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Ketley et al.

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[54] **GRAVURE PRINTING PLATE OF
PHOTOCURABLE MATERIAL**

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[51] **Int. Cl.**.....**G03c 5/00**

[58] **Field of Search****96/35.1, 48, 115**

[56]

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[57]

ABSTRACT

This invention relates to a gravure printing plate and methods of making same, said plate comprising a photocurable composition, i.e., a polyene, polythiol and photosensitizer, optionally having a screen or grid embedded in the photocurable composition.

3 Claims, No Drawings

GRAVURE PRINTING PLATE OF PHOTOCURABLE MATERIAL

In present gravure image carriers, the image is broken up into a large number of minute discrete cells, which are formed by selective chemical etching on a metallic, usually copper, surface. The cells carry unit deposits of ink to the printed surface. The printing element may be a flat plate wrapped around the cylinder of a sheetfed press or a cylinder for the commercially more important process of rotogravure. The rotogravure cylinder rotates continuously in a bath of highly fluid printing ink, the excess being removed from the raised areas by means of a doctor blade. The printing cylinder is manufactured to a very high tolerance to allow control of web tension and color register, and it is chromium plated to prolong its working life. In addition, the cylinder is carefully balanced to avoid vibrations that would cause excessive wear. The doctor blade is normally constructed of sheet steel and is mounted parallel to the cylinder and pressure may be applied if required. The angle of contact may be varied and during operation the blade is oscillated from side to side. The web is printed by contact between the inked cylinder and a friction-driven rubber-covered impression roller. For color work, there are as many cylinders as there are colors. Normally three process colors are used, yellow, magenta and cyan which can be combined additively to form almost all colors in the visible spectrum. Black is added for greater detail and density in the shadow areas. Since rotogravure is essentially a high speed printing process, gravure inks are required to be extremely fast drying, with drying units placed between each color printing station to enable satisfactory superimposition to be accomplished.

The gravure process is capable of reproducing continuous tone pictures as well as line drawings and type images. It is distinguished from other processes in that all copy must be screened, both to separate the individual ink carrying cells and to form a bearing surface for the doctor blade. The area of an individual cell is determined by the size of the screen used, which varies between 120-300 lines per inch, usually 150 lines per inch in commercial work. Gravure enables tonal values to be produced in three ways:

(1) by using cells of constant area but varying depth known as conventional gravure, (2) by using cells of constant depth and varying area known as the Henderson process and (3) by using cells of both varying area and varying depth known as the News-Deltgen or Hurlton Processes.

The conventional half-tone methods produce different tones by utilizing a constant thickness of ink and different dot sizes as in two (2) supra. Gravure processes (1) and (3) supra in addition to using a variable dot size, enable an ink film of variable thickness to be applied by virtue of the cells of variable depth. The capability of printing ink layers of variable thicknesses accounts for the superior quality of the gravure printing over the other major methods.

The production of a rotogravure cylinder begins with the electroplating of a steel cylinder with a 0.040 inch thick layer of copper, which is subsequently machined and polished to the required diameter. The Ballard process offers an alternative by using a thin 0.006 inch thick removable copper sleeve. Photographically, conventional gravure requires continuous tone intermediates, the Henderson process requires half-tone intermediates and the Hurlton or mixed process requires both continuous and half-tone intermediates. The intermediate transparencies are used to expose the photochemical resistance materials, which control the etching operation. The resists, usually carbon tissue or Dupont (Rotofilm) are hardened differentially and respond differentially to etchants of varying density. The exposed resist is mounted on the cylinder, developed in hot water and rotated in the etching solution. The etching process is a critical and time consuming operation, and up to six solutions (usually FeCl_3) of different concentrations are used. It is usual to apply corrective re-etching in local areas. If the cells are too shallow, the cylinder is either locally or completely re-etched. The top surface is carefully protected during this operation. Cells that are etched

too deeply may be corrected by spot electroplating and the application of lacquer to the bottom of the cells. The proofed cylinder is finally electroplated with chromium with 0.0002 inch thick to minimize cylinder wear in long run work.

One object of the instant invention is to eliminate the laborious chemical etching process of present-day gravure plate making. Another object of the instant invention is to substitute a photocurable material for the metal e.g., copper, gravure image carrier. Another object is to prepare a photocurable polymer gravure printing plate in which the discrete gravure cells are produced by selective photocuring to replace the conventional method of preparation by chemical etching of copper through a selectively hardened resist. Still another object is to prepare a photocurable gravure printing plate which requires no wet chemicals in the etching or development step. These and other objects will be apparent from a reading hereinafter.

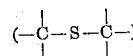
Summarily this invention is directed to forming an image carrier for gravure printing comprising a photocurable composition i.e., a polyene, polythiol and photosensitizer or curing rate accelerator which on exposure through conventional screens and image-bearing transparencies can be readily etched or hardened to form a gravure image carrier on a cylinder. The cylinder can be electroplated with chromium to minimize wear for long run workings. Any of the three aforesaid methods to obtain tonal values are operable by the use of the instant invention. For purposes of description tonal values by using cells of constant area but varying depth will be exemplified hereinafter unless otherwise noted.

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

Photocurable systems which are operable in the instant invention are set out in copending applications having U.S. Ser. No. 674,773 filed Oct. 12, 1967 and U.S. Ser. No. 779,596 filed Nov. 27, 1968 assigned to the same assignee and both 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. These compositions when in contact with a UV transparent film layer or substrate adhere thereto on exposure when the film layer is between the composition and the light source.

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

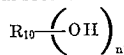
As used herein the term "reactive" unsaturated carbon to carbon groups means groups which will react under proper conditions as set forth herein with thiol groups to yield the thioether linkage



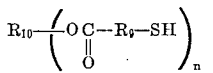
, as contrasted to the term "unreactive" carbon to carbon unsaturation which means



HS-R₉-COOH where R₉ is an organic moiety containing no "reactive" carbon to carbon unsaturation with polyhydroxy compounds of the general formula:



where R₁₀ 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 R₉ and R₁₀ 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-CH₂-COOH), α-mercaptopropionic acid (HS-CH(CH₃)-COOH) and β-mercaptopropionic acid (HS-CH₂CH₂COOH) 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 gravure image carrier.

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, crosslinked three dimensional network polythioether polymer systems on curing. In order to achieve such infinite network formation, the individual polyenes and polythiols must each have a functionality of at least 2 and the sum of the functionalities of the polyene and polythiol components must always be greater than 4. Blends and mixtures of the polyenes and the polythiols containing said functionality are also operable herein.

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

One method of employing the photocurable composition of this invention as a gravure image carrier involves exposing through a suitable screen a uniformly thick layer of the photocurable composition sandwiched between two films at least one of which transmits actinic radiation. It is also possible to merely have the photocurable composition on one substrate which transmits actinic radiation without the necessity for a top layer, especially when the photocurable composition is highly viscous. In this instance, the substrate transmits actinic radiation and the exposure to UV light is through the substrate. The system is exposed to collimated UV light for sufficient time to allow photocuring of the exposed areas to take place throughout the thickness of the photocurable layer. This exposure results in the formation of discrete cells of uncured photocurable material separated by cell walls of solidified photocured material. The screen is replaced with a screenless, continuous tone, image-bearing positive transparency and the photocurable layer is reexposed through the transparency for sufficient time to cause the tonal range of the positive to be reproduced by selectively curing the photocurable material to a solid of variable depths. Exposure of the photosensitizable material to UV light causes the photosensitizable material to adhere to the film proximate the actinic radiation light source. Thus, if a sandwich is employed, the other film away from the light source is peeled off the photocurable material and the remaining uncured portion of the photocurable layer is removed by dissolution in a solvent for the photocurable

material leaving discrete cells of varying depth for printing.

Another method of using the photocurable composition of the instant invention for forming a gravure plate is to employ a metal shell containing a grid system whose holes extend partially or completely through the entire shell said shell being easily removable from a metal printing roller or cylinder. The holes in the shell are filled with the photocurable composition and the image placed on the grid by either of the following systems:

a. if the holes do not extend completely through the shell, the outside surface is covered with a U.V. transparent film to which cured photocurable composition adheres over which is positioned a continuous tone, negative transparency of the image. After exposure through the negative to collimated UV light, the negative is removed, the UV transparent film and adhering photocured composition is stripped from the shell and the residual photocurable composition in the grid is reexposed to UV collimated light to cure and harden same and form a gravure image carrier for printing.

b. if the holes in the grid system extend completely through the outside shell, the process outlined in (a) can still be used. In addition, a positive, continuous tone, image bearing transparency can be placed on the inside surface of the shell and exposed to collimated UV light from the inside of the shell. The solid photocured composition remains in the grid and the uncured portion of the photocurable composition is removed from the outside surface of the shell by solvent extraction leaving a gravure image carrier in the shell. Both process (a) and (b) allow reuse of the shell containing the grid system by complete solvent extraction of the cured photocurable composition after use. The addition of a metal shell or grid system in the aforesaid method enables the image carrier to be employed for a printing of longer duration than a photocured image carrier per se.

A third method of employing a photocurable composition to make an image carrier for gravure printing by the instant invention has the added advantage that no wet chemicals are needed for the preparation of the plates and that they require only a UV light source. This dry process method comprises etching a gravure plate or cylinder with a grid work to provide a multitude of cells and lands. The cells are filled with the photocurable composition and then covered with a U.V. transparent film so that contact is made with the surface of the photocurable material. A continuous, image-bearing, negative transparency is placed in contact with the film and exposed to collimated UV light. The negative is removed and the film together with adhering cured portion of the photocurable material is stripped off from the surface of the plate or cylinder. The residual photocurable material is then reexposed to collimated UV light to cause the composition to solidify by curing. The amount of photocurable material which remains in the cells after stripping off the film with the adhering cured portion of the photocurable material is proportional to the amount of light passing through the negative. Hence a clear portion of the negative will allow light to cure most of the photocurable material beneath it which will be removed with the film leaving no photocurable material in the cell. This cell will be completely filled with ink during the printing process producing a very black impression. Conversely, a dark portion of the negative will produce a white portion during the printing. Gray areas will result in varying depths of residual photocurable material and hence proportional ink pick-up. The plates can be reused by soaking in a solvent in which the cured polymer is partially or completely soluble. The surface can be wiped clean without damage to the original grid system.

The following examples will explain, but should in no way limit, the instant invention. Unless otherwise noted, all parts and percentages are by weight.

PREPARATION OF POLYENES

EXAMPLE 1

1 mole diglycidyl ether of Bisphenol A having a molecular weight in the range 370-384 and commercially available from Shell Chemical Company under the tradename "Epon 828" and 2 moles of allyl amine were dissolved in 500 ml. benzene 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 benzene solvent was removed by vacuum. The thus formed allyl terminated liquid prepolymer will hereinafter be referred to as Prepolymer A.

EXAMPLE 2

Example 1 was repeated except that 2 moles of diallyl amine was substituted for the 2 moles of allyl amine and no benzene solvent was used. The thus formed allyl terminated liquid prepolymer will hereinafter be referred to as Prepolymer B.

EXAMPLE 3

1 mole of commercially available tolylene diisocyanate was charged to a resin kettle equipped with a condenser, stirrer, thermometer, and gas inlet and outlet. 2 Moles of the diallyl ether of trimethylpropane was slowly added moles the kettle. After the addition was complete 4.0 grams of dibutyl tin dilaurate as a catalyst was added to the kettle and the reaction was continued for 30 minutes at 70° C. under nitrogen. The thus formed allyl terminated liquid prepolymer will hereinafter be referred to as Prepolymer C.

PREPARATION OF PHOTOCURED GRAVURE PRINTING PLATE

EXAMPLE 4

A photocurable composition comprising 10 parts by weight of Prepolymer B from Example 2, 8.5 parts of pentaerythritol tetrakis (β -mercaptopropionate) commercially available from Carlisle Chemical Co. under the tradename "Q-43" and 0.015 parts of dibenzosuberone were admixed together. The mixture was degassed by heating at 70° C. under vacuum and cast into a painted black glass mold $4 \times 3 \times 0.037$. Sufficient volume was used to fill the mold and a thin film of polyvinyl alcohol (1 ml. thick) was stretched and held in contact with the mixture. A screen containing 40 lines per inch and a transparent/opaque ratio of 1:2.33 was placed with the emulsion side in contact with the polyvinyl alcohol film. The system was mounted in a vacuum table to provide intimate contact and exposed through the screen to UV light from an Ascorlux lamp providing a surface intensity of 2,500 microwatts/cm.² for 4 minutes. The screen was removed and the procedure was repeated with a continuous tone, image bearing, positive transparency for an exposure period of 2 and $\frac{1}{4}$ minutes. The resulting plate with the polyvinyl alcohol backing layer was removed from the mold, washed in ultrasonically agitated ethanol for 5 minutes and post-exposed to the same lamp with the same intensity for 7 minutes on each side to harden it. Microscopic examination revealed that cells of constant area and variable depth had been attained. The flexible gravure plate was mounted on a $2\frac{1}{2}$ inch diameter roller using a proprietary adhesive. A doctor blade was constructed from rubber (Shore A Hardness 80), chamfered to an edge and mounted between metal plates. This assembly was held at 80° to the printing plate with the sharp rubber edge in intimate contact with the plate surface. The plate roller was continually rotated in a bath of gravure printing ink, (Sinclair and Valentine vinyl black no 3.) mounted underneath. A white paper web $3\frac{1}{2}$ inches wide passed through the nip formed between the plate and a $2\frac{1}{2}$ inch diameter rubber covered impression roller. The paper roll was maintained in tension and was

wound after printing. The resultant prints were of good quality.

EXAMPLE 5

Example 4 was repeated except that the film covering the mold was 1 mil thick cellulose acetate and the gravure screen contained 150 lines per inch and a ratio of space to line of 2.5 to 1. The resultant prints were of good quality.

EXAMPLE 6

A copper cylinder was etched by conventional means after being exposed through a screen with 150 lines to the inch in a ratio of space to line of $2\frac{1}{2}$ to 1. A photocurable mixture consisting of 10 parts of prepolymer A from Example 1, 5 parts of pentaerythritol tetrakis (β -mercaptopropionate) and 0.2 parts benzophenone were admixed together and degassed by heating at 70° C. under vacuum. The wells of the etched cylinder were then filled with the photocurable mixture and covered with a UV transparent cellulose acetate film (1 mil thick) so that contact is made with the surface of the photocurable material. A continuous-tone, image-bearing, negative transparency was placed in contact with the cellulose acetate film and exposed to UV light from an Ascorlux lamp providing a surface intensity of 25,000 microwatts/centimeter² for 3 minutes. The negative was removed and the cellulose acetate film together with the photocured portion of the photocurable material was stripped from the cylinder. The residual uncured portion of the photocurable material was then exposed to light from the same light source at the same intensity for a period of 5 minutes to form cells of varying depth. The use of the thus formed gravured cylinder in a conventional gravure press resulted in prints of excellent quality.

EXAMPLE 7

Example 6 was repeated except that Prepolymer A was replaced by 10 grams of poly (1,3-butadiene) of approximately 2,000 molecular weight. The resulting prints were of excellent quality.

EXAMPLE 8

Example 6 was repeated except that Prepolymer A was replaced with 2.7 grams of the triacrylate of the reaction product of trimethylol propane with 20 moles of ethylene oxide. The resulting prints were of good quality.

EXAMPLE 9

A copper cylinder (3 mil thick) was etched clear through by conventional means after exposure through a screen with 150 lines to the inch and a ratio of space to line of 2.5 to 1. The cells in the cylinder were filled with a photocurable mixture comprising 10 parts of prepolymer C from Example 3, 8.2 parts of pentaerythritol tetrakis (β -mercaptopropionate) and 0.02 parts dibenzosuberone which mixture had previously been degassed by heating at 70° C. under vacuum. Since the cells extended through the copper cylinder, a continuous tone image-bearing positive transparency was placed inside the cylinder proximate its surface and exposed to UV light from an Ascorlux lamp providing a surface intensity of 25,000 microwatts/cm² for 5 minutes to cure the photocurable admixture. The cylinder was then washed in ultrasonically agitated ethanol for 1 minute to remove the uncured photocurable material. The cylinder was fitted on a metal roller and employed as a gravure printing plate. The prints resulting from the process were of excellent quality. The use of these cylinders instead of conventional rollers alleviates the handling and storage problems.

EXAMPLE 10

A copper cylinder (25 mil thick) was etched to a depth of 2.5 mils by conventional means after being exposed through a screen with 150 lines to the inch in a ratio of space to line of 2.5 to 1. The etched cylinder was placed on a metal roller and

the cells in the cylinder were filled with a photocurable material consisting of 10 parts by weight of Prepolymer B from Example 2, 25 parts of pentaerythritol tetrakis (β -mercaptopropionate) and 0.015 parts of dibenzosuberone which had previously been degassed by heating at 70° C. under vacuum. A 1 mil thick film of cellulose acetate was placed over the cylinder in contact with the photocurable material and a continuous tone, image-bearing, negative transparency was placed on top of the cellulose acetate film. The system was exposed through the transparency to UV light from an Ascorlux lamp providing a surface intensity of 25,000 microwatts/cm² for 5 minutes. After exposure, the negative was removed and the cellulose acetate film along with the adhering photocured material was stripped off the cylinder. The residual uncured portion of the photocurable material in the cylinder was then reexposed to UV light from the same light source and intensity for a period of 5 minutes to form a gravure image carrier. Prints resulting from the use of said image-carrier on a roller were of good quality.

The photocurable compositions of this invention are especially useful in producing gravure printing plates after exposure through conventional screens and continuous tone negative or positive image-bearing transparencies. The methods herein are especially useful since the exposure and subsequent development or etching can be carried out on the same or different side of the plate as desired.

The photocurable compositions to be converted to solid gravure printing plates, 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 polyene or polythiol prior to or during the compounding or admixture step. Additives, however, should not be substantially opaque when present in the photocurable compositions. The aforesaid additives may be present in quantities up to 500 parts or more per 100 parts of the photocurable 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 reaction or other required steps in the process.

The support to which the photocured composition adheres is preferably a plastic having the characteristics of being flexible, adherable to the photocurable composition on exposure to UV radiation or by other means and can transmit a substantial amount of UV light. Operable plastics include but are not limited to, polyethylene, polypropylene, poly-4-methylpentene, polystyrene, "Mylar" i.e., polyethylene terephthalate, cellulose 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 photocurable 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 photocuring reaction can be initiated by actinic radiation from sunlight or from special light sources which emit significant amounts of actinic light suitably in the wave-length range of 2,200-4,000Å. Thus, it is possible merely to expose the photocurable composition with or without a transparent support or cover film to actinic radiation preferably in the range 2200-4000 Å, under ambient conditions or otherwise and obtain a solid elastomeric or resinous product useful as a gravure printing plate after development.

The photocuring reaction rate can be increased by the use of a photosensitizer. As used herein a photosensitizer means a curing rate accelerator as used in a curing reaction. 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,

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'-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 are usually added in an amount ranging from 0.0005 to 50 percent by weight, suitably 0.0005 to 33% by weight, preferably 0.5 to 25 percent, of the photocurable composition in the instant invention.

The compounding of the components of the photocurable 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, are admixed in an inert atmosphere and charged to an aerosol can, drum, tube, or cartridge for subsequent use. Exposure of said admixed components to actinic radiation under ambient or elevated temperature conditions will initiate photocuring.

Another useful method of compounding the photocurable composition is to prepare by conventional mixing techniques but in the absence of actinic radiation a composition consisting of polyene, antioxidant (to inhibit spontaneous oxygen-initiated curing), polythiol, UV sensitizer, 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 suitable as gravure printing plates.

Conventional curing inhibitors or retarders operable with the photocurable compositions in the instant invention when desired, 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 photocurable 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 cured polymer, very dense areas in the negative to substantially no polymer and intermediate densities to intermediate thicknesses of polymer.

What is claimed is:

1. A process for forming a gravure printing plate which comprises supporting a substantially uniformly thick layer of a composition consisting essentially of (1) 98 to 2 percent by

weight of said composition of a polyene containing at least 2 reactive unsaturated carbon to carbon bonds per molecule, (2) 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, and (3) 0.0005 to 50 percent by weight of said composition of a photosensitizer, on a support film which is transparent to actinic radiation, exposing said composition to actinic radiation through the support film firstly through a conventionally gravure screen and secondly through an image-bearing, continuous tone positive transparency, said screen and said transparency being maintained adjacent to 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 solidified cured reverse image relative to said transparency in a solidified cured grid pattern and removing uncured portions of the composition to form a gravure printing plate.

2. The process of forming a gravure printing plate which comprises filling the cells of a grid-etched metal cylinder with a composition consisting essentially of (1) 98 to 2 percent by weight of said composition of a polyene containing at least 2 reactive unsaturated carbon to carbon bonds per molecule, (2) 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, and (3) 0.0005 to 50 percent by weight of said composition of a photosensitizer, covering the thus filled cells with a film transparent to actinic radiation exposing said composition to actinic radiation through an image-bearing continuous tone negative transparency thereby causing portions of the composition exposed to actinic radiation to adhere to the film, and form a solidified cured reverse image relative to said transparency, stripping the film and the adhering cured composition from the cylinder and exposing the residual portion of the composition in the cells of the cylinder to actinic radiation.

3. A process for forming a gravure printing plate which comprises filling the cells of a metal cylinder shell which has been grid-etched through its thickness with a composition consisting essentially of (1) 98 to 2 percent by weight of said composition of a polyene containing at least 2 reactive unsaturated carbon to carbon bonds per molecule, (2) 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 uncured carbon to carbon bonds per molecule in the polyene and (b) the thiol groups per molecule in the polythiol being greater than 4, and (3) 0.0005 to 50 percent by weight of said composition of a photosensitizer, exposing said composition on the inside of the shell to actinic radiation through an image-bearing, continuous tone, positive transparency thereby causing portions of the composition exposed to actinic radiation to form a solidified cured reverse image relative to said transparency and thereafter removing uncured portions of the composition on the outside of the shell to form a gravure printing plate.

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