

[54] **METHOD FOR ULTRASONIC ETCHING OF POLYMERIC PRINTING PLATES**

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[*] Notice: The portion of the term of this patent subsequent to Oct. 4, 1987, has been disclaimed.

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[21] Appl. No.: **68,257**

Related U.S. Application Data

[60] Division of Ser. No. 764,849, Oct. 3, 1968, which is a continuation-in-part of Ser. No. 707,299, Feb. 21, 1968, abandoned.

[52] U.S. Cl. **156/14, 156/2, 156/5, 156/345, 134/1**

[51] Int. Cl. **B41n 3/02, C23g 1/00**

[58] Field of Search **156/2, 14, 5; 134/1**

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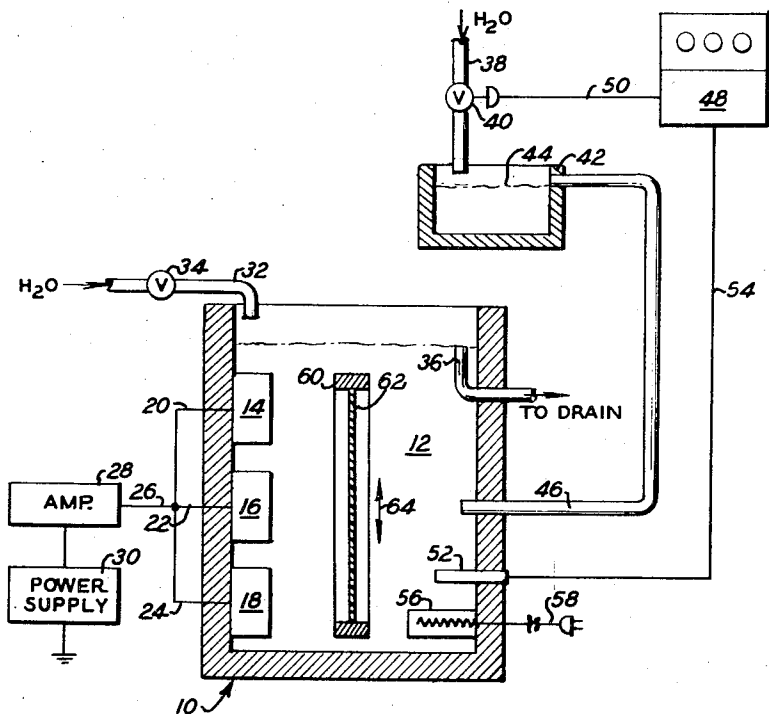
Ultrasonics in Industry by Steinberg, p. 1293

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[57] **ABSTRACT**

The invention disclosed is a method for ultrasonic etching of polymeric printing plates. The method includes an etching bath energized by means of ultrasonic energy, a water spray bath, and an air dryer. The method for ultrasonic etching of polymeric printing plates includes the steps of immersing a polymeric printing plate in an etching bath, energized by ultrasonic energy, washing the polymeric printing plate in a water spray cleaning bath after ultrasonic etching, and air drying the water washed polymeric printing plate in a current of heated air.

3 Claims, 4 Drawing Figures



Patented May 9, 1972

3,661,660

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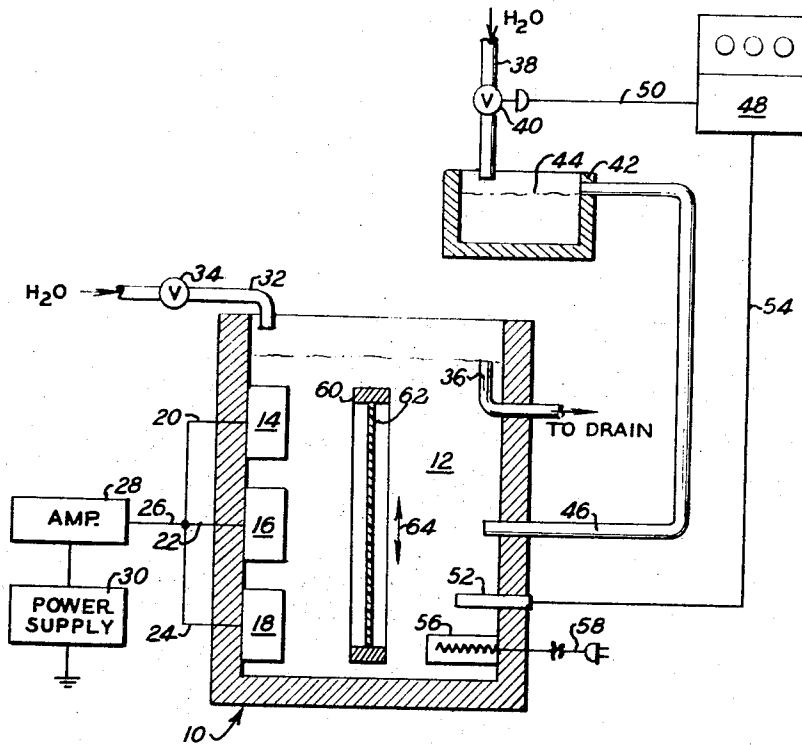


FIG. 1

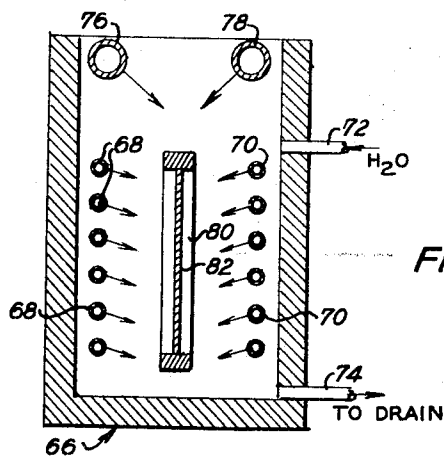


FIG. 2

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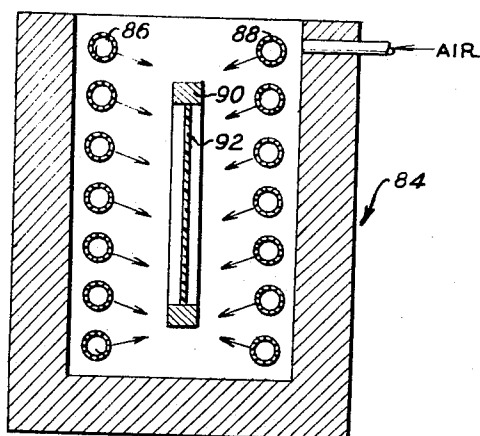


FIG. 3

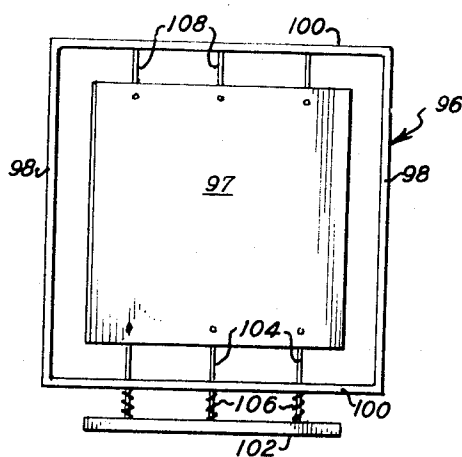


FIG. 4

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METHOD FOR ULTRASONIC ETCHING OF POLYMERIC PRINTING PLATES

This application for U.S. letters Pat. is a divisional application of Ser. No. 764,849 filed Oct. 3, 1968 which in turn is a continuation-in-part application of U.S. Ser. No. 707,299 filed Feb. 21, 1968 now abandoned.

The present invention relates to an apparatus and method for ultrasonic etching of polymeric printing plates. More particularly, the present invention provides an apparatus including an etching bath energized by ultrasonic energy, a water spray bath for cleaning the etched printing plate, and an air dryer for drying the water washed printing plate in a current of heated air. In one embodiment, the present invention provides an etching bath energized by means of ultrasonic energy and containing a solvent or aqueous detergent solution, while in another embodiment the present invention provides a solvent or detergent flow system for use in association with the etching bath.

In the printing art, where time is of the essence, preparation of relief printing plates usually made of zinc or magnesium metal by photoengraving requires relatively long etching periods until sufficient relief is obtained on the metal plate. Recently, the art has discovered that polymeric compositions may be substituted for the metals in the formation of printing plates. However, even with polymeric compositions in which images are formed usually by photopolymerization or photocuring thereof, the time necessary to develop or etch the plate in a solvent or an aqueous solution is bordering on that which is commercially acceptable. In addition, it is necessary to also mechanically aid the etching by removal of the un-polymerized or uncured portion of the material with a spray, brush, blotter, sponge or other mechanical means. Such mechanical means, relying on physical contact, cause image surface or edge distortion and the total removal of all the non-image polymeric material is difficult. A further drawback to the etching systems for photopolymerizable or photocurable plate materials which use a solvent system is the flammability and toxicity of the solvent and the possible harm that may result to the person handling said system over the relatively long periods of time required to etch to a commercially acceptable degree. It has now been found that by the practice of the present invention, an apparatus and method are provided for etching photopolymerizable or photocurable polymeric printing plates using time cycles of relatively short duration to provide a polymeric printing plate with a relief image far superior to that obtained by the presently used combination of chemical and mechanical etching.

The present invention generally stated provides a method and apparatus for ultrasonic etching of polymeric printing plates wherein the method includes the steps of immersing a printing plate formed of a photocurable or photopolymerizable polymeric composition which has been exposed to actinic light through an image bearing, line or halftone, positive or negative transparency consisting solely of substantially opaque and substantially transparent areas until substantially complete photocuring or photopolymerization takes place in the exposed areas and substantially no photocuring or photopolymerization takes place in the non-exposed areas, in an aqueous solution or in a solvent for said unexposed photopolymerizable or photocurable material at a temperature wherein said unexposed material is a liquid and ultrasonically activating said solvent or solution to the degree necessary to cause cavitation and removal of substantially all of the unexposed liquid composition.

The apparatus of the present invention generally includes an etching bath energized by ultrasonic energy, a water spray bath for cleaning the etched printing plate, and an air dryer for drying the water washed printing plate. Desirably, the etching bath contains a solvent or aqueous detergent solution and a system therefore which continuously monitors the concentration of the solvent or detergent in the etching bath and as required, replenishes depleted solvent or detergent thereby maintaining a desired, substantially constant bath concentration.

Practice of the present invention will become more apparent from the following detailed description taken in conjunction with the drawings wherein:

FIG. 1 diagrammatically illustrates an etching bath energized by means of ultrasonic energy and having a system associated therewith which continuously monitors the bath concentration and replenishes depleted solvent or detergent as required;

FIG. 2 diagrammatically illustrates a water spray bath for cleaning etched printing plates;

FIG. 3 diagrammatically illustrates an air dryer for drying the water washed printing plates; and

FIG. 4 shows a frame for conveniently mounting a flexible printing plate for use in processing the plate through the several stations of the apparatus of the present invention.

In the drawings wherein similar elements are referred to by similar numerals, FIG. 1 illustrates etching bath tank 10 formed of a suitable material such as a metal for retaining a cleaning liquid or etching solution 12 therein.

Disposed relative to tank 10 and desirably along one side wall thereof is a means to energize the bath with ultrasonic energy generated by transducers 14, 16 and 18 positioned within the solution and receiving through lines 20, 22 and 24 respectively and power line 26 electrical energy from amplifier 28 and power supply 30. It is found that more effective etching results by positioning the transducers along the side wall of bath 10 since more direct cavitation is available and materials are readily removed by currents generated in solution 12. The removed materials may either float to the surface of the solution or may sink to the tank bottom when the plate is substantially vertically disposed therein as illustrated without undue interference with the cavitation of other areas.

The ultrasonic activation of the bath to produce cavitation may be provided by various known methods employing transducers. The transducers most commonly used for ultrasonic cleaning are either magnetostrictive made of nickel, or its alloys or electrostrictive units made of barium titanate and/or lead zirconate.

One method is to place transducers on the sides or bottom of the tank 10 containing the bath solution 12 and connect said transducers to generators to energize same at between about 18 to about 40 kilocycles/sec. and preferably about 20 kilocycles/sec. or more and a power density level nominally in the range of 5-20 watts/sq. in. or more. It is obvious that longer cleaning or etching periods are required at the lower power density level, i.e. of the order of 3-10 minutes and that rapid cleaning of the order of 0.5 to 2 minutes may be obtained at the upper power density level for a newspaper page about 15½ × 24 inches.

Etching tank 10 may further include in addition to a solution 12, a system therefore which continuously monitors the concentration of the solvent or detergent in the etching bath and as required, replenishes depleted solvent or detergent thereby maintaining a desired, substantially constant bath concentration. One useful system may include pipe 32 having a standard valve 34 receiving water from a convenient source for continuously transporting the water at a fixed constant rate to tank 10. Excess solution in tank 10 may be conveniently removed such as by overflow drain tube 36 if desired.

The system may further include a second pipe 38 receiving water from a convenient source for transporting water at a rate regulated by solenoid controlled valve 40 to detergent tank 42 containing a detergent or solution 44 therein. As water is received in detergent tank 42, a corresponding amount containing detergent or etching solvent is received by overflow line 46 which transports the overflow to solution 12 in etching tank 10. Control 48 is used to regulate the output through solenoid controlled valve 40 by electrical line 50. The concentration of solution 12 may be monitored by electrode 52 in the etching tank which measures the strength of the solution and transmits the signal to control 48 by electrical line 54. If the concentration of the solution is low, power is supplied to the solenoid valve causing it to open and admit water into the

detergent reservoir. The concentration of the solution contained in the reservoir is caused to overflow into the etching tank, thus building up the solution strength. When the strength of the solution attains the proper level, the solenoid valve is closed until the strength of the solution again falls below the predetermined level at which the solenoid valve is again opened to correct the depletion.

If desired, heater 56 receiving electrical energy through line 58 may be included in etching tank 10 to maintain the temperature of the solution 12 at a temperature whereat the unexposed area of a photocurable or photopolymerizable composition is in the liquid or molten phase. Bath temperatures may range from room temperature up to the boiling point of water at atmospheric pressure and even higher if a pressurized system is maintained. A preferred temperature is in the range of about 150° F. to about 200° F.

Mounting frame 60 described hereinafter in greater detail may be employed to support a photocured polymeric printing plate 62 within solution 12 of etching bath 10. It is found that movement of plate 62 in an up and down direction indicated by arrow 64 further facilitates removal of uncured polymeric composition from the printing plate.

It has been found that using an aqueous solution of detergent and soap in combination with ultrasonic activation of bath 10 to impart cavitation thereto, the etching time may be reduced to periods of 5 seconds to 10 minutes without enlisting mechanical aids such as brushes, sponges, or the like and the relief obtained is far superior in topographical quality and in fidelity of image reproduction to that previously obtained using photopolymerizable or photocurable materials and, in most cases, far superior to the relief formed from a photoengraved metal plate.

The greater the difference in solubility, viscosity, or emulsifiability between the solidified areas in the photosensitized plate and portions of said plate which remain liquid, the greater the efficiency of the etching process to make the relief plate. Thus, it is important to select the right detergent, soap or solvent in the etching bath to facilitate removal by the use of ultrasonics. For the aforementioned photocurable system, the preferred bath is an aqueous bath containing a suitable, commercially available inorganic or organic detergent in an amount ranging from about 0.05 percent to about 30 percent by weight of the aqueous bath. For the aforementioned photopolymerizable system in British Pat. No. 1,102,910, the preferred bath consists of an organic solvent such as acetone or petroleum ether. Etching baths for other liquid photosensitizable compositions are dependent on the aforesaid difference in solubility between the liquid and solidified portion of the photosensitized relief plate.

Although usually commercially available inorganic or organic detergent compositions may be added to the etching bath, a detergent formed of an alkali metal polyphosphate, an alkali metal silicate, and a linear alkyl benzene sulfonate is preferred to greatly facilitate removal of uncured liquid polymeric composition from selectively photocured printing plates. Although most any alkali metal salt may be employed with the sodium salt being preferred.

The amounts of the alkali metal polyphosphate, alkali metal silicate, and linear alkyl benzene sulfonate forming the detergent preferred for use herein may vary provided the amount of the alkali metal silicate comprises a major portion, the amount of the alkali metal polyphosphate comprises a lesser and intermediate portion, and the amount of the linear alkyl benzene sulfonate comprises the minor portion thereof. Desirably, the amount of the alkali metal silicate is greater than the combined amounts of the alkali metal polyphosphate plus the amount of the linear alkyl benzene sulfonate.

The amount of alkali metal silicate forming the preferred detergent may vary from about 51 to about 97 parts by weight of the detergent. An example of a useful alkali metal silicate is sodium meta-silicate pentahydrate or the like.

The amount of alkali metal polyphosphate forming the preferred detergent may vary from about 2 to about 48 parts

by weight of the detergent. An example of a useful alkali metal polyphosphate is sodium tripolyphosphate or the like.

The amount of the linear alkyl benzene sulfonate forming the preferred detergent may vary from about 1 to about 30 parts by weight of the detergent. An example of a useful linear alkyl benzene sulfonate is linear dodecyl benzene sulfonate or the like.

Although the preferred detergent for use herein may be added to form an aqueous bath solution in an amount ranging from about 0.05 percent to about 30 percent by weight of the aqueous bath solution, amounts in the range of about 0.5 percent to about 10 percent are usually sufficient and are thus preferred. An amount of about 0.5 percent by weight has been found to be effective as a concentration for the preferred detergent.

The dwell time in the bath for the printing plate is of the order of about 5 seconds to about 10 minutes, depending upon the photocurable or photopolymerizable material employed, the thickness of the plate, the temperature of the bath, and the cleaning detergent employed in the bath. The relief obtained in such a system constitutes substantially the entire thickness of the photocurable or photopolymerizable layer right down to the support. The printing plate is thereafter removed from the etching bath and passed into water spray rinse tank 66 of FIG. 2 formed desirably of metal and having a series of spray units 68 disposed along one side with a second series of spray units 70 disposed along an opposite side of the interior of tank 66. The spray units 68 and 70 may be formed of a series of pipes having water spraying elements for directing water under pressure received from water supply 72 against frame 80 and printing plate 82 substantially vertically disposed in the rinse tank. The spray of water may be heated if desired and directed such to wash the printing plate free of any detergent solution remaining thereon as well as any undesired materials including uncured polymeric materials if present. The water wash may be drained from tank 66 by outlet drain 74, or other suitable means as desired.

In order to facilitate rinsing wash water from the surface of printing plate 82, air spraying units 76 and 78 oppositely disposed to receive the plate therebetween may be included to serve to provide an air curtain or air knife which removes substantially most of the water accumulating on the surface of the printing plate as it is removed vertically from the water spraying operation. The air to units 76 and 78 may be heated if desired.

FIG. 3 illustrates air dryer 84 formed as a metal tank if desired, with oppositely disposed air tubes 86 and 88 therein. The air tubes may be used to direct air at elevated temperatures up to about 150° C. to facilitate drying of printing plate 92 in mounting frame 90 substantially vertically disposed in the air dryer. The air for units 86 and 88 may be received from a pressurized air supply through tube 94 and may be connected to the several units by a manifold arrangement as may be the case for the water spray pipes 68 and 70 of FIG. 2 receiving water from supply line 72.

The direction at which the air spray or water spray for the rinse tank and the air dryer may vary as desired against the printing plate. Variations in the spray pattern may be employed or the spray pattern may be uniform against the printing plate in one or another direction.

FIG. 4 illustrates mount 96 for printing plate 97 to usefully serve as a means for passing the plate through the several processing stations of the present apparatus. It is recognized that other means may be employed, if desired. Mount 96 may appear having a first and a second vertical element 98 conveniently joined to a first and a second horizontal element 100 forming the base frame thereof. Mount handle 102 having L-shaped members 104 slidably projecting through a first horizontal element 100 is biased thereagainst by springs 106 disposed about a longer leg of the L-shaped elements while the perpendicular leg thereof grips plate 97 by holes punched therethrough. The edge opposite the printing plate to that supported by elements 104 may be similarly secured by L-shaped

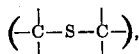
members 108 fixed to the second horizontal element 100 forming the frame.

A convenient method of carrying out this invention is to place an image-bearing, line or halftone, stencil or positive or negative transparency parallel to the surface of a layer of a photocurable or photopolymerizable composition which has been cast directly on a support. The image-bearing transparency and the surface of the composition may be in contact or have an air gap there between, as desired. The photocurable or photopolymerizable layer is exposed through the transparency to a source of actinic light, preferably a point or collimated light source when a liquid photocurable composition is used, until the layer is cured or polymerized to an insoluble stage in the exposed areas. The thickness of the ultimate relief in such a method may be controlled by varying the thickness of the layer of the composition. The thus cured plate is then immersed in an aqueous solution of a detergent in a bath and the bath is ultrasonically activated to the degree necessary to cause cavitation in the bath. Thereafter, the photocured printing plate is washed in a spray of water and dried in an air dryer.

One photocurable system which is suitable for use herein is that set out in a copending application having U.S. Ser. No. 674,773 filed Oct. 12, 1967, assigned to the same assignee hereof and incorporated by reference herein. In said photocurable system a printing plate is formed from a layer of a photocurable polymeric composition consisting of a polyene containing at least two unsaturated carbon to carbon bonds per molecule, a polythiol containing two or more thiol groups per molecule and a photosensitizer. The layer of photocurable polymeric composition may be adhered to a support such as one formed of rubber, plastic, paper, glass, metal and the like.

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

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

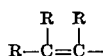


as contrasted to the term "unreactive" carbon to carbon unsaturation which means



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

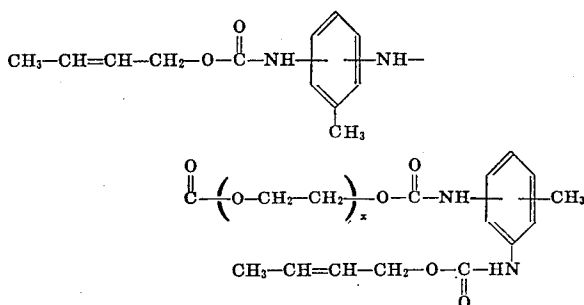
One group of operable polyenes to react with polythiols to form printing plates is that taught in a copending application having Ser. No. 617,801 filed Feb. 23, 1967 and assigned to the same assignee. This group includes those materials having a molecular weight in the range 300 to 20,000, a viscosity ranging from 0 to 20 million centipoises at 70° C. of the general formula: $[A-\text{X}]_m$ wherein X is a member of the group consisting of



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

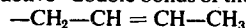
Examples of operable polyenes from this group include, but are not limited to

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

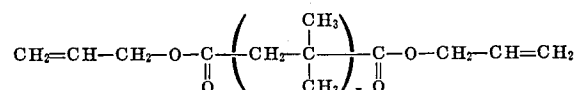


wherein x is at least 1,

2. ethylene/propylene/non-conjugated diene terpolymers, such as "Nordel 1040" manufactured by duPont which contains pendant "reactive" double bonds of the formula:

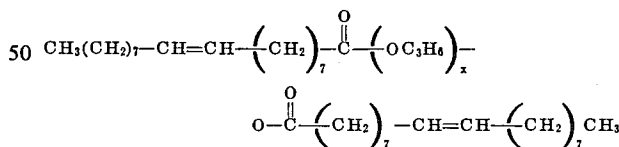


3. the following structure which contains terminal "reactive" double bonds:



where x is at least 1.

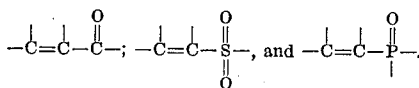
4. the following structure which contains near terminal "reactive" double bonds:



where x is at least 1.

Another group of operable polyenes includes unsaturated polymers in which the double or triple bonds occur also within the main chain of the molecules. Examples include conventional elastomers (derived primarily from standard diene monomers) such as polyisoprene, polybutadiene, styrene-butadiene rubber, isobutylene-isoprene rubber, polychloroprene, styrene-butadiene-acrylonitrile rubber and the like; unsaturated polyesters, polyamides, and polyurethanes derived from monomers containing "reactive" unsaturation, e.g., adipic acid-butenediol, 1,6-hexanediamine-fumaric acid and 2,4-tolylene diisocyanate-butenediol condensation polymers and the like. Included in the term "polyenes" as used herein are those materials which in the presence of an inert solvent, aqueous dispersion or plasticizer fall within the viscosity range set out above at 70° C.

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



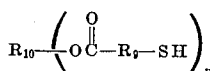
A few typical examples of polymeric polyenes which contain conjugated reactive double bond groupings such as those described above are polyethylenether glycol (600 M.W.) diacrylate; polytetramethylenether glycol (1,000 M.W.) dimethacrylate; the triacrylate of the reaction product of trimethylol propane with 20 moles of ethylene oxide; and the like.

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

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

The operable polythiols may 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 operable polythiols with polyenes to obtain essentially odorless cured polythioether printing plates are esters of thiol-containing acids of the general formula: $HS-R_9-COOH$ where R_9 is an organic moiety containing no "reactive" carbon to carbon unsaturation with polyhydroxy compounds of the general structure: $R_{10}-OH$, where R_{10} is an organic moiety containing no "reactive" carbon to carbon unsaturation and n is 2 or greater. These components will react under suitable conditions to give a polythiol having the general structure:



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

Certain polythiols such as the aliphatic monomeric polythiols (ethane dithiol, hexamethylene dithiol, decamethylene dithiol, tolylene-2,4-dithiol, etc.) and some polymeric polythiols such as a thiol-terminated ethycyclohexyl 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 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 polypropylene ether glycol bis (β -mercaptopropionate) which is prepared from polypropylene-ether glycol e.g. Pluracol

P2010, Wyandotte Chemical Corp.) and β -mercaptopropionic acid by esterification.

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

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

The term "functionality" as used herein refers to the average number of ene or thiol groups per molecule in the polyene or polythiol, respectively. For example, a triene is a polyene with an average of three "reactive" carbon to carbon unsaturated groups per molecule and thus has a functionality (f) of 3. A dithiol is a polythiol with an average of two thiol groups per molecule and thus has a functionality (f) of 2.

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

In general, it is preferred, especially at or near the operable lower limits of functionality in the polyene and polythiol, to use the polythiol and the polyene compounds in such amounts that there is one thiol group present for each ene group, it being understood that the total functionality of the system must be greater than four, and the functionality of the thiol and the diene must each be at least two. For example, if two moles of a triene are used, and a dithiol is used as the curing agent, making the total functionality have a value of five, it is preferable to use three moles of the dithiol. If much less than this amount of the thiol is used, the curing rate will be lower and the product will be weaker in some respects because of the reduced 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 may lead to a plasticized cross-linked product which may not have the desired properties. However, the relative amounts of polyenes and polythiols may be adjusted to any values above the minimum scope disclosed herein which give desirable properties to the cross-linked polythioether. It must be emphasized that regardless of the ratio of polythiol to polyene,

the total functionality of the system must be greater than four, or a crosslinked network will not result, and the product will be a swellable, chain-extended composition which is unsuitable. Thus, to obtain a solid crosslinked printing plate it is necessary to use a polyene containing at least two reactive unsaturated carbon to carbon bonds per molecule in an amount that the combined functionality of the reactive unsaturated carbon to carbon bonds per molecule and the thiol groups per molecule is greater than 4.

Another composition operable to form a relief printing plate by the process of the instant invention is that set out in British Pat. No. 1,102,910 and 1,007,345. Therein the liquid composition consisting of:

A. 0.001 to 5 percent weight of a polyboron acid salt of the formula $M'_2(B_nH_{n-p-q}X_pY_q)_m$ (1) wherein M' is a silver (I) or cerium (III) cation, X is halogen; Y is a hydroxyl group, or a hydrocarbyloxyalkoxy or hydrocarbylcarbonyl group free of aliphatic unsaturation and containing at most 12 carbon atoms; n is 10 or 12; p is 1 to 12 and is equal to n minus q when q is greater than zero; q is 0 to 2, p + q being at most equal to n; and M' is the valence of M' ; (when p is greater than 1, the halogens represented by X may be the same or different);

B. a halide promoter in which the halogen is chlorine, bromine or iodine and which is dissociable by actinic light of wavelength between 2,500 Å; and 7,000 Å; and

C. at least one substance capable of undergoing cationic polymerization is cationically polymerized on exposure to actinic light having a wavelength in the range 2,500 to 7,000 Å. Thus, in carrying out the process in the instant invention any liquid photosensitive composition capable of being photopolymerized or photocured or both upon exposure to actinic radiation to a solid polymer is operable in the process of the instant invention to form a relief printing plate.

Another liquid photocurable composition useful to form printing plates by the process of this invention is that set out in French U.S. Pat. No. 1,471,432. Generally, liquid photosensitive compositions disclosed in this patent comprise as essential constituents, an unsaturated polyester, an ethylenically unsaturated monomer leading itself to a reaction of additional polymerization, and a photosensitizer. The unsaturated polyester may be produced from an alcohol monomer containing at least a polyol comprising at least 5 ether-oxygen radicals linked to carbon atoms in its main chain and not having more than 3 carbon atoms between the ether-oxygen radicals, and a monomer of acidic character containing at least an unsaturated dicarboxylic acid and/or one of its derivatives.

The liquid photosensitive compositions to be converted to printing plates may if desired, include such additives as antioxidants, accelerators, dyes, inhibitors, activators, fillers, pigments, antistatic agents, flame-retardant agents, thickeners, thixotropic agents, surface active agents, light scattering agents, viscosity modifiers, extending oils, plasticizers, detackifiers and the like. Such additives are usually preblended with the monomer or compound to be photopolymerized or with the polyene or polythiol prior to or during the compounding step. Operable fillers include natural and synthetic resins, carbon black, glass fibers, wood flour, clay, silica, alumina, carbonates, oxides, hydroxides, silicates, glass flakes, glass beads, borates, phosphates, diatomaceous earth, talc, kaolin, barium sulfate, calcium sulfate, calcium carbonate, antimony oxide and the like. The aforesaid additives may be present in quantities up to 500 parts or more per 100 parts polymer by weight and preferably about 0.005 to about 300 parts on the same basis. Each additive must be present in an amount which will not interfere with or inhibit the necessary photocuring or photopolymerization image-producing reaction or other required steps in the plate making process.

The support to which the photosensitive composition is adhered may be formed from various materials such as rubber, plastic, paper, glass, metal and the like. The support is preferably a plastic having the characteristics of being flexible,

adherable to the photosensitive composition on exposure to actinic radiation or by other means and capable of transmitting a substantial amount of the radiation therethrough. The thickness of the support is dependent on its relative strength and dimensional stability to hold a specified thickness of the photosensitive composition and may be empirically determined by one skilled in the art. For example when an oriented polyethylene terephthalate in film form sold under the tradename "Mylar" is employed as the support and a 20 mil relief is desired, the "Mylar" film will have a thickness of about 1 to 10 mils. Non-actinic radiation transmitting metal plates such as aluminum for the same thickness of photosensitive composition usually have a thickness of about 1 to 8 mils.

The photosensitive reaction may be initiated by actinic radiation from sunlight or from special light sources which emit significant amounts of actinic light suitably in the wavelength range of 2,500–7,000 Å. For liquid photosensitive compositions it is preferred that the light emanate from a point source or in the form of parallel rays. However, divergent beams are also operable under certain circumstances as a source of actinic light in the instant invention. Thus it is possible merely to expose the liquid photosensitive composition to actinic radiation, preferably in the range 3,000–4,000 Å, under ambient conditions or otherwise and obtain a solid elastomeric or resinous product useful as a printing plate material after development. Additionally, in liquid photosensitive compositions which are photocured, chemical photoinitiators or sensitizers such as benzophenone, acetophenone, acenaphthene-quinone, methyl ethyl ketone, thioxanthene-9-one, Xanthene-9-one, 7-H-Benz [de] anthracene-7-one, dibenzosuberone, 1-naphthaldehyde, 4,4'-bis(dimethylamino) benzophenone, fluorene-9-one, 1'-acetoneaphthone, 2'-acetoneaphthone, 2,3-butanedione, anthraquinone, 1-indanone, 2-tert-butyl anthraquinone, valerophenone, hexanophenone, 8-phenylbutyrophenone, p-mor pholinopropiophenone, 4-morpholinobenzophenone, 4'-morpholinodeoxybenzoin, p-diacetylbenzene, 4-aminobenzophenone, 4'-methoxyacetophenone, benzaldehyde-tetralone, 9-acetylphenanthrene, 2-acetylphenanthrene, 10-thioxanthene, 3-acetylphenanthrene, 3-acetylindole 1,3,5-triacetylbenzene, etc. and blends thereof, to greatly reduce the exposure times and thereby when used in conjunction with various forms of energetic radiation yield very rapid, commercially practical cures. The curing rate accelerators are usually added in an amount ranging from about 0.0005 to about 10 percent by weight of the photocurable composition.

Curing inhibitors or retarders operable in the instant invention include but are not limited to hydroquinone; P-tertbutyl catechol; 2,6-ditert-butyl-p-methylphenol; phenothiazine and N-phenyl-2-naphthylamine.

The thickness of the layer of the liquid photosensitive composition employed depends on the thickness desired in the relief image and on the alignment between the relief figures. That is, if the printing areas are closely aligned less relief is necessary than if the printing areas are further apart. This is to assure that the non-printing areas are not contacted with the surface of the material on which the printing is to occur. In the case of photosensitized half-tones formed from the process of the instant invention, the screening used must be taken into consideration when selecting the proper thickness. In general, the thickness of the layer to be solidified and employed as a printing plate may vary from 3 to 250 mils or more. For letter-set (dry offset) plates, the thickness may be customarily in the 3 to 25 mil range; for letterpress printing, thicknesses of 10 to 500 mils are common. For letterpress newspaper or magazine printing plates, the thickness of the photosensitive layer will be about 10 to about 50 mils. Thicker layers are sometimes employed for the flexographic printing of designs and relatively large areas with letterpress printing plates.

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

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

EXAMPLE 2

A liquid photocurable composition was prepared by mixing 102.3 g. of Polymer A from Example 1 herein, 7.7 g. of pentaerythritol tetrakis (α -mercaptopropionate), 1.5 g. benzophenone and 0.1 g. of 2,6-ditertiary-butyl-methyl phenol. The mixture was heated to 80° C. to dissolve the benzophenone and produce a clear homogeneous mixture. A suitable mold for making a printing plate was prepared using a 4 mil thick "Mylar" film as a support edged on two sides with a 20 mil thick rubber electric tape thereby forming a frame or mold to partially contain the liquid curable polymer. The mold was leveled on an adjustable flat table and the liquid photocurable composition at a temperature of 80° C. was poured into the mold along an edge of the frame and distributed evenly throughout the mold by means of a doctor blade to form a printing plate of 20 mil thickness on top of the 4 mil Mylar support. Shims were placed at the top of the edge of the mold and a test negative of a combination of an 85 line halftone, standard type and reverse type, 65 line gray scale and a solid area under a glass plate was placed on top of the shims leaving an air gap of 7-12 mils between the surface of the liquid curable composition and the test negative. The photocurable composition was exposed through the negative to light from a 4,000 watt Ascorlux pulsed xenon arc printing lamp commercially available from American Speed Light Co. placed 26 inches above the plate. The exposure was for about 2 minutes during which time the liquid photocurable composition gelled in the image areas. The non-image areas remained a liquid essentially of the same viscosity as prior to exposure.

The photocured printing plate was transferred to an aqueous bath at 180° F. containing 10 percent of a detergent commercially available under the tradename "Liqui-nox" from Alconox Inc., New York, New York. The bath was ultrasonically activated to produce cavitation in the bath by means of 3 transducers (each 1 kilowatt) on the bottom of the bath connected to separate generators, each energized at about 20 kc/sec. After 6¼ minutes in the bath, the printing plate was removed therefrom. The resultant etched plate was completely clear of uncured liquid polymer and had a solid relief image of 20 mils in depth in the exposed photocured areas of the plate. The relief was sharp with complete recesses in the bowls of letters such as o, p, etc. and the image areas had smooth surfaces and shoulders. The glossy plate was inked and employed in letterpress printing on a Davidson Press Model 816 manufactured by Davidson Corp., Chicago, Ill. The lines were distinct and separate and the dots in the halftone area had excellent definition.

A control run using the reactants and procedure set out herein as in Example 2 except that the bath was not ultrasonically activated resulted in substantially no etching or removal of uncured polymer after 30 minutes immersion in the bath.

EXAMPLE 3

Example 2 was repeated except that the detergent added to the bath consisted of 3 percent ethylene glycol and 5 percent by weight of a commercially available detergent sold under the tradename "Liqui-Nox" commercially available from Alconox Inc., New York, New York and the bath was maintained at 170° F. The resultant etched plate was completely free of uncured liquid polymer and had a solid relief image of 20 mils in depth in the exposed photocured areas of the plate within 6 minutes. The plate was inked and printed resulting in distinct and separate lines and excellent definition of the dots in the halftone area.

EXAMPLE 4

Example 2 was repeated except that the detergent in the bath consisted of 1 percent "Liqui-Nox" commercially available from Alconox Inc., New York, New York and 1 percent "D-Lite" commercially available from DuBois Chemicals, Cincinnati, Ohio and the bath was maintained at 170° F. After 7 minutes the plate was completely etched, free of uncured polymer and had a solid relief image, 20 mils in depth in the exposed photocured areas. The relief was well defined with complete recesses in the letters. The plate was inked and printed and a clear image of distinct and clear lines and excellent definition of the dots was transferred to the paper.

EXAMPLE 5

Example 2 was repeated except that the detergent consisted of 5.6 percent by weight of "New Score" commercially available from Economics Laboratory, Inc., New York, New York and 5 percent "Liqui-Nox" and the bath was maintained at 180° F. After 5 minutes the resultant etched plate was completely free of uncured polymer and had a solid relief image of 20 mils in depth in the exposed photocured areas of the plate. The plate gave excellent copies when used on the Davidson Press Model 816.

EXAMPLE 6

Example 2 was repeated except that the detergent in the bath was 2.5 percent by weight of a commercially available detergent sold under the tradename "D-Lite" commercially available from DuBois Chemicals, Cincinnati, Ohio and the bath was maintained at 170° F. After 1 minute and 35 seconds, the etched plate was substantially completely free of uncured polymer and had a solid relief image with the main bodies of the letters penetrating to the support. The plate gave excellent copies when used on the printing press.

EXAMPLE 7

Example 2 was repeated except that the detergent in the bath was 0.5 percent by weight of a detergent formed of 59 parts by weight of sodium metasilicate pentahydrate, 19 parts by weight of sodium tripolyphosphate, and 9 parts by weight of linear dodecyl benzene sulfonate (commercially available under the trademark Santomerse 85-B by Monsanto Chemical Co.) The bath was maintained at about 170° F. After about 1 minute and 15 seconds, the etched plate was substantially completely free of uncured polymer and had a solid relief image with the main bodies of the letters penetrating to the support. The plate gave excellent copies when used on the printing press.

EXAMPLE 8

A liquid photocurable composition was prepared by mixing 102.3 g. of Polymer A from Example 1 herein, 7.7 g. of pentaerythritol tetrakis (β -mercaptopropionate), 1.5 g. benzophenone and 0.1 g. of 2,6-ditertiary-butyl-methyl phenol. The mixture was heated to 70° C. to dissolve the benzophenone and produce a clear homogeneous mixture. A sheet of "Mylar" 4 mil thick film was placed on an adjustable

flat table and a portion of the photo-curable composition at a temperature of 70° C. was poured on the "Mylar" support. The liquid photocurable composition was distributed evenly over the support by means of a doctor blade to a uniform thickness of 20 mils on top of the 4 mil "Mylar" support. Shims were placed around the edge of the support to maintain an air gap of 12 mils between the surface of the liquid curable composition and a test negative of a combination of an 85 line halftone, standard type and reverse type, 65 line gray scale and a solid area. The negative was adhered to a glass plate to maintain it parallel to the surface of the liquid photocurable composition. The photocurable composition was exposed through the glass plate and negative to light from an 8,000 Ascorlux pulsed xenon arc printing lamp commercially available from American Speed Light Co. placed 54 inches above the plate. The exposure was for about 2 minutes during which time the liquid photocurable composition solidified in the image areas. The non-image areas remained a liquid essentially of the same viscosity as prior to exposure to actinic light.

The photocured printing plate was back exposed and cured through its "Mylar" support by a 9 lamp bank of GEF24T12 black light high output tubes at a distance of 21 inches therefrom for about 15 seconds to more firmly adhere the photosensitized composition to the support and form a solid 1 mil layer of the photosensitized composition on the support.

The photocured printing plate with a latent image thereon was transferred to an aqueous bath maintained at 170° F. containing 2 percent weight of a commercially available detergent sold under the tradename "DuBois TK" by DuBois Chemical Co., Cincinnati, Ohio. The bath was ultrasonically activated to produce cavitation in the bath by means of 3 transducers (each 1 kilowatt) on the bottom of the bath connected to separate generators, each energized at about 21 kc/sec. After 1½ minutes in the bath, the printing plate was removed therefrom. The resultant etched plate was completely clear of uncured liquid polymer and had a solid relief image of 20 mils in depth in the exposed photocured line image areas of the plate. The relief was sharp with complete recesses in the bowls of letters such as o, p, etc. and the image areas had smooth surfaces and shoulders. To further harden the image and prepare it for printing, the plate was post cured for 2 minutes at a distance of 3 inches from a 4,000 watt Ascorlux pulsed xenon arc printing lamp commercially available from American Speed Light Co. Thereafter the glossy plate was inked and employed in letterpress printing on a Davidson Press Model 816 manufactured by Davidson Corp., Chicago, Illinois. The lines were distinct and separate and the dots in the halftone area had excellent definition.

The printing plates etched by the instant invention can be employed in various types of printing plates including, but not limited to intaglio printing, lithographic printing, letterpress printing, dry offset printing, flexographic printing and the like.

The various elements of the present apparatus unless otherwise indicated, may be secured to adjoining elements by any suitable means such as bolts, welding, rivets or the like. In addition, auxiliary support or reinforcement members may also be included as part of the apparatus where required.

Although a preferred embodiment of the invention has been illustrated herein, it is to be understood that various changes and modifications may be made in the construction and arrangement of elements without departing from the spirit and scope of the invention as defined.

What is claimed is:

1. A method of etching a printing plate formed of a photocurable polymeric composition comprising (1) a polyene containing at least two reactive unsaturated carbon to carbon bonds per molecule, (2) a polythiol containing at least two 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) a curing rate accelerator, which composition has been exposed to actinic light projected through an image bearing, line or halftone, positive or negative transparency consisting solely of substantially opaque and substantially transparent areas until substantially complete photocuring takes place in the exposed areas and substantially no photocuring takes place in the non-exposed areas which comprises, immersing said plate formed of a photocurable polymeric composition in an etching bath containing a liquid maintained at a temperature sufficient to keep the non-image area of the plate in the liquid or molten phase, energizing the etching bath by means of ultrasonic energy to a degree necessary to cause cavitation and removal of substantially all of the unexposed non-image area, washing the etched polymeric printing plate by means of a water spray, and air drying the water washed polymeric printing plate in a current of heated air.

2. The method of claim 1 wherein the ultrasonic energy level of the bath varies between about 18 to about 40 kilocycles.

3. The method of claim 1 wherein the curing rate accelerator is selected from the group consisting of benzophenone, acetophenone, acenaphthenequinone, methyl ethyl ketone, dibenzosuberone, thioxanthene-9-one, xanthene-9-one, 7-H-benz anthracene-7-one, fluorene-9-one, 1-indanone, and mixtures thereof.

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