

July 30, 1974

S. I. SCHLESINGER

3,826,650

EPOXY PHOTOPOLYMER DUPLICATING STENCIL

Filed Aug. 25, 1972

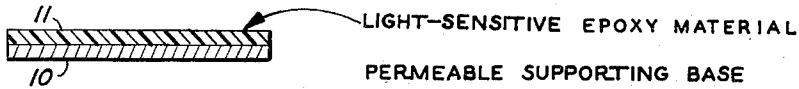


Fig-1

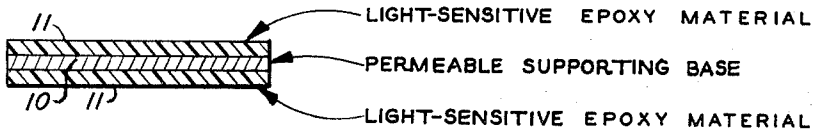


Fig-2

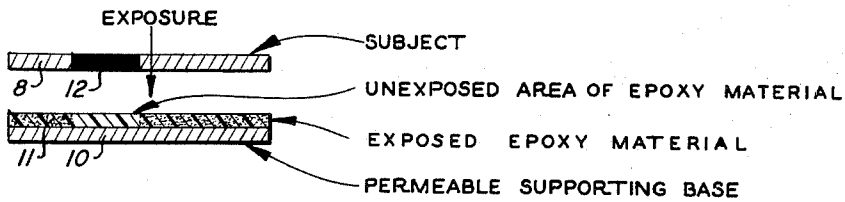


Fig-3

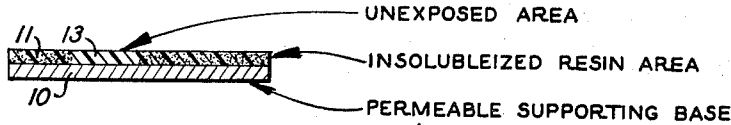


Fig-4

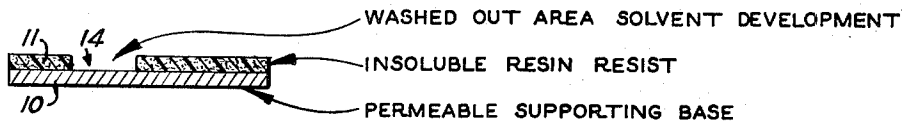


Fig-5

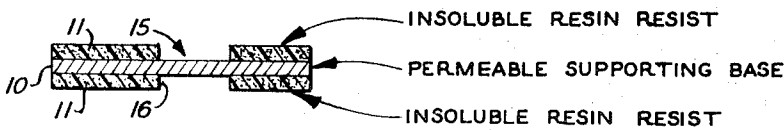


Fig-6

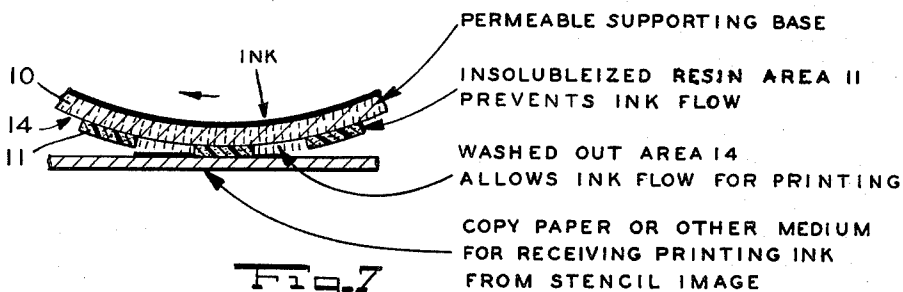


Fig-7

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EPOXY PHOTOPOLYMER DUPLICATING STENCIL

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Continuation-in-part of application Ser. No. 753,869, Aug. 20, 1968, now Patent No. 3,708,296, dated Jan. 2, 1973. This application Aug. 25, 1972, Ser. No. 283,629

The portion of the term of the patent subsequent to Jan. 2, 1990, has been disclaimed

Int. Cl. G03c 1/70

U.S. Cl. 96—35.1

19 Claims

ABSTRACT OF THE DISCLOSURE

A stencil is prepared from a support such as paper, silk or nylon, metal or metal coated material which is coated with an epoxy-diazonium composition, the surface of the material is exposed to an energy source, preferably actinic radiation, in an image wise manner to effect polymerization of said composition and unpolymerized composition is removed, preferably by washing with a solvent.

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of my pending application Ser. No. 753,869, filed Aug. 20, 1968, now U.S. Pat. 3,708,296, issued Jan. 2, 1973.

BACKGROUND OF THE INVENTION

Duplicating paper or the like has been cut, die-impressed and embossed in the preparation of stencils for use on mimeograph and other types of duplicating machines. Further, an electrolytic method of marking metals through a die-impressed pressure sensitive resist or engraved plastic resist has been widely accepted by the metal marking industry and is now preferred in contrast to the older methods utilizing steel die stamps, acid and ink stamps, and pantograph or engraving tools. Such electrolytic method has utilized a die-impressed pressure-sensitive paper stencil which has been reinforced with various types of synthetic or natural resins and waxes adapted to be readily displaced by pressure rolling or by impact against electrolyte or etched plates. After die-impressing, a liquid marking medium which may be either an ink or an electrolytic fluid, for example, is then applied to the stencil sheet and will pass through the porous fibrous layer where thus exposed and mark an underlying work surface accordingly.

Stencils of the type above discussed are very convenient of use and give satisfactory results when first employed. They are, however, not very long-lived and the results obtained from any one stencil tend to become less and less satisfactory until the stencil must eventually be discarded. Many interested in the stencil problem has attempted to solve it through the technique of applying water soluble colloids containing photosensitive compounds to a supported porous member. After the coating has dried, a photonegative or a photopositive transparency is placed in contact with the coating, and by exposure to a proper light source, some curing of the light exposed coating may be caused to take place. The unexposed area may then be washed out with water and the exposed area treated in a hardening solution.

It will be appreciated that while the techniques described above have certain advantages, they have certain features which are not good for the instant purposes. Colloidal proteins which have been light sensitized with bichromates produce fairly well-defined copy but since they are hydrophilic they never become truly water impermeable but will imbibe water (including electrolytes) and thus serve as electrical conductors. This renders them un-

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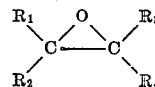
suitable for electrolytic and other types of stencil work. There is a continued need for stencils that are devoid of the problems discussed and for methods for their preparation.

SUMMARY OF THE INVENTION

The present invention relates to novel duplicating stencils and their preparation from coating materials which include a polymerizable epoxy monomer and a photosensitive catalyst.

This invention relates then to the use of a process for polymerizing epoxy monomers and more particularly to a process for effecting the photopolymerization of epoxy monomers by use of organic compounds which are photosensitive and release an active catalyst upon application of energy. This material is used as a coating material to produce a stencil.

The term epoxy monomer or prepolymer in the description of this invention includes any molecule containing one or more 1,2-epoxy or oxirane rings, whether the molecule consists of a small grouping of atoms or of a chain of repeating units as in commercial resins. Thus, this invention includes the treatment of commercial epoxy resins, sometimes referred to as prepolymers, which consist of smaller molecular units which have been linked together to give longer chains with pendant epoxy groups which are capable of further polymerization. All of the epoxy compounds treated in the present invention regardless of whether they are referred to as monomers, resins or prepolymers will contain the 1,2-epoxy or oxirane ring structure



which will be identified hereinafter as an epoxy ring and where R_1 , R_2 , R_3 , and R_4 can be alkyl, aryl, alkoxy, alkenyl, halogen and hydrogen.

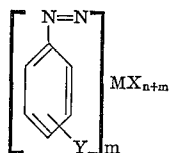
In order to effect the polymerization of the above defined monomers, it is necessary to open the epoxy ring through cleavage of a carbon-oxygen bond. A reactive intermediate is then formed, which can subsequently open up another epoxy ring. This reaction may repeat itself many times in a chain reaction to form a polymer of repeating ether units.

The method of the present invention proposes the use of novel aryldiazonium compounds as photosensitive agents, which upon exposure to an energy source, such as radiation or electron beam scanning, releases an active catalyst which initiates the polymerization of epoxy monomers to produce epoxy polymers. However, many of similar such photosensitive compounds proposed by the prior art, for example aryl diazonium fluoroborates, tend to be chemically unstable resulting in disadvantages of extremely short pot life and being potentially explosively hazardous. It has been discovered herein that the catalyst activity and resulting usefulness of aryldiazonium compounds cannot be determined on a random basis. Moreover, it has been unexpectedly discovered that many aryldiazonium compounds do not possess the requisite properties necessary to catalyze the wide variety of epoxy monomers previously defined herein. Accordingly, it is desirable to identify and discover new and improved epoxy monomer catalyzing agents useful in the photopolymerization process which are not subject to and overcome the deficiencies now existing in the art.

Accordingly, a new and improved class of aryldiazonium compounds has been discovered which upon admixture with an epoxy monomer or prepolymer followed by application to a stencil and subsequent exposure to an

energy source release an active catalyst which effects the polymerization of the epoxy monomer. This new class of photosensitive compounds possess the properties of increased speed and efficiency in catalyzing polymerization and in yielding epoxy polymers which possess inherent superior toughness, abrasion resistance, and resistance to chemical attack.

The photosensitive latent curing agents utilized in accordance with the present invention may be classified as aromatic diazonium salts of a complex anion, this anion being selected from the group consisting of haloantimonates, haloarsenates, halobismuthates, haloferrates, halostannates and halophosphates wherein each halogen atom is a lower atomic weight halogen selected from the group consisting of fluorine and chlorine, the latent curing agent initially having had substantially no application of energy thereto. The preferred photosensitive compounds of the present invention can be defined by the following formula:



where MX_{n+m} is a halogen containing complex anion selected from the group consisting of hexachlorostannate IV, tetrachloroferrate III, hexafluorophosphate, hexafluoroarsenate V, hexachloroantimonate V, hexafluoroantimonate V and pentachlorobismuthate III; and Y is selected from at least one of the group consisting of nitro, halogen, N-morpholino, alkyl, alkoxy, aryl, amino, arylamino, alkylamino and arylmercapto and arylthio radicals, indicating the variety of substituted aryl compounds which may carry the diazonium group forming the cation in the photosensitive aromatic diazonium salts having the formula shown above. In the above formula it will be understood that n is equal to the oxidation state of the element M and m is equal to the number of halogen atoms which are given up upon application of energy such as actinic radiation to yield a Lewis acid, m thus being the number of diazonium groups in the diazonium salt as determined by the net charge on the complex anion (MX_{n+m}).

Specific examples of photosensitive compounds which can be used in the present invention include:

p-nitrobenzenediazonium hexafluorophosphate
 o-nitrobenzenediazonium hexafluorophosphate
 2,5-dichlorobenzenediazonium hexafluorophosphate
 p-N-morpholinobenzenediazonium hexafluorophosphate
 2,5-diethoxy-4-(p-tolyl) benzenediazonium hexafluorophosphate
 2-chloro-4-(dimethylamino)-5-methoxybenzenediazonium hexafluorophosphate
 2,5-diethoxy-4-(p-mercapto) benzenediazonium hexafluorophosphate
 2,5-dimethoxy-4-N-morpholinobenzenediazonium hexafluorophosphate
 4-(dimethylamino)-naphthalene diazonium hexafluorophosphate
 2,5-diethoxy-4-ethoxyphenylbenzenediazonium hexafluorophosphate
 2,5-diethoxy-4-(p-tolyl) benzenediazonium hexafluoroarsenate
 p-nitrobenzene diazonium hexafluoroarsenate
 p-N-morpholinobenzenediazonium hexafluoroarsenate
 2,5-diethoxy-4-(p-tolyl) benzenediazonium hexafluoroantimonate

2,4-dichlorobenzenediazonium hexachloroantimonate
 p-nitrobenzene diazonium hexafluoroantimonate
 p-N-morpholinobenzenediazonium hexafluoroantimonate
 2,5-dichlorobenzenediazonium hexachloroantimonate
 2,5-dichlorobenzenediazonium hexafluoroantimonate
 2,4-dichlorobenzenediazonium pentachlorobismuthate III
 o-nitrobenzenediazonium pentachlorobismuthate III
 2,4-dichlorobenzenediazonium tetrachloroferrate III.

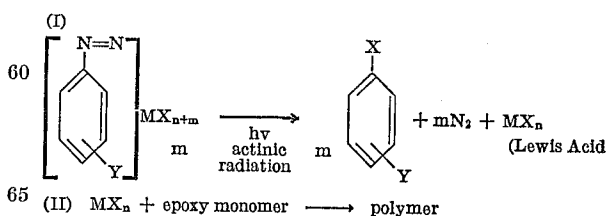
The diazonium compounds of the present invention may be prepared from procedures known in the art and such preparation forms no part of the present invention. Thus the chlorometallic complexes may be prepared for example in accordance with the method set forth by Lee et al. in *Journal of the American Chemical Society*, 83, 1928 (1961). Diazonium hexafluorophosphates can be prepared by diazotizing the corresponding aniline with $NOPF_6$, an $HCl-NaNO_2$ combination with subsequent addition of HPF_6 or a PF_6^- salt, or by addition of such a hexafluorophosphate salt to another diazonium salt to effect precipitation. The N-morpholino complexes can be prepared either from the aniline derivative or by adding an aqueous solution of the desired inorganic complex salt to a solution of p-N-morpholinobenzenediazonium fluoroborate.

The epoxy monomers which can be employed in the present invention can be defined by the following formula:



where R_1 , R_2 , R_3 , and R_4 can be alkyl, aryl, alkoxy, alkenyl, halogen and hydrogen. Specific examples of such monomers include, but are not limited to, ethylene oxide and homologues thereof; glycidic and glycidyl esters; glycidyl (2,3-epoxypropyl) methacrylates, acrylates and crotonates; and allyl glycidyl ethers. Additionally, commercial synthetic resins as heretofore defined can be employed. Examples of such resins can be those derived from the diglycidyl ether of bisphenol A, epoxidized polyolefins and epoxyated novolacs. Combinations of the above epoxies may be used and additionally they may be in solid or liquid form. Such epoxies may preferably also include the copolymer of glycidyl methacrylate and allyl glycidyl ether prepared as disclosed in the Schlesinger et al. copending application Ser. No. 297,829, filed Oct. 16, 1972 entitled "Copolymer of Glycidyl Methacrylate and Allyl Glycidyl Ether and Polymerization Thereof" the disclosure of which is incorporated herein by the foregoing reference.

The overall reaction which occurs in carrying out the present invention can be depicted by the following equations:



where MX_{n+m} is a complex anion as defined previously, and Y is as defined previously. It will be seen that in equation I, exposure of the particular aryl diazonium photosensitive compound of the present invention produces a Lewis Acid represented by the formula MX_n . By Lewis Acid is meant an electron pair acceptor such as PF_5 , $FeCl_3$, AsF_5 , SbF_5 , $SnCl_4$ and $BiCl_3$. The Lewis Acid produced in equation I initiates or catalyzes the

photopolymerization process depicted in equation II, wherein the epoxy monomer is polymerized as the result of the action of applied energy. While not essential to the functioning of the present invention, it is believed that certain intermediates such as carbonium ions are formed during photolysis of the diazonium compound which aid in the polymerization reaction.

A general application of the process embodied by equations I and II in the preparation of a stencil can be as follows: a diazonium compound, as heretofore defined, is admixed, with or without the use of a suitable solvent, with an epoxy monomer. The mixture is thereafter coated on a suitable substrate to prepare a stencil. After evaporating solvent which may be present, the stencil is exposed, for example, to ultraviolet light through a mask or negative. When the light strikes the stencil the diazonium compound decomposes to yield a catalyst in the form of a Lewis Acid which initiates the polymerization of the epoxy monomer. The resulting polymer is resistive to most solvents and chemicals in the exposed areas. The unexposed areas can be washed away with suitable solvents to leave a reversal image in the form of an epoxy polymer which produces the stencil design. With certain solventless liquid epoxies, however, it is possible to remove the unexposed material by blotting away the liquid. That is, the unexposed liquid epoxy may be removed from the exposed (now solid) epoxy resin by pressing between absorbent sheets.

The energy source required for effective decomposition of the latent catalysts employed in the invention may be energy applied by bombardment with charged particles, notably by high-energy electron beam irradiation. In such an application of energy, the electron beam is used as a "pen" to scan the desired pictorial or alphanumeric information on the epoxy layer after which development and processing is the same as when electromagnetic radiation is the energy source. However, the catalyst precursors described hereinbelow are primarily photosensitive and the required energy is preferably imparted by actinic irradiation which is most effective at those regions of the electromagnetic spectrum at which there is high absorption of electromagnetic energy by the particular catalyst precursor used. More than one of these types of energy may be applied to the same system: e.g. ultraviolet light followed by electron beam irradiation, etc. The preferred energy, actinic radiation, can be any produced by any suitable source such as a mercury, xenon, carbon arc or tungsten filament lamp. The only limitations placed on the type of instrumentation used is that it must have a frequency range and energy level sufficient to impart to the monomer or prepolymer system energy at a high enough intensity to reach the decomposition level of the photosensitive compounds. Table I below lists some of the photosensitive compounds of the present invention including absorption maxima in acetonitrile.

TABLE I

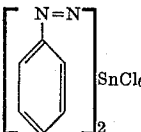

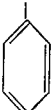
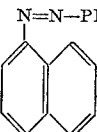
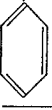

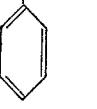
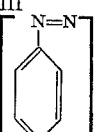
Complex type	Ring substituents	Decomposition melting point, ° C.*	Absorption maxima, μ **
Hexachlorostannate, IV 	2,4-dichloro.....	190	285
	p-Nitro.....	126	258, 310
Tetrachloroferrate, III 	2,4-dichloro.....	62-64	259, 285, 360
	p-Nitro.....	98-95	243, 257, 310, 360
	p-N-morpholino.....	121.5	240, 267, 313, 364

TABLE I—Continued

Complex type	Ring substituents	Decomposition melting point, ° C.*	Absorption maxima, μ **
5 Hexafluorophosphate 	p-Chloro.....	162-164	273
	p-Nitro.....	156	258, 310
	p-(N-morpholino)....	162	377
	2,4,6-trichloro.....	240-250	294, 337
	2,4,6-tribromo.....	237-250	306
	2,5-dimethoxy-4-(p-tolyl).....	167	210, 405
	2,5-diethoxy-4-p-tolylmercapto, 2,5-dimethoxy-4-N-morpholino, 2,5-diethoxy-4-p-ethoxyphenyl.....	147	247, 400
	2-chloro-4-dimethylamino-5-methoxy, o-Nitro.....	135	266, 396
	2,5-dimethoxy-4-chloro, 2,5-dimethoxy-4-p-tolylmercapto, 2,4-dimethyl-6-nitro, 2-nitro-4-methyl, 2-methyl-4-nitro.....	136	265, 415
	111	273, 405	
15 Hexafluorophosphate	4-dimethylamino....	148	280, 310, 410
			
25 Hexafluoroarsenate, V	p-Nitro.....	141-144	257, 310
	p-(N-morpholino)....	162	257, 378
30 	p-Nitro.....	140-141	257, 308
	2,5-dichloro.....	161-162.5	238, 358
35 Hexafluoroantimonate, V	p-(N-morpholino)....	163	254, 374
			
40 Hexachloroantimonate, V	2,4-dichloro.....	178-180	282, 322
			
45 Pentachlorobismuthate, III	2,4-dichloro.....	193.5-195	285, 313
	O-nitro.....	166.5	285, 313
50 			

*By capillary tube method. Higher melting points can be obtained in differential thermal analysis apparatus under nitrogen.

**In acetonitrile.

The procedures for admixing the photosensitive compounds of the present invention with epoxy monomers are relatively simple and can be carried out in the following manner. An epoxy monomer, resin or prepolymer as heretofore defined containing oxirane groups is combined with a photosensitive aryldiazonium compound of the present invention. Suitable inert solvents may be employed if desired in effecting this mixture. By a suitable inert solvent is meant one that does not react appreciably with the monomer or the aryldiazonium compound before exposure to actinic radiation. Examples of such solvents include acetone, methyl benzoate, acetonitrile, butyronitrile, benzonitrile, toluene, o-chlorotoluene, xylene, methyl ethyl ketone, cellosolve ether, monochlorobenzene, tri-

chloroethylene, anisole, tetrachloroethane, o - dichlorobenzene, and propylene carbonate. Mixtures of these solvents have been found useful in the present invention. Furthermore, a liquid epoxy may serve as solvent for another epoxy, liquid or solid in nature. It is to be understood, however, that the use of solvents is not mandatory in carrying out the present invention. The exact amount of solvent necessary will depend upon the particular photosensitive compound employed. However, the solvent is used in sufficient quantity to dissolve both the aryldiazonium compound and the epoxy monomer.

Table II below summarizes some of the epoxy compounds treated by the above process.

TABLE II

Epoxy	Type	Average molecular weight	Epoxy equivalent weight
Dicyclopentadiene dioxide.	Alicyclic monomer	162.2	81.1
Glycidyl methacrylate allyl glycidyl ether copolymer.	Polyvinyl epoxy prepolymer.		
Ciba araldite 6084 ¹	Bis-phenol-A glycidyl ether polymer.	875-1,025	
Ciba ECN1273 ¹	Epoxy-cresol novolac	1,820	225
Ciba ECN1299 ¹	do	1,270	235
Shell Epon 1009 ² (with 10% Ciba ECN1299).	Bis-phenol-A glycidyl ether polymer.		2,500-4,000

¹ Sold commercially by Ciba Pharmaceutical Products, Inc., Summit, New Jersey.

² Sold commercially by Shell Chemical Corporation, New York, New York.

The epoxy compounds listed in Table II illustrate the variety of epoxy compounds suitable for use in the present invention; however, the epoxy compounds listed in the above table are by no means limiting. Further, as illustrated hereinbelow, the epoxy compound may be solid or liquid.

The amount of photosensitive compound employed in the admixture need not be specifically ascertained but is generally related to the amount of epoxy monomer being polymerized. It has been found that quite satisfactory results are obtained by using from about one to about ten parts by weight of aryldiazonium compound to each one hundred parts by weight of the dry epoxy monomer. Additionally, the photosensitivity of the diazonium compound, and hence the speed of photopolymerization may be further enhanced by the inclusion of certain photosensitizers known in the art of the chemistry of diazonium compounds. Among such sensitizers, but not limited to these, are anthraquinone, 1-chloroanthraquinone, primuline, acenaphthylene, naphthalene and anthracene.

DETAILED DESCRIPTION OF THE INVENTION

To the accomplishment of the foregoing and related ends, said invention then comprises the features herein-after fully described and particularly pointed out in the claims, the following description and the annexed drawings setting forth in detail certain illustrative embodiments of the invention, these being indicative, however, of but a few of the various ways in which the principle of the invention may be employed.

In the drawing:

FIG. 1 diagrammatically illustrates the layer of permeable supporting base material coated with a layer of a light sensitive epoxy monomer, prepolymer, or resin;

FIG. 2 diagrammatically illustrates such permeable material coated on both sides with layers of such epoxy material;

FIG. 3 shows the manner in which such material may be exposed to light passing through an appropriate negative to produce exposed and unexposed areas;

FIGS. 4 and 5 illustrate the production of a finished stencil through solvent development;

FIG. 6 corresponds to FIG. 5 but with both sides of the permeable supporting base coated with the resin;

FIG. 7 schematically illustrates the duplicating stencil in operation.

Accordingly, an impervious film or layer of an epoxy monomer, prepolymer, or resin is employed on a sheet of pervious material such as Yoshino long fiber paper, such resin being photosensitive and rendered insoluble due to photochemical action upon exposure to light. The photosensitive epoxy containing material may be applied to one or both sides of such pervious material in a conventional manner, such as by whirl coating, weir coating or by roll coating on automatic equipment. It may be applied, for instance, simply by immersing the supporting medium therein and wiping off the surplus through fixed wiping bars. Conventional spraying techniques familiar in the paint industry may be employed, but this will ordinarily require that the pervious supporting medium be supported in an appropriate frame.

As exemplified in FIG. 1 of the drawing which is the preferred embodiment of the invention, the photosensitive coated material comprises a permeable supporting base 10 of sheet material such as Yoshino long fiber paper coated on one side with the preferred light sensitive epoxy containing material 11, or, alternatively as shown in FIG. 2, such permeable sheet material may be coated on both sides with the epoxy containing material as a film or layer 11. When the coated material of FIG. 1 is exposed to light passing through negative 8 having a light impermeable area 12, the coating 11 will include exposed and unexposed areas corresponding to the light transmitting and light impermeable areas of the negative. Thus, as shown in FIGS. 4 and 5, the unexposed region 13 remains soluble and may be washed out by appropriate solvent development as shown in FIG. 5 to expose the underlying permeable material 10 in a sharply defined area 14 forming the stencil design. Similarly, as shown in FIG. 6, when both sides of the thin permeable layer 10 have been coated with the epoxy containing material, the stencil design will be formed by solvent development of the unexposed regions 15 and 16 on directly opposite sides of permeable sheet 10. When both sides of sheet 10 are thus coated with the epoxy resist layers, it is especially important that sheet 10 be thin and of good light transmitting quality so that the epoxy material on the underside of the sheet will be exposed sufficiently to render the same insoluble. The epoxy material on the underside of the sheet will, moreover, in such cases likewise preferably be in the form of a relatively thin film.

Within the purview of the invention the epoxy containing material has been applied as a film as thin as the permeable sheet itself and up to a thickness of 0.01 inch. Ordinarily, the epoxy containing film should have a thickness of from about 0.0002 to 0.002 inch. The permeable supporting sheet will preferably be from 1/2 mil to 1 mil in thickness for the production of fine line stencils and from 1 to 3 mils in thickness for production of broad line stencils.

The following formulations and Examples are given to illustrate the instant invention:

EXAMPLE I

Formulation:

(a) Epoxy-cresol novolac (ECN 1299) having an average M.W. of 1270 and epoxy equivalent weight of 235 in 50% solution in monochlorobenzene	g	16.25
(b) Butyronitrile	ml	22.5
(c) p-Nitrobenzenediazonium hexafluorophosphate	g	0.225
(d) Monochlorobenzene	ml	17.5

A sheet of tissue paper was impregnated with the above solution. After drying, the impregnated paper was exposed through a transparency image and a half-tone to a Gates Raymaster lamp for two minutes and then developed in acetone. A reversed photoresist image of the copy was left on the paper. The image on the paper was duplicated by superimposing the stencil on a sheet of

ordinary paper and wiping over it with an aqueous dye solution. Thus a positive copy of the original was obtained.

EXAMPLE II

This example illustrates a preferred embodiment of the invention wherein the epoxy material is applied to one side of a permeable base material.

(a) Glycidyl methacrylate allyl glycidyl ether copolymer in a 60% solution of toluene	g	97
(b) Acetonitrile	ml	95
(c) p - Chlorobenzenediazonium hexafluorophosphate	g	2.91

The procedure of Example I was repeated employing the above formulation except that the paper was exposed for 30 seconds. The results obtained were the same as in Example I.

EXAMPLE III

Formulation:

(a) Bisphenol-A-glycidyl ether polymer having an epoxide equivalent of 250-400 in 50% toluene	g	30.5
(b) Butyronitrile	ml	50
(c) p-N-morpholinobenzene diazonium hexafluorophosphate	g	0.763

The above formulation was applied to one side of a sheet of paper and the coated paper exposed to actinic radiation through a positive transparency image employing the procedure of Example I. It is heated for 3 minutes at 100° C., prior to development. With the photopolymer stencil image thus prepared, the stencil is employed for duplicating with the photopolymer side held toward the copy medium. The paper side, held away from the copy medium is inked with the ink passing through the stencil spaces to print while the polymer coating prevents absorption in non-image areas of the stencil as illustrated in FIG. 7 of the drawing.

EXAMPLE IV

In this example no additional solvent was employed so that the epoxy containing monomers selected were of the liquid type.

Formulation:

- 20 parts by weight of an epoxy phenol novolak
- 6 parts by weight of bis (3,4-epoxy-6-methylcyclohexyl methyl) adipate
- 2 parts by weight of vinyl cyclohexene dioxide
- 4 parts by weight of an aliphatic glycidyl ether where the alkyl groups are predominantly C₈ and C₁₀.

To 20 parts by weight of this master batch was added 1 part of a 20% solution of p-chlorobenzene diazonium hexafluorophosphate in acetonitrile. The catalyzed formulation was applied to a stencil using a roller coater. The coated stencil was then exposed through a negative to a 360 watt high pressure mercury lamp at a distance of three inches for five seconds. The unexposed area was removed by passage through absorbent rollers to remove the unexposed liquid and copies were duplicated by passage of ink through these unexposed areas.

The following examples illustrate the use of electron beam as the energy source:

EXAMPLE V

Formulation:

- 75 g. of glycidyl methacrylate-allyl glycidyl ether copolymer
- 364.3 g. of butyronitrile
- 60.7 g. of o-chlorotoluene
- 3.75 g. of 2,5-diethoxy-4-(p-tolylmercapto) benzene diazonium hexafluorophosphate.

The above formulation was applied to aluminum coated paper. After drying, the coated sample was ex-

posed to a raster line scan pattern of an electron beam in a commercially available electron microprobe. With a beam potential of 20 kv., a charge of 10⁻⁸ coulombs/cm.² was used to effect insolubilization of the areas receiving the electron beam. After development as in Example I, the aluminum was removed from the unexposed areas by etching in 10% sodium hydroxide solution, thus yielding the stencil.

EXAMPLE VI

Formulation:

(a) Epoxy-cresol novolac (ECN 1299)	g	75
(b) Butyronitrile		364.3
(c) o-Chlorotoluene		60.7
(d) 2,5-diethoxy-4-(p-tolylmercapto) benzene diazonium hexafluorophosphate		3.75

The procedure of Example V was repeated employing the above formulation except that a charge of 10⁻⁶ coulombs/cm.² was employed to effect insolubilization of the areas receiving the beam. After development in trichloroethylene, the stencil was prepared as in Example VI.

By means of the present invention, excellent stencils may be produced using various substances as the supporting medium. Examples of such supports are paper, silk, glass fiber, nylon, rayon, acrylic resins, polyester resins, linen, cotton, wool, metal cloth, metal-coated paper, metal-coated fabrics etc. They should, of course, be selected to provide the proper uniform distribution of voids or interstices for passage of the marking material therethrough. Likewise, they should be selected to satisfactorily effect the desired application of the energy source and etching where such is desired.

The method of producing stencils is suitable for use with any copy which lends itself to photographing and from which a photonegative or photopositive transparency may be prepared. Where the number of copies desired is sufficient to justify, entire pages of print, for example, may be reproduced with excellent detail and stencils produced in accordance with the invention may readily be applied to the silk screen process. The new stencils are especially useful for employment with electrolytes for electrolytic etching and marking, particularly of metals. They have proved extremely wear-resistant, are not hydrophilic, and produce very sharp and definite outlines.

As stated in the above the stencil image is formed by washing the stencil sheet in a suitable developing solvent that will remove the material in the unexposed areas, but leave the exposed (polymerized) areas together with etching to remove metal in the unexposed areas where such are employed. Thus, the unpolymerized epoxy monomer is removed from areas corresponding to the printed matter. The image may be duplicated by the passage of ink through these areas of the stencil.

The developing solvent is not necessary if a liquid epoxy monomer system is used as in Example IV. In such a situation the unexposed area is removed by blotting to absorb the unexposed liquid monomer. With either technique, the development, i.e., solvent washing step can be eliminated if the ink chosen for the duplication process contains a solvent that would dissolve through the unexposed areas when the first few copies are printed.

While there have been shown and described particular embodiments of the invention, it will be obvious to those skilled in the art that various changes and modifications may be made therein without departing from the invention, and, therefore, it is aimed to cover all such changes and modifications as fall within the true spirit and scope of the invention.

What is claimed is:

1. A process for producing a stencil which comprises (1) applying a composition comprising a liquid epoxy monomer or prepolymer and an aromatic diazonium

salt of a complex anion, said anion being selected from the group consisting of haloantimonates, haloarsenates, halobismuthates, haloferrates, halostannates and halophosphates wherein each halogen is selected from the group consisting of fluorine and chlorine to a permeable base substrate;

(2) exposing at least a portion of said composition to electromagnetic or electron-beam irradiation through an article having opaque and transparent areas, to effect polymerization and to render the exposed areas of said composition insoluble;

(3) removing said unexposed areas of said liquid composition to produce the stencil design.

2. The process of claim 1 wherein said composition contains from about 1 percent to about 10 percent by weight of photosensitive aromatic diazonium salt based on the dry weight of the epoxy monomer.

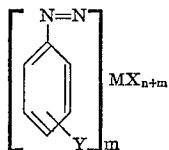
3. The process of claim 1 wherein said aromatic diazonium salt is a halophosphate.

4. The process of claim 3 wherein said halophosphate is hexafluorophosphate.

5. The process of claim 1 wherein said irradiation is electromagnetic radiation.

6. The process of claim 1 wherein said irradiation is electron beam irradiation.

7. A process for producing a stencil which comprises applying a composition comprising a liquid polymerizable epoxy containing material and a photosensitive aryl diazonium compound having the formula:



where MX_{n+m} is a halogen containing complex anion selected from the group consisting of hexachlorostannate IV, tetrachloroferrate III, hexafluorophosphate, hexafluoroarsenate V, hexachloroantimonate V, hexafluoroantimonate V and pentachlorobismuthate III; X is the halogen, n is the oxidation state of M, m is the number of diazonium groups in the diazonium compounds as determined by the net charge on said complex anion, and Y is selected from at least one of the group consisting of halogen, nitro, N-morpholino, alkyl, alkoxy, aryl, amino, arylamino, alkylamino and arylmercapto and arylthio radicals to a permeable supporting base; exposing a portion of said composition through a screening means to electromagnetic radiation of predetermined intensity and frequency to effect said polymerization and removing un-

polymerized portions of said liquid composition to produce the stencil design.

8. The process of claim 7 wherein the composition contains from about 1 percent to about 10 percent by weight of photosensitive aryl diazonium compound based on the dry weight of the epoxy monomer.

9. The process of claim 7 wherein the composition is subjected to heat after exposure to said electromagnetic radiation.

10. The process of claim 7 wherein the screening means includes projecting an image onto said permeable base having said composition.

11. The process of claim 7 wherein the screening means includes impinging a shadow arrangement onto said permeable base having said composition.

12. The process of claim 7 wherein said unpolymerized portions of said composition is removed without the use of solvent.

13. The process of claim 7 wherein said composition is applied to one side of a permeable supporting base.

14. The process of claim 13 wherein said supporting base is paper.

15. A stencil comprising a permeable supporting base having applied to portions of at least one surface thereof as the non-image area, a photopolymerized hardened, organic solvent-insoluble reaction product of an epoxy monomer or prepolymer and an aromatic diazonium salt of a complex anion, said anion being selected from the group consisting of haloantimonates, haloarsenates, halobismuthates, haloferrates, halostannates and halophosphates wherein each halogen is selected from the group consisting of fluorine and chlorine.

16. A stencil as claimed in claim 15 wherein the permeable substrate has the reaction product applied to both sides thereof.

17. A stencil as claimed in claim 16 in which said substrate is paper.

18. A stencil as claimed in claim 15 wherein the permeable substrate has the reaction product applied to one side thereof.

19. A stencil as claimed in claim 15 in which said substrate is paper.

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U.S. Cl. X.R.

96-36.4; 101-128.3; 117-8.5, 93.31; 204-159.18, 159.23