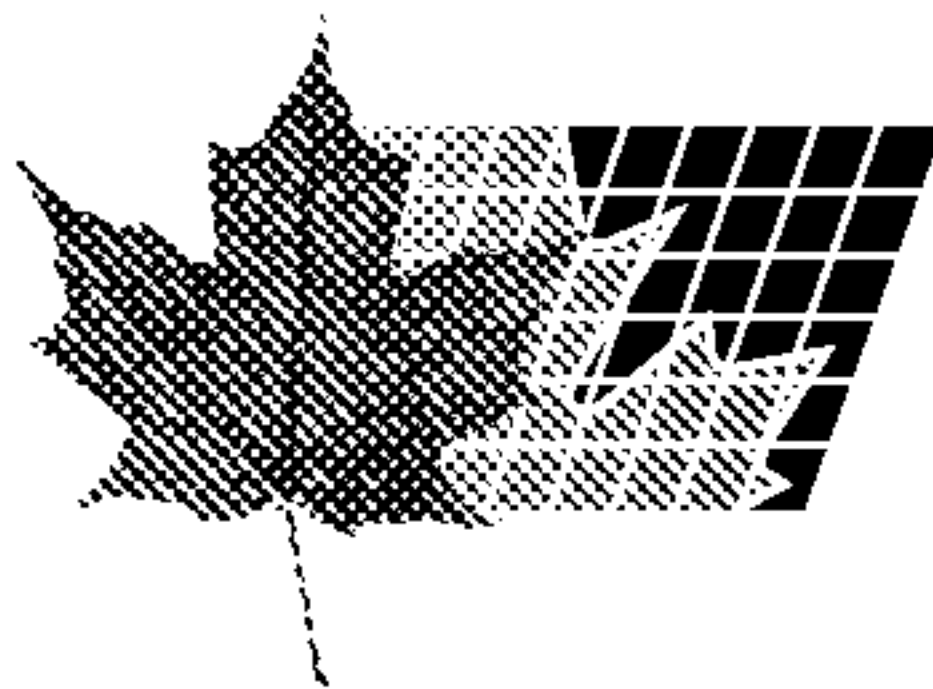




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(54) **ARTICLE ET PROCEDE HYBRIDE DE MODIFICATION D'UNE
SURFACE**

(54) **HYBRID SURFACE MODIFICATION PROCESS AND ARTICLE**

(57) The combination or hybridization of chemical machining (especially photochemical machining, chemical resist machining or thermal resist machining) with electrical discharge machining provides an increased efficiency machining process with unique etch characteristics and improved economics. The ability of chemical machining to accurately and rapidly machine a substrate to significant depths is combined with the increased flatness of wall or slope facings of the slower, but more precise, electrical discharge machining to provide three-dimensional patterning of surfaces with facial characteristics that are unique, rapidly obtained, and of high quality. The process is performed by either (a) first chemical machining to obtain the fundamental pattern and approximate depth of texturing desired in the final product and refining the grooves, walls and troughs of the patterned surface by subsequent electrical discharge machining or (b) using electrical chemical machining to define a pattern of troughs, grooves and walls, and then extending the depth of those grooves with chemical machining (in combination with a resist over the surface of the plateaus of the initial pattern). The initial product from alternative (b) may be followed by a further electrical discharge machining to refine the groove characteristics.

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(54) Title: HYBRID SURFACE MODIFICATION PROCESS AND ARTICLE

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HYBRID SURFACE MODIFICATION PROCESS AND ARTICLE

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BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to methods and apparatus for producing surfaces with designed texture thereon and articles having those surfaces. The processing technology relates to a combination of chemical milling (such as photochemical
10 milling) and Electrical Discharge Machining (EDM).

2. Background of the Art

Modern technology requires a vast array of manufacturing techniques to meet the specialized needs of different operating systems. One of the most important aspects of efficient machines is the control of the surface properties,
15 particularly at the interface of different parts. The most usual design consideration of surface properties is attempting to reduce the friction between moving parts that contact each other. However, controlled friction is also a major design consideration as friction between parts is often essential to their performance, as with a clutch plate, nip rollers, coating rollers, tires, drive
20 wheels and the like. The earliest forms of controlling or modifying the friction properties contributed by surfaces comprised various forms of grinding, lapping, polishing or abrading surfaces to make them as smooth or as rough as the task required.

The requirements of many technical fields has required significant
25 advances in the ability of manufacturers to provide consistent, repeatable, and precisely designed surface characteristics at a reasonable cost. Simple abrading of surfaces by manually rubbing sand paper over surfaces has been easily surpassed by the high speed application of diamond abrasive sheeting moving at thousands or tens of thousands of linear feet per minute in sophisticated lapping
30 apparatus, as shown in EPO Published Application EP 98/301690.8, filed on March 6, 1998 in the name of Wayne O. Duescher and Keltech Engineering. This type of surface treatment is able to provide between one and two lightbands of smoothness on metal surfaces in minutes.

The provision of designed texture on surfaces tends to be highly dependent upon the nature of the material that is being surfaced. For example, polymers and resins are capable of being molded to form microreplicated surfaces, with complex textures and patterns thereon (e.g., 3M Trizact™ surfaces). This technology is completely inappropriate for use with metals, however, primarily because the material forming the replication has to be thermally or chemically softened to a state above its flow temperatures. Those flow temperatures tend to be very high for most useful metals, particularly machineable metals, and the replication molds must endure high temperatures and extreme cooling conditions, and tend to suffer extreme wear with metals being molded. Metals can have their surfaces textured by mechanical milling (e.g., diamond milling, lapping, abrading, roughening), chemical milling (e.g., chemical etching, photochemical etching), high energy milling (e.g., ablation or etching with high energy beams such as with plasma, excimer lasers, laser diodes, and the like), and other treatments capable of controlled removal of material in designed or patterned areas. Other materials are formed or molded with the surface characteristics and shapes determined by the walls of the mold.

Another technology that has found its way into the field of surface modification is electrical discharge machining (EDM). This technology is represented in its simplest form as a wire that is held under tension and electrically heated (resistively heated) to very high temperatures, and then the wire is brought into contact with a surface that is desired to be cut, shaped or etched. Simple apparatus of this type may be purchased in retail stores or hobby stores for the cutting of foams, thin plastic sheets, or other materials that will melt without quickly catching fire at the temperature of the wire. Much more complex EDM equipment exists that has an electrode cutting device that is accurately moved over a workpiece surface, with the heated electrode selectively melt-etching or melt-ablating material. The electrode cutting device may be a wire or a shaped head (e.g., with a tapered or pointed cutting extension) that literally melts its way through the surface to be textured as would a hot knife through butter. The mechanism for texturing the surface is not precisely melting.

In actuality, the electrode is moved towards the workpiece until the space between the electrode and the workpiece is such that the voltage in the gap can

ionize a dielectric fluid (coolant) that is placed on the workpiece surface. The ionization allows a spark to pass from the electrode to the workpiece. The EDM operates by providing these spark discharges at a very high frequency of at least 50,000 discharges per second, usually at least 100,000 discharges per second and preferably at least 250,000 discharges per second. The spark move the shortest distance across the gap, to the nearest or highest place on the workpiece. The amount of material removed from the surface with each spark is proportional to the amount of energy in each pulse. Each spark melts, ablates or vaporizes a small area of the workpiece surface. This vaporized material will then be cooled in the dielectric fluid (explaining its alternative description as the coolant). The removed material (swarf) is carried away from the surface by movement of the dielectric. By appropriately directing and positioning the electrode and the amount of energy discharged, the workpiece surface can be precisely textured according to the pattern of movement of the electrode. The texturing may be essentially two dimensional or three dimensional, depending upon the workpiece and the design sought in the texturing.

Because EDM removes metal with electrical discharges instead of with an actual mechanical or abrading action, the hardness of the workpiece does not determine whether or not a material can be machined by EDM. A relatively soft electrode made of graphite or metal can easily machine hardened steel tools or tungsten carbide.

The basic principles of wire-cut EDM are essentially the same as the die-sinking or plunge EDM described above. The major difference is that instead of using an electrode with a specific shape, in wire EDM the electrode is a simple wire, typically with a 5 to 15 mil diameter. The wire will follow a horizontal path through the workpiece. Filtered water (e.g., filtered deionized water) is typically used as the coolant in wire EDM processes. Although EDM is a very desirable and effective method of providing specific textures and patterns to surfaces, it is relatively expensive when a large and/or deep pattern must be machined. The process is also relatively slow, with the die-sinking electrode machining only a narrow path with long durations needed for deeper patterns, and wire EDM is also relatively slow and is limited to making linear machine

tooling as the wire must maintain significant tension to prevent gravity bowing or mechanical deflection.

Other well known surface texturing technologies include chemical milling, photochemical milling, or mechanical milling. Chemical milling is the generic term applied to any surface modification of a material by the application of chemical materials to the surface and the resulting chemical activity removing or texturing the surface. Although chemical milling usually applies to the removal of material to generate a patterned or uniform topography to a surface, it has also been used in the art to encompass anodization, controlled oxidation, reduction and the like. The term milling, however, is referred to in the present invention as applicable to only the removal of material from the surface.

Photochemical milling, for example, is a technology wherein a photosensitive response usually in the form of a photoresist layer) is provided to a surface. After chemical milling compositions are then applied to the surface after exposure to activating (actinic) radiation, the milling tends to result in a patterned removal of material from the surface. The photoresponsive material in a photochemical milling process may be, for example, photoresist materials, whether positive-acting or negative-acting. Thermal resist materials (that are responsive to differential patterns of heat) and electrographic resists (that are responsive to differential patterns of charge, as, for example, applied by a stylus) are essential equivalent formats for providing imaged resist patterns, with photoresists being more generally accepted by the art. Photoresist materials are layers that alter their solubility in a specific or general class of solvents after sufficient irradiation by electromagnetic radiation to which the layer is sensitive. For example, in a water-developable positive-acting photoresist layer sensitive to ultraviolet (UV) radiation within the wavelength range of 230 to 380 nanometers, the initial (unexposed to UV radiation) layer will not be highly soluble in water. After exposure to the UV radiation in the actinic range for the positive-acting photoresist composition, the areas of the layer that have been sufficiently irradiated (a fluence of radiation that exceeds a threshold amount) will display increased solubility in water. The imagewise exposed layer is then washed (sprayed, immersed, scrubbed, mildly agitated, etc.) With water and the more soluble areas are removed, leaving a pattern of coating on the surface

corresponding to the non-imaged areas of the original coating. Upon application of chemical milling agents to the substrate with the patterned coating thereon, the chemical milling agents contacts only exposed areas of the substrate and thereof only those exposed areas of the substrate that contact the chemical
5 milling surface are milled (or etched) by the activity of the solution.

Negative-acting photoresists are used in a similar manner, except that the coating becomes less soluble where exposed to actinic radiation. For example, where a coating composition comprising organic solvent soluble binder, polymerizable components (e.g., monomers, comonomers, polymerizable
10 oligomers, or polymerizable polymers) and a photosensitive compound that assists in or initiates the polymerization (e.g., a photocatalyst, photoinitiator, photolabile halogen materials, photolabile acid generators, and the like, with or without spectral sensitizers). Upon irradiation by electromagnetic radiation to which the composition is sensitive, the coated composition polymerizes (often
15 referred to in certain arts as hardening), becoming less soluble in the organic solvent. The imagewise exposed layer is then washed (sprayed, immersed, scrubbed, mildly agitated, etc.) with the appropriate organic solvent and the more soluble areas are removed, leaving a pattern of coating on the surface corresponding to the imaged areas of the original coating. Upon application of
20 chemical milling agents to the substrate with the patterned coating thereon, the chemical milling agents contacts only exposed areas of the substrate and thereof only those exposed areas of the substrate that contact the chemical milling surface are milled (or etched) by the activity of the solution.

SUMMARY OF THE INVENTION

25 The combination or hybridization of chemical machining (especially photochemical machining, chemical resist machining or thermal resist machining) with electrical discharge machining provides an increased efficiency machining process with unique etch characteristics and improved economics. The ability of chemical machining to accurately and rapidly machine a substrate
30 to significant depths is combined with the increased flatness of wall or slope facings of the slower, but more precise, electrical discharge machining to provide three-dimensional patterning of surfaces with facial characteristics that are unique, rapidly obtained, and of high quality. The process is performed by either

- a) first chemical machining to obtain the fundamental pattern and approximate depth of texturing desired in the final product and refining the grooves, walls and troughs of the patterned surface by subsequent electrical discharge machining or
b) using electrical chemical machining to define a pattern of troughs, grooves
5 and walls, and then extending the depth of those grooves with chemical machining (in combination with a resist over the surface of the plateaus of the initial pattern). The initial product from alternative b) may be followed by a further electrical discharge machining to refine the groove characteristics.

BRIEF DESCRIPTION OF THE DRAWINGS

- 10 Figures 1a), 1b) and 1c) show perspective illustrations of the profile of plateaus created by Photochemical Milling, Electrical Discharge Machining, and the hybrid process of the present invention combining PCM and EDM, respectively.

DETAILED DESCRIPTION OF THE INVENTION

- 15 In many different fields of technology, the ability to design and manufacture surfaces with detailed surface structure with three dimensions of features has become extremely important. In addition to the need for good resolution and reproducibility in the manufacture of articles with specific surface features, it is essential to be able to provide unique characteristics and subtle
20 variations in the substructure of the detail, as with shaping, surfacing, sloping, and sub-microstructuring to the overall pattern or details of the surface. For example, in the manufacture of chips, it is often necessary to determine a specific microcircuits' electrical performance characteristics based on correlation to its physical dimensions. To do so reliably, the electrical and physical test
25 measurement equipment must be extremely accurate and precise to resolve the absolute abscissic and ordinal coordinate locations of features on a plane to single Angstrom units.

- Heretofore, the combination of physical and electrical impulse algorithms to position linear stepper motors has allowed these types of test instruments to
30 perform satisfactorily given the present semiconductor feature geometries. However, with the advent of the multiplicity of integrated circuits populating, an increased surface area on wafers and the converse trend of miniaturization of semiconductors, the performance of these instruments has actually lagged behind

the technology and product capabilities in integrated circuit (IC) manufacture, rendering the testing instrumentation's validation of a circuits' integrity to become a gating time factor and a detriment to efficiency in the fabrication process.

5 An improvement in the speed and position accuracy of linear motors' utilized in these instruments would be realized by changing critical dimensional features of key subassemblies of the equipment. The article described herein and the description of the feature geometry's elucidated in the diagram allow for a significant increase in performance characteristics desired in the trade.

10 It is recognized in many technical fields that processes are capable of leaving fingerprints that are unique to that process. One skilled in a particular art is often able to microscopically examine or chemically analyze a product and determine the nature of the composition and/or the process used to manufacture that product. This characteristic holds reasonably well for machined surfaces,
15 particularly those machined with features having maximum topographic dimensions of about 15 mils (0.38 mm, preferably less than 0.38 mm, for example in a range of from about 0.000038 to 0.38 mm or 0.000038 to 10 mils) that were machined by PCM or Plunge EDM. This can be partially noted by reference to Figures 1a) and 1b), wherein plateaus having maximum heights (h)
20 as measured from the lowest level of an adjacent trough are shown. The plateaus illustrated in Figure 1a) represent plateaus produced by photochemical machining. The plateaus illustrated in Figure 1b) represent plateaus produced by electrical discharge machining. Significant differences can be seen in the characteristics of the plateaus made by the various processes. For purposes of
25 comparing the illustrations, a valid assumption that the height (h) of each plateau is the same. The dashed line **t** represents a line within the plane at the top of the plateau and an extension of an edge 2. The dashed line **b** represents a line parallel to **t** that lies within a plane defined by the lowest point in a trough adjacent a plateau. A corner 10 is formed by intersection of edge 2 with edge 8.
30 Line **v** represents a vertical line that passes through corner 10. As can be seen, the edge 12 of the face extending from edge 8 rapidly diverges away from vertical line **v**. Ordinarily, the angle theta formed by a line defining the slope of the edge 12 or the face 14 diverges from vertical line **v** by at least 30 degrees

when about 30% of **h** has been achieved moving down from **t** in the case of photochemical machining. The slope of the edge **12** or the face **14** diverges from vertical line **v** by at least 30 degrees when about 25%, about 20%, or even 15% of **h** has been surpassed moving down from **t** in the case of photochemical machining. The slope characteristics of the chemical machining are important from a number of perspectives. Manufacturers and technical personnel that use these textured and patterned surfaces in subsequent processes, particularly where those surfaces are used in highly detailed and sophisticated processing, rely upon the subtleties of the performance characteristics (e.g., flow characteristics of fluids such as liquids and gases through the grooves) of the texturing that are in large part controlled by the details of the topography. The Gauss or magnetic flux applied across or over the surface may also be affected, as later described for use with linear motor systems. These processes have themselves been refined to rely upon the configuration and properties of the texturing. These personnel also feel more comfortable working with a surface structure that appears consistent with structures that have been used for many years. Also, the sloped structure that is characteristic of chemical machining provides a high level of structural support for the plateaus, reduces their ability to flex or shift under lateral stresses, and reduces shearing of plateaus from the underlying substrate.

In considering Figure 1b), representing an illustration of a plateau formed by electrical discharge machining, the relative characteristics of edges, faces and angles is quite different from those of plateaus formed by photochemical machining. The plateau more nearly represents a cubic structure, with very little curve to the faces or downward aligned edges. In terms used to characterize the faces and edges in Figure 1a), the same lines would be better described as ordinarily, the angle θ formed by a line defining the slope of the edge **12** or the face **14** diverges from vertical line **v** by less than 20 degrees when about 60% of **h** has been surpassed moving down from **t** in the case of photochemical machining. The slope of the edge **12** or the face **14** diverges from vertical line **v** by less than 25 degrees when about 70%, about 75%, or even 85% of **h** has been surpassed moving down from **t** in the case of photochemical machining. As noted above, there can be unique properties attributed to the textured material

because of the slope pattern. Although the electrical discharge machined grooves, troughs, plateaus and channels offer a very sharp design (with smooth walls, sharp, unrounded features, uniform angles, etc.), these characteristics are not necessarily beneficial in all technical environments. The sharp features and right angles reduce the structural support of the plateaus, providing areas where stress can attack the bases of plateaus. The sharp right angles create vortex generating points for the flow of fluids, which can assist in causing bubbles or foaming with liquids. The sharp angles at the base of the plateaus also allows the raised areas to shift more easily under lateral stress.

10 The plateau configuration of the product of the present invention is also unique, and is not identifiable as the product of PCM or EDM, alone. In terms used to characterize the faces and edges in Figure 1a), the same lines would be better described as ordinarily, the angle theta formed by a line defining the slope of the edge 12 or the face 14 diverges from vertical line v by less than 20 degrees when about 30% of h has been surpassed moving down from t in the case of the hybridized process of electrical discharge machining and photochemical machining. The slope of the edge 12 or the face 14 diverges from vertical line v by more than 25 degrees when about 60%, 70%, about 75%, or even 85% of h has been surpassed moving down from t in the case of the hybridized process of electrical discharge machining and photochemical machining. As can be seen from this illustration, many of the beneficial characteristics of both the electrical discharge machining and the chemical machining are provided in the finished surface of the present invention. A slightly curved facing, more typical of chemical machining is provided (enabling plateau support, distortion reduction, and controlled inter-groove flow characteristics), while the sharpness of the faces, the initial straightness of the edges moving down from the plateaus, and smoothness of the faces are more characteristic of electrical discharge machining. These characteristics are provided by a process that approaches the economics and speed of chemical machining, yet provides the sharper detail available from electrical discharge machining.

The process according to the present invention may be practiced by first photochemical etching (or any other chemical etching process, such as thermal chemical etching) and then performing electrical discharge machining, or vice

versa. It is preferred to practice chemical machining first, as that is a more rapid and economical method of deep machining, and the electrical discharge machining tends to provide a smoother face surface than chemical machining. That is another characteristic that can be microscopically seen that distinguishes
5 between surfaces and plateaus that have been chemically machined versus EDM. The surface that was chemically machined will show ripples, or wavy striations on the surface, a result of the liquid motions (e.g., eddies, vortexes, channeling etc.) of the chemical machining solution or etch solution on the surface. If electrical discharge machining is used before chemical machining, it may be
10 desirable to refine the chemically machined surfaces by further electrical discharge machining. The chemical machining would be performed, for example, by applying a resist to the surface of the plateaus or plateau outlines after electrical discharge machining (to significantly less than the final depth ultimately desired, e.g., from about 1-25% of the ultimate depth) to provide the
15 resist pattern. The resist pattern could be applied by printing the resist onto the plateaus (e.g., by roller application), avoiding significant penetration into the mini-troughs obtained by general application of a resist and imagewise exposure in register with the pattern from the electrical discharge machining, followed by wash-off development of the resist.

20 A wide variety of photocurable compositions and photo-reactive materials are known in the prior art. Two main approaches exist in the art for producing photocurable compositions: (1) photocurable (photoinduced radical) compositions based upon polymerizable ethylenically unsaturated groups, and (2) photocurable compositions based upon photoacid generating
25 compounds which function as photoinitiators for cationic polymerization. Both these approaches are reviewed in UV Curing; Science and Technology, S. P. Pappas, Editor, Technology Marketing Corporation, Norwalk, Conn. (1980). Illustrative ethylenically unsaturated compositions are described in U.S. Pat. Nos. 4,544,621; 4,564,580, 4,668,601, and 4,798,877. In
30 one embodiment these photocurable compositions can comprise a photoinitiator, such as the onium compounds described in U.S. Pat. No. 4,632,891, and a polymerizable material which is activated by the photoinitiator. U.S. Pat. No.

4,229,519 discloses that polymers containing quaternary nitrogen groups bearing ethylenically unsaturated groups may be cured with radiation under nitrogen in the presence of a suitable photoinitiator.

Illustrative of photocurable compositions which comprise a photoacid generating initiator are those described in U.S. Pat. Nos. 4,081,276; 4,551,418 and 4,610,952. The most common photoacid generating systems are diaryliodonium and triarylsulfonium salts. Recent work in photoacid generating compounds are described in proceedings of ACS Division of Polymeric Materials, Science and Engineering, Vol. 61, Fall Meeting 1989, in Miami Beach, Fla. J. V. Crivello, "Chemistry of Photoacid Generating Compound", p. 62. Generally, those photocurable compositions are water incompatible and require organic solvents for preparation of coatings.

U.S. Pat. No. 4,118,297 describes aromatic cyclic sulfonium Zwitterions which polymerize upon exposure to ultraviolet light. Japanese Kokai No. 34,445, published Feb. 28, 1983 describes photosensitive Zwitterions of aryl cyclic sulfonium.

In conventional processes a photocurable composition is selectively exposed to actinic or other radiation in a desired pattern. The portions of the composition which are not subjected to radiation can be removed or developed by immersion in a suitable solvent. This is commonly referred to as a negative photoresist. In some applications, a photocurable composition is rendered more soluble by exposure to radiation and this photoreacted area is removed during developing. Such compositions are referred to as positive photoresists.

Photocurable compositions are commonly used to form lithographic printing plates, inks cured with ultraviolet (UV) radiation or printed circuits. After development of the image on the desired substrate, the exposed surface may be etched by conventional techniques. Similar techniques can be used to manufacture integrated circuits and other microelectronic components. However, photoresists used in such applications must afford a very high degree of resolution because of the fine detail required in these miniaturized images.

For accurate image formation in microlithographic applications it is desirable to have a relatively thin coating (typically about 0.1 to 2.5 microns, or more preferably from about 0.4 to 1.2 micrometers) of the photo-sensitive

composition material. Further, it is desirable that the composition photocure (either polymerize or crosslink) relatively rapidly. The need for thin coatings of a photo-sensitive composition is related to the limited depth of focus of typical exposure patterning equipment and to the minimization of light scatter from the film deposited. The diffusing and spreading effect of the diffraction pattern of the exposing actinic radiation can limit the resolution of fine detail of the photoresist pattern. The very short wavelength of the exposing wavelength of this resist will (proportionately) decrease the width of the diffraction pattern and increase the resolution of fine detail of the resist pattern. In addition, the coating on the surface should be substantially free from pinholes and other blemishes, which would result in defects in the image produced.

Suitable photoinitiation systems for use in the invention are those which are thermally inactive but which generate free radicals upon exposure to actinic light at or below 185.degree. C. Typically, the photoinitiation systems make up about 3 to 9 wt. % of the organic medium, with preferably 5 to 7 wt. %. These include the substituted or unsubstituted polynuclear quinones which are compounds having two intracyclic carbon atoms in a conjugated carbocyclic ring system, e.g., 9,10-anthraquinone, 2-methylanthraquinone, 2-ethylanthraquinone, 2-tert-butylanthraquinone, octamethylanthraquinone, 1,4-naphthoquinone, 9,10-phenanthrenequinone, benz(a)anthracene-7,12-dione, 2,3-naphthacene-5,12-dione, 2-methyl-1,4-naphthoquinone, 1,4-dimethyl-anthraquinone, 2,3-dimethylanthraquinone, 2-phenyl-anthraquinone, 2,3-diphenylanthraquinone, retenequinone, 7,8,9,10-tetrahydronaphthracene-5,12-dione, and 1,2,3,4-tetrahydrobenz(a)anthracene-7,12-dione. Other photoinitiators which are also useful, even though some may be thermally active at temperatures as low as 85 degree. C., are described in U.S. Pat. No. 2,760,863 and include vicinal ketaldonyl alcohols such as benzoin, pivaloin, acyloin ethers, e.g., benzoin methyl and ethyl ethers; alpha.-hydrocarbon-substituted aromatic acyloins, including .alpha-methylbenzoin, alpha-allylbenzoin and alpha-phenylbenzoin. Photoreducible dyes and reducing agents disclosed in U.S. Pat. Nos. 2,850,445, 2,875,047,

3,097,096, 3,074,974, 3,097,097, and 3,145,104, as well as dyes of the phenazine, oxazine, and quinone classes, Michler's ketone, benzophenone, 2,4,5-triphenylimidazolyl dimers with hydrogen donors including leuco dyes and mixtures thereof as described in U.S. Pat. Nos. 3,427,161, 3,479,185, and
 5 3,549,367 can be used as initiators. Also useful with photoinitiators and photoinhibitors are sensitizers disclosed in U.S. Pat. No. 4,162,162.

As used in this application:

"catalytically effective amount" means a quantity sufficient to effect
 10 polymerization of the curable composition to a polymerized product at least to a degree to cause an increase in viscosity of the composition under the conditions specified;

"monomer" and "ligand" means a chemical species that allows for substitution or
 15 which may be substituted by conventional substituents, in addition to what may be described and that do not interfere with the desired product, e.g., substituents can be alkyl, alkoxy, aryl, phenyl, arylalkoxy, hydroxyl, cyano, carboxyl, amino, nitro, acetyl, halo (F, Cl, Br, I), etc;

20 "organometallic salt" means an ionic salt of an organometallic complex cation, wherein the cation contains at least one carbon atom of an organic group that is bonded to a metal atom of a transition metal series (F. A. Cotton, G. Wilkinson Basic Inorganic Chemistry, Wiley, 1976, p. 497);

25 "polymerizable composition" means a mixture of an initiator or catalyst and polymerizable monomer(s); and

"polymerize" and "cure" are interchangeable and mean to supply sufficient energy to a composition to alter the physical state of the composition, to make it
 30 transform from a fluid to less fluid state, to go from a tacky or non-tacky state, to go from a soluble to insoluble state, or to decrease the amount of polymerizable monomer by its consumption in a reaction.

"Photosolubilize" means to cause a composition to become more soluble in a specific solvent at a fixed temperature by the application of energy (usually by irradiation) to alter the chemical composition of at least one species within the composition.

5

Catalysts

In general, catalyst or initiator salts initiator system contains an acid generator selected from the group consisting of diazonium, phosphonium, sulfonium, iodonium salts, halogen compounds, organometal/organohalogen combinations, benzoin esters and o-nitrobenzyl esters of strong acids, and N-hydroxyamide and N-hydroxyimide sulfonates, and aryl naphthoquinonediazide-4-sulfonates. of the instant invention can be prepared by anion exchange or metathesis reactions by combining initiator or catalyst salts that contain conventional counteranions, such as chloride, PF_6 , SbF_6 , or BF_4 , with simple salts, such as alkali or alkaline earth metal salts or alkylammonium salts, of the nonnucleophilic anions of the invention in a suitable solvent. Generally, the initiated reactions may be carried out at temperatures ranging from about -80 degree. to about 150 degree. C., preferably at ambient temperature, or slightly elevated temperature.

Nonlimiting examples of suitable solvents include, water, alkaline solutions, aqueous organic solutions (e.g., water and alcohols); chlorocarbons, such as methylene chloride, and chloroform; ethers; aromatic hydrocarbons, such as toluene, and chlorobenzene; nitriles, such as, acetonitrile; alcohols, such as methanol and ethanol; nitrobenzene; nitromethane; ketones, such as acetone and methyl ethyl ketone; and other similar classes of organic solvents. Mixtures of solvents are often desirable to control solubility of reagents and product salts.

25

Polymerizable Compositions and Polymers

In the negative-acting photoresist systems, the typical photoresist comprises at least one crosslinkable or polymerizable component. To provide substantivity to the coating before the application or radiant energy to cure the layer in an image-wise manner, the polymerizable component may be a relatively higher molecular weight material (e.g., an oligomer or polymer with polymerizable groups, or may contain an inert binder ingredient to solidify the coating and prevent it from

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dripping or evaporating before photoinitiation of the cure or polymerization. Pigments or dyes may be present to assist in visualization of the layer, and even acid/base sensitive dyes may be present that change color during the polymerization or cure of the layer to enable prewash visualization of the resist layer. The layer may contain solvents or be free of solvents in the coating composition. Typically, most negative acting resist compositions tend to comprise materials having polymerizable groups, such as polymerizable groups selected from the classes of ethylenically unsaturated groups (e.g., vinyl, acryloyl, [meth]acryloyl, allyl, styryl, and the like), epoxy groups, silane groups, and the like. Typical monomers might include acetic anhydride, acrylic acid, methacrylic acid, butyl acrylic acid, gamma-glycidoxytrimethoxysilane, gamma-acryloylpropyltrimethoxysilane, polymer backbones having pendant or terminal polymerizable groups (e.g., acryloyl or methacryloyl groups). Additional conventional monomer components (having no pendant acid labile groups) which may be used to modify the polymeric material include, but are not limited to, acrylic alkyl esters such as methyl methacrylate; ethyl methacrylate; 2-ethyl hexyl methacrylate; propyl methacrylate; cyclohexyl methacrylate; butyl methacrylate; benzyl methacrylate; benzyl acrylate; methyl acrylate; ethyl acrylate; propyl acrylate; butyl acrylate; styrene; acrylic alkyl amides such as N-butylacrylamide; N-octylacrylamide; acrylonitrile, styrene, p-methyl styrene; butadiene, isoprene. Preferred monomers for resistance to alkaline processing solutions include aromatic monomers such as styrene or benzyl methacrylate or hydrophobic aliphatic monomers such as 2-ethylhexyl, butyl or cyclohexyl methacrylate. Small quantities (typically less than 5 mole %) of glycidyl methacrylate may be added as an adhesion promoter.

Photosensitive Acid Generator

Some polymerizable or photosolubilizable compositions are initiated by the liberation of acid groups within the composition. Examples of compounds and mixtures which can be used as photoacid generators include diazonium, phosphonium, sulfonium and iodonium salts; halogen compounds; organometal/organohalogen combinations; benzoin esters and o-nitrobenzyl esters of

strong acids, e.g., toluenesulfonic acid; and N-hydroxy amide and N-hydroxyimide sulfonates as disclosed in U.S. Pat. No. 4,371,605. Also included are aryl naphthoquinone-diazide-4-sulfonates. Preferred photosolubilizing agents are the diaryliodonium or triarylsulfonium salts. These are generally present in the form of salts with complex metal halide ions such as tetrafluoroborate, hexafluoroantimonate, hexafluoroarsenate, and hexafluorophosphate.

Another useful group of photosensitive acid generators include oligomers and polymers comprising appended anionic groups having an aromatic onium acid photogenerator as the positive counter ion. Examples of such polymers include those described in U.S. Pat. No. 4,661,429, column 9, lines 1 to 68, and column 10, lines 1 to 14, incorporated herein by reference.

It may be desirable to add a spectral sensitizer to the system to adjust the spectral sensitivity to the available wavelength of actinic radiation. The need will depend on the requirements of the system and the specific photosensitive compound used. For example, iodonium and sulfonium salts that only respond to wavelengths below 300 nm may be sensitized to longer wavelengths using benzophenone and derivatives thereof, polycyclic aromatic hydrocarbons such as perylene, pyrene, and anthracene, and derivatives thereof. The decomposition of diaryliodonium and triarylsulfonium salts has been sensitized by bis-(p-N,N-dimethylaminobenzyliden)-acetone. Anthracene bound sulfonium salts, with chain lengths of three to four atoms, are efficient photosolubilizing agents. These compounds, which are disclosed in M. G. Tilley, Ph.D. Thesis, North Dakota State University, Fargo, ND (1988) [Diss. Abstr. Int. B, 49, 3791 (1989); Chem. Abstr., 111, 39942u], are a preferred class of photosolubilizing agents. Another preferred acid generator is ATASS, i.e., 3-(9-anthracenyl)propyldiphenylsulfonium-, hexafluoroantimonate. In this compound the anthracene and the sulfonium salt are bonded by a three carbon chain. Additional examples of acid generators that may be used herein are diphenyliodonium tosylate, benzoin tosylate, and triarylsulfonium hexafluoroantimonate.

The amount of acid generator in the photoresist composition should generally be as low as possible without unduly sacrificing sensitivity, generally from about 0.1% to about 10% by weight of the photoresist composition. Less than about 0.1% generally lead to insensitive compositions while weight percentages greater than 10% produce compatibility and control problems. For most acid-labile polymers, 0.5 to 6% by weight acid generator in the photoresist composition is preferred.

A sufficient amount of acid labile ester in the polymer is necessary to allow the exposed areas of the resist to be developable in all aqueous base either by dissolution or dispersion. Preferred all aqueous developing solutions include, but are not limited to 0.5% sodium hydroxide or 1.0% sodium carbonate. The addition of small amounts of surfactants or defoamers can be useful to aid development or to control foaming in the solution. The exact amount of acid labile ester depends on the resist formulation, the polymer composition and molecular weight, and the glass transition of both. Experiments have demonstrated that as little as 25 mole % of tetrahydropyranyl methacrylate in a tetrahydropyranyl methacrylate/butyl methacrylate copolymer was sufficient for all aqueous development in 0.5% sodium hydroxide solution.

It is possible to add other monomers or additives such as polyketals and acetals, plasticizers and/or crosslinkers into the resist composition to modify certain properties.

Colorants

Colorants such as dyes and pigments are useful adjuvants in dry film photoresists because the developed resist image can be inspected for defects and a determination of when the resist has been cleaned from the substrate during development is possible. A preferred example of a colorant is Victoria Green dye. This material imparts a deep green color to a resist and upon exposure of the resist, it lightens in color in the irradiated areas. This creates an image of the artwork which is useful for inspecting the exposed sample for defects that might have been present in the artwork or dirt that accidentally was present during the exposure. Additives that create a visible image by forming a color or by a color change, e.g., leucolactones, would also be useful.

The present invention also provides polymerizable compositions comprising (a) at least one of cationic addition polymerizable monomers, ethylenically-unsaturated free radical monomers, mixtures of multifunctional monomers polymerizable by catalyzed step-growth polymerization or mixtures thereof and (b) a catalyst or initiator salt of the present invention and a method for the polymerization comprising the steps of:

(a) providing a monomer mixture comprising at least one of a cationically polymerizable monomer, an ethylenically-unsaturated free radical monomer, or mixtures of multifunctional monomers polymerizable by catalyzed step-growth polymerization and mixtures thereof,

(b) adding a catalytically effective amount of a curing agent to the monomer mixture, thereby forming a polymerizable composition, and

(c) causing the polymerizable composition to polymerize in an imagewise manner by adding energy in an imagewise distribution according to a desired pattern, with a sufficient amount of energy to the mixture to effect imagewise polymerization over the substrate to be etched or chemically milled.

It may be desirable to add solvent to solubilize components and aid in processing. Solvent, preferably organic solvent, may be present in an amount up to 99 weight percent, preferably in the range of 0 to 90 weight percent, and most preferably in the range of 0 to 75 weight percent, of the polymerizable composition can be used.

In the polymerizable compositions of this invention, the catalyst or initiator salts can be present in a catalytically effective amount to initiate polymerization, and is generally in the range of 0.01 to 20 weight percent (wt %), preferably 0.1 to 10 wt % of the total composition.

Cationically Polymerizable Monomers

Another particular subclass of polymerizable monomers that can be used in the practice of the present invention include 1-ethoxyethyl methacrylate,

1-ethoxyethyl acrylate, 1-butoxyethyl methacrylate, 1-butoxyethyl acrylate, 1-ethoxy-1-propyl methacrylate, 1-ethoxy-2-propyl acrylate, tetrahydropyranyl methacrylate, tetrahydropyranyl acrylate, tetrahydropyranyl p-vinylbenzoate, 1-ethoxy-1-propyl p-vinylbenzoate, 4-(2-tetrahydropyranyloxy)benzyl
5 methacrylate, 4-(2-tetrahydropyranyloxy)benzyl acrylate, 4-(1-butoxyethoxy)benzyl methacrylate, and 4-(1-butoxyethoxy)benzyl acrylate.

A wide variety of monomers can be energy polymerized using the catalysts and initiators of the invention. Suitable cationically polymerizable monomers and/or oligomers typically contain at least one cationically
10 polymerizable group such as epoxides, cyclic ethers, vinyl ethers, vinylamines, unsaturated hydrocarbons, lactones and other cyclic esters, lactams, cyclic carbonates, cyclic acetals, aldehydes, cyclic amines, cyclic sulfides, cyclosiloxanes, cyclotriphosphazenes and other cationically polymerizable groups or monomers described in G. Odian, "Principles of Polymerization" Third
15 Edition, John Wiley & Sons Inc., 1991, N.Y. and "Encyclopedia of Polymer Science and Engineering", Second Edition, H. F. Mark, N. M. Bikales, C. G. Overberger, G. Menges, J. I. Kroschwitz, Eds., Vol. 2, John Wiley & Sons, 1985, N.Y., pp. 729-814. Particularly useful examples include cyclic ether monomers, including epoxide monomers and are described in U.S. Pat. No.
20 4,985,340 and such description is incorporated herein by reference, vinyl organic monomers are described in U.S. Pat. No. 4,264,703, and such description is incorporated herein by reference.

Free-radically Polymerizable Monomers

25 Another subclass of polymerizable species that may be used in the polymerizable photoresist compositions of the present invention includes free-radically polymerizable compounds containing at least one ethylenically unsaturated double bond, may be monomers and/or oligomers, such as acrylates and methacrylates, acrylamides, methacrylamides, and other vinyl compounds
30 capable of undergoing free-radical polymerization. Such monomers and specific examples are more fully described in U.S. Pat. No. 4,985,340, and such description is incorporated herein by reference.

Catalyzed Step Growth Polymerizable Monomers

A further subclass of polymerizable species is referred to in the art as catalyzed step growth polymerizations include but are not limited to, the reaction of multifunctional isocyanates (polyisocyanates) with multifunctional alcohols (polyols) to form polyurethanes, the reaction of multifunctional epoxies with multifunctional alcohols, and the cyclotrimerization of multifunctional cyanate esters to crosslinked polytriazine resins.

Particularly useful multifunctional alcohol, isocyanate, and epoxide components that can be cured by catalyzed step-growth polymerization using catalysts of the present invention are described in U.S. Pat. Nos. 4,985,340, 4,503,211 and 4,340,716, and such description is incorporated herein by reference.

Suitable multifunctional cyanate esters that can be cured by catalyzed cyclotrimerization, using catalysts of this invention are described in U.S. Pat. Nos. 5,143,785 and 5,215,860 and such description is incorporated herein by reference.

Where mixtures of two or more polymerizable monomers are used in combination, the polymerizable components can be present in any proportion preferably with the minor component comprising at least 1.0 wt %.

Mixtures of aforementioned classes of monomers with additives such as tackifiers, hardeners, co-curatives, curing agents, stabilizers, sensitizers etc. can also be used in the polymerizable compositions of this invention. Furthermore, adjuvants, such as pigments, abrasive granules, stabilizers, light stabilizers, antioxidants, flow agents, bodying agents, flattening agents, colorants, inert fillers, binders, blowing agents, fungicides, bacteriocides, surfactants, plasticizers, and other additives as known to those skilled in the art can be added to the compositions of this invention. These can be added in an amount effective for their intended purpose.

Optionally, it is within the scope of this invention to include photosensitizers or photoaccelerators in the radiation-sensitive compositions. Use of photosensitizers or photoaccelerators alters the wavelength sensitivity of radiation-sensitive compositions

employing the latent catalysts and initiators of this invention. This is particularly advantageous when the latent catalyst or initiator does not strongly absorb the incident radiation. Use of photosensitizers or photoaccelerators increases the radiation sensitivity, allowing shorter exposure times and/or use of less powerful sources of radiation. Any photosensitizer or photoaccelerator may be useful if its triplet energy is at least 45 kilocalories per mole. Examples of such photosensitizers are given in Table 2-1 of the reference Steven L. Murov, Handbook of photochemistry, Marcel Dekker Inc., N.Y., 27-35 (1973), and include those described in U.S. Pat. No. 4,985,340, and such description is incorporated herein by reference. When present, the amount of photosensitizer or photoaccelerator used in the practice of the present invention is generally in the range of 0.01 to 10 and preferably 0.1 to 1.0 wt % of photosensitizer or photoaccelerator based on the weight of the curable composition.

Solvents, preferably organic, can be used to assist in dissolving the curing agent in the polymerizable monomers described supra and as a processing aid. Representative solvents include acetone, methyl ethyl ketone, cyclopentanone, methyl cellosolve acetate, methylene chloride, nitromethane, methyl formate, acetonitrile, gamma-butyrolactone, and 1,2-dimethoxyethane (glyme). In some applications it may be advantageous to adsorb the curing agents onto an inert support such as silica, alumina, clays, etc., as described in U.S. Pat. No. 4,677,137.

In general, energy-induced polymerization of the polymerizable compositions of this invention, which incorporate a latent, light or radiation sensitive catalyst or initiator, may be carried out at room temperature for the majority of energy curable compositions, although low temperature (e.g., -10.degree. C.) or elevated temperature (e.g., 30.degree. to 400.degree. C., preferably 50.degree. to 300.degree. C.) can be used to subdue the exotherm of polymerization or to accelerate the polymerization, respectively. Temperature of polymerization and amount of catalyst will vary and be dependent on the particular curable composition used and the desired application of the polymerized or cured product. The amount of curing agent (catalyst or initiator) to be used in this invention should be sufficient to effect polymerization of the monomers (i.e., a catalytically effective amount) under the

desired use conditions. Such amount generally will be in the range of about 0.01 to 20 wt %, and preferably 0.1 to 10 wt %, based on the weight of the curable composition.

For those compositions of the invention that are radiation sensitive, any
5 source of radiation including accelerated particles (e.g., electron beam radiation) and radiation sources emitting active radiation in the ultraviolet and visible region of the spectrum (e.g., about 200 nm to 800 nm) can be used. Infrared radiation may also be used, either as a source of heat that is focused in an
10 imagewise manner (initiating thermal cure or thermally initiating a catalyst) or by spectrally sensitizing the composition to the infrared (e.g., with merocyanine dyes, squarine dyes, or the other classes of dyes known to spectrally sensitize in the infrared). Suitable sources of radiation include fluorescent lamps, mercury vapor discharge lamps, carbon arcs, tungsten lamps, xenon lamps, lasers, light-emitting diodes, luminescent semiconductors, sunlight, etc. The required amount
15 of exposure to effect polymerization is dependent upon such factors as the identity and concentrations of the curing agent, the particular monomers, the temperature and thickness of the exposed material, type of substrate, intensity of the radiation source and the amount of heat associated with the radiation. Thermal
20 polymerization using direct heating or induction heating, infrared or microwave electromagnetic radiation, as is known in the art, can be used to cure the compositions according to the teachings of this invention. Curing conditions, for both photocuring and thermal curing, including duration, wavelength, temperature are readily ascertainable by those skilled in the art.

25 It is within the scope of this invention to include two-stage polymerization (curing), by first activating the curing agent by irradiating the curable compositions and subsequently thermally curing the activated precursors so obtained, the irradiation temperature being below the temperature employed for the subsequent heat-curing. The activated precursors may normally be
30 cured at temperatures that are substantially lower than those required for the direct thermal curing, with an advantage in some cases in the range from 50.degree. to 110.degree. C. This two-stage curing also makes it possible to control the polymerization in a particularly simple and advantageous manner.

Compositions of this invention may be applied, preferably as a liquid, to a substrate such as metals (e.g., steel, aluminum, copper, brass, tin, alloys, cadmium, zinc, ceramic, glass, paper, composites, wood or various plastic films such as poly(ethylene terephthalate), plasticized poly(vinylchloride), polypropylene, polyethylene, and the like, and irradiated. By polymerizing part of the coating, as by irradiation through a mask, those sections which have not been exposed may be washed with a solvent to remove the unpolymerized portions while leaving the photopolymerized, insoluble portions in place. Thus, compositions of this invention may be used in the production of articles useful in the graphic arts and electronics industry such as printing plates and printed circuits. Methods of producing printing plates and printed circuits from photopolymerizing compositions are well known in the art (cf., British Patent Specification No. 1,495,746).

The system may be arranged for use with an optical imagery unit such as a wafer stepper, for adequately illuminating a photoresist surface with an extremely detailed very high resolution image. Details of the control, positioning, autofocus and associated mechanisms of the wafer stepper are known and are not included for brevity. Energizing light of a specific character is generated starting with an illuminator 10 including an excimer laser 12 of the KrF type, generating a rectangular beam of approximately Gaussian distribution at 248 nm in the ultraviolet region. The excimer laser 12 generates a pulse series, at approximately 150 pulses per second, each pulse being of 1.2×10^{-8} seconds in duration and about 375 mJ/pulse. As is shown hereafter, this system can direct radiation of sufficient intensity onto a photoresist layer to record an image, and can do so within a usefully short time since the optical imaging system is of sufficiently high efficiency. A suitable laser of this type is provided by the Lumonics Hyperex-460 Model HE-SM excimer laser, although a number of other systems are available that can be utilized with appropriate recognition of various factors enumerated hereafter.

The beam from the laser is spatially coherent to a substantial degree, and temporally coherent to about 1 part in 620, factors which are not consistent with the spatial and temporal distributions desired. Accordingly, the laser operates in conjunction with a resonant tuning cavity, generally referred to as an etalon,

which can raise the Q factor and the predictability of the lightwave train to be in step for as much as 124,000 wavelengths. Alternatively a laser with intracavity etalon tuning may be used to produce the same degree of temporal coherence. However, excessive tuning is not desirable because of the possibility of
5 introduction of interference fringe effects, so that the etalon is slightly detuned to reduce the temporal coherence to in the range of 1 in 10,000 wavelengths.

After emergence from the laser, the beam may be enlarged in a double-prism beam expander which turns the rectangular beam of the excimer laser into a square beam about 1" on a side. This beam passes into a spatial
10 coherence randomizer that includes a first quasi-random phase surface defined by quasi-random patterns of SiO_2 deposited on an SiO_2 substrate. The randomizer structure provides a light transmissive element that imparts a degree of phase randomization across its cross-sectional area. Such a quasi-random phase surface may be achieved by evaporated patterns having average
15 thicknesses of about 1 micron and average widths of about 10 microns. A first field lens may transfer the beam to a reticle masking assembly which may, if desired, be motor driven. The masking assembly limits the beam peripherally to a controllable object field outline of a selectable size, the beam then passing through onto a movable corner mirror that is dynamically shifted through a small
20 arc as described below. From this corner mirror the beam is directed through an imaging relay lens which images the first quasi-random surface 19 onto a second quasi-random phase surface of similar character. The beam then passes onto a beam combining corner mirror toward the associated optics including a second field lens and to the wafer plane to which the image is directed. This angled
25 beam path enables the laser, which requires substantial power and volume, to be placed well away from the image forming part of the system.

Positive Acting Resist Compositions

The positive acting resists normally comprise one of two types of
30 systems. In one system, a polymer or resin has a natural resistance to solubility in a solvent, but the action of the light or light-generated species (e.g., an acid, a base, a catalyst, etc.) causes the polymer or resin to undergo a chemical reaction that alters its relative solubility in the solvent. Such chemical reactions include,

for example, an internal rearrangement, a cleavage, neutralization, splitting off of a group, acidification, or the like. In a second type of system, the polymer or resins (e.g., usually a phenol-formaldehyde resin) contains a species that resists solubilization or prevents the solvent from penetrating the polymer that would normally be soluble in the solvent. The species breaks down when struck by radiation, and the native solubility of the polymer is reinstated. Ortho-quinone diazides are an example of the type of photosolubilizing species that are conventional used in phenol formaldehyde resins, although certain onium salts are also recognized as being able to perform that function, particularly diaryliodonium salts.

The phenol formaldehyde resins useful in the compositions are known to include products derived from hydrocarbon-substituted phenols having two available positions ortho or para to a phenolic hydroxy group for aldehyde condensation to provide polymers suitable for the preparation of epoxy novolaks include o- and p-cresols, o- and p-ethyl phenols, o- and p-isopropyl phenols, o- and p-tert-butyl phenols, o- and p-secbutyl phenols, o- and p-amyl phenols, o- and p-octyl phenols, o- and p-nonyl phenols, 2,5-xylenol, 3,4-xylenol, 2,5-diethyl phenol, 3,4-diethyl xylenol, 2,5-diisopropyl phenol, 4-methyl resorcinol, 4-ethyl resorcinol, 4-isopropyl resorcinol, 4-tert-butyl resorcinol, o- and p-benzyl phenol, o- and p-phenethyl phenols, o- and p-phenyl phenols, o- and p-tolyl phenols, o- and p-xylyl phenols, o- and p-cyclohexyl phenols, o- and p-cyclopentyl phenols, 4-phenethyl resorcinol, 4-tolyl resorcinol, and 4-cyclohexyl resorcinol. Various chloro-substituted phenols which can also be used in the preparation of phenol-aldehyde resins suitable for the preparation of the epoxy novolaks include o- and p-chloro-phenols, 2,5-dichloro-phenol, 2,3-dichloro-phenol, 3,4-dichloro-phenol, 2-chloro-3-methyl-phenol 2-chloro-5-methyl-phenol, 3-chloro-2-methyl-phenol, 5-chloro-2-methyl-phenol, 3-chloro-4-methyl-phenol, 4-chloro-3-methyl-phenol, 4-chloro-3-ethyl-phenol, 4-chloro-3-isopropyl-phenol, 3-chloro-4-phenyl-phenol, 3-chloro-4-chloro-phenyl-phenol, 3,5-dichloro-4-methyl-phenol, 3,5-dichloro-5-methyl-phenol,

3,5-dichloro-2-methyl-phenol, 2,3-dichloro-5-methylphenol,
 2,5-dichloro-3-methyl-phenol, 3-chloro-4,5-dimethyl-phenol,
 4-chloro-3,4-dimethyl-phenol, 2-chloro-3,5-dimethyl-phenol,
 5-chloro-2,3-dimethylphenol, 5-chloro-3,5-dimethyl-phenol,
 5 2,3,5-trichlorophenol, 3,4,5-trichloro-phenol, 4-chloro-resorcinol,
 4,5-dichloro-resorcinol, 4-chloro-5-methyl-resorcinol,
 5-chloro-4-methyl-resorcinol.

Typical phenols which have more than two positions ortho or para to a
 10 phenolic hydroxy group available for aldehyde condensation and which, by
 controlled aldehyde condensation, can also be used are: phenol, m-cresol,
 3,5-xylenol, m-ethyl and m-isopropyl phenols, m,m'-diethyl and diisopropyl
 phenols, m-butyl-phenols, m-amyl phenols, m-octyl phenols, m-nonyl phenols,
 resorcinol, 5-methyl-resorcinol, 5-ethyl resorcinol.

15 Examples of specific dihydroxy polynuclear phenols include, among
 others, the bis-(hydroxyphenyl)alkanes such as
 2,2'-bis-(4-hydroxyphenyl)propane, 2,4'-dihydroxydiphenylmethane,
 bis-(2-hydroxyphenyl)methane, bis-(4-hydroxyphenyl)methane,
 bis(4-hydroxy-2,6-dimethyl-3-methoxyphenyl)methane,
 20 1,1'-bis-(4-hydroxyphenyl)ethane,
 1,2'-bis-(4-hydroxyphenyl)ethane, 1,1'-bis-(4-hydroxy-2-chlorophenyl)ethane,
 1,1'-bis(3-methyl-4-hydroxyphenyl) ethane,
 1,3'-bis-(3-methyl-4-hydroxyphenyl)propane,
 2,2'-bis-(3-phenyl-4-hydroxyphenyl)propane,
 25 2,2'-bis-(3-isopropyl-4-hydroxyphenyl)propane,
 2,2'-bis(2-isopropyl-4-hydroxyphenyl)pentane, 2,2'-bis-(4-hydroxyphenyl)
 heptane, bis-(4-hydroxyphenyl)phenylmethane,
 bis-(4-hydroxyphenyl)cyclohexylmethane,
 1,2'-bis-(4-hydroxyphenyl)-1,2'-bis-(phenyl)propane and
 30 2,2'-bis-(4-hydroxyphenyl)-1-phenyl-propane; di(hydroxyphenyl)
 sulfones such as bis-(4-hydroxyphenyl)sulfone, 2,4'-dihydroxydiphenylsulfone,
 5'-chloro-2,4'-dihydroxydiphenyl sulfone, and 5'-chloro-4,4'-dihydroxydiphenyl

sulfone; di(hydroxyphenyl)ethers such as bis-(4 -hydroxyphenyl)ether, the 4,4'-, 4,2'-, 2,2'-, 2,3'-, dihydroxydiphenyl ethers, 4,4'-dihydroxy-2,6-dimethyldiphenyl ether, bis-(4-hydroxy-3-isobutylphenyl)ether, bis-(4-hydroxy-3-isopropylphenyl)ether, 5 bis-(4-hydroxy-3-chlorophenyl)ether, bis-(4-hydroxy-3-fluorophenyl) ether, bis-(4-hydroxy-3-bromophenyl)ether, bis-(4-hydroxynaphthyl)ether, bis-(4-hydroxy-3-chloronaphthyl) ether, bis-(2-hydroxydiphenyl)ether, 4,4'-dihydroxy-2,6-dimethoxydiphenyl ether, and 4,4'-dihydroxy-2,5-diethoxydiphenyl ether.

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As condensing agents, any aldehyde may be used which will condense with the particular phenol being used, including formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, heptaldehyde,, cyclohexanone, methyl cyclohexanone, cyclopentanone, benzaldehyde, and nuclear alkyl-substituted 15 benzaldehydes, such as toluic aldehyde, naphthaldehyde, furfuraldehyde, glyoxal, acrolein, or compounds capable of engendering aldehydes such as para-formaldehyde, hexamethylene tetramine. The aldehydes can also be used in the form of a solution, such as the commercially available formalin. The preferred aldehyde is formaldehyde.

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The products of the present invention find use in a wide variety of applications. For example, platens are provided for the manufacture and testing of circuit boards, chips, wafers, lenses, screens, and the like that comprise flat surfaces having patterns of grooves thereon to allow fluid flow under the article being manufactured or inspected. The allowance of fluid flow prevent any air 25 seals from restricting the movement of the article being manufactured, and actually reduces the resistance to movement of an article supported on the grooved surface.

Additionally, abrasive sheeting is manufactured with columns and rows of abrasive elements thereon, to enable the passage of coolant fluids and swarth 30 below the abrading height of the sheet. The present process would be highly adaptable for manufacture of precisely structured abrasive surfaces. A non-limiting particular field within which the practice of the present technology is applicable includes a linear step motor positioning stage. An open lopp linear

step motor provides an economical linear motor driven positioning stage for integrated circuit manufacture and the manufacture of other precision elements. Linear step motors incorporate a motor, positioning system and bearings (e.g., air bearings) into two components, a moving forcer and a stationary platen. The invention provides a unique method for manufacturing the platen and unique resulting platen. The platen is ordinarily a photochemically etched steel plate filled (in the grooves or troughs) with epoxy resin. The surface is usually further ground and hard-chrome plated to provide an appropriate magnetically responsive differential on the surface. The magnetic force between the forcer and the platen provides a preload for the bearing system. The integral bearing system (e.g., air bearings), maintains the required air gap. The uniformity and slope detail of the platen become important in enabling the linear motor to provide direct linear motion without mechanical transmission, without mechanical transmission devices. The flatness and uniformity of the surface is important in providing uniform and controlled movement of the linear motor and associated workpiece over the surface.

WHAT IS CLAIMED:

1. A process for the provision of a pattern on a surface of a substrate comprising, in any order:
 - 5 a) providing a pattern of resist material onto the surface of a substrate, and chemically machining the substrate through the pattern of resist; and
 - b) electrical discharge machining said substrate in a pattern that at least overlaps the pattern of resist material.
- 10 2. The process of claim 1 wherein step a) is performed before step b).
3. The process of claim 2 wherein said providing a pattern of resist material is performed by applying a coating of photosensitive resist material to the surface of said substrate, exposing the coating to a distribution of radiation that alters the
15 solubility of the coating, and developing coating to remove portions of the coating, leaving the pattern of resist on said surface.
4. The process of claim 3 wherein said photosensitive resist is a positive-acting resist.
20
5. The process of claim 3 wherein said photosensitive resist is a negative acting resist.
6. The process of claim 2 wherein said pattern comprises columns and rows of
25 flat plateaus separated by troughs.
7. The process of claim 2 wherein the pattern comprises at least one flat area adjacent to a trough, the difference in height between the highest point on the edge of a plateau and the lowest point in a trough defining a value of height, h ,
30 and a line, v , passing vertically through said edge and a face of the plateau that defines a part of said trough forming an angle θ , the angle θ diverges from vertical line v by less than 20 degrees when 30% of h has been surpassed moving down from said edge, and the angle θ diverges from vertical line v

by more than 25 degrees when 60% of h has been surpassed moving down from said edge.

8. The process of claim 1 wherein the maximum depth of features machined into
5 said substrate is 0.5 mm.

9. The process of claim 2 wherein the maximum depth of features machined into said substrate is 0.4 mm.

10 10. The process of claim 4 wherein the maximum depth of features machined into said substrate is 0.3 mm.

11. A process for the provision of a pattern on a surface of a substrate comprising, in any order:

15 a) providing a pattern of resist material onto the surface of a substrate, and chemically machining the substrate through the pattern of resist to provide a three-dimensional pattern on said surface, said three-dimensional pattern comprising plateaus and troughs, the plateaus having flat tops and sides that slope farther away from the plateaus as the sides reach the troughs; and

20 b) electrical discharge machining said substrate in a pattern that at least overlaps the pattern of resist material, the electrical discharge machining altering the slope of the sides so that at least some of the sides slope away from the plateaus as the sides approach the troughs by a lesser amount than immediately after chemical machining has been completed in a).

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12. The process of claim 11 wherein said pattern consists of a uniform repeating pattern of plateaus over an area of at least 200mm².

13. An article of manufacture comprising a surface having a three-dimensional
30 pattern thereon, the pattern comprises multiple flat areas defined by plateaus having edges, said plateaus having a difference in height from adjacent troughs, the difference in height between the highest point on the edge of a plateau and the lowest point in a trough defining a value of height, h , and a line, v , passing

vertically through said edge and a face of the plateau that defines a part of said trough forming an angle theta, the angle theta diverges from vertical line v by less than 20 degrees when 30% of h has been surpassed moving down from said edge, and the angle theta diverges from vertical line v by more than 25 degrees
5 when 60% of h has been surpassed moving down from said edge.

14. The article of claim 13 wherein said pattern consists of a uniform repeating pattern of plateaus over an area of at least 200mm².

10 15. The article of claim 13 wherein h is between 0.000038 and 0.38 mm.

16. The article of claim 14 wherein h is between 0.000038 and 0.38 mm.

15 17. The article of claim 13 wherein said pattern comprises rows and columns of plateaus, the plateaus having diameters of less than 1mm.

18. The article of claim 13 wherein said pattern comprises rows and columns of plateaus, the plateaus having diameters of less than 0.5mm.

20 19. The article of claim 16 wherein said pattern comprises rows and columns of plateaus, the plateaus having diameters of less than 0.5mm.

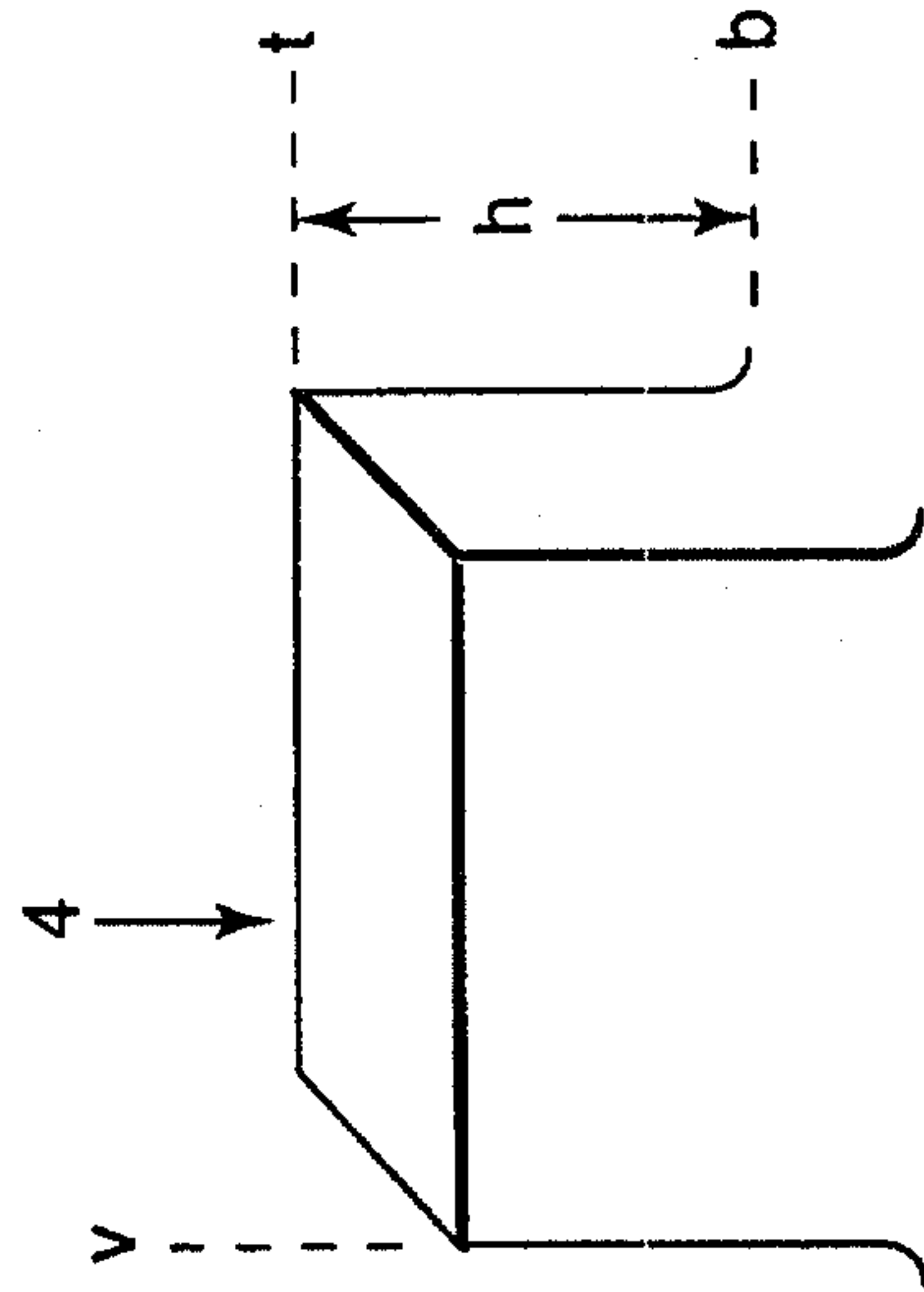


Fig. 1b

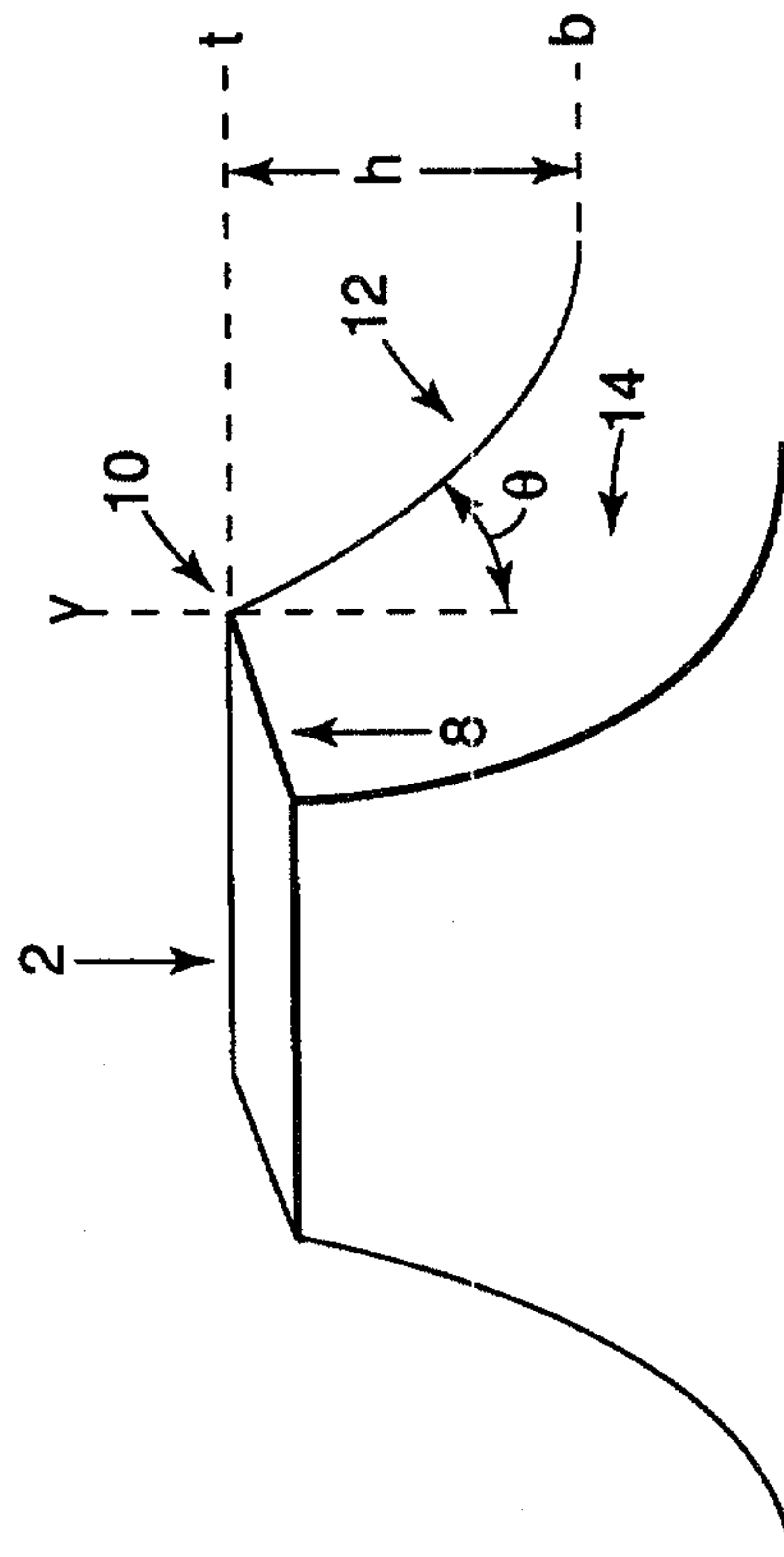


Fig. 1a

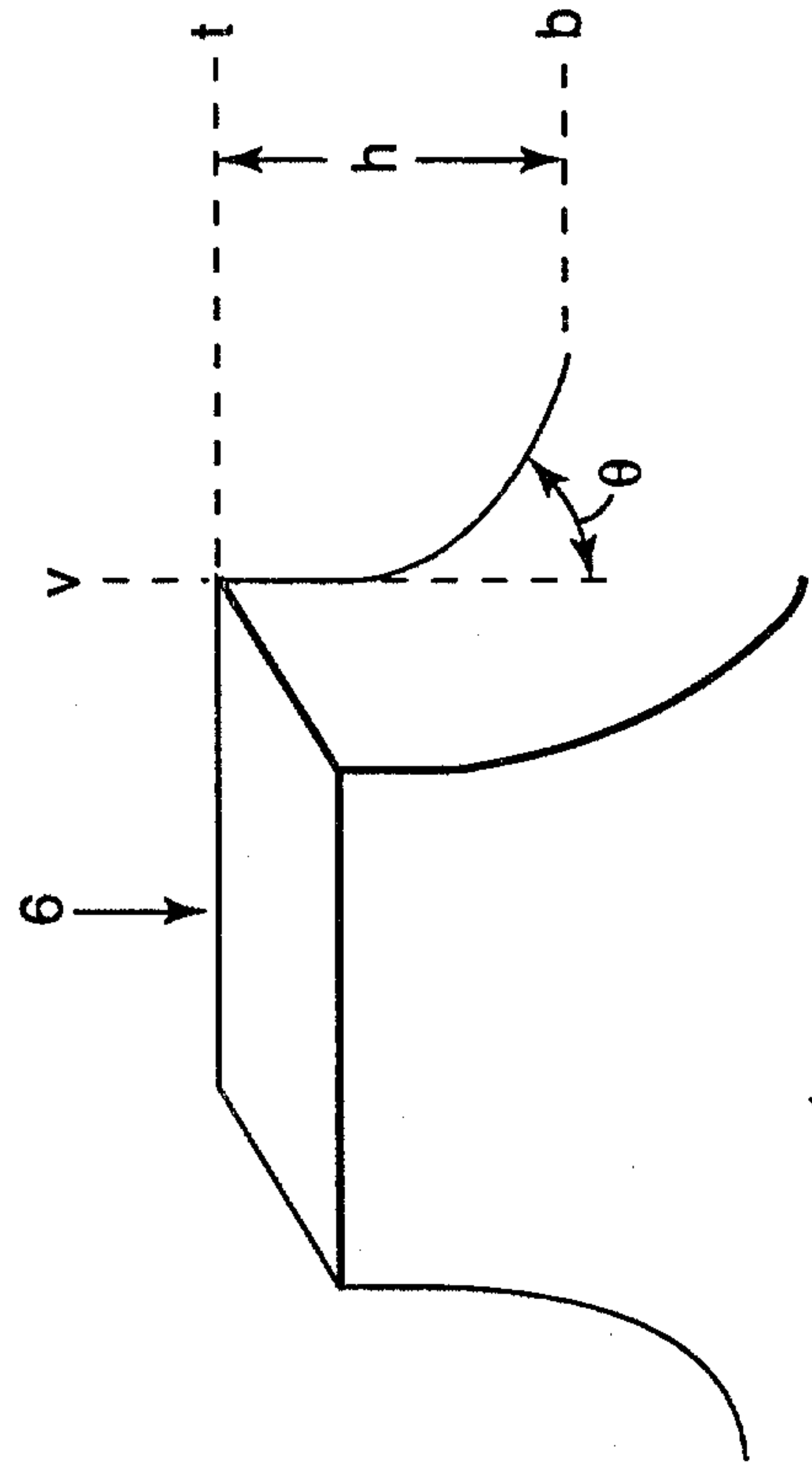


Fig. 1c