United States Patent [19]

De Angelo

[11] **3,821,016**

[45] **June 28, 1974**

[54] **METHOD OF FORMING AN ADHERENT METALLIC PATTERN ON A POLYIMIDE SURFACE**

[75] Inventor: **Michael Anthony De Angelo,** Hamilton Township, Mercer County, N.J.

[73] Assignee: **Western Electric Company Incorporated,** New York, N.Y.

[22] Filed: **Oct. 17, 1973**

[21] Appl. No.: **407,356**

Related U.S. Application Data

[62] Division of Ser. No. 255,124, May 19, 1972.

[52] **U.S. Cl.** ..... **117/47 A,** 117/93.3, 117/71, 117/130, 117/160, 117/212, 96/49, 96/88, 96/92

[51] **Int. Cl.** **B44d 1/50,** H05k 3/12, H05k 3/18

[58] **Field of Search** ..... 117/47 A, 93.3, 71, 130, 117/160; 96/49, 88, 92

[56] **References Cited**

UNITED STATES PATENTS

2,869,267	1/1959	Holman	242/79.5
3,033,703	5/1962	Schneble et al.	117/47 A
3,179,614	4/1965	Edwards	260/30.2
3,361,589	1/1968	Lindsui	117/47 A
3,394,023	7/1968	Wilhelm	117/47 A
3,686,016	8/1972	NaGuire	117/47 A
3,702,285	11/1972	Knorre	117/47 A

FOREIGN PATENTS OR APPLICATIONS

2,012,123	Germany	117/47 A
2,016,111	France	117/47 A
1,160,675	Great Britain	117/47 A

OTHER PUBLICATIONS

Developing Pattern In Polyimide Films, Anderson, Pg. 1,834, Vol. 10, No. 12, 1968, IBM Disc. Bult. 156–2.

Metalization of KTFR, Holl et al., pg. 533, Vol. 10, No. 5, Oct. 1967, IBM Disc. Bult. 156–2.

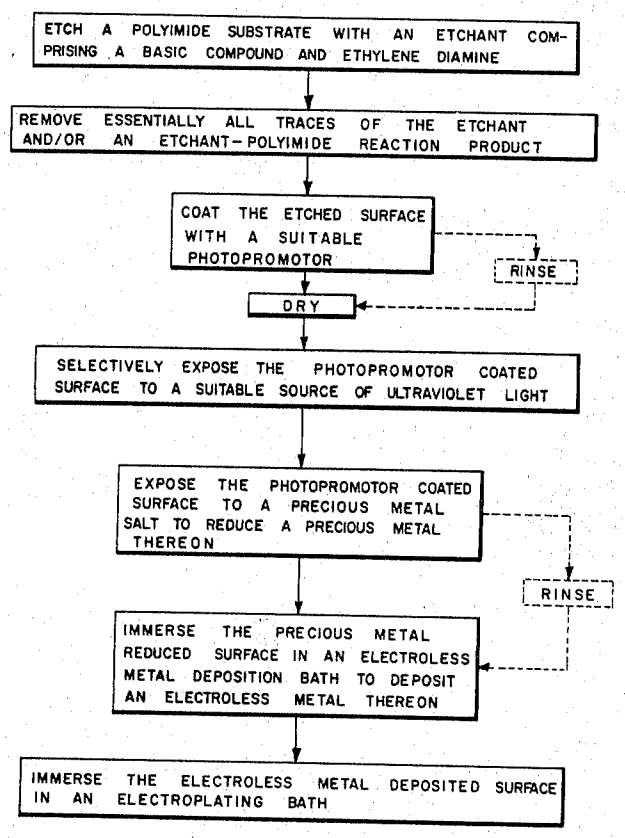
Improved Adhesion Between Polyimide Surfaces, pg. 518, Vol. 13, No. 2, July 1970, IBM Disc. Bult. 156–2.

Primary Examiner—Michael Sofocleous
Assistant Examiner—William R. Trenor
Attorney, Agent, or Firm—J. Rosenstock

[57] **ABSTRACT**

An etching composition and a method utilizing such a composition for etching a surface of a polyimide is disclosed. The method comprises exposing the polyimide surface to an etching composition comprising an aqueous solution of a basic compound and ethylene diamine. The ethylene diamine synergistically increases the etching rate of the polyimide. When the ethylene diamine is present in an amount in excess of its degree of solubility the etching of the polyimide results in a frosted or matte finish thereof.

5 Claims, 3 Drawing Figures



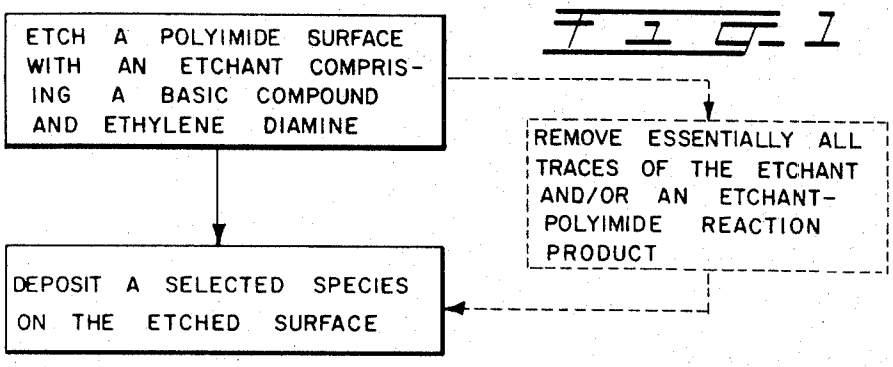

ETCH A POLYIMIDE SURFACE WITH AN ETCHANT COMPRISING A BASIC COMPOUND AND ETHYLENE DIAMINE
REMOVE ESSENTIALLY ALL TRACES OF THE ETCHANT AND/OR AN ETCHANT-POLYIMIDE REACTION PRODUCT
DEPOSIT A SELECTED SPECIES ON THE ETCHED SURFACE

FIG. 1

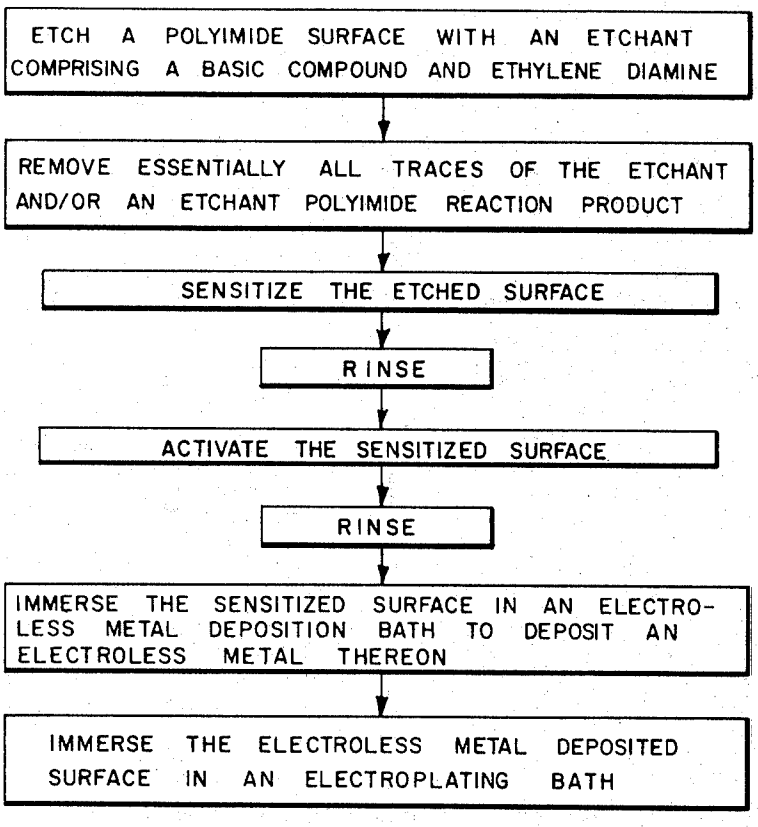

ETCH A POLYIMIDE SURFACE WITH AN ETCHANT COMPRISING A BASIC COMPOUND AND ETHYLENE DIAMINE
REMOVE ESSENTIALLY ALL TRACES OF THE ETCHANT AND/OR AN ETCHANT POLYIMIDE REACTION PRODUCT
SENSITIZE THE ETCHED SURFACE
RINSE
ACTIVATE THE SENSITIZED SURFACE
RINSE
IMMERSE THE SENSITIZED SURFACE IN AN ELECTROLESS METAL DEPOSITION BATH TO DEPOSIT AN ELECTROLESS METAL THEREON
IMMERSE THE ELECTROLESS METAL DEPOSITED SURFACE IN AN ELECTROPLATING BATH

FIG. 2

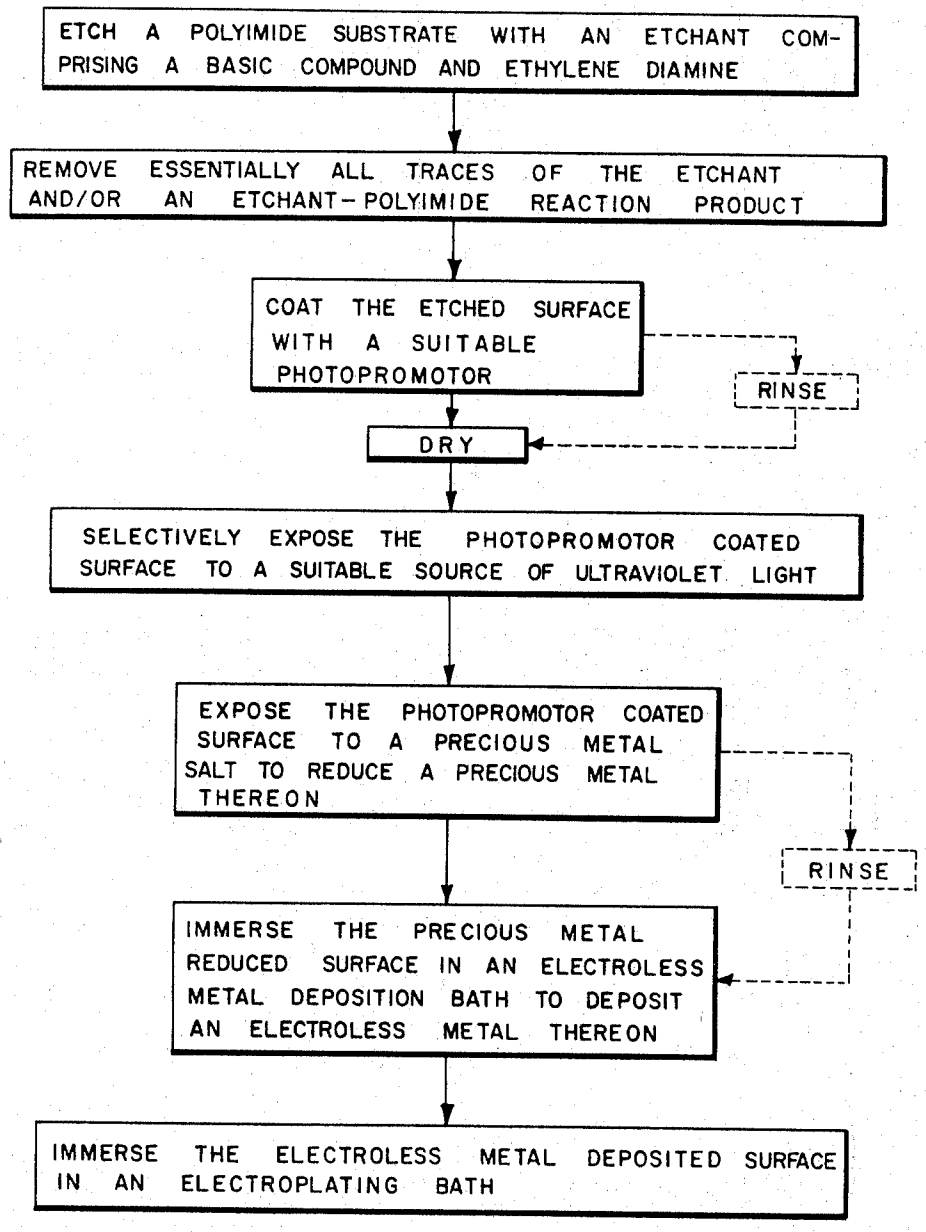

ETCH A POLYIMIDE SUBSTRATE WITH AN ETCHANT COMPRISING A BASIC COMPOUND AND ETHYLENE DIAMINE
REMOVE ESSENTIALLY ALL TRACES OF THE ETCHANT AND/OR AN ETCHANT-POLYIMIDE REACTION PRODUCT
COAT THE ETCHED SURFACE WITH A SUITABLE PHOTOPROMOTOR
RINSE
DRY
SELECTIVELY EXPOSE THE PHOTOPROMOTOR COATED SURFACE TO A SUITABLE SOURCE OF ULTRAVIOLET LIGHT
EXPOSE THE PHOTOPROMOTOR COATED SURFACE TO A PRECIOUS METAL SALT TO REDUCE A PRECIOUS METAL THEREON
RINSE
IMMERSE THE PRECIOUS METAL REDUCED SURFACE IN AN ELECTROLESS METAL DEPOSITION BATH TO DEPOSIT AN ELECTROLESS METAL THEREON
IMMERSE THE ELECTROLESS METAL DEPOSITED SURFACE IN AN ELECTROPLATING BATH

FIG 3

METHOD OF FORMING AN ADHERENT METALLIC PATTERN ON A POLYIMIDE SURFACE

This is a division, of application Ser. No. 255,124 filed May 19, 1972.

BACKGROUND OF THE INVENTION

1. Field of the Invention

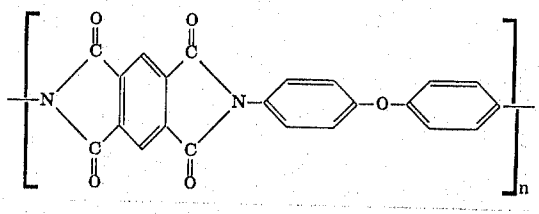
This invention relates to a method of etching a polyimide surface, and more particularly, to a method of etching a polyimide surface to produce a matte finish thereof.

2. Discussion of the Prior Art

During the past few years, the markets for metal plated plastic parts have grown rapidly as manufacturers have begun to appreciate the beautiful appearance of such parts when plated with bright, metallic finishes, and to take advantage of the economies in cost and weight afforded by substituting molded plastic parts for metal. Furthermore, such plated finishes are not as susceptible to pitting and corrosion because there is no galvanic reaction between the plastic substrate and the plated metal.

Because plastic materials do not conduct electricity, it is common practice to provide a conductive layer, such as copper, by electroless deposition so that an additional thickness of metals, particularly copper, nickel and chromium, can be electrolytically plated onto the electroless copper layer. Electroless deposition refers to a chemical deposition of an adherent metal coating on a conductive, non-conductive or semi-conductive substrate in the absence of an external electrical source. While there are several methods of applying this metallic coating by the combined use of electroless and electrolytic procedures, it was not until quite recently that processes were developed which can provide even minimal adhesion of the conductive coating to the plastic. This is because overall adhesion is governed by the bond strength between the plastic substrate and the electroless copper layer. Even with these improved processes, reasonable adhesion can be obtained with only a very few plastics, and then only when great care is taken in all of the steps for the preparation and plating of the plastic substrate.

In the printed circuit field, extensive use is being made of substrates comprising polyimides. One type of polyimide that is especially preferred as a substrate is the polyimide sold under the trademark "Kapton" (DuPont). Kapton^R is a polyimide polymer made from the anhydride of pyromelittic acid and **4,4'** diaminodiphenyl ether and is represented by the general formula



where n is an integer ranging from 150 to 650. Kapton^R has an average molecular weight ranging from 60,000 to 250,000.

Difficulties have been encountered heretofore in attempting to deposit a layer of metal or metal ions upon

polyimides, such as Kapton^R, in that this type of material, like many other plastics is not normally receptive to the aqueous solutions employed in metal plating processes. Prior efforts to overcome this deficiency have not been particularly successful. Moreover, the adhesion properties at the surface of this particular type of plastic is low thereby leading to metal deposits thereon which are easily flaked or stripped during normal usage. This makes it highly desirable that some way be found to activate polyimide substrates so as to increase their adhesive properties at their surfaces and to render their surfaces hydrophilic while, at the same time, retaining their normal strength and their other desirable physical properties.

In the present state of the art, various methods are available for rendering the surface of a polymer or a plastic material hydrophilic. One method in common practice in plating plastic materials entails mechanical roughening of the surface of the plastic. Initially, this surface roughening is accomplished by some form of mechanical deglazing, such as scrubbing with an abrasive slurry, wet tumbling, dry rolling or abrasive (sand) blasting. However, the mechanical deglazing process is extremely costly in that many parts have to be finished by hand, and, in the case of relatively small parts, or parts with complex contours, it is very difficult to abrade the surface uniformly by conventional means. Another disadvantage to mechanical abrading is that it is hard to control and many problems are encountered when the surface abrasion is carried too far. Of greatest disadvantage, however, is in the formation of printed circuits utilizing a photoimaging process, such as the photoselective metal deposition process revealed in DeAngelo et al., Ser. No. 719,976, filed April 1968, now U.S. Pat. No. 3,562,005, assigned to the assignee hereof. The photoimaging process inherently requires a high pattern resolution. This resolution is limited by the topography of the surface on which the pattern is generated. When mechanical deglazing is employed, e.g., by sand blasting, the resolution of the pattern may suffer because of the mechanically roughened surface.

Adhesion is defined as the attraction which exists between molecules at an interface. [See Adhesion, D. D. Eley, Ed., University Press, Oxford (1961)]. As stated in Goldie, Metallic Coating of Plastics, Vol. 1 (Electrochemical Publications Limited, 1969), there are various categories of adhesion. The adhesion of printing inks to plastics involves one type, whereas use of adhesives on plastics involves another and electroplating of plastic involves yet another. A method of improving adhesive properties of a polyimide surface with respect to a selected deposited species thereon, including in part, printing inks, adhesives and electroplated metals, especially in aqueous form is needed.

A method extensively employed to improve the adhesive properties of plastics includes the use of chemical roughening agents or etchants thereof. Various basic compounds, typical of which are revealed in U.S. Pat. No. 3,361,589, are capable of acting as etchants for polyimides. However, it has been found that the type of etching resulting from such basic etchants does not lead to a large adhesion enhancement of a selected species deposited thereon. The etched surface produced by most of the basic polyimide etchants is "smooth" to the naked eye. An etched surface which is frosted or of a matte finish to the eye is preferred, rather than the

above-described "smooth" finish. Such a frosted or matte finish would enhance the adhesive properties of the polyimide surface to a selected species deposited thereon. A method whereby such a matte surface is produced is therefore needed.

SUMMARY OF THE INVENTION

The present invention is directed to a method of etching a polyimide surface and, more particularly, to etching a polyimide surface to improve adhesive properties thereof with respect to a species deposited thereon.

The method includes etching a polyimide surface with an etching composition which comprises an aqueous solution comprising a basic compound and ethylene diamine. A suitable etching, which improves the adhesive properties of the polyimide, occurs when the finish of the polyimide surface becomes frosted or matte to the naked eye. Such a frosted or matte finished surface is produced when the etching composition is in the form of a dispersion, wherein the ethylene diamine is present in an amount in excess of its degree of solubility, which is defined as a concentration of a saturated solution at a given temperature. A suitable species, e.g., a printing ink, an aqueous solution, an electroless metal deposit, etc., destined to be retained on the etched polyimide surface, may now be deposited thereon.

DESCRIPTION OF THE DRAWING

The present invention will be more readily understood by reference to the following drawing taken in conjunction with the detailed description, wherein:

FIG. 1 is a general flow chart of the novel process of the invention;

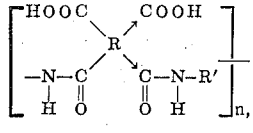
FIG. 2 is a flow chart of the process of the invention directed to an electroless metal deposition; and

FIG. 3 is a flow chart of the process of the invention directed to a photosensitive electroless metal deposition.

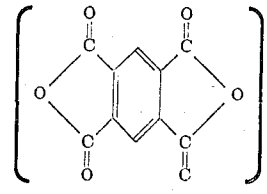
DETAILED DESCRIPTION

The present invention is described primarily in terms of improving the adherence of a metal deposit, deposited from an electroless plating bath, upon a polyimide surface. However, it will be understood that such description is exemplary only and is for purposes of exposition and not for purposes of limitation. It will be readily appreciated that the inventive concept described is equally applicable to improve adhesion between the polyimide surface and other conventional species well known in the art which may be utilized in cementing, printing and metallizing the polyimide surface.

A polyimide substrate is selected. A suitable polyimide includes any polyimide of a polyamide-acid having the formula

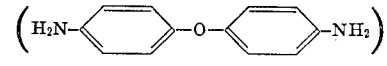


where the arrows denote isomerism, R is an organic tetravalent radical containing at least 2 carbon atoms, no more than 2 carbonyl groups of each polyamide-acid unit being attached to any one carbon atom of said tetravalent radical; R′ is a divalent radical containing at least 2 carbon atoms, the amide groups of adjacent polyamide-acid units each attached to separate carbon atoms of said divalent radical; and n is a positive integer sufficient to provide the polyamide acid with an inherent viscosity of at least 0.1. Typical of such a polyimide is Kapton^R. Kapton^R is a polyimide formed from pyromellitic dianhydride

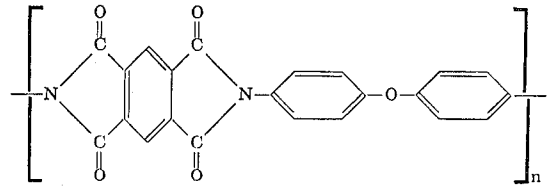


and

4,4′-diamino-diphenyl ether



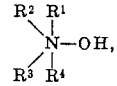
and which has a general formula



where n is an integer ranging from 150 to 650, and which has an average molecular weight ranging from 60,000 to 250,000. The above polyimides and their preparation are fully described in Edwards, U.S. Pat. No. 3,179,614, incorporated by reference hereinto.

A surface of the polyimide, e.g., Kapton^R, etc., is treated with a suitable etchant thereof for a period of time sufficient to obtain an adequate etching or roughening. Generally an adhequate etching of the surface, in the case of clear polymeric materials, such as the polyimide Kapton^R, for purposes of improving adhesive properties of the surface, occurs when the surface becomes uniformly translucent or frosted to the naked eye. Typically, such frosted surfaces have pores or pits of 1μ or less in diameter and typically exhibit a depth of 10μ or less.

A suitable etching for the polyimide class of polymers comprises a suitable basic compound and ethylene diamine contained in a suitable carrier medium, e.g., alcohols of 1–4 carbons (methanol, ethanol, etc.). A preferred carrier, however, is water. Some suitable basic compounds are those revealed in Lindsey, U.S. Pat. No. 3,361,589, and incorporated by reference hereinto. Specifically, these are (1) a carbonate, hydroxide, cyanide, borate, phosphate, pyrophosphate, sulfite, sulfide or silicate of an alkali metal including sodium, potassium, lithium, rubidium and cesium; (2) a carbonate, hydroxide, cyanide, borate or sulfide of ammonia; (3) an alkoxide of an alkali metal and (4) quarternary ammonium hydroxides having a general formula



where R^1 and R^2 are the same or different alkyl radicals of 1 through 4 carbons, R^3 is alkyl of 1 through 18 carbons or alkenyl of 1 through 18 carbons and R^4 is alkyl of 1 through 18 carbons, alkenyl of 1 through 18 carbons, phenyl, alkylphenyl where the alkyl portion has 1 through 18 carbons, benzyl or alkylbenzyl where the alkyl portion has 1 through 18 carbons. However, a preferred basic compound is the hydroxide of the alkali metals, including sodium, potassium, lithium, rubidium and cesium.

The concentration of the basic compound and the ethylene diamine respectively, is determined by the type and degree of etching desired. The concentration of the basic compound may range over a broad spectrum, depending again upon the degree of etching and the rate of etching desired. Typically, for NaOH, a practical and operational concentration ranges from 1 mole to 15 moles/liter of water. It is to be noted and stressed that adding ethylene diamine to an aqueous solution of a suitable basic compound results in an unexpected synergism in the etch rate of the selected polyimide, e.g., Kapton^R, etc. Ethylene diamine by itself has no effect on the polyimide with respect to the etching thereof. However, upon adding ethylene diamine to a suitable basic etchant of the polyimide, e.g., an aqueous NaOH solution, a synergism is obtained whereby the rate of etch by the basic etchant, e.g., the aqueous NaOH solution, is increased. The amount of ethylene diamine necessary for this synergism ranges from a minimum, e.g., approximately 20 weight percent of the total solution in a 1N aqueous NaOH solution at 25°C, 0.67 weight percent of the total solution in a 10N aqueous NaOH solution at 25°C, which may be easily determined experimentally by one skilled in the art using conventional techniques, to a maximum representing saturation of the basic solution at a particular temperature, e.g., approximately 6.2 to 7.6 weight percent of the total solution of ethylene diamine in a 10 normal aqueous NaOH solution at a temperature of 25°C.

With respect to the saturation limit of ethylene diamine, it is of course understood that using less concentrated aqueous basic solutions allows more ethylene diamine to go into solution with, of course, the converse being true. In this regard, also, it should be noted that the synergistic effect of ethylene diamine occurs above the saturation limit, i.e., when the ethylene diamine is present in an amount in excess of its degree of solubility, which is defined as a concentration of a standard solution at a given temperature. The above maximum, representing saturation, has been merely used to distinguish the synergistic concentration of the ethylene diamine from a concentration of ethylene diamine which leads not only to the synergism but also to the production of a frosted or matte polyimide surface finish.

It is to be noted that where the polyimide surface is to be etched to a matte-free finish, it may be either immersed in the basic compound — ethylene diamine solution or alternatively, it may be first immersed in ethylene diamine, whereafter it is immersed in an aqueous solution comprising the basic compound, e.g., NaOH. In this regard, it is hypothesized that the ethylene diamine is first absorbed onto the polyimide surface whereafter it penetrates the polymer in depth and opens up or expands, in a spatial sense, the crosslinking network of the polymer. Subsequently upon exposure to the basic solution, e.g., aqueous NaOH, the ethylene diamine either combines therewith to cause the increased etch rate or else provides "swelled" [spatially expanded] sites which are more rapidly etched by the basic solution. Some support to the above hypothesis resides in the fact that water rinsing of the ethylene diamine exposed or treated polyimide surface does not prevent the synergistic effect. However, it is to be understood that the above explanation is in the nature of a hypothesis and the invention is not to be restricted thereby. Where the polyimide surface is first immersed in an ethylene diamine solution, the period of exposure therein should be sufficient to allow the absorption of the ethylene diamine on the surface. Such exposure, typically, is in the range of several seconds, e.g., approximately 30 seconds at a temperature of 25°C. It is also to be noted that surprisingly, etching the polyimide surface in this manner leads to a resultant basic compound-polyimide etching reaction product which is not readily analyzable or identifiable. This reaction product does not have the appearance of products resulting from etching the polyimide with the various suitable basic compounds alone or the basic compounds combined with the ethylene diamine.

The synergistic etching of polyimides, e.g., Kapton^R, etc., with the aqueous etching solution, comprising the suitable base and ethylene diamine, may be carried out over a broad temperature spectrum, whereby an etched matte-free finish is obtained. A practical, operational temperature ranges from 20°C to the boiling point of the etching solution. It is, of course, understood, that the concentration of the basic compound and the ethylene diamine and the temperature employed should be selected as to give a desired etch within a resonable time. It is also to be understood and stressed that the concentration, temperature and time parameters are all interdependent and that variations in temperature will produce variations in the other parameters, whereby optimum results will be attained. In this regard, the various parameters and their interdependency are well known in the art and their interactions between one another is also well known or can be easily ascertained experimentally by one skilled in the art.

As stated previously, an adequate and a preferred etching of a polyimide surface, for improving the adhesive properties thereof, occurs when a frosted or matte finish is obtained. Such a surface is obtained only when the ethylene diamine is present, in the aqueous solution of the suitable basic compound, in an amount in excess of saturation, i.e., only when the ethylene diamine is in excess of its degree of solubility. Typically, for a 10 molar aqueous NaOH solution, an ethylene diamine concentration of at least 7.6 weight percent of the total weight of the solution is required at a temperature of 25°C. Typically, for a 15 molar aqueous NaOH solution, an ethylene diamine concentration of at least 1.8 weight percent of the total weight of the solution is required at a temperature of 25°C. When such is the situation, a two-phase system comprising (1) an aqueous phase containing ethylene diamine and the suitable base, e.g., NaOH, and (2) an ethylene diamine phase, immiscible with the aqueous phase, is obtained. Preferably, the two-phase system should be in the form of a dispersion whereby the ethylene diamine is dispersed throughout the aqueous phase. This is preferred since it leads to a uniformly frosted polyimide surface rather than one which may be spotty. The dispersion may be attained by standard means well known in the art, including, in part, mechnical stirring or agitation, ultra-

sonic cavitation, and chemical additives, such as surfactants.

Referring to FIG. 1, the polyimide surface destined to be frosted is immersed in the two-phase dispersion for a period of time sufficient to attain an adequate etch, as evidenced by the frosted or matte finish thereof. As mentioned above, an adequately etched surface, having improved adhesive properties, typically exhibits pores or pits of 1μ or less in diameter, which typically have a depth of 10μ or less. After the polyimide, e.g., Kapton^R, etc., has been etched, whereby a frosted or matte finish is obtained, the frosted surface is then subjected to a deposition of a suitable species thereon. The frosted surface may first be subjected to an optional treatment or step which comprises removing essentially all traces of a deposit residing on the etched surface. The deposit comprises the etchant and/or an etchant-polyimide reaction product which forms. The removal may be best accomplished by rinsing the frosted surface with water or any other suitable cleaning agent for approximately 1 minute. In this regard, it is to be noted that the rinsing may extend beyond 1 minute since there is not adverse affect from long duration rinsing with water and in fact long duration rinsing with water, e.g., typically, about 15 minutes with water maintained at a temperature of 20°C, 5 minutes with water at a temperature of 60°C, is preferred when an electroless metal deposit is to be deposited on the frosted surface. It is also to be understood that the removal step may involve in whole or in part a mechanical removal, e.g., by doctor blading, or the etchant and/or etchant-polyimide reaction product which forms or remains on the frosted surface. It is to be understood and stressed that although the removal step is preferred, where traces of the etchant and/or etchant-polyimide reaction product can be tolerated on the frosted surface of the polyimide, this removal step may be eliminated.

A suitable selected species is then deposited on the frosted polyimide surface, which may or may not have traces of the etchant and/or etchant-polyimide reaction product thereon. A suitable species may be any of a multitude of materials, well known in the art, which can be deposited upon a polyimide type polymer and comprises in part conventional aqueous or organic based paints, lacquers, inks and adhesives, aqueous or non-aqueous solutions of inorganic salts, aqueous or non-aqueous electroless metal deposition solutions, e.g., sensitizers and activators, and the metal deposits resulting therefrom, metals, etc. The suitable species may be deposited or applied to the frosted or matte surface by any standard means known in the art including dipping, brushing, spray coating, spin coating, vapor depositing, electroless depositing with or without electrodepositing, sputtering, etc.

Where the selected species is an electrolessly deposited metal, a standard technique may be employed. A typical standard method of electroless deposition is outlined in the flow diagram of FIG. 2. It is, of course, understood that any conventional electroless metal deposition technique may be employed and the outline in FIG. 2 is illustrative only and not restrictive. The frosted polyimide surface is thoroughly rinsed with water, typically about 5 minutes with water maintained at 60°C, to remove essentially all traces of the etchant and/or etchant-polyimide reaction product which forms. It is, of course, understood that the removal or cleaning step may be carried out with any suitable agent, including a mechanical one. The rinsing is to avoid contaminating a sensitizing, an activating and an electroless metal plating solution to which the frosted polyimide surface is destined to be subjected. Contamination, particularly of the plating bath, is undesirable because the stability of such plating baths is frequently adversely affected by such a condition.

After rinsing, the frosted polyimide surface is sensitized. Sensitization consists of depositing or absorbing on the frosted surface a sensitizing species, e.g., Sn^{+2} ion, which is readily oxidized. Conventionally, the rinsed, frosted surface is dipped into a standard sensitizing solution, e.g., aqueous stannous chloride with a supporting medium such as HCl, ethanol, ethanol and caustic, or ethanol and hydroquinone. It is to be understood that the sensitizing solutions and the conditions and procedures of sensitizing are well known in the art and will not be elaborated herein. Such sensitizers and procedures may be found, in part, in Metallic Coating of Plastics, William Goldie, Electrochemical Publications Limited, 1968.

After sensitizing the frosted surface, the sensitized surface is rinsed, then activated. It is to be noted that it is important that the sensitized frosted surface be rinsed thoroughly in a cleaning medium, e.g., deionized water, after sensitizing. If such is not done, there is a possibility that excess sensitizer on the roughened surface will cause reduction of an activating species, e.g., Pd^{+2}, to which the sensitized surface is destined to be exposed, in non-adherent form on the frosted surface. Activation relates to providing a deposit of a catalytic metal, e.g., Pd, over the frosted surface of the polyimide substrate in sufficient quantities to successfully catalyze a plating reaction once the frosted surface is introduced into an electroless plating bath. The sensitized, frosted surface is exposed to a solution containing the activating species, e.g., a noble metal ion, wherein the sensitizing species is readily oxidized and the noble metal ion, e.g., Pd^{+2}, is reduced to the metal, e.g., Pd, which in turn is deposited on the frosted surface. The deposited activating metal, e.g., Pd, acts as a catalyst for localized further plating. Again, it is to be understood that the various activating metal ions and their solutions, the conditions and procedures of activation are well known in the art and will not be elaborated herein. Such activators and procedures may be found, in part, in Metallic Coating of Plastics, previously referred to.

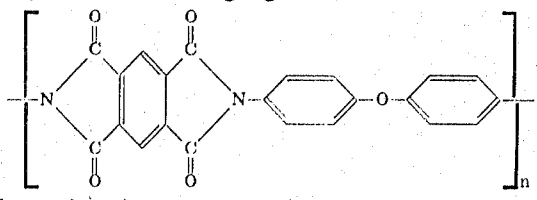
After the activating step, the activated polyimide surface is immersed in a standard electroless plating bath containing a metal ion, e.g., Cu^{+2}, destined to be reduced by the catalytic metal species, e.g., Pd. The metal ion, e.g., Cu^{+2}, is reduced by the catalytic metal, e.g., Pd, and is electrolessly deposited on the frosted surface. Again it is to be pointed out that the electroless baths, the electroless plating conditions and procedures are well known in the art and will not be elaborated herein. Reference is again made to Metallic Coating of Plastics, previously referred to, for some typical examples of electroless baths and plating parameters. It is to be noted that in some cases, it is possible to go directly from the sensitizing step to the electroless plating solution exposure step. It is also noted that the electroless metal deposition may then be subjected to a conventional electroplating bath whereby the electroless metal deposit is built up.

A preferred method of electrolessly depositing a metal on the abraded polymeric surface is the method revealed in DeAngelo et al., Ser. No. 719,976, filed Apr. 9, 1968, and now U.S. Pat. No. 3,562,005, assigned to the assignee hereof and incorporated by reference hereinto. Referring to FIG. 3, the method entails applying a photopromoter solution to the frosted polyimide surface, utilizing procedures revealed in M. A. DeAngelo et al. It is to be noted that the frosted surface is treated, prior to the photopromoter coating, so as to remove a portion of the deposit, representing essentially all traces of the etchant and/or etchant polyimide reaction product which forms, from the surface. A photopromoter is defined as a substance which, upon being exposed to appropriate radiation, either (a) dissipates chemical energy already possessed thereby or (b) stores chemical energy not previously possessed thereby. When the substance possesses or has stored chemical energy it is capable of promoting, other than as a catalyst, a chemical reaction whereby it, the photopromoter, undergoes a chemical change in performing its function (unlike a catalyst). The resultant photopromoter-covered, frosted polyimide surface may then be rinsed with deionized water (depending on the type of photopromoter employed), and is then dried. The photopromoter-coated surface is then selectively exposed to a source of ultraviolet radiation, through a suitable mask, to form at least one region which is capable of reducing a precious metal from a precious metal salt, e.g., $PdCl_2$. The region so capable is exposed to the precious metal salt, e.g., $PdCl_2$, whereby the precious metal salt is reduced to the precious metal, e.g., Pd, which in turn is deposited thereon. The precious metal-deposited region is then exposed to a suitable electroless metal plating bath, e.g., copper, wherein the metal, e.g., copper, is plated on the region, forming an adherent metal deposit on the frosted polyimide surface. The electroless metal deposit may then be subjected to a conventional electroplating bath treatment.

A suitable photopromoter solution may be either a positive type or a negative type as discussed in DeAngelo et al. A suitable mask, either positive or negative depending on whether the photopromoter is positive or negative, is one as discussed in DeAngelo et al., and typically comprises a quartz body having a radiation opaque pattern thereon. The ultraviolet radiation source is a source of short wavelength radiation (less than 3,000A, and typically about 1,800A to about 2,900A).

EXAMPLE I

A. For comparison purposes, a 2 mil thick Kapton^R film, which is a polyimide made from the anhydride of pyromellitic acid and 4,4′ diamino-diphenyl ether, and is represented as having a general formula



where n is an integer ranging from 150 to 650, and having an average molecular weight of 60,000 to 250,000, was chemically etched in a 10N-NaOH aqueous solution, commercially obtained, at a temperature of 25°C. After 10 minutes there was a loss of about 0.1 mil of thickness. There was no pitting or frosting observed.

B. The procedure of Example I-A was repeated except that the etching solution comprised 2.1 weight percent, of the total weight of the resultant solution, of anhydrous ethylene diamine, commercially obtained, in the 10N aqueous NaOH solution. After 10 minutes there was a loss of 0.2 mil of thickness. There was no pitting or frosting observed.

C. The procedure of Example I-B was repeated except that 4.3 weight percent of the total weight of the resultant solution, of ethylene diamine was used. After 10 minutes there was a loss of 0.5 mil of thickness.

D. The procedure of Example I-B was repeated except that 7.6 weight percent, of the total weight of the resultant solution, of ethylene diamine was used. A two-phase system resulted. The Kapton^R film was immersed in the two-phase system without agitation thereof. After 10 minutes there was a loss of 0.7 mil of thickness. The resultant Kapton^R surface was frosted or had a matte finish.

E. The procedure of Example I-D was repeated except that 9.1 weight percent, of the total weight of the resultant solution, of ethylene diamine was employed. After 10 minutes a loss of 0.8 mil was obtained. The resultant Kapton^R surface was frosted.

F. The procedure of Example I-D was repeated except that 16.8 weight percent, of the total weight of the resultant solution, of ethylene diamine was employed. After 10 minutes a loss of approximately 1.0 mil was obtained. The resultant Kapton^R surface was frosted.

EXAMPLE II

A. For comparison purposes a 2 mil thick Kapton^R film was immersed in a 100 percent ethylene diamine solution, commercially obtained, at a temperature of 25°C. After 10 minutes there was no etching of the Kapton^R film.

B. For comparison purposes the procedure of Example II-A was followed except the solution was an aqueous 10N-NaOH solution. After 10 minutes 0.1 mil of the film was removed.

C. The procedure of Example II-A was followed except that the film was first immersed in the ethylene diamine for 10 minutes, followed by a water rinse for 15 seconds. The film was then immersed in the solution of Example II-B for 10 minutes at 25°C. A removal of 0.2 mil of the Kapton^R film resulted. There was no observable frosting. A film or residue representing a polyimide-etchant reaction product was observed. The reaction product was unknown and was not readily analyzable.

D. The procedure of Example II-C was followed except that the film was immersed in the ethylene diamine for 5 minutes at 25°C, followed by a 15-second water rinse. A removal of approximately 0.115 mil of the film resulted.

E. The procedure of Example II-C was followed except that the film was immersed in the ethylene diamine for two minutes. A removal of approximately 0.16 mil of the film resulted.

F. The procedure of Example II-C was followed except that the film was immersed in the ethylene diamine for 30 seconds at a temperature of 25°C. A removal of approximately 0.15 mil of the film resulted.

G. The procedure of Example II-C was followed except that the film was immersed in the ethylene dia-

mine for 30 minutes at a temperature of 25°C. A removal of approximately 0.5 mil of the film resulted.

EXAMPLE III

A. For comparison purposes, a 2 mil thick Kapton^R film was chemically etched in a 10N-NaOH aqueous solution, commercially obtained, at a temperature of 25°C. After 1 hour, there was a loss of about 0.1 mil of thickness.

B. The procedure of Example III-A was repeated except that the etching solution comprised 0.67 weight percent, of the total weight of the resultant etching solution, of anhydrous ethylene diamine, commercially obtained, in the 10N aqueous solution. After 1 hour there was a loss of 0.5 mil of thickness.

EXAMPLE IV

A. For comparison purposes, a 2 mil thick Kapton^R film was immersed in a 1.0N-NaOH aqueous solution maintained at a temperature of 25°C. After 30 minutes there was no etching of the polyimide film.

B. The procedure of Example IV-A was repeated except that the etching solution comprised 20.17 weight percent, of the total weight of the resultant etching solution, of anhydrous ethylene diamine, commercially obtained, in the 1N aqueous NaOH solution. After 30 minutes there was a loss of 0.1 mil of thickness. There was no pitting or frosting observed.

C. The procedure of Example IV-B was repeated except that 22 weight percent, of the total weight of the resultant etching solution, of ethylene diamine was used. After 30 minutes there was a loss of 0.1 mil of thickness. There was no pitting or frosting observed.

EXAMPLE V

A. For comparison purposes, a 2 mil thick Kapton^R film was immersed in a 15N-NaOH aqueous solution maintained at a temperature of 25°C. After 30 minutes there was a loss of about 0.2 mil of thickness. There was no pitting or frosting observed.

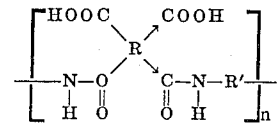
B. The procedure of Example V-A was repeated except that the etching solution comprised 1.8 weight percent, of the total weight of the resultant etching solution, of anhydrous ethylene diamine, commercially obtained, in the 15N aqueous NaOH solution. After 10 minutes there was a loss of about 0.5 mil of thickness. There appeared a very slight frosting of the polyimide surface.

C. The procedure of Example V-B was repeated except that 3.1 weight percent, of the total weight of the resultant solution, of anhydrous ethylene diamine was used. After 10 minutes there was a loss of about 0.1 mil. The resultant Kapton^R surface was frosted or had a matte finish.

It is to be understood that the abovedescribed embodiments are simply illustrative of the principles of the invention. Various other modifications and changes may be devised by those skilled in the art which will embody the principles of the invention and fall within the spirit and scope thereof.

What is claimed is:

1. In an improved method of forming an adherent metallic pattern on a surface of a substrate comprising a polyimide of a polyamide-acid having the formula



where the arrows denote isomerism; R is an organic tetravalent radical containing at least 2 carbon atoms, no more than 2 carbonyl groups of each polyamide-acid unit being attached to any one carbon atom of said tetravalent radical; R′ is a divalent radical containing at least 2 carbon atoms, the amide groups of adjacent polyamide-acid units each attached to separate carbon atoms of said divalent radical; and n is a positive integer sufficient to provide said polyamide acid with an inherent viscosity of at least 0.1, which consists essentially of the steps of:

a. coating the surface with a photopromoter;

b. producing a pattern capable of reducing a precious metal from a precious metal salt by selectively exposing a portion of the photopromoter-coated surface to a source of short wavelength ultraviolet light;

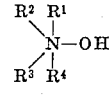
c. immersing the substrate in a precious metal salt solution to reduce on the pattern the precious metal; and

then

d. placing the precious metal pattern in an electroless plating bath which is catalyzed by the reduced precious metal to produce the metallic pattern, the improvement comprising:

a^1 prior to step (a) above, treating the polyimide surface with an aqueous etchant solution consisting essentially of:

1. a basic compound selected from the group consisting of a carbonate, hydroxide, cyanide, borate, phosphate, pyrophosphate, sulfite, sulfide and silicate of an alkali metal; a carbonate, hydroxide, cyanide, borate and sulfide of ammonia; alkali metal alkoxides where the alkylate portion has 1 through 4 carbons; and a quarternary ammonium hydroxide of the formula



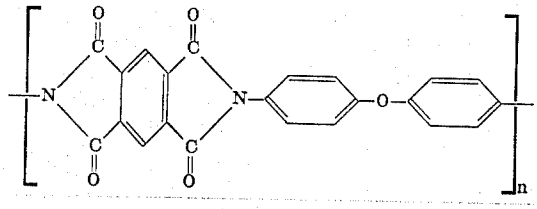
where R^1 and R^2 are each alkyl of 1 through 4 carbons, R^3 is selected from the group consisting of alkyl of 1 through 18 carbons and alkenyl of 1 through 18 carbons; and R^4 is selected from the group consisting of alkyl of 1 through 18 carbons, alkenyl of 1 through 18 carbons, phenyl, alkylphenyl where the alkyl portion has 1 through 18 carbons, benzyl and alkylbenzyl where the alkyl portion has 1 through 18 carbons; and

2. ethylene diamine, in an amount in excess of saturation of said aqueous solution, to etch the surface.

2. The method as defined in claim **1** which further comprises removing a deposit residing on said etched surface, said deposit being one of the group consisting of said etchant, an etchant-polyimide reaction produce and mixtures thereof.

3. The method as defined in claim **1** wherein in step (a^1) the polyimide surface comprised a polyimide made

from the anhydride of pyromellitic acid and **4,4'** diamino-diphenyl ether, having a general formula



where n is an integer ranging from 150 to 650, and having a weight average molecular weight of 60,000 to 250,000.

4. The method as defined in claim **1** wherein said basic compound comprises an alkali hydroxide.

5. The method as defined in claim **4** wherein said basic compound comprises NaOH.

* * * * *

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,821,016 Dated June 28, 1974

Inventor(s) Michael Anthony DeAngelo

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 44, "Adhesion" should read -- Adhesion --; line 46, "Metallic Coating of Plastics" should read -- Metallic Coating of Plastics -. Column 4, line 40, "adhequate" should read -- adequate --. Column 6, line 31, "or the" should read -- of the --. Column 8, lines 20 and 21, "Metallic Coating of Plastics" should read -- Metallic Coating of Plastics --; line 48, "Metallic Coating of Plastics" should read -- Metallic Coating of Plastics --; lines 59 and 60, "Metallics Coating of Plastics" should read -- Metallic Coating Coating of Plastics --. Column 11, line 59, "abovedescribed" should read -- above-described --.

Signed and sealed this 24th day of June 1975.

(SEAL)
Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents
and Trademarks

FORM PO-1050 (10-69)

USCOMM-DC 60376-P69
U.S. GOVERNMENT PRINTING OFFICE : 869-930