

[54] **METHOD OF MAKING PATTERNED METAL COATINGS BY SELECTIVE ETCHING OF METAL**

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[22] Filed: Aug. 27, 1968

[21] Appl. No.: 755,627

[52] U.S. Cl.117/38, 117/8, 156/7, 156/4, 252/79.4, 252/79.5

[51] Int. Cl.B44c 1/22

[58] Field of Search117/38, 8; 156/1-10; 252/79.1-79.4, 79.5; 96/36

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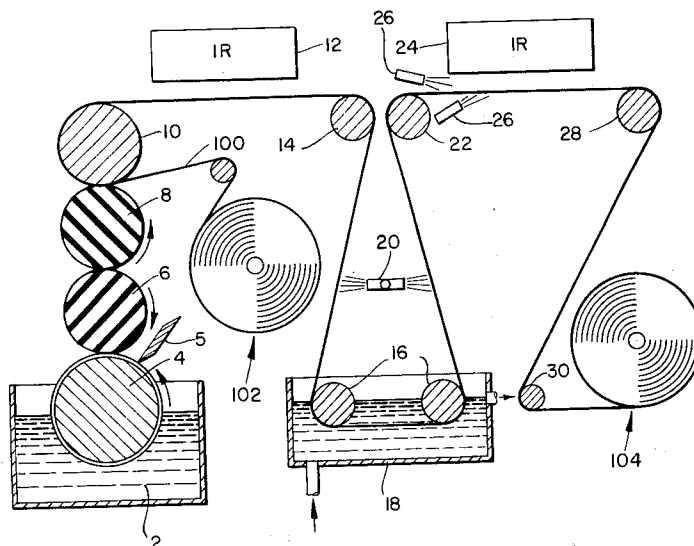
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[57] **ABSTRACT**

Web substrates (such as plastic film) are coated with metal (as by vacuum aluminizing) and etched in selected areas of the metal coating. The etching medium comprises an etchant, a body-forming member to trap the etchant, a volatile carrier and a dispersing member which holds the etchant and body-forming member in intimate mixture.

8 Claims, 3 Drawing Figures



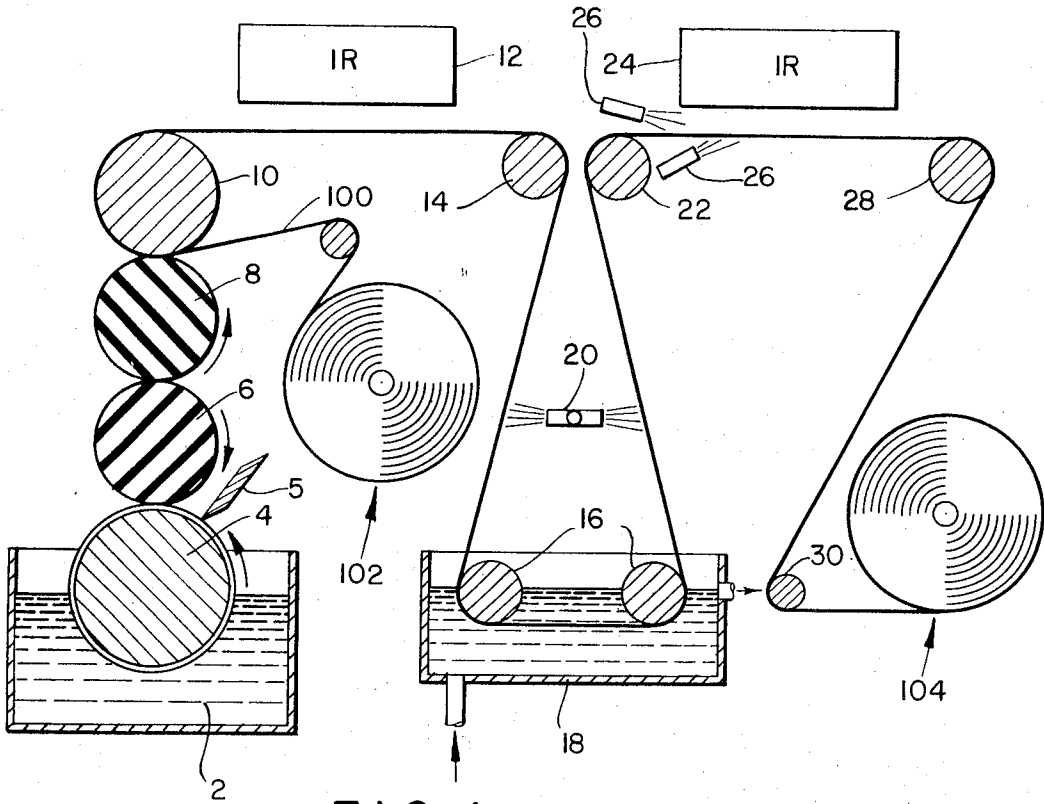


FIG. 1

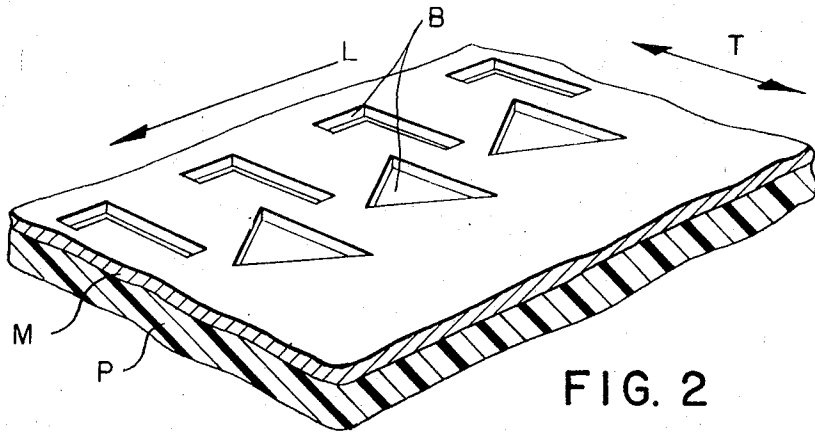


FIG. 2

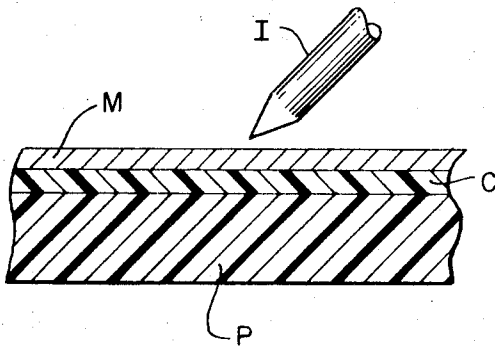


FIG. 3

METHOD OF MAKING PATTERNED METAL COATINGS BY SELECTIVE ETCHING OF METAL

The present invention relates to the art of metal coating and particularly to metal coatings deposited on flat web substrates. Examples of common products in this field are plastic film or strip coated with tin by dipping, paper coated with aluminum foil by lamination. The metal coating may be for decorative purposes and/or functional purposes, based on the essential characteristics of adhesion, reflectivity and conductivity of the metal coating. Some of the uses for such metallized webs are packaging, hot stamp printing, draperies, clothing and blankets, capacitors, resistors, electrical circuitry, microwave and light reflectors and thermal insulation.

BACKGROUND

It is a longfelt need in the art of metallizing and several of the various fields of application of metallized webs to establish patterns in the metal coating. This can be done by electrically sparking away portions of the metal coating as in U.S. Pat. No. 1,909,079, etching longitudinal stripes in the coating by contacting with an etch coated wheel as taught in U.S. Pat. No. 2,897,066, use of masking or stencils in the original application of the coating, multiple coating steps with different masks, and photoresist masking followed by etching. It is also known to pattern metal surfaces by anodizing and selectively etching the oxide as shown for instance in U.S. Pat. Nos. 3,016,293 and 3,017,285. It was also suggested in the above-cited U.S. Pat. No. 2,897,066 that an etchant used for demetallizing longitudinal stripes of aluminum might, if its viscosity were adjusted to that of printer's ink, be applied by printing rolls or galleys. The likelihood of success of the latter suggested method is limited by the conflicting requirements of viscosity adjustment to prevent the etch from spreading and complete etching of the desired pattern area and is not known to have been successfully applied, even for the limited striping function contemplated by the patentee. The coating while masking, sparking and etch methods are all essentially limited to producing straight lines in the longitudinal direction of the web. The photoresist and etch method can produce bidirectional patterns of coating metal removal, but is expensive.

OBJECTS

It is an object of the present invention to provide an improved method of making metal coated webs with patterns in the coatings which is more practically feasible and economical than prior art methods. In general the object is achieved by printing an etch medium on the web, the medium containing an etchant and other components as herein described.

It is a further object of this invention to achieve a high degree of control of the pattern formed so that formation can be limited to selected areas of the coating. It is a related further object of the invention to form bidirectional patterns — that is, patterns which extend transversely to the web as well as longitudinally, in contrast to capacitor electrode patterns which are simple longitudinal stripes of metal removal running along the length of a metal coated plastic film. Examples of bidirectional patterns are repetitive transverse stripes, circles, stars, number or letter patterns of metal removal contained singly or in a repetitive pattern along the length of a metal-coated plastic film.

It is a further object of the invention to provide for alternative mass production utilization or custom use of the metal removal technique and to similarly provide alternative products of metal coated webs with preformed patterns of metal removed or metal coated web which are in precursor form and capable of patterned metal removal by a simple final step.

GENERAL DESCRIPTION

The invention comprises an improved method of preparing patterned webs by metal coating and patterned metal removal

by etching, including species of applying etching medium before or after metal coating, an improved method of patterning metal-coated webs, the products of the foregoing methods and new etching media and their preparation for use in the above-stated methods.

The etching medium comprises a mixture of an etchant, a body-forming member and a volatile carrier. It may also comprise a separate dispersing member, if necessary to hold the etchant and body-forming member in intimate mixture. The medium is applied to the coating in the desired pattern by print techniques and heated for drying. Alternatively, the medium may be applied in a latent form and activated in precise pattern areas only. In either case, etching proceeds in the pattern area simultaneously with solidification of the body-forming member to form a spongelike trap for the etchant limiting its spread to the pattern area.

The resultant chemical complex is easily removed to expose the web substrate in the pattern area. Whether the etch residue is retained or washed away, the etched pattern area differs in essential characteristics of conductivity adhesion and/or reflectivity from the remainder of the metal coating. The patterned web can then be cut to desired size for use as packaging, draperies, printed circuits, etc.

The present invention is particularly flexible in its various methods of usage. The principal metal coating, print-etching and size-coating steps (with appropriate adjustments described below) (1) can be any sequential order, (2) can be done separately or in close-together sequence, (3) can utilize conventional materials or methods and apparatus such as commercially available metallized webs, commercially available printing facilities and web handling, cutting and heating facilities, and conventional cheap chemicals and (4) allows economic material usage in that major components, such as metallized web can be mass produced and doled out in portions for custom print-etching of desired patterns.

Other objects, features and advantages of the present invention will in part be obvious and will in part be stated herein.

SPECIFIC DESCRIPTION AND DRAWINGS

The invention is now specifically described with reference to the accompanying drawings wherein:

FIG. 1 is a diagram of an apparatus for carrying out the method of the invention,

FIG. 2 is a segment of finished product produced by the invention according to a preferred embodiment,

FIG. 3 is a cross section view showing a product according to another embodiment of the invention and indicating its mode of utilization.

This specific description is made with respect to the illustrative application of the invention to aluminum-coated web stock.

The invention can be practiced with the use of a felt-tipped pencil or ink stamp for applying etch to the aluminum coating. However, it is preferred and distinctly advantageous to utilize the invention in connection with mass production of patterned metal coated web stock.

In this preferred embodiment, the method steps are:

I. Vacuum aluminize a substrate roll through evaporation of aluminum in a vacuum chamber and condensation on a substrate web which is unrolled from a roll supply in the vacuum chamber, passed over the evaporating aluminum and then rerolled.

II. Removal of the coated web roll from the vacuum chamber and print-etching in the apparatus of FIG. 1.

The FIG. 1 print-etching apparatus is essentially a conventional printing apparatus modified for use in the present invention. A rolled up web 100 of metallized plastic is unrolled from a supply roll 102 and fed to a takeup roll 104. The print etch mixture bath 2 is picked up by an etched gravure roll 4 containing a screen pattern etched on its face. The pickup roll 4 rotates past a doctor blade 5 and into contact with a print roll (gravure or mountable type) which has a printed face enforc-

ing to the desired pattern, the etch area being raised and it picks up the print etch mixture in the desired pattern and transfers it to the web via transfer roll 8. The transfer roll 8 is optional. The screen count of roll 14 is preferably 50 to 100 mesh per inch for most etch mixtures. But this is variable over a wider range.

The web passes over press roll 10 while receiving the pattern of print-etch mixture and then goes past an infrared heater 12 where the applied print etch mixture is dried to set up the pattern of metal removal. The web is then passed over guiding rolls 14, 16, 22, 28, 30 to roll 104. On the way it passes through a water bath 18 and spray water rinses 20, infrared heater 24 and blowing air jets 26 to dry the water.

A typical resultant product is shown in FIG. 2 which illustrates a section of plastic film web (1,000 feet long or longer) P with a metal coating M. The length direction of the web is indicated by L and the transverse dimension by T.

Running along the length of the web are two repetitive etch patterns B which are bidirectional, that is — extending transversely as well as merely longitudinally. In a sense, the interruptions between like patterns along the length are also part of the bidirectional character of the pattern. The two repetitive patterns shown for illustration are of triangle and L-form. But far more complex patterns have been etched, including the letters of the alphabet in normal type face with a central island of metal remaining intact in the etched letter "O." It should be appreciated that the etchant could be applied over very large areas of the metal coating to leave discrete islands of metal rather than etching small areas out of the metal coating, as in the preferred embodiment illustrated in FIGS. 1-2.

The print-etch mixture as described above in the general description has an etchant component, a body-forming member, a volatile carrier and, preferably a dispersing agent for extending stability, or shelf life, of the mixture. Also, the mixture may optionally include viscosity adjusting components; however, viscosity control is less important than etchant and mixture stability. In the FIG. 1-2 embodiment, the mixture is preferably wet when applied. Alternatively, it may be applied dry and wetted in situ to begin etching. The next and critical step (III) in the etching is drying the mixture by driving off the volatile carrier to allow the body-forming member to harden. The drying may be done by letting stand in room temperature air. But preferably it is done by assisted heating. The cured body forming member forms a spongelike structure which limits the etchant to the pattern area where it attacks the aluminum metal coating to form a complex of aluminum and the mixture in the pattern area lacking the essential characteristics of adhesion reflectivity and conductivity of the original metal coating.

In the next (and optional) step IV, the chemical complex is removed by rinsing with water or solvents and/or brushing to leave the pattern area bare.

For aluminum, the etchant is preferably sodium hydroxide or potassium hydroxide. In order to increase the intensity of etching for attacking thick aluminum coatings at high rates for mass production, the etchant is preferably highly concentrated.

The body-forming member is selected from any of several classes of natural or synthetic resins including vinyl, acetal, acrylic and polyurethane resins. Several of these are known for usage in printers inks or paint thickeners. Stability is a principal criterion.

The volatile carrier is a common economic organic solvent such as methyl ethyl ketone.

The dispersing agents include methyl alcohol and other ethereal solvent extenders, sodium carboxy methyl cellulose and silicones.

The carrier and dispersing agent may be initially associated with the body-forming member, the etchant or both.

The same material may be the carrier in one combination and a dispersing agent in another combination. For instance, in one combination methyl ethyl ketone would be a dispersing agent, or diluent for a boy of acetal resin dissolved in a toluol

carrier and mixed with an aqueous etchant. In many other combinations, methyl ethyl ketone is the carrier.

A particularly critical problem is the avoidance of shocking out of the mixture through formation of precipitates or layers of liquid (the common antipathy of oil and water — oil from the carrier, water from the etchant).

The balancing of the various criteria of etchant concentration, solution stability and high speed etching will best be understood by reviewing the following nonlimiting illustrative examples which show instances of successful, and unsuccessful, print-etching achieved through various mixture formulations and mixing procedures.

EXAMPLE 1

A sheet of green open weave polyester fiber cloth (Dacron T.M. of E. I. DuPont de Nemours) was vacuum metallized to produce a decorative grade coating with a bright metallic appearance which was complete across the face of the sheet. The sheet was hand stamped with an ink stamp containing a variety of printed matter which was inked by rolling on the stamp an etchant mixture liquid prepared as follows:

1. Mix 10 parts of 55 percent acrylic solution (Union Carbide 00200) with 20 parts of ethylene glycol monoethyl ether (Cellosolve solvent) and 20 parts of water;
2. Mix (1) with 60 parts of 50 percent sodium hydroxide solution;
3. Mix 60 parts methyl ethyl ketone with 30 parts water;
4. Mix (2) with (3).

All mixing steps are carried out with stirring and without heat addition. The resultant liquid was very fluid and spread easily on the stamp.

After the stamp was inked and applied to the cloth, the cloth was held up to a radiant heater with a fan for a few seconds. After the heating the etch took place rapidly in the stamped area of the cloth — a few seconds formed a powdery residue which was then rinsed away with water.

The resultant stamped pattern on the cloth was very sharp and essentially complete within the pattern area. The original green cloth surface in the stamp area made a sharp contrast with the metallic brightness in the surrounding. For comparison, the same stamp was inked on a conventional stamp inking pad and applied to a piece of white paper. The resultant "A" pattern was no more defined and was less complete within the pattern areas than the "B" pattern formed on metallized cloth by etching.

EXAMPLE 2

The mixture of Example 1 was applied to a nylon cloth with the same good results.

EXAMPLE 3

A half-mil film of polyethylene terephthalate polyester (Mylar-T.M. of E. I. DuPont de Nemours) was vacuum aluminized to a decorative grade thickness of 5 ohms per square. The metallized film was hand-stamped by a stamp prewet with an etching mixture prepared as follows:

1. Mix 50 parts of 55 percent acrylic solution with 100 parts methyl ethyl ketone.
2. Mix 50 parts methyl alcohol with 10 parts Cellosolv and 50 parts of 50 percent sodium hydroxide.
3. Mix (1) and (2).

The metallized film was stamped and heated to dry the etching mixture as in Example 1. Good etching was obtained.

EXAMPLE 4

220 parts of the mixture of Example 3 were added to 55 parts of additional 55 percent acrylic solution and used for etching as in Example 3 with good results.

EXAMPLE 5

200 parts of the mixture of Example 3 were added to 50 parts of a polyvinyl butryal (PVB) solution (5 percent in a

mixed solvent of 1:1 ratio isopropyl alcohol and Cellosolv) and used for etching as in Example 3 with good results.

EXAMPLE 6

The following formulation failed to etch when used for etching as in Example 3.

1. Mix 50 parts of the acrylic solution with 50 parts of the PVB solution and 50 parts of methyl ethyl ketone.
2. Mix 50 parts of the sodium hydroxide (50 percent) solution with 40 parts methyl alcohol and 10 parts Cellosolv.
3. Mix (1) and (2). It was observed that after mixing step (3) a precipitate formed within the mixture.

EXAMPLE 7

200 parts of the mixture of Example 3 were added to 50 parts of sodium hydroxide solution and used for etching as in Example 3 with good results. The mixture formed a gel instead of the usual fluid liquid, but was nevertheless readily picked up and applied by the hand stamp.

EXAMPLE 8

Aluminum coatings were vacuum deposited on vinylidene-chloride coated cellophane and polyester film substrates and etched as in Example 3 with a mixture formulation prepared as follows:

1. Mix 50 parts acrylic with 100 parts methyl ethyl ketone and 50 parts methyl alcohol.
2. Mix 10 parts Cellosolv and 50 parts of the sodium hydroxide solution.
3. Mix (1) and (2). The etching results were good, but the etching process took a few seconds longer after drying than the previous successful examples.

EXAMPLE 9

240 parts of the Example 8 mixture were added to 30 parts of sodium hydroxide solution. The resultant mixture gave good etching at the usual high speed.

EXAMPLE 10

A mixture formulation was prepared as follows and had a viscosity of about 30 seconds on a No. 3 Zahn cup. It was used for etching and gave good results.

1. Mix 50 parts of the PVB solution with 10 parts Cellosolv and 50 parts methyl ethyl ketone.
2. Mix 50 parts sodium hydroxide solution (50 percent) with 50 parts methyl alcohol.
3. Mix (1) and (2), adding (2) to (1) while stirring.

EXAMPLE 11

100 parts of the Example 10 mixture were mixed with 25 parts water and 25 parts acrylic solution. The resultant mixture gave good etching effect.

EXAMPLE 12

Metallized plastic and cloth sheets were patterned etch with good results using the following mixture formulation:

1. Mix 50 parts water with 5 parts of 5 percent solution of sodium carboxymethyl cellulose in water.
2. Mix 50 parts methyl alcohol with 50 parts methyl ethyl ketone and 50 parts of 55% acrylic solution.
3. Mix (1) and (2).
4. Mix (3) with 50 parts of 50 percent sodium hydroxide solution.

EXAMPLE 13

Aluminum coated Mylar was etched well, but at a slower rate, with the following formulation:

1. Mix 100 parts 55 percent acrylic solution with 50 parts methyl ethyl ketone and 50 parts isopropyl alcohol.
2. Mix 20 parts Cellosolv and 50 parts of 50 percent sodium hydroxide solution.

EXAMPLE 14

Fast and good etching of aluminized Mylar was achieved using a formulation of 20 parts of 50 percent sodium hydroxide solution mixed with 200 parts of the Example 13 mixture.

EXAMPLE 15

The following formulation was attempted.

1. Mix 80 parts of the Example 14 mixture with 10 parts of Cellosolv.
2. Mix 20 parts of 50 percent sodium hydroxide with (1).
3. Mix 40 parts methyl ethyl ketone with (2). The mixture shocked out — separating into layers on standing.

EXAMPLE 16

The Example 15 mixture was restirred and 20 parts of it were mixed with 30 parts of water and 20 parts of 50 percent sodium hydroxide. The resulting mixture shocked out.

EXAMPLE 17

Etching was unsuccessful with the following formulation:

1. Mix 20 parts glyoxal with 10 parts methyl ethyl ketone.
2. Mix (1) with 20 parts 55 percent acrylic solution.
3. Mix (2) with 10 parts 50 percent sodium hydroxide solution.

EXAMPLE 18

The following formulation was attempted.

1. Mix 20 parts methyl ethyl ketone with 10 parts 50 percent sodium hydroxide solution.
2. Mix 10 parts glyoxol with (1).
3. Mix 20 parts 55 percent acrylic solution with 5 parts Cellosolv.
4. Mix (2) and (3).

This formulation was successfully used in etching aluminized Mylar.

EXAMPLE 19

10 parts of 50 percent sodium hydroxide solution were mixed with 15 parts Cellosolv and the Example 18 mixture. The resultant was very cloudy but nevertheless successfully used in etching aluminized Mylar.

EXAMPLE 20

A series of etching mixtures were made with solid alkali metal hydroxide to increase intensity of etching action. These were

- a. 100 grams of potassium hydroxide dissolved overnight in a solvent mixture of 100 ml. methyl ethyl ketone and 100 ml. Cellosolv to produce a dark brown thick mixture.
- b. 2 grams of sodium hydroxide partially dissolved overnight in 20 ml. Cellosolv to produce a yellow solution and mixed with a mixture of 20 ml. 55 percent acrylic solution in 20 ml. methyl ethyl ketone and finally mixed with 15 ml. Dow Corning DC 600 silicone to produce a light brown mixture.
- c. 10 ml. of 55 percent acrylic solution with 20 ml. of (a) above.
- d. 15 ml. of (a) above in 15 ml. of methyl alcohol and mixed with 10 ml. 55 percent acrylic.

All the foregoing mixtures were picked up on the tip of a glass rod and applied to aluminized Mylar and successfully etched small spots in the aluminum coating. All the etches were repeated by using the rod to add a drop of water to the contact zone which speeded etching. The mixtures of (c) and (d) were completely homogeneous and (a) and (b) had some initial undissolved caustic. However, all four mixtures demonstrated good shelf life of several days before shocking out via layering or precipitate compared to 1-2 days for most of the previous examples. An odor of evolving ammonia was noted over mixtures (b), (c) and (d) which contained acrylic resin.

EXAMPLE 21

10 parts of the Example 20 (a) mixture were mixed with 10 parts of a 30 percent solution of Lewisol-28 solid (a maleic resin modified resin ester solid) dissolved overnight in methyl ethyl ketone and formed a completely homogeneous solution with shelf life of several days. Since it was completely free of acrylic-amide body member it did not evolve ammonia.

The mixture did not, per se, etch metal noticeably when applied with a rod and to aluminized Mylar, but did etch when as little as a trace droplet or as much as 1 ml. of water was added to the contact area.

EXAMPLE 22

18 ml. of the Example 21 mixture (including 1 part water in 18) and 12 ml. of the Example 20 (a) mixture were mixed and applied to an artist's hand roller and used for etching aluminized Mylar with good results over the very large area of roller contact with the metal coat.

EXAMPLE 23

To further increase shelf life consistent with high intensity etching, a new series of mixtures was made as follows:

- a. 20 ml. of the Example 21 mixture (including 1 part water in 20) mixed with 0.1 ml. DC-600 silicone.
- b. -20 ml. of etch solution (of 100 grams NaOH dissolved in a 100 ml. Cellosolv - 100 ml. methyl ethyl ketone solvent) were mixed with 30 ml. of methyl ethyl ketone and 30 ml. of the above described solution of Lewisol-28.
- c. 20 ml. of the etch solution of (b) with 50 ml. of the (b) mixture and 0.5 ml. water.

All three mixtures gave good roll-etching results and exhibited shelf lives of several weeks. The etching was carried out on a very thick aluminum coating (half-ohm per square).

EXAMPLE 24

100 ml. of methyl ethyl ketone was mixed with 100 ml. Cellosolv and 20 ml. water and heated to boiling 100 grams of KOH solid was added to the boiling mixture. Upon cooling, there was some solution separation. 80 ml. of methyl ethyl ketone was added and solution separation was arrested.

This component demonstrated good shelf life and etching.

EXAMPLE 25

An etchant substantially similar to that of Example 24 etched well after mixing with a body component of Turco Guard - 100 polyurethane resin solution in equal amounts with etching speed increased by adjusting the mixture to a 60 - 40 ratio of etchant (including dispersing agent and carrier) to resin solution.

The foregoing examples illustrate some of the variety of factors involved in choosing the components of the etching medium or adjusting the print-etch process steps to suit a particular print etch application. Some of the key criteria may be summarized as follows:

1. Where the print etching is to be accomplished by hand stamps or flexographic printing or the like, increased viscosity for handling on the applicator is desired and this can be achieved by increasing the body-forming member content and/or water content of the etching medium. On the other hand, viscosity normally has very little significant effect on the behavior of the etching medium on the metal since it is the solidification of the body forming member, rather than wettability of the metal surface or viscosity of the medium which primarily controls pattern definition. For high speed printing, such as gravure or offset, lower viscosity (achieved by more solvent, less body and less dispersing agent or diluent or water) is preferred.

2. Another way of controlling viscosity is in the choice of body member-carrier subsystem. For instance a solution of Lewisol-28 in methyl ethyl ketone has a lower viscosity than a

solution of PVB in the isopropyl alcohol — methyl ethyl ketone solvent, even though the two solutions have the same solids content.

3. Where it is desired to fully remove the etch residue, choice of body forming member is important in regard to adhesion to the web substrate. Acrylic resins are easily washed off. In using some other body-forming members, it may be desirable to add soap or a wetting agent to the etching medium to expedite washing away.

Where it is desired to dispense with washing away residue and leave it in place, then the body choice factors are opposite.

Another degree of control over adhesion of the body is in the heating for drying. In all the foregoing examples, heating was carried out to temperatures allowing the body-forming resin to reach its green state (e.g., about 180°-200° F. for acrylic) but below the curing point (about 150° C.). If it is desired to retain the etch residue to physically protect the substrate in the etch pattern area, this can be facilitated by heating to curing. In this case, optical clarity can be enhanced by adding siloxanes to the etch medium.

4. For etching metal coatings of great thickness or at high production rates, choices of more active etchants and higher concentration of etchant are in order. The effective activity of the etchant can also be increased by adding a salt to the etching medium which has opposite electrochemical characteristics compared to the etchant per se.

5. Shelf life or stability, is governed by choice of resin as noted in the above examples. Reduction of water content and increase of solvent and dispersant to increase stability is also significant factors.

6. The choice of thick depositing method for application of medium, such as gravure printing, can compensate for the inherent dilution of etchant involved in (5) above.

OTHER COATINGS AND SUBSTRATES

In applying the invention to other materials, the principal substitution in the above aluminum-attacking mixtures (media) would be that of the etchant. Acid-stable body-forming members, carriers and dispersing agents would be used. Suitable etchants for other metal coatings are well known. Some examples are

for copper coatings
tin
gold
nickel
chromium
cobalt,
magnesium
iron

caustic or hydrochloric acid
hydrochloric acid
aqua regia
nitric or hydrochloric acid
hydrochloric or dilute sulfuric acid

most acids
ferric chloride or ferric sulfate
solutions.

Metal alloys can be similarly etched by proper selection of etchant. For instance a film of nickel-chromium resistive alloy could be deposited on plastic and cuttings could be sold to electric circuit makers for drawing out circuit patterns with a felt pencil impregnated with an etch medium.

The invention can be applied to multilayer metal coatings with preferential attack of one layer. For instance, a copper coat could be deposited over a silver coat and ferric chloride could be used to attack the copper without substantial effect on the silver undercoat. Alternatively, a silver overcoat, over a copper undercoat, could be attacked by a nitric acid solution rich in copper ion, to pattern the silver coat while leaving the copper coat intact. As another example, a nickel iron magnetic alloy could be applied to a plastic film and overcoat; with aluminum to provide a magnetic shield. Windows could be print-etched in the aluminum shield using a medium containing caustic etchant as described above.

Similarly metal web substrates can be coated with other metals (e.g., aluminized steel, gold-steel clads) and the metal coating can be preferentially etched without affecting the substrate.

Other substrates such as packages, rods, spheres can be metal coated and the coating can then be print-etched as described herein using rollers, stamps, pencils or automatic printing equipment.

OTHER BASIC EMBODIMENTS

The foregoing discussion in this specific description of the invention has been essentially limited to the preferred and distinctly advantageous approach of using the sequence of steps of (a) metal coating a substrate or obtaining a commercially available metal coated substrate, (b) print-etching a desired pattern in the metal substrate, including the steps of applying the etching medium to the coating in a defined pattern, drying the medium and optionally removing the etch residue, and (c) optionally cutting to a desired size for final use.

There are several general variations within the general scope of the present invention, many of which will be obvious and some of which are now stated.

First, one may apply the print-etch pattern to the coated substrate in a latent form and activate it by heating and/or water addition at a much later time and/or after cutting to a desired final-use sizes. The latent etch may be applied broadly or in defined pattern areas, using a partial drying and solidification of the body member to hold the pattern. Alternatively, the heating and/or water addition may be limited to specific pattern areas. The water addition may be done by adding drops of water or liberating water from a source in situ by heating. The in situ source may, for instance, be hydrated crystals contained in the etching medium, e.g., sodium silicate.

Second, the etching medium might be applied to the substrate directly in a latent form, and the metal deposited over the etching medium deposit. Such an embodiment would involve use of a precursor product which is illustrated in FIG. 3 — a substrate, such as a plastic film web P, coated with an etching medium C and overcoated with a metal layer M. If the metal is applied by vacuum deposition, the substrate P with etch medium surface C should be cooled during the deposition. Etching in desired pattern areas is initiated by holding a soldering iron I near the desired pattern areas. As a specific variation of this embodiment, a suitable source of moisture for etching would be a choice of a high moisture content substrate, e.g., cellulose acetate. As another specific variation of this embodiment, the etching medium could be made to act as a release agent, either as applied or after degradation through time or chemical treatment. Thus, the metal film M could be stripped away after completion of the etch-patterning operation. This would be an excellent economical source of ultrathin patterned metal for use in printed circuit work.

In connection with the embodiment illustrated in FIG. 3 it should be noted that the etching medium could be selected to make a moisture-containing substrate suitable for vacuum deposition of metal and that the metal M protects the coating C from extraneous atmospheric moisture during any storage period prior to etch activation.

Still further embodiments and variation in usage and practice of the invention will be apparent to those skilled in the art once given the benefit of the present disclosure. It is therefore intended that the foregoing specification and drawings shall not be construed as limiting except as set forth in the claims appended to this specification.

What is claimed is:

1. A continuous method of producing decorative or functional bidirectional surface patterns on metal-coated substrate articles utilizing adjacent areas of metallized and unmetallized surface on the substrate article by a print-etch process comprising contacting the metallic coating with a substantially nonspreading etching mixture in regions of the coating constituting the desired bidirectional pattern and drying the mixture to form a chemical complex of the metal and the etchant

mixture which contains essentially all the metal in the pattern region and which lacks at least one of the essential characteristics of adhesion, reflectivity and conductivity of the metal coating per se,

5 wherein the substrate is of web form and, wherein the etching mixture comprises two components in intimate contact and admixture, a first one of said components comprising a body-forming solid dispersed in a volatile carrier the second component comprising the etchant so that drying of the mixture produces a solid which entraps the etchant in the region of application of the mixture to limit spreading of the etchant during the period while the etchant attacks the metal coating.

2. A continuous method of producing decorative or functional bidirectional surface patterns on metal-coated substrate articles utilizing adjacent areas of metallized and unmetallized surface on the substrate article by a print-etch process comprising contacting the metallic coating with a substantially nonspreading etching mixture in regions of the coating constituting the desired bidirectional pattern and drying the mixture to form a chemical complex of the metal and the etchant mixture which contains essentially all the metal in the pattern region and which lacks at least one of the essential characteristics of adhesion, reflectivity and conductivity of the metal coating per se,

5 wherein the substrate is of web form and, wherein the inhomogeneous wet etching mixture comprises a solution of resin in an organic carrier and an aqueous etching solution, the organic carrier having a higher volatility than water so that upon drying the mixture, solidification of the resin is quickly obtained to prevent spreading of the etchant.

3. A continuous method of producing decorative or functional bidirectional surface patterns on metal coated substrate articles utilizing adjacent areas of metallized and unmetallized surface on the substrate article by a print-etch process comprising contacting the metallic coating with a substantially nonspreading etching mixture in regions of the coating constituting the desired bidirectional pattern and drying the mixture to form a chemical complex of the metal and the etchant mixture which contains essentially all the metal in the pattern region and which lacks at least one of the essential characteristics of adhesion, reflectivity and conductivity of the metal coating per se,

5 wherein the etchant mixture comprises an etchant which is suitable for removing the particular metallic coating, a body-forming component to prevent spreading of the etchant mixture when applied to the particular coated substrate surface involved and a volatile carrier therefor and a component which prevents the etching and body-forming chemicals from shocking out when contacted with each other, and heating the contacted area to remove the volatile component of the etchant mixture to form a complex of the metal coating contacted with the mixture and the etchant component only in the selected portion of the coating contacted by the mixture.

4. The method of claim 1 wherein the etching mixture is applied to the metal coating by precoating a solid applicator having a pattern face conforming to the desired pattern and then contacting the coating with the pattern face of the applicator.

5. The method of claim 2 wherein the etching medium is applied in latent form to an area of the metal coating broader than the desired pattern and activated only in the desired pattern area.

6. The method of claim 1 combined with the step of metal coating the substrate.

7. The method of claim 6 wherein metal coating precedes etching medium application.

8. The method of claim 6 wherein metal coating follows etching medium application.

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