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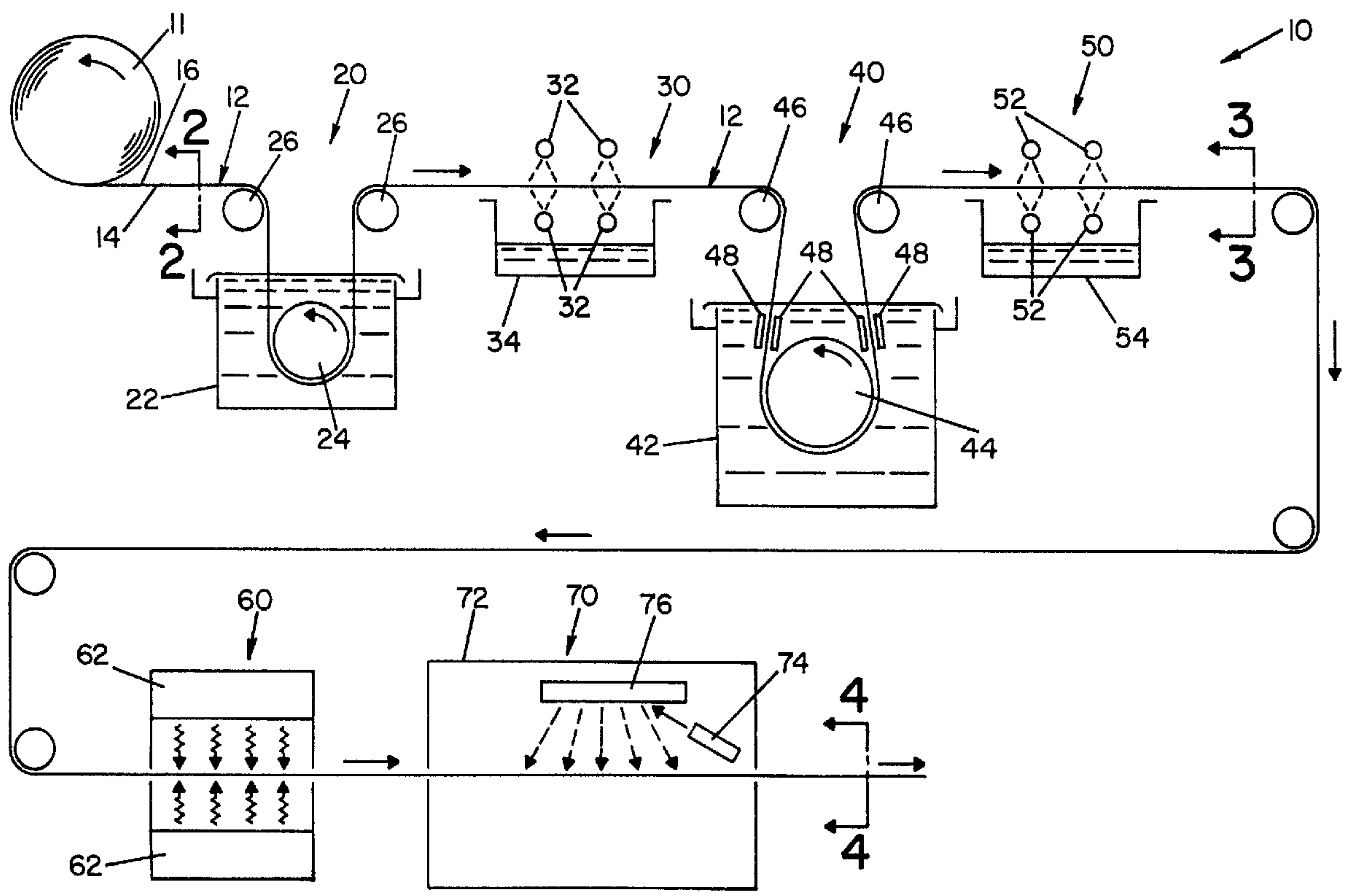
(54) Titre : METHODE POUR LA FORMATION DE CUIVRE CHROME POUR LES CARTES DE CIRCUIT IMPRIME
(54) Title: METHOD OF FORMING CHROMIUM COATED COPPER FOR PRINTED CIRCUIT BOARDS



(57) Abrégé/Abstract:
A method of applying a metal onto a copper layer, comprising the steps of: stabilizing a surface of a copper layer by applying a stabilization layer thereto, the stabilization layer comprised of zinc oxide, chromium oxide, nickel, nickel oxide or a combination thereof and having a thickness of between about 5Å and about 70Å; and vapor depositing a metal selected from the group consisting of aluminum, nickel, chromium, copper, iron, indium, zinc, tantalum, tin, vanadium, tungsten, zirconium, molybdenum and alloys thereof onto the stabilized surface of the copper layer, and a sheet material formed thereby.

Abstract

A method of applying a metal onto a copper layer, comprising the steps of:

stabilizing a surface of a copper layer by applying a stabilization layer thereto, the stabilization layer comprised of zinc oxide, chromium oxide, nickel, nickel oxide or a combination thereof and having a thickness of between about 5Å and about 70Å; and

vapor depositing a metal selected from the group consisting of aluminum, nickel, chromium, copper, iron, indium, zinc, tantalum, tin, vanadium, tungsten, zirconium, molybdenum and alloys thereof onto the stabilized surface of the copper layer, and a sheet material formed thereby.

METHOD OF FORMING CHROMIUM COATED COPPER FOR PRINTED CIRCUIT BOARDS

Field of the Invention

This invention relates to a process for treating copper and, more particularly, to a process for applying a metal to at least one side of a copper foil.

Background of the Invention

Copper foil is used in the production of printed circuit boards. In the production of printed circuit boards, it is generally necessary to bond a copper foil to a dielectric substrate to provide the foil with dimensional and structural stability. Although an excellent electronic conductor, there are problems inherent with the use of copper foil. For example, copper is easily oxidized and corroded, and copper itself, whether plated or rolled, does not adhere well to such substrates. Copper is also known to accelerate or catalyze the decomposition of the dielectric substrates. For these reasons, copper foil is typically sold with one or more protective layers applied to its surface.

It is known that a thin, chromium layer deposited onto copper foil has many applications for printed circuit boards. There are two ways to deposit the thin chromium layer onto a copper surface. One is by an electrodeposition process, and the other is by a vacuum deposition process.

The electrodeposition process has several disadvantages. Foremost, the process uses environmentally hazardous material that is difficult and costly to handle and dispose of. Further, this type of process is inexact and inefficient.

With respect to the vacuum deposition process, in order to insure a satisfactory adhesion between the applied chromium and copper, an extensive and rigorous pre-treatment of the copper is required to remove copper oxide from the surface thereof prior to the vacuum deposition of the chromium.

The present invention overcomes these and other problems and provides a method of forming a metal coated copper by a vacuum deposition process that does not require an extensive rigorous pre-treatment process.

Summary of the Invention

In accordance with a preferred embodiment of the present invention, there is provided a method of applying a metal onto a copper layer, comprising the steps of stabilizing a surface of a copper layer by applying a stabilization layer thereto, the stabilization layer comprised of zinc oxide, chromium oxide, nickel oxide or a combination thereof and having a thickness of between about 5Å and about 70Å, and vapor depositing a metal selected from the group consisting of aluminum, nickel, chromium, copper, iron, indium, zinc, tantalum, tin, vanadium, tungsten, zirconium, molybdenum and alloys thereof onto the stabilized surface of the copper layer. One specific alloy contemplated herein is nickel-chromium alloy.

In accordance with another aspect of the present invention, there is provided a sheet material comprised of a layer of copper and a stabilization layer on a surface of the copper. The stabilization layer is comprised of zinc oxide, chromium oxide, nickel oxide or a combination thereof and has a thickness between about 5Å and about 70Å. A vapor deposited metal is provided on the stabilized layer.

It is an object of the present invention to provide a chromium coated copper layer for use in manufacturing printed circuit boards.

Another object of the present invention is to provide a method of forming a chromium coated copper layer as described above by a vacuum deposition process that does not require an extensive, rigorous pre-cleaning of the copper surface prior to deposition of the chromium.

Another object of the present invention is to provide a method of vacuum depositing a metal onto a copper surface.

A still further object of the present invention is to provide a generally continuous process as described above.

These and other objects will become apparent from the following description of a preferred embodiment taken together with the accompanying drawings and the appended claims.

Brief Description of the Drawings

The invention may take physical form in certain parts and arrangement of parts, a preferred embodiment of which will be described in detail in the specification and illustrated in the accompanying drawings which form a part hereof, and wherein:

FIG. 1 is a schematic view of a process for applying a metal onto a surface of a copper foil in accordance with the present invention;

FIG. 2 is an enlarged sectional view taken along lines 2-2 of FIG. 1 showing a sheet of copper foil;

FIG. 3 is an enlarged sectional view taken along lines 3-3 of FIG. 1 showing the sheet of copper foil of FIG. 2 with stabilization layers thereon; and

FIG. 4 is an enlarged sectional view taken along lines 4-4 of FIG. 1 showing a sheet of copper having a vapor deposited metal on the matte side thereof.

Detailed Description of Preferred Embodiment

The present invention relates to a process for applying a metal onto a copper surface. As used herein the term "metal" refers to metals and alloys capable of vacuum deposition by the methods disclosed herein. The invention is particularly applicable to applying chromium onto copper foil and will be described with particular reference thereto, it being appreciated however, that the disclosed process may also be used in applying a metal such as aluminum, nickel, copper, iron, indium, zinc, tantalum, tin, vanadium, tungsten, zirconium, molybdenum and alloys thereof onto copper foil.

The copper foils used with this invention can be made using one of two techniques. Wrought or rolled copper foil is produced by mechanically reducing the thickness of a copper or copper alloy strip or ingot by a process such as rolling. Electrodeposited foil is produced by electrolytically depositing copper ions on a rotating cathode drum and then peeling the deposited foil from the cathode. Electrodeposited copper foils find advantageous application with this invention.

The copper foils typically have nominal thicknesses ranging from about 0.0002 inch to about 0.02 inch. Copper foil thickness is sometimes expressed in terms of weight and typically the foils of the present invention have weights or thicknesses ranging from about ⅛ to about 14 ounces per square foot (oz/ft^2). Especially useful copper foils are those having weights of ⅓, ½, 1 or 2 oz/ft^2.

Electrodeposited copper foils have a smooth or shiny (drum) side and a rough or matte (copper deposit growth front) side. The stabilization layer applied by the inventive process can be applied to either side of the foil, and in some instances it is applied to both sides. In one embodiment, the layer applied by the inventive process is applied to the shiny side of the foil.

The side or sides of the foil, to which the layer applied by the inventive process overlies, can be a "standard-profile surface," low-profile surface" or "very-low-profile surface." Useful embodiments involve the use of foils with low-profile surfaces and very low-profile surfaces. The term "standard-profile surface" is used herein to refer to a foil surface having an R_{tm} (IPC-MF-150F) of greater than 10.2 microns. The term "low-profile surface" refers to a foil surface having an R_{tm} (IPC-MF-150F) of less than 10.2μ. The term "very-low-profile surface" refers to a foil surface having an R_{tm} (IPC-MF-150F) of less than 5.1μ. R_{tm} (IPC-MF-150F) is the mean of the maximum peak-to-valley vertical measurements from each of five consecutive sampling measurements, and can be measured using a SURTRONIC® 3 profilometer marketed by Rank Taylor Hobson, Ltd., Leicester, England.

It will be appreciated by those skilled in the art that the present invention not only applies to copper foil having a stabilization layer on a surface thereof, but also applies to copper layers that have been deposited or adhered to other substrates and that have a stabilization layer applied on a surface thereof, after deposition or before or after being adhered to another substrate. Such substrates include, but are not limited to, polyimide (see U.S. Patent Nos. 5,685,970 and 5,681,443 which are expressly incorporated by reference herein), other polymeric substrates, organic substrates, aluminum (see U.S. Patent No. 5,153,050 which is expressly incorporated by reference herein), metal substrates (see U.S. Patent No. 5,674,596 which is expressly incorporated by reference herein) or laminates of copper and INVAR.

Referring now to the drawings wherein the showings are for the purpose of illustrating the preferred embodiment of the invention only, and not for the purpose of limiting same, FIG. 1 is a schematic view of a generally continuous manufacturing process 10 for applying a metal onto a copper surface illustrating a preferred embodiment of the present invention. In the embodiment shown, a roll 11 provides a generally continuous strip of copper foil 12. FIG. 2 is an enlarged cross-sectional view of copper foil 12. The copper foil 12 has a shiny side 14 and a matte side 16. (In the drawings, matte side 16 of copper foil 12 is shown exaggerated for the purpose of illustration).

Copper foil 12 preferably undergoes a first cleaning process, designated 20 in the drawings, to remove oxide film on the surfaces thereof. In the embodiment shown, copper foil 12 is conveyed into a tank 22 around a guide roll 24 by means of guide rollers 26. Tank 22 contains a cleaning solution to remove oxide film from the surfaces of copper foil 12. An acid solution is preferably used to remove the copper oxide layer from copper foil 12. A typical acid solution for cleaning copper foil 12 may include 10-80 g/l H_2SO4. In one embodiment, 50 g/l H_2SO4 is used to remove the copper oxide layer from copper foil 12.

After cleaning process 20, copper foil 12 undergoes a rinsing process, designated 30, wherein spray elements 32 disposed above and below copper foil 12 spray the surfaces of copper foil 12 with water. A tank 34 disposed beneath spray elements 32 collects the water sprayed therefrom.

Following cleaning process 20 and rinsing process 30, copper foil 12 undergoes a stabilization process, designated 40. Copper foil 12 is directed into a tank 42 and around a guide roll 44. Copper foil 12 is positioned relative to guide roll 44 by guide rollers 46. Tank 42 contains an electrolytic solution. In accordance with one embodiment of the present invention, the electrolytic solution contains zinc ions and chromium ions. The source of zinc ions for the electrolytic solution can be any zinc salt, examples include $ZnSO_4$, $ZnCO_3$, $ZnCrO_4$, etc. The source of chromium ions for the electrolytic solution can be any hexavalent chromium salt or compound, examples include $ZnCrO_4$, CrO_3, etc.

The concentration of zinc ions in the electrolytic solution is generally in the range of about 0.1 to about 2 g/l, preferably about 0.3 to about 0.6 g/l, and more preferably about 0.4 to about 0.5 g/l. The concentration of chromium ions in the electrolytic solution is generally in the range of about 0.3 to about 5 g/l, preferably about 0.5 to about 3 g/l, and more preferably about 0.5 to about 1.0 g/l.

In another embodiment, nickel oxide or nickel metal may also be deposited by itself or co-deposited with either zinc oxide or chromium oxide or both to form the stabilization layer. The source of nickel ions for the electrolytic solution can be any of the following individually or in combination: Ni_2SO_4, $NiCO_3$ etc.

The concentration of nickel ions in the electrolytic solution is generally in the range of about 0.2 g/l to about 1.2 g/l.

In another embodiment, other stabilization layers such as those containing phosphorous as is disclosed in U.S. Patent No. 5,908,544, which is expressly incorporated by reference herein, may be used.

The electrolytic solution can include other conventional additives such as Na_2SO_4 at concentrations in the range of about 1 to about 50 g/l, preferably about 10 to about 20 g/l and more preferably about 12 to about 18 g/l. The pH of the electrolytic solution is generally in the range of about 3 to about 6, preferably about 4 to about 5, and more preferably about 4.8 to 5.0.

The temperature of the electrolytic solution is generally in the range of about 20°C. to about 100°C., preferably about 25°C. to about 45°C., and more preferably from about 26°C. to about 44°C.

As seen in FIG. 1, anodes 48 are disposed adjacent to each side of copper foil 12 to apply a current density to copper foil 12. Guide rollers 46 are cathodic rollers wherein a stabilization layer 49 comprised of zinc oxide and chromium oxide is deposited on the exposed shiny side 14 and matte side 16 of copper foil 12 when anodes 48 are energized by a power source (not shown). FIG. 3 is a cross-sectional view showing copper foil 12 with stabilization layers 49 on shiny side 14 and matte side 16.

The current density is generally in the range of about 1 to about 100 amps/ft^2, preferably about 25 to about 50 amps/ft^2, and more preferably about 30 amps/ft^2. Where multiple anodes are employed, the current density may be varied between the anodes.

The plating time that is used is generally in the range of about 1 to about 30 seconds, preferably about 5 to about 20 seconds, and more preferably about 15 seconds. In one embodiment, the total treatment time on the shiny or smooth side is from about 3 to 10 seconds, and on the matte side is from about 1 to about 5 seconds.

In one embodiment, the mole ratio of chromium ions to zinc ions in the electrolytic solution is in the range of about 0.2 to about 10, preferably about 1 to about 5, and more preferably about 1.4.

In accordance with the present invention, the thickness of stabilization layers 49 that are applied to copper foil 12 are between about 5Å to about 70Å, and preferably about 20Å to about 50Å.

In the embodiment heretofore described, stabilization layer 49 is comprised of chromium oxide and zinc oxide. In accordance with another aspect of the present invention, stabilization layer 49 is comprised of only chromium oxide. The bath chemistries and process conditions for applying a chromium oxide stabilization layer are as follows:

1 - 10 g/l C_rO_3 solution

Preferred 5 g/l C_rO_3

pH - 2

Bath temperature: 25°C

10 - 30 amps/ft^2 for 5 - 10 seconds

or dip treatment: 10 seconds

Following stabilization process 40, copper foil 12 with stabilization layers 49 thereon then undergoes a rinse process, designated 50 in the drawings. Spray elements 52, disposed above and below copper foil 12, spray water onto the surfaces of copper foil 12 (with stabilization layers 49) to rinse and clean the same and to remove any residual electrolytic solution therefrom. A tank 54 disposed below spray nozzles 52 collects the rinsing solution.

Copper foil 12 with stabilization layers 49 thereon undergoes a drying process 60 schematically shown in FIG. 1. In the embodiment shown, forced air dryers 62 are disposed above and below copper foil 12 to direct air onto copper foil 12 to dry the surface thereof.

In accordance with the present invention, following application of stabilization layers 49, a metal is vacuum deposited onto one or both stabilized surfaces of copper foil 12. In the embodiment shown in FIG. 1, the metal is applied to matte side 16 of copper foil 12. The metal may be any metal capable of vacuum deposition including those selected from the group consisting of aluminum, nickel, chromium, copper, iron, indium, zinc, tantalum, tin, vanadium, tungsten, zirconium, molybdenum and alloys thereof. In accordance with the present invention, the metal is vacuum deposited onto the stabilization layer 49 on copper foil 12 without additional cleaning or surface preparation. The metal is applied directly onto stabilization layer 49 by vacuum deposition techniques such as sputtering, chemical vapor deposition, electron beam deposition, thermal evaporation, ion plating (via substrate) or a combination of such processes. In the embodiment shown, a sputtering process 70 is schematically illustrated. As seen in FIG. 1, copper foil 12 with stabilization layers 49 thereon is conveyed into a deposition chamber designated 72. An electron beam gun 74 directs a stream of electrons at a target 76 comprised of a metal such that metallic species are knocked loose and deposited onto a surface of copper foil 12. In the embodiment shown, the deposition process applies a metal onto the matte side of copper foil 12. The applied metal preferably has a thickness of between about 50Å and 5,000Å. In the embodiment shown, a single target 76 is illustrated. As will be appreciated, multiple targets may be used and, if desired, the metal may be applied to both matte side 16 and shiny side 14 of foil 12.

In a preferred embodiment of the present invention, chromium is sputter deposited onto matte side 16 of copper foil 12 as an adhesion layer to enhance the adhesion of the copper foil to a substrate. It has been found that the foregoing process provides a chromium coated copper foil having good adhesive properties.

The following examples are provided for purposes of illustrating the invention. Unless otherwise indicated, in the following example as well as throughout the specification and claims, all parts and percentages are by weight, all temperatures are in degrees Celsius, and all pressures are atmospheric.

EXAMPLE 1

Both sides of raw electrodeposited copper foil ⅓ oz/ft^2, are pretreated with stabilization layers as follows:

Stabilization Treatment:

0.53 g/l Zinc as $ZnSO_4$,0.6 g/l Cr as CrO_3, 11 g/l Na_2SO_4

Bath pH: 5.0

Bath temperature: 42°C.

Current density: 8-15 amps/ft^2 for matte side

2-2.5 amps/ft^2 for shiny side

Plating time: shiny side: 6-8 seconds

matte side: 3-4 seconds

Chromium is then applied to the stabilization layer(s) as follows:

Chromium Sputtering:

14" sputter machine

Power: 5-8 kilowatts

Linear speed: 1.4 to 2.2 ft/min

Chromium Thickness: 1,200Å for matte side

1,300Å for shiny side

EXAMPLE 2

Both sides of polyimide film are plated with copper (18μ copper/50μ polyimide film/5μ copper; this product is one of a family of Gould®flex products manufactured by Gould Electronics Inc.) and treated as follows:

Stabilization Treatment:

0.53 g/l Zinc as $ZnSO_4$, 0.6 g/l Cr as CrO_3, 11 g/l Na_2SO_4

Bath pH: 5.0

Bath temperature: 42°C.

Current density: 25 amps/ft^2 for both sides

Plating time: for either or both sides: 3-8 seconds

Chromium is then applied to the stabilization layer(s) as follows:

Chromium Sputtering:

14" sputter machine

Power: 5-8 kilowatts

Linear speed: 1.8 to 2.8 ft/min

Chromium Thickness: 1,000Å for 18μ copper side

No chromium applied to 5μ copper side

EXAMPLE 3

Both sides of polyimide film are plated with copper (18μ copper/50μ polyimide film/5μ copper; this product is one of a family of Gould®flex products manufactured by Gould Electronics Inc.) and treated as follows:

Stabilization Treatment:

5 g/l Cr as CrO_3

Bath pH: 2.0

Bath temperature: 25°C.

Dip treatment

Chromium is then applied to the stabilization layer(s) as follows:

Chromium Sputtering:

14" sputter machine

Power: 5-8 kilowatts

Linear speed: 1.8 to 2.8 ft/min

Chromium Thickness: 1,000Å for 18μ copper side

EXAMPLE 4

Both sides of electroplated 8μ copper on INVAR (8μ Cu/ 1.5 mil INVAR/8μ Cu), are pretreated with stabilization layers as follows:

Stabilization Treatment:

0.53 g/l Zinc as $ZnSO_4$, 0.6 g/l Cr as CrO_3, 11 g/l Na_2SO_4

Bath pH: 5.0

Bath temperature: 42°C.

Current density: 25 amps/ft^2

Plating time: 3-4 seconds

Chromium is then applied to the stabilization layer(s) as follows:

Chromium Sputtering:

14" sputter machine

Power: 5-8 kilowatts

Linear speed: 1.8 to 2.8 ft/min

Chromium Thickness: 1,000Å for 8μ copper side

The foregoing description is a specific embodiment of the present invention. It should be appreciated that this embodiment is described for purposes of illustration only, and that numerous alterations and modifications may be practiced by those skilled in the art without departing from the spirit and scope of the invention. For example, cleaning process 20 may not be required if process 10 is an extension of an electroforming process wherein virgin copper is being formed and directed into process line 10. Further, while the foregoing process has been described with respect to a copper foil, the process may be used to apply a metal, such as chromium, onto copper that is part of a copper coated polymer. It is intended that all such modifications and alterations be included insofar as they come within the scope of the invention as claimed or the equivalents thereof.

Having described the invention, the following is claimed:

1. A method of applying a metal onto a copper layer, comprising the steps of:

stabilizing a surface of a copper layer by applying a stabilization layer thereto, said stabilization layer comprised of zinc oxide, chromium oxide, nickel, nickel oxide or a combination thereof and having a thickness of between about 5Å and about 70Å; and

vapor depositing a metal selected from the group consisting of aluminum, nickel, chromium, copper, iron, indium, zinc, tantalum, tin, vanadium, tungsten, zirconium, molybdenum and alloys thereof onto the stabilized surface of said copper layer.

2. A method as defined in claim 1, wherein said copper layer is selected from the group consisting of copper foil, copper on polyimide and copper on INVAR.

3. A method as defined in claim 2, wherein said metal is chromium.

4. A method as defined in claim 3, wherein said stabilization layer is comprised of the combination of zinc oxide and chromium oxide.

5. A method as defined in claim 4, wherein said copper foil has a shiny side and a matte side and said chromium is applied to said matte side or said shiny side.

6. A method as defined in claim 3, wherein said stabilization layer is comprised of chromium oxide.

7. A method as defined in claim 6, wherein said copper foil has a shiny side and a matte side and said chromium is applied to said matte side or said shiny side.

8. A method as defined in claim 1, wherein said copper layer is a generally continuous strip and said stabilization layer and vapor deposited metal are applied in a generally continuous process.

9. A sheet material, comprised of:

a layer of copper;

a stabilization layer on a surface of said copper, said stabilization layer comprised of zinc oxide, chromium oxide or a combination thereof having a thickness between about 5Å and about 70Å; and a vapor deposited metal on said stabilization layer.

10. A sheet material as defined in claim 9, wherein said metal is selected from the group consisting of aluminum, nickel, chromium, copper, iron, indium, zinc, tantalum, tin, vanadium, tungsten, zirconium, molybdenum and alloys thereof.

11. A sheet material as defined in claim 10, wherein said metal is chromium.

12. A sheet material as defined in claim 11, wherein said stabilization layer is comprised of zinc oxide and chromium oxide.

13. A sheet material as defined in claim 11, wherein said stabilization layer is comprised of chromium oxide.

14. A sheet material as defined in claim 10, wherein said chromium has a thickness of about 50Å to about 5,000Å.

15. A sheet material as defined in claim 10, wherein said vapor deposited metal is sputtered onto said stabilization layer.

16. A sheet material as defined in claim 15, wherein said stabilization layer is applied by an electrodeposition process.

17. A sheet material as defined in claim 15, wherein said stabilization layer is applied by a mechanical dip process.

18. A sheet material as defined in claim 10, wherein said copper foil is electrodeposited.

19. A sheet material, comprised of:

a layer of copper;

a stabilization layer on a surface of said copper, said stabilization layer having a thickness of from about 5Å to about 70Å; and

a vapor deposited metal on said stabilization layer.

20. A sheet material as defined in claim 19, wherein said stabilization layer is selected from the group consisting of nickel, nickel oxide and a combination thereof.

21. A sheet material as defined in claim 19, wherein said stabilization layer contains phosphorous.

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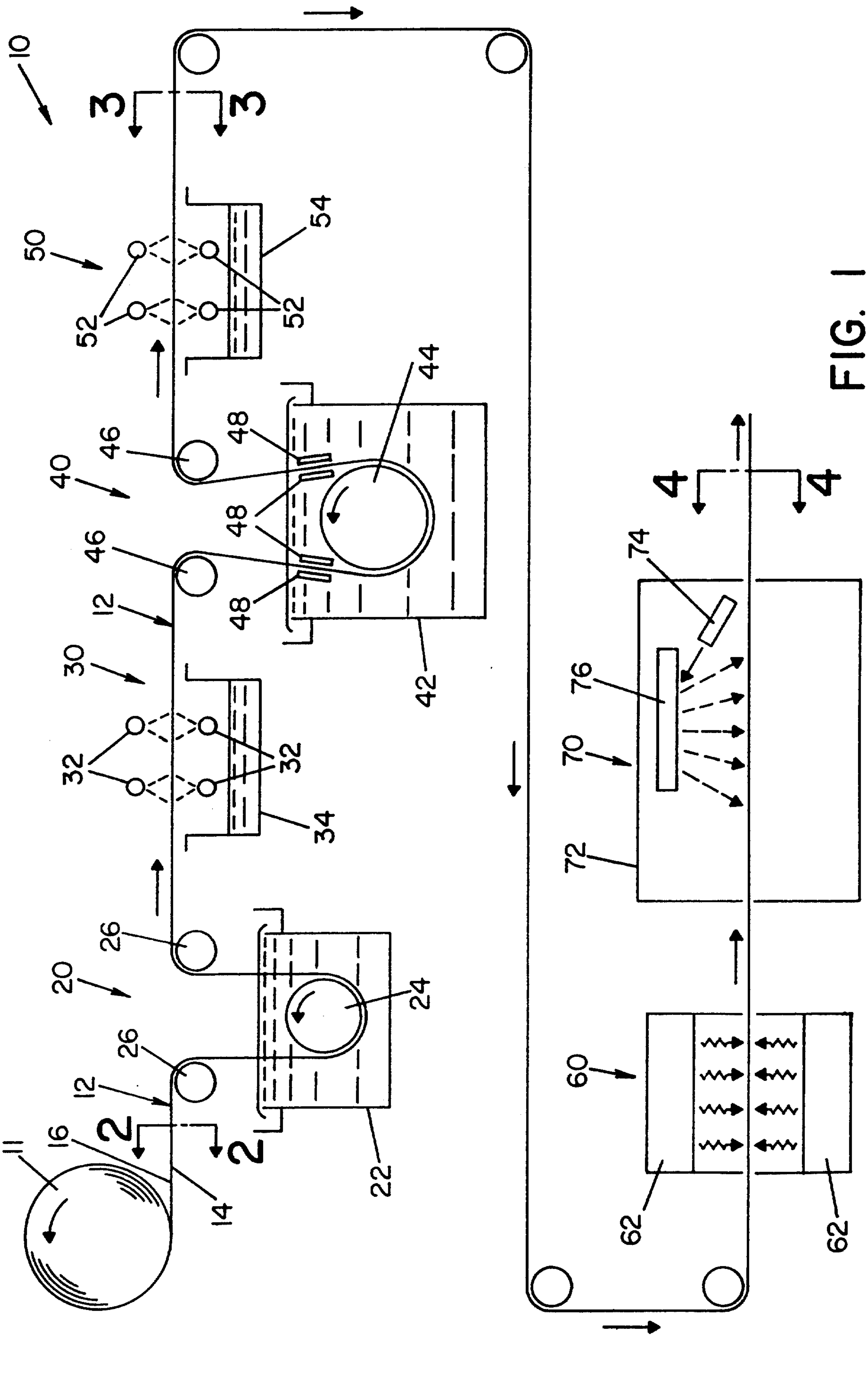
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FIG. 1

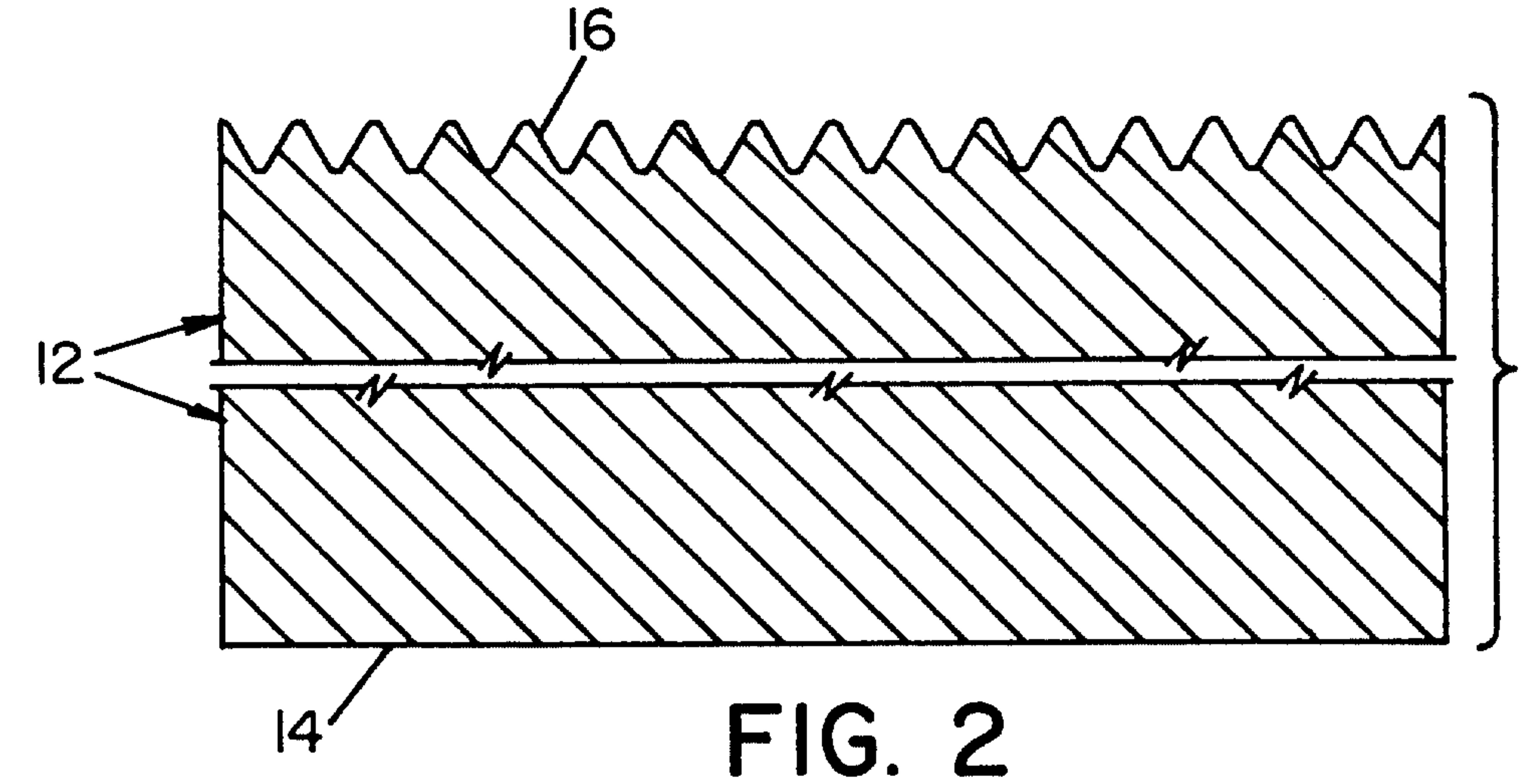


FIG. 2

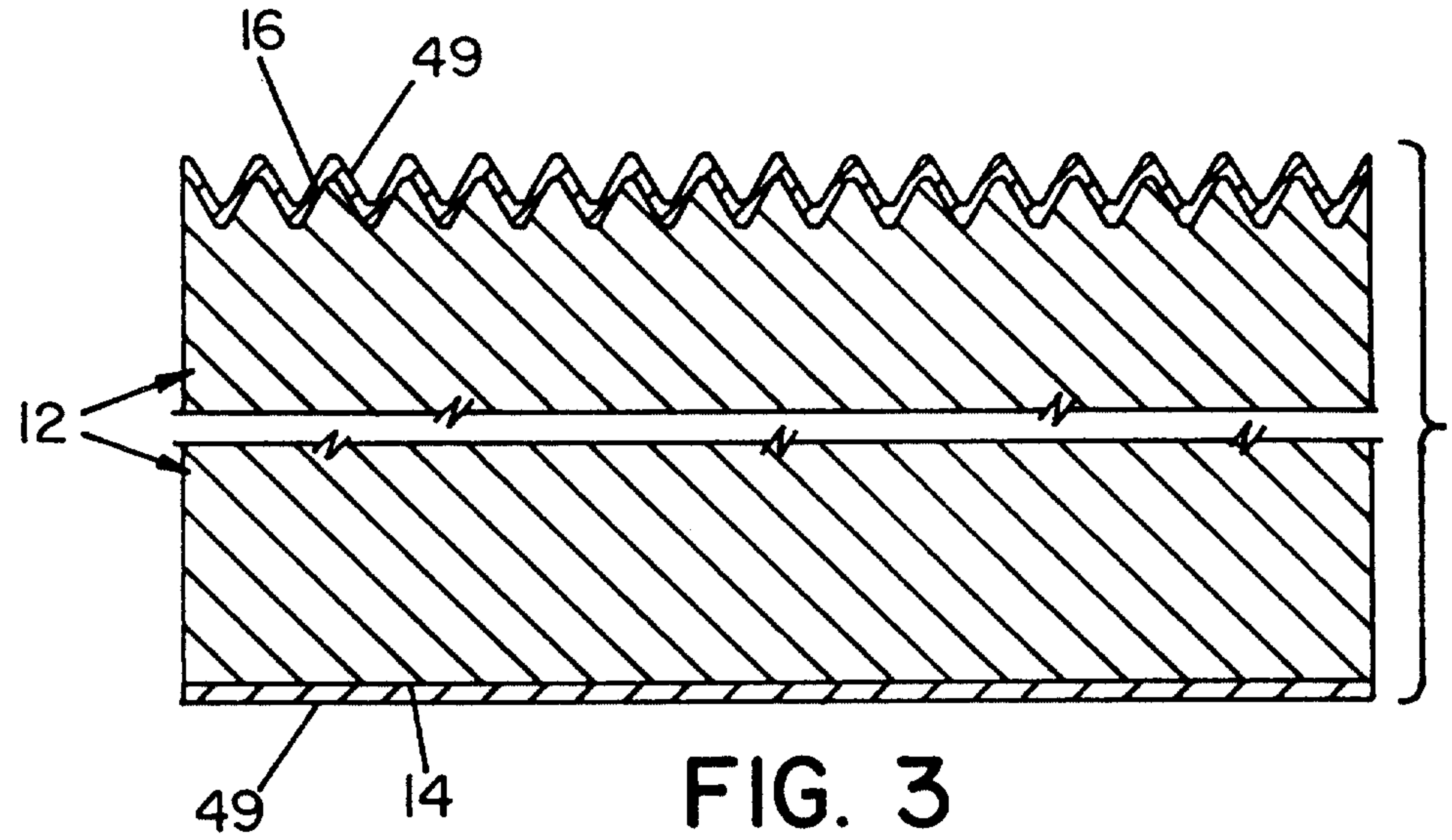


FIG. 3

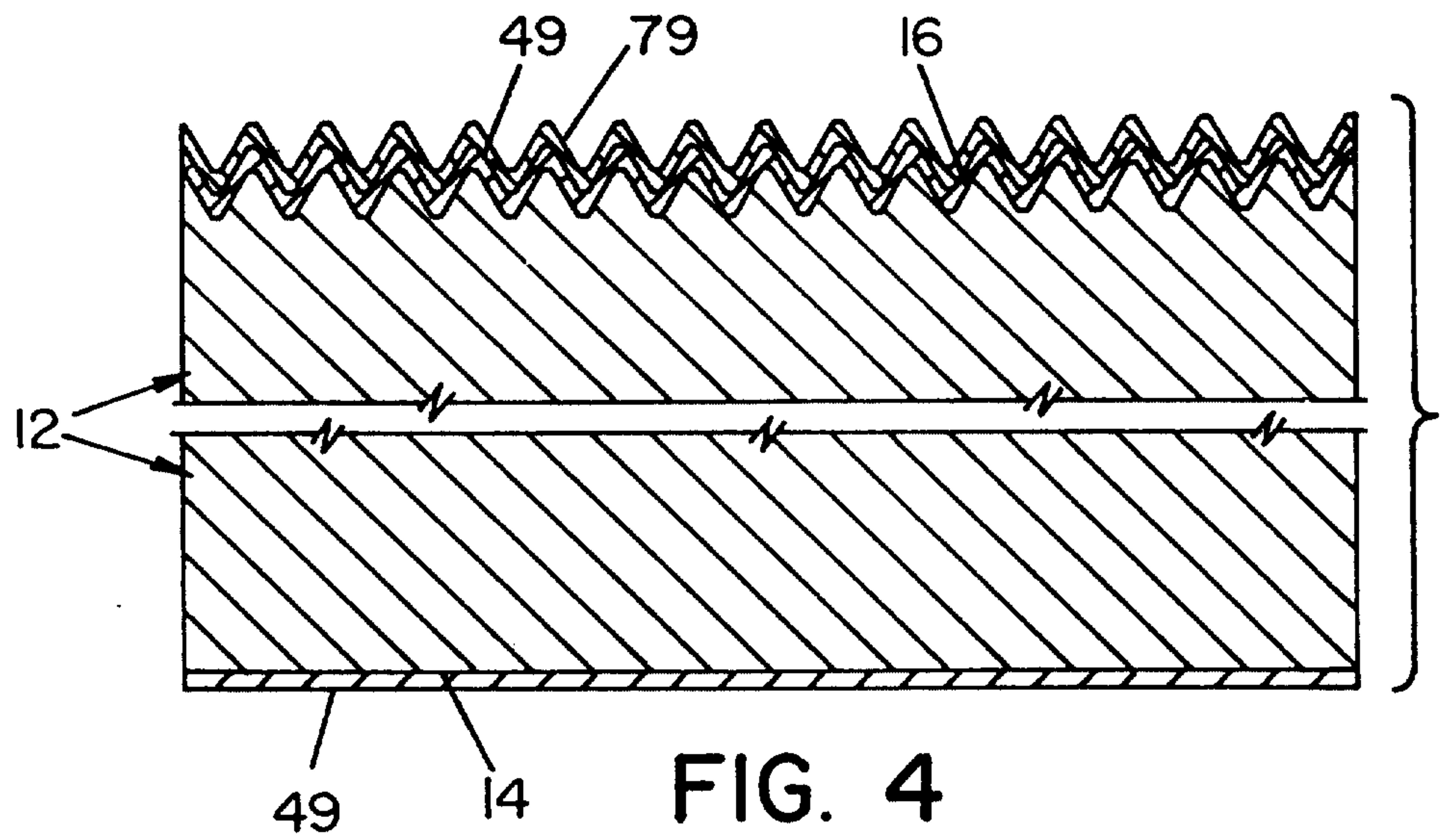
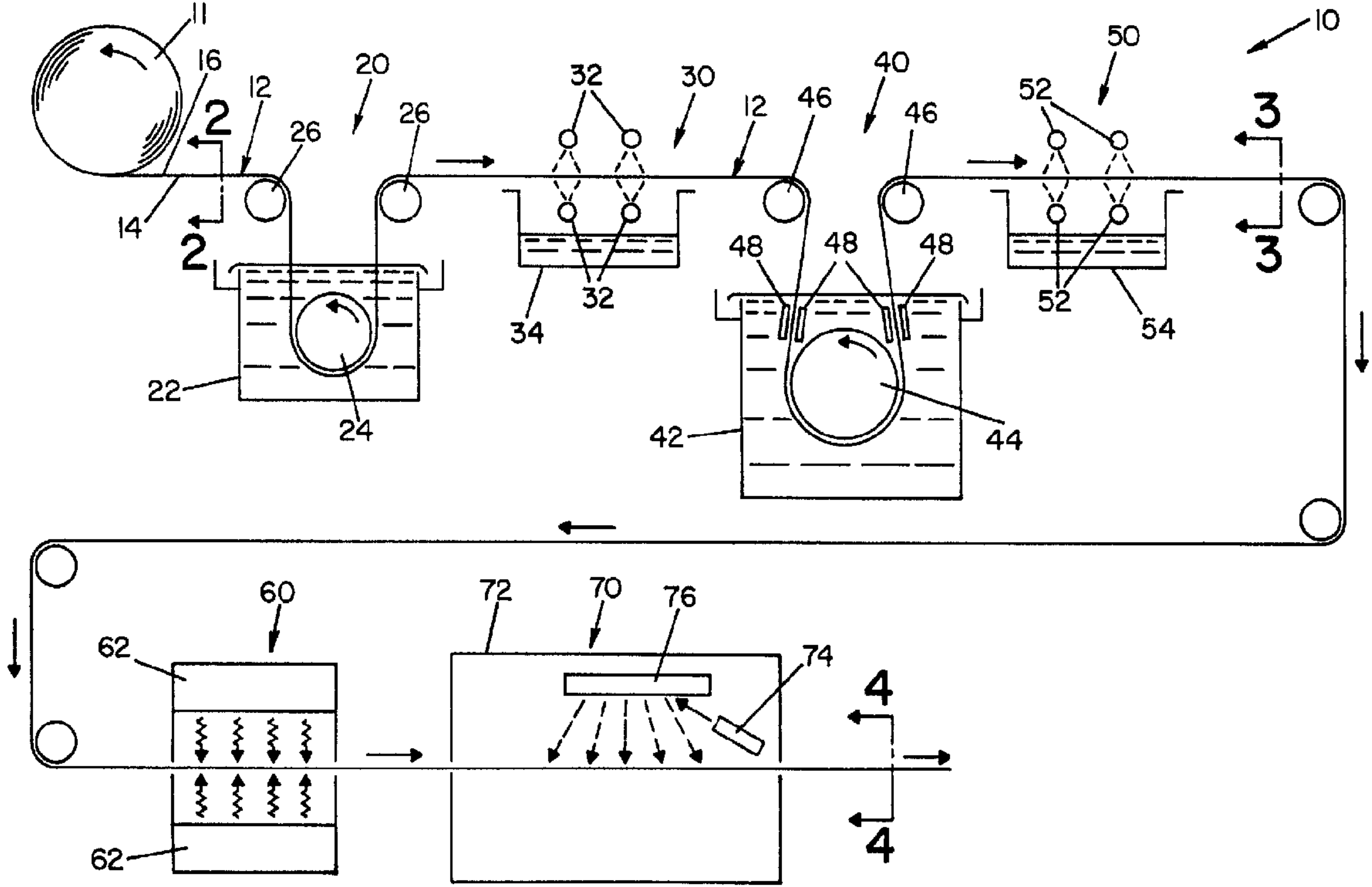


FIG. 4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