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S. KATZ ET AL
PROCESS FOR UNIFORMLY ELECTROFORMING INTRICATE
THREE-DIMENSIONAL SUBSTRATES
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3,694,325

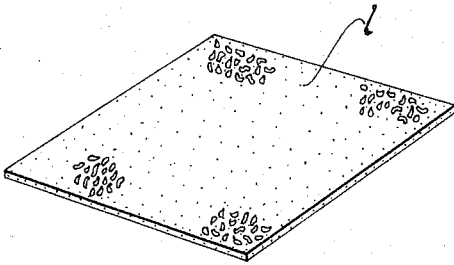


Fig. 1

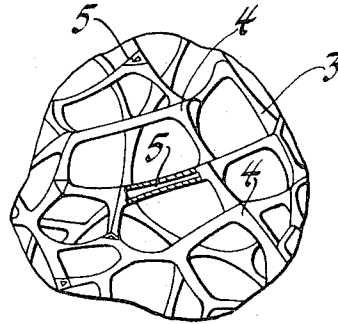


Fig. 2

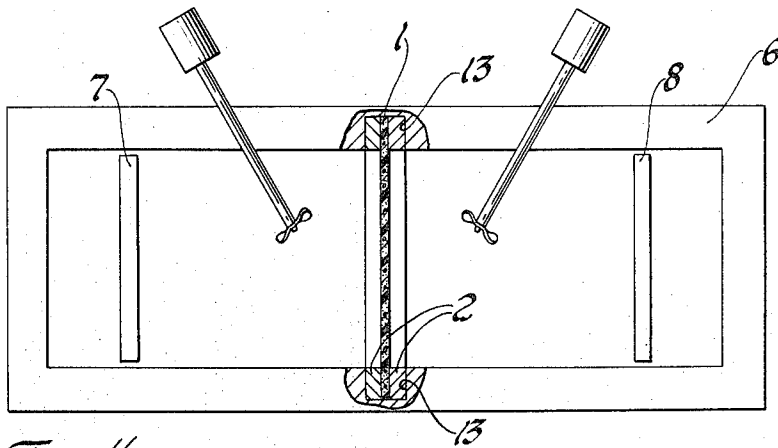


Fig. 4

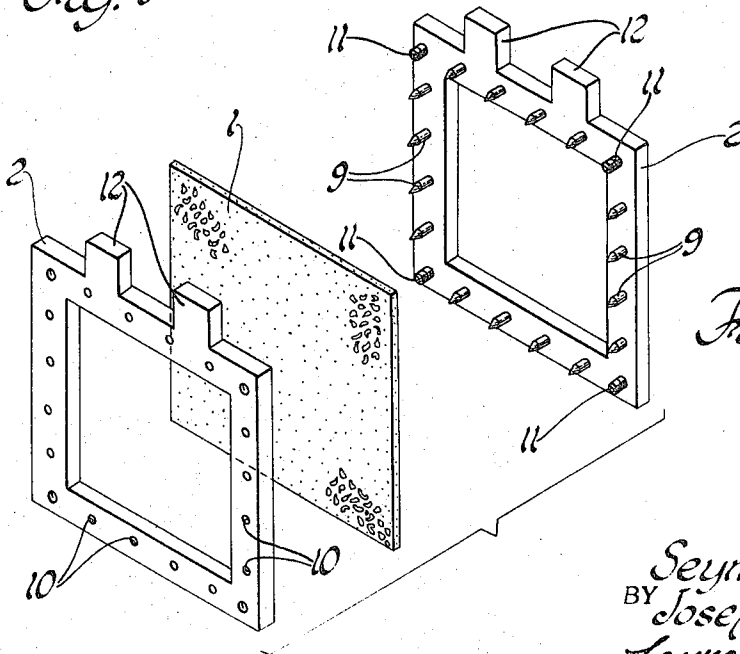


Fig. 3

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PROCESS FOR UNIFORMLY ELECTROFORMING INTRICATE THREE-DIMENSIONAL SUBSTRATES

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Continuation-in-part of application Ser. No. 724,544,

Apr. 26, 1968. This application June 21, 1971, Ser.

No. 155,160

Int. Cl. C23b 7/00, 5/60; C23f 17/00

U.S. Cl. 204—11

2 Claims

ABSTRACT OF THE DISCLOSURE

A process for making a substantially homogeneous, intricate, three-dimensional, reticulated electroform particularly an open cell metal foam.

This is a continuation-in-part of application Ser. No. 724,544 now abandoned filed Apr. 26, 1968 in the name of Katz et al. and assigned to the assignee of this application.

A variety of porous cellular metal structures and techniques for producing same are known. One technique produces substantially closed-cell, foam-like metal structures and involves grinding a temperature-decomposable, gas-forming solid into a molten metal. Upon decomposition of this solid, gas bubbles form and cause the molten metal to foam prior to and during cooling. Another technique involves impregnating an open-cell, porous structure with a suspension of powdered metal, driving off the suspension medium, and sintering the metal particles together. The ability of this slurry and sinter process to very closely reproduce a completely open-cell structure from an open-cell porous substrate is limited, owing to the formation of webs between adjacent cells and its ability to duplicate the substrate's shape becomes less and less as the metal content of the product is increased or the cell size of the substrate decreased.

It is the object of this invention to substantially uniformly electroform, and in so doing replicate in metal, intricate, three-dimensionally, reticulated, open-cell substrates. Other objects of this invention will become more apparent from the detailed description which follows.

Reference is made to the drawings in which:

FIG. 1 is a perspective view of a panel of a type of product produceable using the process of this invention.

FIG. 2 is an enlarged view of a portion of the panel of FIG. 1.

FIG. 3 is an exploded perspective view of a panel and plating frame used in this invention.

FIG. 4 is a plan view of a plating cell arrangement used in this invention.

Briefly stated, this invention resides in a method of making a substantially homogeneous, intricate, three-dimensionally reticulated electroform.

This invention involves a unique combination of steps and plating techniques acting together to homogeneously electroform a substrate replete with high and low connect density areas and including fibrils extending in virtually every direction throughout a three-dimensional network. More particularly the invention comprehends the combined use of (1) a conductive frame mounted contiguous the border of a conductive, reticulated substrate panel, (2) precise positioning of the frame-mounted panel between two anodes in an elongated plating cell such that the panel is transverse and substantially fills the cross section of the cell, and (3) current densities less than about 10 amps/ft.². Substantially homogeneous three-dimensionally reticulated electroforms made in accordance with this invention will generally have a metal con-

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tent of about 0.5%–30% metal, by volume and the substrate may or may not be removed after plating.

EXAMPLE

An appropriate, intricate, three-dimensional, reticulated, substrate having the desired shape of the finished electroform is selected. For this example a material known as etched premium grade Scott Industrial Foam was selected. It is a flexible ester-type polyurethane produced by the Scott Paper Company. This material comprises a plurality of filaments or fibrils interconnected via a plurality of junctions in a three-dimensional lattice-like arrangement resulting in an approximately isotropic skeletal outline of a multitude of polyhedrally shaped cells. The cells' faces are polygonal and are common to adjacent polyhedrally shaped cells. While sheets of this material ranging in thickness from 1/32 inch to 1/2 inch have been used, the following discussion relates to 1/4 inch sheets. The material has cell sizes from about 10 to about 100 cells per lineal inch (c.p.i.), but the following discussion relates to sheets having about 100 cells per lineal inch (c.p.i.). The sheet is first washed for about 1 minute in an organic solvent to remove any undesirable organic contaminants, such as oil. We prefer to use alcohol or acetone. This first step not only removes any undesirable organic contaminants but also significantly improves the wettability of the substrate's fibers. This improved wettability significantly contributes to the effectiveness of subsequent steps in the operation. The solvent is best applied using a squeezing technique wherein the foam is alternately compressed and released while immersed in the solvent. When using other than etched premium grade foam, it is desirable to also soak the plastic for about 2–5 minutes in 8% NaOH solutions to improve its wettability. Following the solvent treatment, the sheet is washed and sensitized by alternately squeezing for 3 minutes in a solution containing 2.5 g./l. SnCl₂, 100 ml./l. conc. HCl, and H₂O. The stannous ion is adsorbed on the surfaces of the sheet. It is next washed and activated by treatment for 4 minutes in a 130–180° F. solution containing 0.2 g./l. PdCl₂, 10 ml./l. HCl and H₂O. The palladium ion is reduced to palladium metal by the action of the adsorbed stannous ion. The palladium metal forms nucleation sites for subsequently applied electrolessly deposited metal. After rinsing, the sheet is immersed at 170° F. in the following solution:

Nickel chloride	grams/l.	22
Sodium hypophosphite	do.	14
Sodium hydroxide	do.	22
Acetic acid	ml./l.	34
Water		
pH, 4–6		

Preferably about 0.1 volume percent electroless metal is deposited. The thusly treated material is cut into about 4 ft.² panels 1 and mounted in a conductive frame 2, such as is shown in FIG. 3. The frame 2 is in two sections, with one section having pins 9 for holding the treated material and the other having holes 10 for receiving the pins. The frames are held together by bolts 11. The framed panel is next placed in a rectangular plating cell 6 (see FIG. 4) having provisions for concurrently depositing metal from both sides (e.g. anodes 7 and 8) of the panel. The plating cell contains the following nickel plating bath:

Nickel sulfate · 6H ₂ O	oz./gal.	20
Ammonium chloride	oz./gal.	4
Boric acid	oz./gal.	4.0
Temperature	° F.	75–90
pH		4–4.5
Current density	a.s.f. (actual)	2.5

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The panel 1 is coated until the desired metal content is reached then subsequently removed, rinsed and dried. It is next heated to about 800° F. in an oxidizing environment, i.e., air, to decompose the plastic substrate and oxidize the carbon. While it is necessary only to heat to about 600° F. for decomposition of polyurethane, it is preferred to exceed this to insure complete oxidation of the carbon. The upper limit, of course, is the melting point of the metal. The panel 1 thus produced has a first micro-void volume 5 having a maze-like configuration and existing within the intercommunicating capillary filaments 3 and junctions 4. A second macro-void volume exists on the outside and around capillary filaments 3.

A second heat treatment, in an inert or reducing atmosphere (e.g., H₂), may be employed to improve the properties of the formed material. In this regard, at least, an annealing treatment is desirable to obtain the improved properties of these materials. We particularly prefer to anneal nickel materials for about one hour at various temperatures depending on the metal content of the material. In this regard, a material containing 1% or less metal is heated to about 1400° F. or less, a 2%–3% metal material to 1500° F. or less, and a 5% or more metal material to 1600° F. or more. The lower temperatures for the lower metal content materials have been found to be necessary if shrinkage of the material is to be avoided. Other heat treatments may be used to develop special properties in the materials. In this regard, carburizing, nitriding, and oxidizing techniques may be employed. Likewise, the capillary filaments may be shrunk using special heat treatments.

A significant aspect of the invention is the substantially homogeneous character of the product produced in that it has a surprisingly uniform deposit thickness distribution, both with respect to the principal planes of the panel and the depth dimensions into its interstices. By principal planes, is meant the major two-dimensional faces of the panels which directly oppose the anodes during forming. With respect to the thickness distribution in the principal planes, 4 ft.² panels have consistently been formed with less than 2% deposit thickness variation. With respect to the depth dimension, 4 ft.² panels have consistently been formed having deposit thickness ratios (DTR) of 1.5 or less. By deposit thickness ratio (DTR) is meant the ratio of the thickness of the metal deposit on the outermost fibers to its thickness on the innermost fibers. In certain instances ¼" panels having 100 cells per inch and 5% metal content have been produced with DTR's of 1.05. While, of course, a DTR of 1.0 is preferred, DTR's of 2.0 or less are satisfactory for most applications. Such materials are herein referred to as being within the intent of the term "substantially homogeneous." Though DTR's approaching 1.0 are possible, for most applications such complete uniformity is not required and, hence, most of our materials have DTR's of about 1.5 or less. DTR's above about 2.0 are much weaker on the inside than on the outside and have much smaller cells on the surface than within the body. During the electroforming process itself, where the DTR is initially large, the surface pores tend to close and inhibit good electroforming into the interstices of the panel. If electroforming continues under these conditions, the DTR gets progressively worse. The deposit thickness distribution, including the DTR, is a function of several variables among which are the size and shape of the panel, its thickness and its cell size, as well as the current density employed, and the throwing power of the bath.

The excellent deposit thickness distributions obtained herein result from a unique combination of techniques essential to and especially adapted for electroforming intricate, three-dimensional, reticulated substrates. One of these techniques involves the placement of the panel in an electrically conductive frame 2, or the like. Such a frame 2 (FIG. 3) comprises two half portions made of copper or other good conductor which are adapted to

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sandwich the panel between them after it has been stretched over the pins 9. Contact blocks 12 serve to connect the frame 2 to the electrolyzing circuit (not shown). The purpose of the frame 2 is to insure a substantially uniform current distribution across the principal planes of the panel. Moreover, it was found that framing significantly contributes to the substantially homogeneous character of the electroform with respect to its depth dimensions, i.e., good DTR's. While it is preferred to have a frame 2 which is conductive on all four sides of the panel, satisfactory forming is possible when only two opposing sides are conductive. When a two-sided conductive frame is used, the spacing between the sides becomes more significant to insure good deposit thickness distributions and to prevent the electroless coating from burning during the initial phases of the electroforming. This is especially true when extremely light loadings of electroless metal are applied. Preferably, those conductive portions of the frame which are not in contact with the panel are covered or masked to prevent scavenging of the metal and the current from the electroforming bath. This can be accomplished by closely fitting the frame 2 into slots 13 in the plating cell's wall.

Another technique essential to obtaining a substantially homogeneous product is the placement of the framed panel 1 in a rectangular plating cell 6 at either end of which are placed anodes (e.g., nickel) 7 and 8. The panel is placed transverse to and substantially centrally of the cell 6. The anodes 7 and 8 are so spaced from the panel 1 as to provide substantially equidistant current paths between the anode and the panel. This arrangement effectively straightens the current paths which, like the frame, contributes to a more uniform current distribution across the face of the panel. As little as possible of the frame should be exposed to the straightened current paths so as not to set up any current baffles which would upset the thickness distribution. In this regard, slots 13 may be provided in the walls of the cell to receive the frame so that the panel fills virtually the entire cross section of the cell. The panels are preferably concurrently coated from both sides. The anodes are preferably independently controlled but for most applications a 1:1 current ratio between the two anodes is preferred, since this produces the most uniform deposit thickness profile through the thickness of the panel. Clearly, however, by varying this ratio, virtually any deposit thickness profile is possible and may, in fact, be desirable for special applications (e.g., fuel cell electrodes) where particular porosity gradients are desirable. Forming solely from one side introduces a current density gradient through the thickness of the panel, i.e., front to back. A corresponding deposit thickness profile results. Forming on both sides, concurrently, causes the current density gradients imposed by the separate anodes to oppose each other such as to substantially cancel each other. Excellent deposit thickness profiles result, which contribute to the substantial homogeneous character of the material.

The respective influences of current density and the bath's throwing power can be directly related to the deposit thickness profile through the panel. The best DTR's (e.g., 1.05) and deposit thickness profiles have been obtained when forming panels ¼" thick or less. One-half inch (½") panels with satisfactory DTR's have been formed using higher throwing power baths such as disclosed in U.S. Pat. 2,802,779. Another factor which contributes significantly to the deposit thickness profile through the material is the nature of the material's porosity. With smaller cells (e.g., 80–100 c.p.i.), more care is required to insure an acceptable deposit thickness profile. During forming, materials having finer cells tend to have their surface pores close thereby limiting or restricting further forming within the interstices of the panel. Both current and electrolyte mobility into the interstices of the panel become more limited. Therefore, if a fine cell material is to be formed, it is preferred to use thinner

panels and high throwing power baths, if possible, to minimize the effects of at least some of the other DTR affecting variables. By way of example, the relationship between the thickness of the panel and its cell size as it relates to some deposit thickness ratios is shown in Table I for three nickel baths and one iron bath.

TABLE I

Thickness (inches)	Cell size (c.p.i.)	Metal content (vol. percent)	Apparent current density (a.s.f.)	DTR
Sulfamate nickel:				
1/8	30	10	40	1.8
1/8	100	5	40	2.1
1/8	100	15	13	1.6
1/8	30	5	40	2.3
1/8	30	10	40	4.0
1/8	10	5	13	1.8
Hard nickel:				
1/8	100	5	13	1.4
1/8	100	15	13	1.7
1/8	10	5	13	2.2
USPN 2,802,779:				
1/8	100	5	40	1.07
1/8	100	10	40	1.21
1/8	100	4	40	1.4
1/8	45	15	40	2.3
1/8	30	15	40	2.1
1/8	10	5	13	1.2
Iron:				
1/8	30	10	40	1.5
1/8	100	5	40	2.0
1/8	100	10	40	2.0
1/8	100	15	40	1.9
1/8	30	5	40	2.4
1/8	30	10	40	4.0

Among the metals susceptible of use herein are iron, nickel, copper, silver, cadmium, tin, zinc, gold and chromium, as well as many alloys, including bronze, Nichrome, iron-chrome, iron-nickel, Monel and others. Among the baths which may be used with this invention are the following:

For nickel

(1)

Nickel sulfate	oz./gal.	20
Ammonium chloride	oz./gal.	4
Boric acid	oz./gal.	4
pH		4-4.5
Temperature	° F.	75-90

(2)

Nickel sulfamate	oz./gal.	60
Boric acid	oz./gal.	4.0
Anti-pitting agent	oz./gal.	0.05
pH		3-5
Temperature	° F.	100-400

(3)

U.S. Pat. 2,802,779, Cowle et al.

For tin

Potassium stannate	oz./gal.	14
Potassium hydroxide	oz./gal.	2
Temperature	° F.	140-160

For silver

Silver cyanide	oz./gal.	16
Potassium cyanide	oz./gal.	19
Potassium hydroxide	oz./gal.	1.5
Potassium carbonate	oz./gal.	4-14
Ammonium thiosulfate	oz./gal.	0.0025
Temperature	° F.	90-120

For cadmium

Cadmium oxide	oz./gal.	2.5-3
Potassium cyanide	oz./gal.	14-17
Potassium carbonate	oz./gal.	8
Potassium hydroxide	oz./gal.	2
Temperature	° F.	75-90
pH		12.6

For zinc

Zinc oxide	oz./gal.	2.5-3
Potassium cyanide	oz./gal.	14-17
Potassium carbonate	oz./gal.	8
Potassium hydroxide	oz./gal.	2
Temperature	° F.	75-90
pH		12.6

For copper

Cuprous cyanide	oz./gal.	12
Potassium cyanide	oz./gal.	20
Potassium hydroxide	oz./gal.	4-6
Temperature	° F.	160
PH		12.5

For iron

U.S. Pat. 3,404,074, 437,276 filed Mar. 4, 1965.

We have found that the best materials made in accordance with this invention are those formed at actual current densities of less than about 10 amperes per square foot (a.s.f.), with from 1-5 a.s.f. being preferred. Actual current density is distinguishable from apparent current density. Actual current density includes all coatable surfaces in all three dimensions, whereas, the apparent current density is that which is based on the dimensions only of the principal plane of the panel. In this regard, for example, we have determined that for a 1/8 inch material such as described in the example and having 100 c.p.i., the ratio of the actual area to the apparent area is about 5.3. Where time is not a significant factor, actual current densities as low as 1/4 a.s.f. can be and have been used. Materials formed at these lower actual current densities tend to have better DTR's and excellent deposit thickness profiles. For most baths tested, except for certain instances where the panels have been about 1/32 inch thick or less, satisfactory materials could not be formed at actual current densities in excess of 10 a.s.f. In one case, however, it has been noted that higher actual current densities (e.g., up to about 15 a.s.f.) could be used with 1/8 inch thick materials when electroforming, using the nickel bath described in U.S. Pat. No. 2,802,779.

While this invention has been disclosed primarily in terms of a particular embodiment thereof, it is not intended to be limited thereto but rather only as defined by the claims which follow.

We claim:

1. A process for preparing a substantially homogeneous intricate, three-dimensionally reticulated electroform comprising the steps of, providing a resin substrate panel having a three-dimensionally reticulated form corresponding to that of the desired electroform said panel having a border and at least one principal plane, treating the coatable surfaces of said panel with an organic solvent to rinse and improve the wettability of said surfaces, sensitizing said surfaces in an aqueous solution containing SnCl₂ and HCl, activating said surfaces in an aqueous solution containing PdCl₂ and HCl, electrolessly depositing a metal coating on said surfaces, mounting said panels in an electrically conductive frame contiguous said border, said frame conducting current directly and substantially uniformly to the borders said panel to provide a substantially uniform current distribution across said principal plane and into the interstices of said panel during the electroforming step, placing said frame-mounted panel in, and substantially centrally of, an elongated electroforming cell defined by substantially straight walls and having electroforming anodes at either end thereof, orienting said framed panel with respect to said cell such that said panel is substantially transverse to said cell and substantially fills the narrow cross section of said cell, isolating said frame from any substantial direct contact with the electroforming electrolyte to avoid scavenging of electrolyzing current by said frame, electrically connecting said panel to said anode through a means for establishing an electrical potential and electrolyzing current to flow between

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said anode and said panel, impressing a sufficient potential between said panel and said anode so as to effect an actual cathode current density of less than about 10 amps/ft.² and for a time sufficient to electrolytically deposit at least about 1.0% by volume metal on said panel, removing said panel and heating same to at least about 600° F. in an oxidizing environment to remove said resin.

2. A process for preparing a substantially homogeneous completely open cell reticulated nickel electroform having a three-dimensional network of interconnecting filaments which are integrally interconnected by a plurality of junctions, which filaments and junctions form a lattice-work corresponding to an approximately isotropic skeletal outline of a multitude of polyhedrally shaped cells whose faces are polygonal and are common to adjacent polyhedrally shaped cells comprising the steps of, treating the coatable surfaces of a polyester, polyurethane resin panel having said reticulated three-dimensional network with an organic solvent to rinse and improve the wettability thereof, said panel having a border and at least one principal plane, sensitizing said surfaces in an aqueous solution containing SnCl₂ and HCl, activating said surfaces in an aqueous solution containing PdCl₂ and HCl, electrolessly depositing a metal coating on said surfaces, mounting said panels in an electrically conductive frame contiguous said border, said frame conducting current directly to said panel so as to provide a substantially uniform current distribution across said principal plane and into the interstices of said panel during the electroforming step, placing said frame-mounted panel in, and substantially centrally of, an elongated electroforming cell de-

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finied by substantially straight walls and having electroforming anodes at either end thereof, orienting said framed panel with respect to said cell such that said panel is substantially transverse to said cell and substantially fills the cross section of said cell, isolating said frame from any substantial direct contact with the electroforming electrolyte to avoid scavenging of electrolyzing current by said frame, electrically connecting said panel to said anode through a means for establishing an electrical potential and electrolyzing current to flow between said anode and said panel, impressing a sufficient potential between said panel and said anode so as to effect an actual cathode current density of less than about 10 amps/ft.² and for a time sufficient to deposit at least about 1.0% by volume nickel on said panel, removing said panel and heating same to at least about 600° F. in an oxidizing environment to remove said resin and further heating said panel in a nonoxidizing environment to at least about 1400° F. to anneal the electroform.

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U.S. Cl. X.R.

204—30, 38 B