

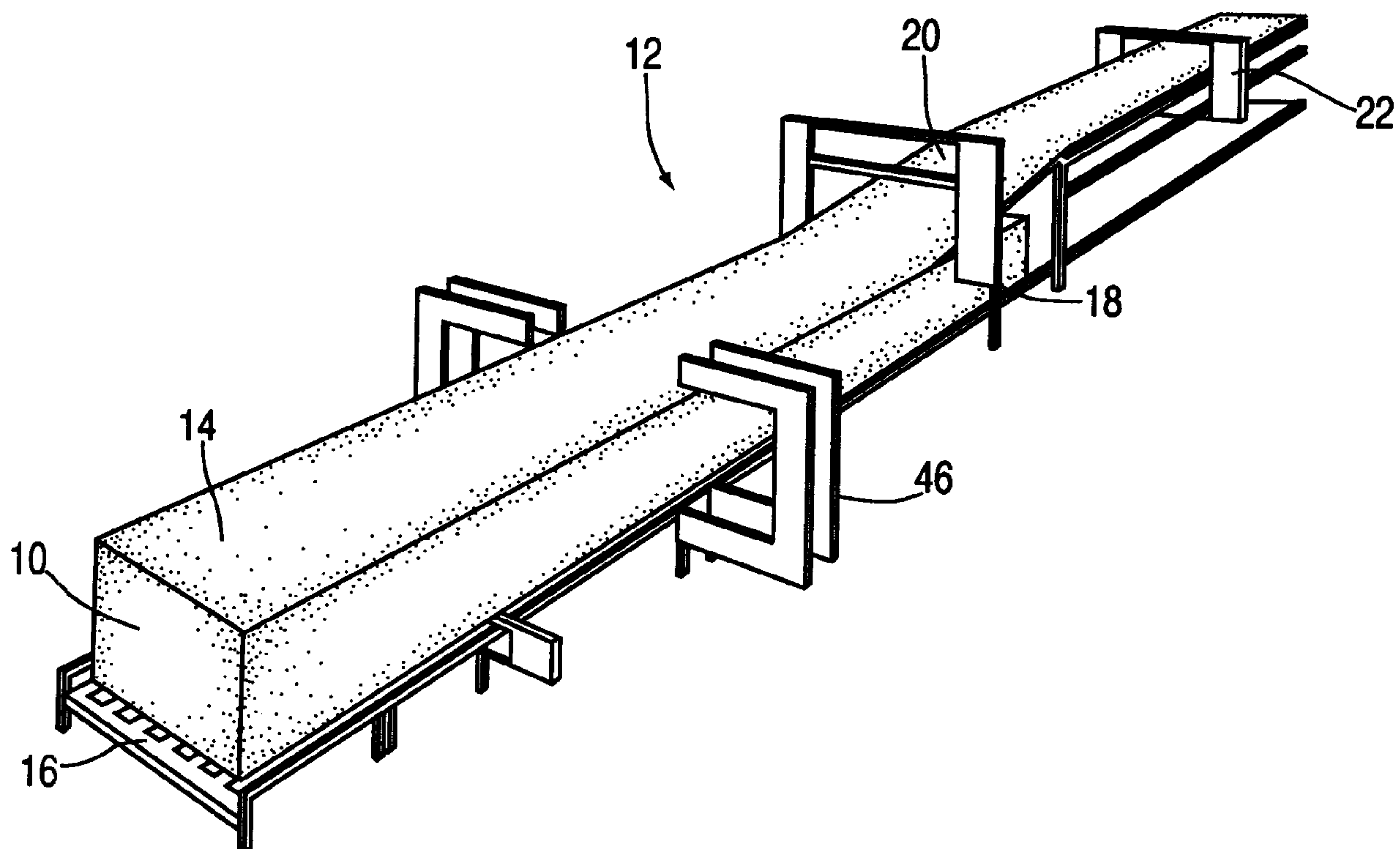


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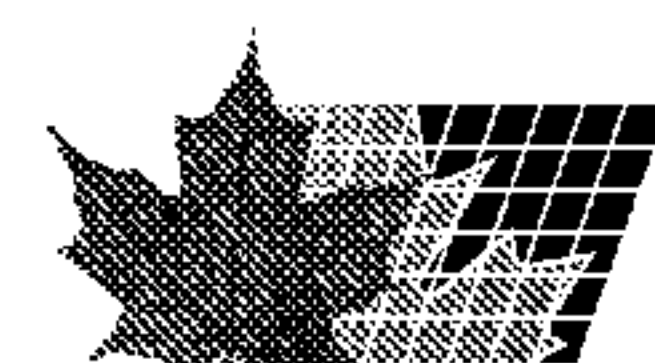
(54) Titre : PROCEDE DE FABRICATION DE MOUSSES METALLIQUES PRESENTANT UNE STRUCTURE
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(54) Title: PROCESS FOR PRODUCING METAL FOAMS HAVING UNIFORM CELL STRUCTURE



(57) Abrégé/Abstract:

A method for producing porous metal plated polymeric foam having uniform pore properties. Polymeric foam buns are horizontally cut along a longitudinal surface thereby lifting off a foam sheet. The sheet is spooled and then reticulated to remove any remaining cell walls and to round off the internal pore struts to enlarge the openings between the adjacent cells. The reticulated foam sheet is unwound and then plated. Slabs may be attached end to end and loop slitted and then reticulated. The resulting plated uniform foam provides a superior substrate for battery plaques and other applications.



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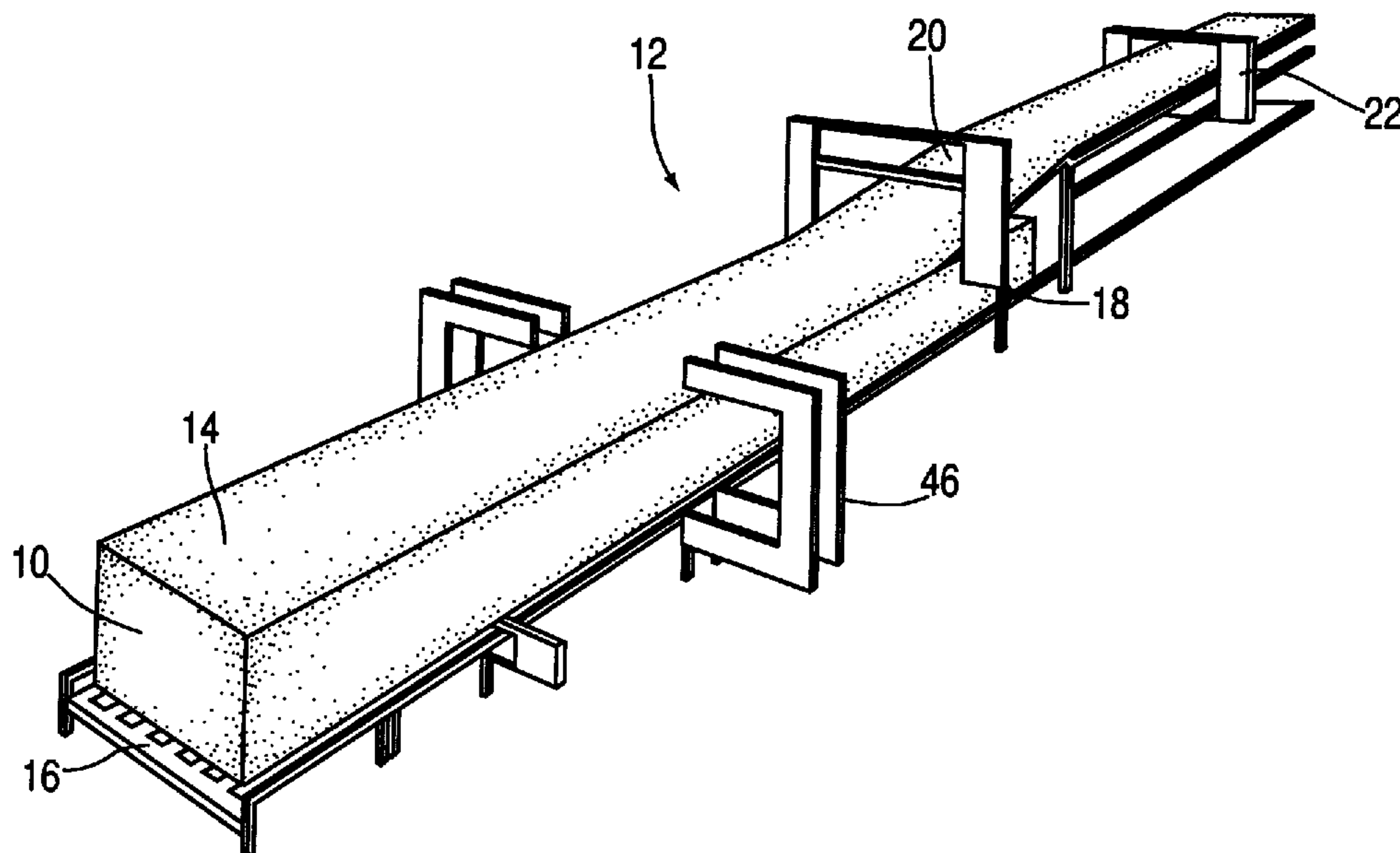
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PROCESS FOR PRODUCING METAL FOAMS
HAVING UNIFORM CELL STRUCTURE

TECHNICAL FIELD

[001] The present invention relates to the production of foams in general, and in particular, to the production of porous metal plated foams having substantially isotropic characteristics.

BACKGROUND OF THE INVENTION

[002] Porous metal plated foams are used in many industrial and commercial applications: battery electrodes, fuel cell components, filters, pollution control equipment, catalyst supports, audio components, etc.

[003] The underlying cell structure is often key to the characteristics of the foam. The three dimensional shape of the repeating cell matrix affects the performance of the foam.

[004] Foams typically come in either open cell or closed cell variants. Different manufacturing techniques are used to produce each type.

[005] Open cell nickel plated foam is predominantly used for electrodes in nickel metal hydride ("NiMH") and nickel cadmium ("NiCd") batteries. In addition to mass production of small consumer cell batteries, large-pack NiMH batteries are a key part of hybrid electrical vehicles ("HEV"). The cell structure of nickel foams affects battery performance; in particular in HEV battery applications. Non-uniform size,

shape and orientation of foam cells lead to non-uniform thickness of nickel, foam conductivity, active mass loading and electrochemical performance of individual battery cells. This in turn will give some of the battery cells different performance characteristics (capacity, impedance, rate of aging) and will eventually cause a premature failure of a large battery pack that often contains as many as 200 battery cells.

[006] Nickel foam is produced through adopting cell structures of polyurethane ("PU") foam substrates as templates by means of electroplating or chemical vapor deposition. In the case of electroplating, a suitable pretreatment of PU foam substrate is required to make the foam conductive. After nickel deposition, sintering is performed to remove the polyurethane substrate, leaving nickel struts arranged in the original three-dimensional framework. Accordingly, a uniform cell structure of the polymeric substrate is key in producing superior nickel foam with a uniform cell structure.

[007] The structure of precursor open cell polyurethane foam is generally described as a pentagonal dodecahedron, which has twelve 5-sided faces with occasional 4- and 6-sided cells found in polyurethane foam structures. With current techniques, it is observed that there exists a geometric anisotropy in the polyurethane cell structure, parallel and perpendicular to the foam rise direction during foaming. Due to gravity, the cells near the bottom of the block of foam (also called a bun or slab) are smaller and more spherical, whereas the cells in the upper part of the block are vertically elongated and larger. Figures 1 and 2 show images of the prior art foam geometric anisotropy, parallel and perpendicular to the foam rise direction respectively. See also U.S. patent 6,383,687.

[008] Currently in commercial nickel foam production, rotary peeled polyurethane foams are widely used as substrates for nickel deposition. The polyurethane foam is peeled by first cutting foam buns into rectangular blocks. After arcuate edge trimming and reticulation the resulting foam roll is peeled via rotary action against a sharp knife blade to produce thin sheets of several millimeters in thickness.

[009] See Figure 5 of V. Paserin et al, "Superior Nickel Foam Production: Starting From Raw Materials Quality Control", in "Porous Metals and Metal Foaming Technology" Metfoam, September 21-23 2005, edited by H. Nakajima and N. Kanetake, p. 317-320, published by The Japan Institute of Metals, (hereinafter "V. Paserin") for a pictorial and written description of metal foams in general and rotary peeling in particular.

[0010] During rotary peeling, since the knife position is along the foam roll perimeter, the resultant foam sheet has circular cell structures from the "parallel" direction (i.e. parallel with the foam rise direction or horizontal position at the time of foaming), and elliptical cell structures from the "perpendicular" direction (perpendicular to the foam rise direction or vertical position at the time of foaming) exhibiting undesirable periodic cell structure variations. On thin sheets, these inconsistencies are sometimes visible as light and dark bands containing cells of different size, shape and orientation. When such foam is used as a substrate for nickel foam production, periodic density perturbation patterns are created, adversely affecting the application performance of the material when used as battery electrodes. See Figures 8 and 9 of V. Paserin. Other important properties of metal foam produced from the rotary peeled polymeric foam are affected as well: periodic variations in electrical conductivity, tensile strength and elongation.

[0011] Another type of thin sheet polyurethane foam production is the "loop slitting" method. A schematic representation of loop slitting is shown in Figure 4. A large foam loop 24 is formed at joint 26 by gluing the two ends of a long (typically 60m) polyurethane slab 28 together. The loop 24 is then rotated in direction 34 by drive belts 44 and is slit by knife 30 in a loop slitting machine as schematically represented in Figure 4 along the slab's surface to continuously form planar sheets 46 which are then rolled into spools 32 of desired thickness.

[0012] Loop slit foam substrates have more uniform cell structures than rotary peeled foams. This is because the foam is cut only in the "perpendicular" direction (the horizontal direction at the time of foaming) so that all cells are essentially circular and their size changes only slowly and over many hundreds of meters of produced foam sheet. Figure 8 of V. Paserin shows the longitudinal density profile of loop slit foam. It

is more consistent than rotary peeled foam. See also Japanese patent JP 9153365. However, the slitting of a large loop 24 requires sophisticated control machinery.

[0013] Nonetheless, most producers of metal plated foam use the rotary peeling technique because the foam can be reticulated by the flame explosion method. After foaming the polymeric buns are cut into foam blocks small enough to be reticulated in an autoclave. The reticulated foam is then cored and rotary peeled as shown in V. Paserin at Figure 5.

[0014] Many foams are reticulated either chemically or thermally to eliminate localized internal obstructions. Residual internal membranes are removed and the edges of the struts of the cells are rounded to create larger and smoother openings in the cell walls. The openings (windows) between adjacent cells are much smaller than the cell diameters and their size and uniformity is critical in many demanding applications, particularly batteries. Well reticulated foams with narrow struts and large openings between cells will improve pasting with active mass and produce higher capacity and higher power batteries than poorly reticulated foams with smaller windows.

[0015] It is preferred to reticulate the foam by the thermal (flame) method. This method produces the largest openings between cells and it doesn't compromise foam strength by reducing the cross section of the struts. Thermal reticulation involves placing the foam into an autoclave, evacuating the autoclave and filling it with an explosive oxygen/hydrogen mixture. After ignition of the mixture, the explosive flame front rapidly travels through the foam while simultaneously melting the residual membranes and the thin edges of the struts.

[0016] The flame front rounds off the edges of the struts and enlarges the pores. Openings between the struts are favorably increased.

[0017] Figure 5A shows typical unreticulated pore struts 36 and 38 separated by opening A. Figure 5B shows typical thermally reticulated pore struts 40 and 42 that are more rounded and are separated by larger opening B.

[0018] Flame fronted reticulated foams are more amenable for metalizing and plating with nickel or any other metal inside the foam structure. Accordingly, the plated foams have enhanced mechanical strengths and preferred geometric framework for battery applications.

[0019] More particularly, Japanese patent JP 9153365, referenced above, recognizes that undesirable periodic variations in the pore size of nickel plated foam can be reduced by the loop peeling method. Loop peeling is used for producing thin sheets of polyurethane foam for laminated fabrics and other non-battery applications.

[0020] Unfortunately, the conventional industry standard size polymeric foam bun, typically 60 meters long, is too large to be placed into an autoclave. It cannot be reticulated by the flame method before loop peeling. Accordingly, the loop slitting method suggested by Japanese patent JP 9152365 does not include thermal (flame) reticulation and it is not believed to be useful for advanced batteries requiring flame reticulated plated foam substrates.

[0021] Because of the inability to properly reticulate the typical 60 meter long foam blocks destined for loop peeling, almost all of the nickel foam produced for battery applications today is rotary peeled foam. However, as noted, rotary peeled foam suffers from disabilities: unavoidable cyclic variations in foam density, conductivity, strength and plating density across the thickness of the foam.

SUMMARY OF THE INVENTION

[0022] There is provided a process for producing metal foams with substantially uniform cell structure. Polymeric foam slabs of desired length are slit with a horizontal slitting knife along the longitudinal bun surface to a desired thickness in a horizontal slitting apparatus. The resulting sheets may be attached to one another end to end to increase their effective length and in any event are typically spooled. Alternatively the horizontal slitting can be done in a loop slitting apparatus, producing a spooled long sheet similar to the long sheet produced by the joining shorter sheets made by the horizontal slitting apparatus. In either case, the rolled or spooled sheets

are subject to thermal reticulation and then plated by chemical vapor deposition, by electrodeposition (preceded by a suitable treatment to make the foam sufficiently conductive) or by other metal deposition process. The resulting metal foam is substantially uniform having consistent and desirable characteristics.

BRIEF DESCRIPTION OF THE DRAWINGS

[0023] Figure 1 is a photomicrograph of conventional metal foam parallel to foam rise direction.

[0024] Figure 2 is a photomicrograph of conventional metal foam perpendicular to foam rise direction.

[0025] Figure 3 is a perspective schematic representation of a horizontal slitting apparatus.

[0026] Figure 4 is a schematic representation of a prior art loop slitting apparatus in plain view.

[0027] Figure 5A is a schematic representation of unreticulated foam struts.

[0028] Figure 5B is a schematic representation of reticulated foam struts.

[0029] Figure 6 is a graph depicting an embodiment of the present invention.

PREFERRED EMBODIMENT OF THE INVENTION

[0030] An object of the present invention is for the production of porous metal plated foam having a uniform cell structure. The metal foam has a consistent distribution of area density, controlled metal strut thickness, and uniform mechanical and electrical properties such as tensile strength, elongation and electrical conductivity.

[0031] Turning to Figure 3, polymeric, preferably polyurethane, foam buns (slabs) 10 of desired length, width and height are slit by a horizontal slitting apparatus 12 along the upper longitudinal bun surface 14.

[0032] The foam bun 10 is repeatedly reciprocated over the slitter bed 16 to cut and raise a planar foam sheet 20 of predetermined thickness from the horizontal longitudinal bun surface 14. Knife 18 slits the bun 10 to generate the foam sheet 20. The foam sheet 20 is transported to a storage section 22 of the apparatus 12. Side trimmer 46 maintains the correct foam slab 10 width. If desired, the foam sheet 20 may be shortened by a blade, heated surface, or similar device (not shown) known to those skilled in the art.

[0033] The horizontally slit foam sheet 20 is subsequently spooled. Individual foam sheets 20 may be joined at their ends by hot compression or by an adhesive to create longer foam sheets 20 prior to spooling. The horizontally slit foam spools are then subject to reticulation — to generate fully open cell foam structures and substrates.

[0034] For better strut structure, it is preferred to use thermal (flame) reticulation when treating the spools. See Figure 5B.

[0035] Alternatively, to overcome the potential size problems associated with a large horizontal slitting apparatus 12, the opposing ends of one or more foam sheets 20 may be affixed to one another to form a loop 24. The loop 24 may be then subjected to conventional loop slitting as shown in Figure 4. The resultant planar foam sheet made initially either by horizontal slitting (20) and joining or by loop peeling (46) may be then subjected to spooling, thermal reticulation, unwinding, metal plating and sizing to predetermined dimensions.

[0036] The present process utilizing horizontal slitting along the longitudinal bun (slab) surface 14 of the bun 10 results in favorable uniform cell structure in the longitudinal direction.

[0037] Indeed, analysis of the resultant horizontally slit foam reveals a similar uniform pore structure as that formed by loop slitting. Figure 6 shows typical

longitudinal density profiles of nickel foam made in accordance with the present horizontal slitting process.

[0038] Horizontal slitting is not limited to the upper longitudinal bun surface 14. A similar process whereas the horizontal slitting occurs along the lower surface of the foam bun 10 will result in equally desirable foam slabs 20. Similarly the loop 24 formed from the long bun (slab) can be made with the original top of the foamed bun facing outward or inward.

[0039] The reticulated foam sheets 20 are then nickel plated by chemical vapor deposition, electroplating, or electroless plating techniques to produce plated nickel foam with uniform cell structures. Deposition techniques include, but are not limited to metal carbonyl decomposition, sputtering, thermal evaporation, etc. Other metals such as copper, chromium, cobalt, platinum, palladium, rhodium, silver, gold, iron, etc. may be plated on to the foam sheets as well.

[0040] The plated foam sheets 20 can be used as-produced, or can be heat-treated, typically by sintering, to remove the internal polymer structure and to stabilize the metal plating. As noted previously, these plated foams may be utilized in a variety of applications. In the case of batteries, the plated foams are impregnated with battery active mass pastes to provide suitable electrodes.

[0041] While in accordance with the provisions of the statute, there is illustrated and described herein specific embodiments of the invention. Those skilled in the art will understand that changes may be made in the form of the invention covered by the claims and that certain features of the invention may sometimes be used to advantage without a corresponding use of the other features.

WHAT IS CLAIMED IS:

1. A method for producing metal plated foam, the method comprising:
 - a) providing polymeric foam having at least one horizontal longitudinal surface;
 - b) cutting the horizontal longitudinal surface to form a planar foam sheet of known thickness; and
 - c) plating the planar foam sheet with metal.
2. The method according to claim 1 including spooling the planar foam sheet.
3. The method according to claim 1 including reticulating the planar foam sheet.
4. The method according to claim 3 including thermal reticulating the planar foam sheet.
5. The method according to claim 2 including unwinding the spooled planar foam sheet.
6. The method according to claim 1 including looping ends of the planar foam sheet together to form a foam loop.
7. The method according to claim 6 wherein the foam loop is slit to form a foam sheet.
8. The method according to claim 7 wherein the foam sheet is spooled and reticulated.
9. The method according to claim 1 including attaching ends of two or more planar foam sheets together to form a longer planar foam slab.

10. The method according to claim 1 wherein the polymeric foam is made from polyurethane.
11. The method according to claim 1 wherein the planar foam sheet is plated by a method selected from at least one of the group consisting of chemical vapor deposition, electroplating, and electroless plating.
12. The method according to claim 10 wherein the chemical vapor deposition method is selected from at least one of the group consisting of metal carbonyl decomposition, sputtering, and thermal evaporation.
13. The method according to claim 1 wherein the metal is selected from at least one of the group consisting of nickel, copper, chromium, cobalt, platinum, palladium, rhodium, silver, gold and iron.
14. A method for producing metal plated foam, the method comprising:
 - a) providing a polymeric foam bun having at least one horizontal longitudinal surface,
 - b) cutting the horizontal longitudinal surface to form a planar foam sheet of known thickness, width and length,
 - c) spooling the planar foam sheet to form a foam coil,
 - d) reticulating the spooled planar foam,
 - e) unwinding the reticulated spooled planar foam,
 - f) plating the unwound reticulated planar foam, and, optionally
 - g) sintering the metal plated foam.
15. The method according to claim 14 wherein plating is a method selected from at least one of the group consisting of chemical vapor deposition, electroplating, and electroless plating.
16. The method according to claim 14 including thermal reticulating the spooled planar foam.

17. The method according to claim 14 wherein the unwound reticulated planar foam is plated with at least one of the group consisting of nickel, copper, chromium, cobalt, platinum, palladium, rhodium, silver, gold and iron.
18. A method for producing metal plated foam, the method comprising:
- a) providing a polymeric foam bun having at least one horizontal longitudinal surface,
 - b) cutting the horizontal longitudinal surface to form a first planar foam sheet of known thickness, width and length,
 - c) looping the opposing ends of the first planar foam sheet to form a continuous foam loop,
 - d) cutting the continuous foam loop to form a second planar foam sheet,
 - e) spooling the second planar foam sheet into a foam coil,
 - f) reticulating the foam coil,
 - g) unwinding the reticulated foam coil to form at least one foam sheet,
 - h) plating the foam sheet, and, optionally,
 - i) sintering the metal plated foam sheet.
19. The method according to claim 18 wherein plating is a method selected from at least one of the group consisting of chemical vapor deposition, electroplating, and electroless plating.
20. The method according to claim 18 including thermal reticulating the foam coil.
21. The method according to claim 18 wherein the foam sheet is plated with at least one of the group consisting of nickel, copper, cobalt, chromium, platinum, palladium, rhodium, silver, gold and iron.

22. A method for producing metal plated foam, the method comprising:
- a) providing a polymeric planar foam sheet of known thickness, width and length,
 - b) looping the opposing ends of the polymeric planar foam sheet to form a continuous foam loop,
 - c) cutting the continuous foam loop to form a second planar foam sheet,
 - d) spooling the second planar foam sheet into a foam coil,
 - e) flame reticulating the foam coil,
 - f) unwinding the reticulated foam coil to form at least one foam sheet,
 - g) plating the foam sheet, and, optionally
 - h) sintering the metal plated foam sheet.
23. The method according to claim 22 wherein plating is a method selected from at least one of the group consisting of chemical vapor deposition, electroplating, and electroless plating.
24. The method according to claim 22 wherein the foam sheet is plated with at least one of the group consisting of nickel, copper, cobalt, chromium, platinum, palladium, rhodium, silver, gold and iron.

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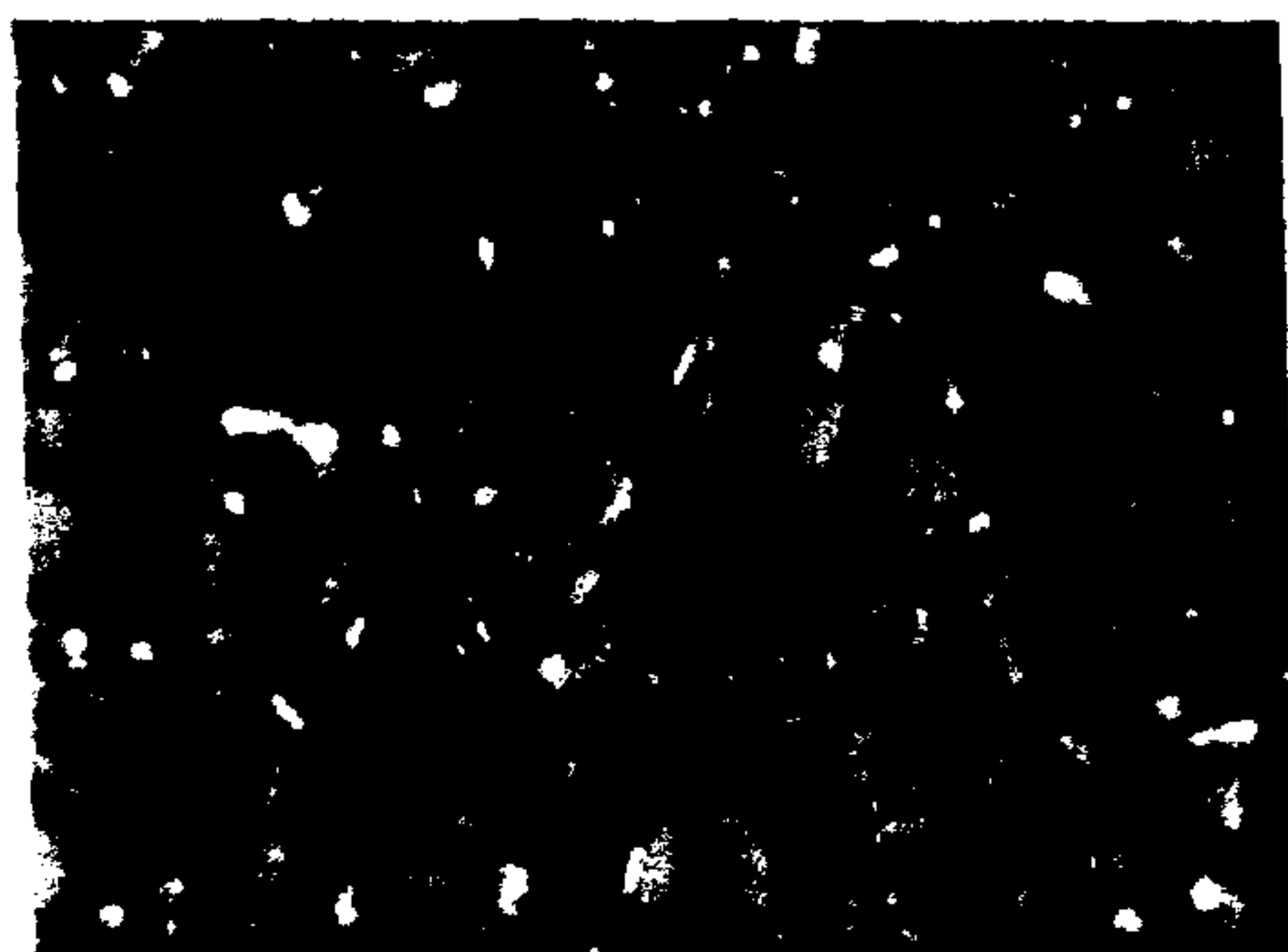


FIG. 1

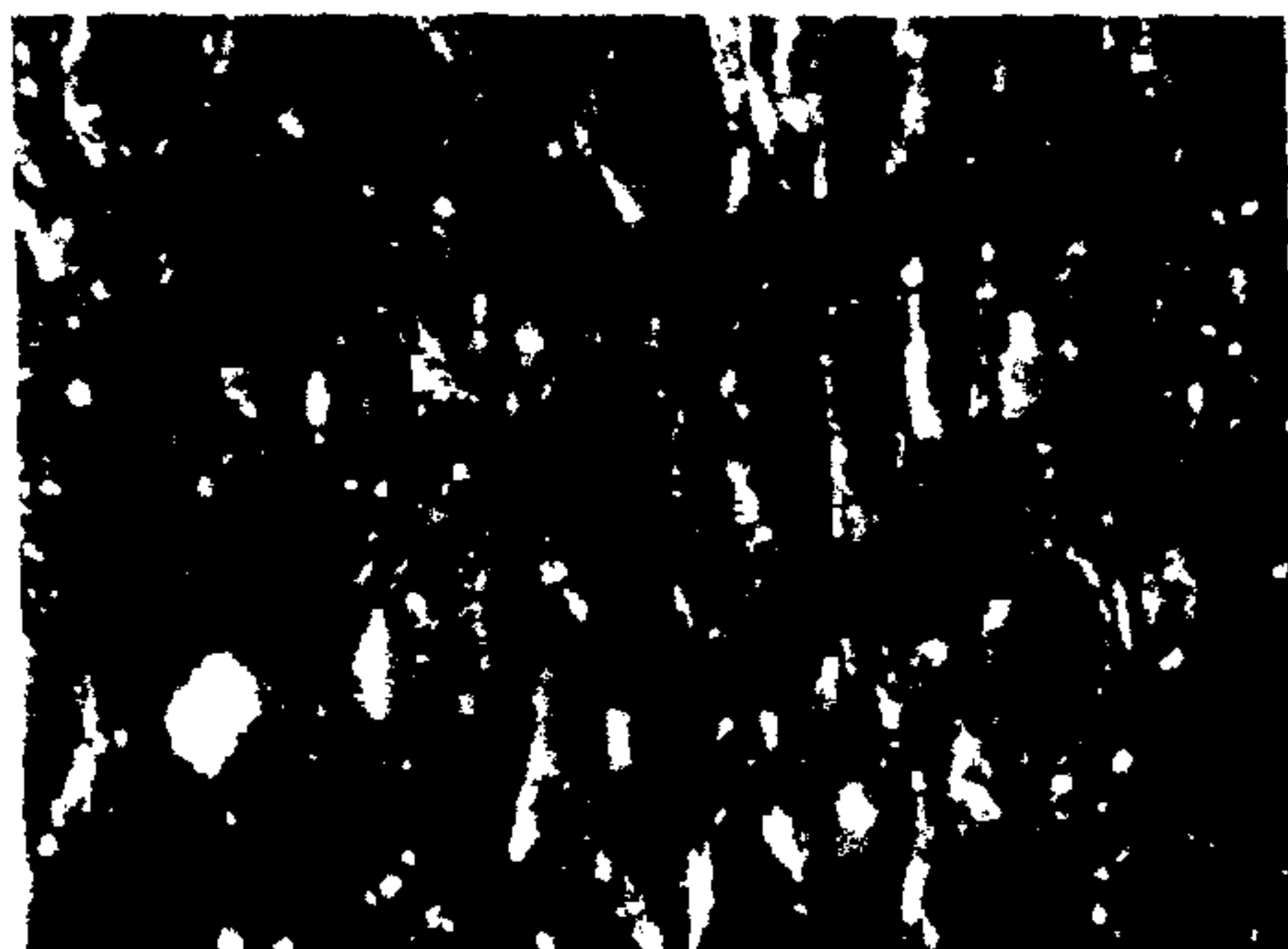
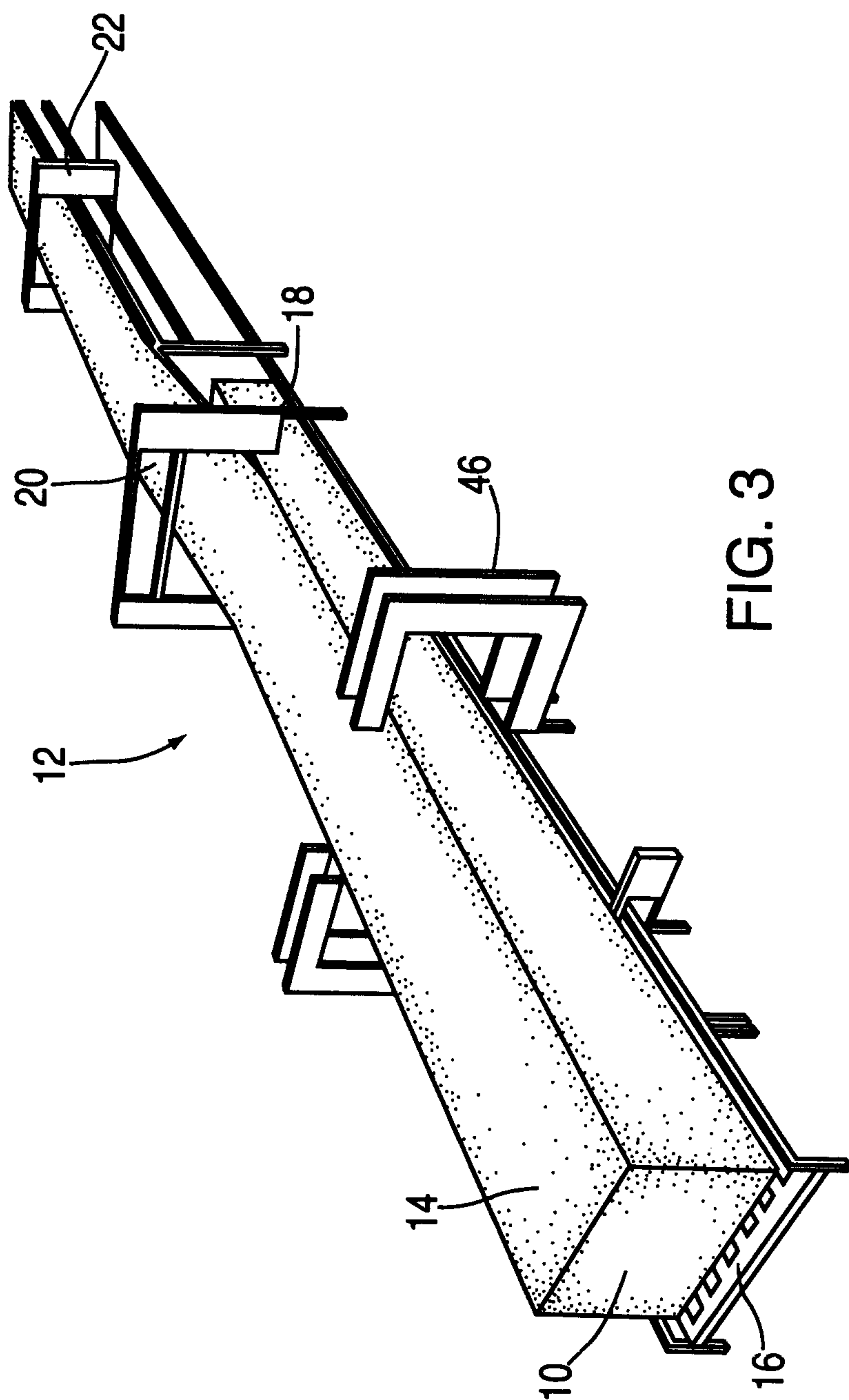


FIG. 2

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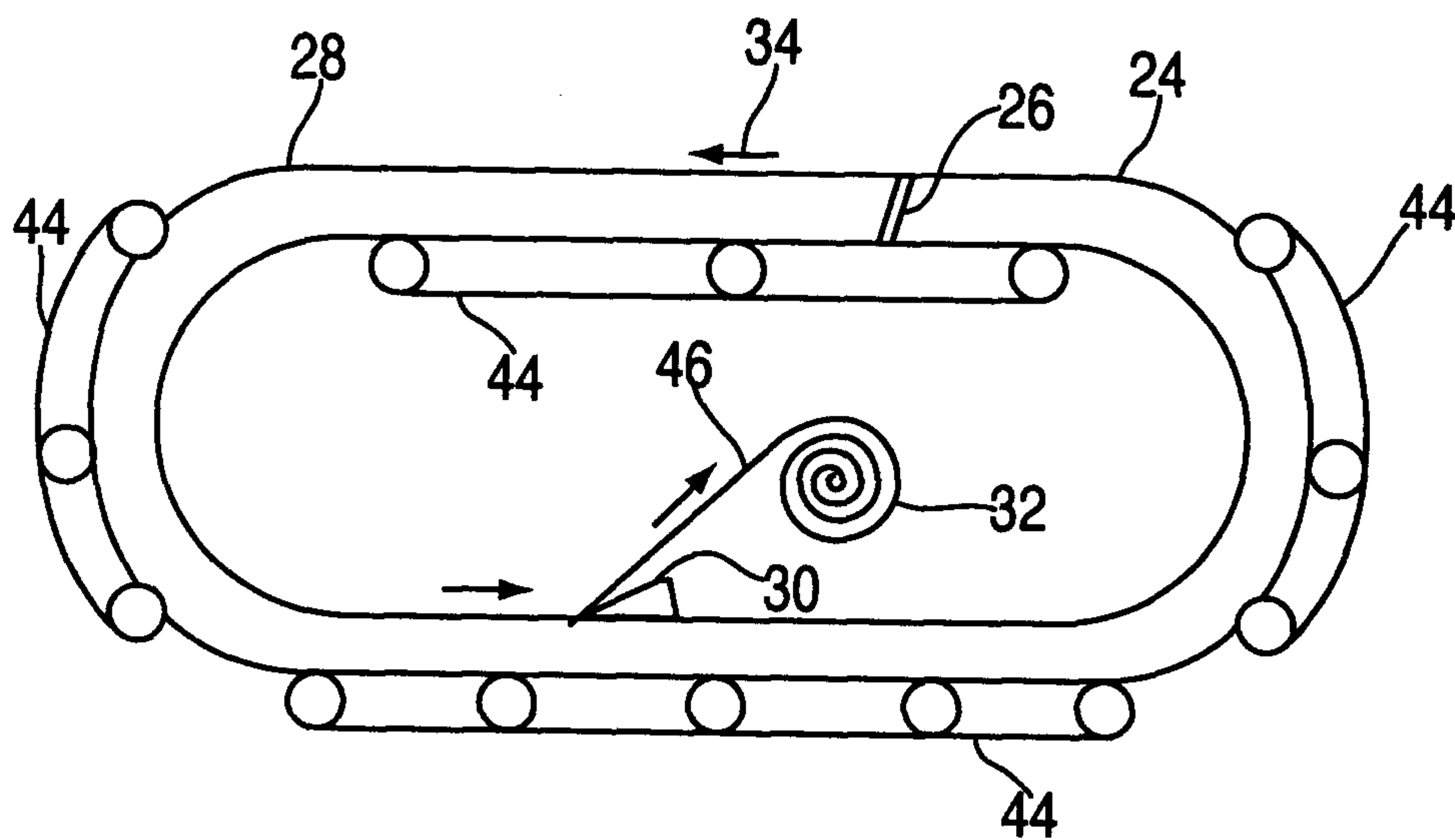


FIG. 4

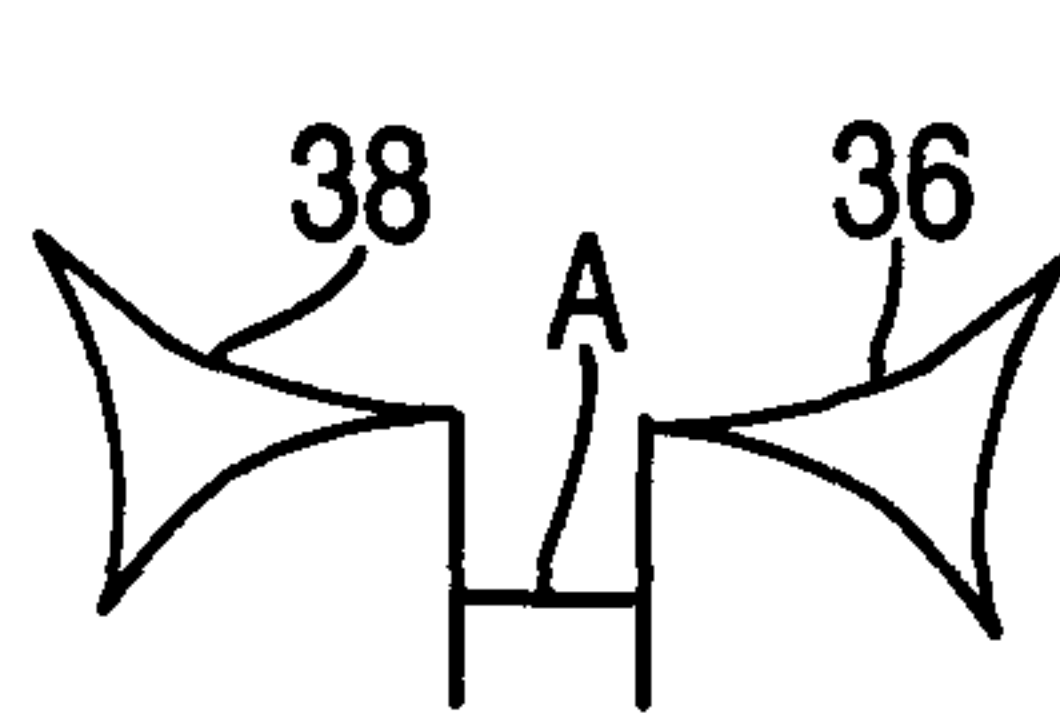


FIG. 5A

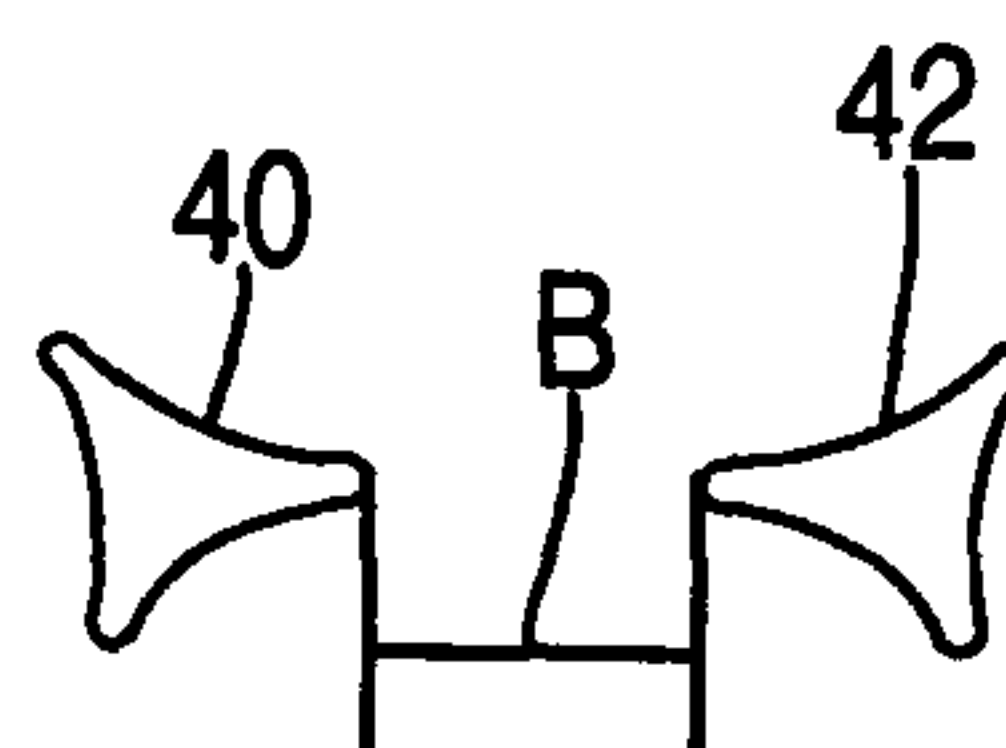


FIG. 5B

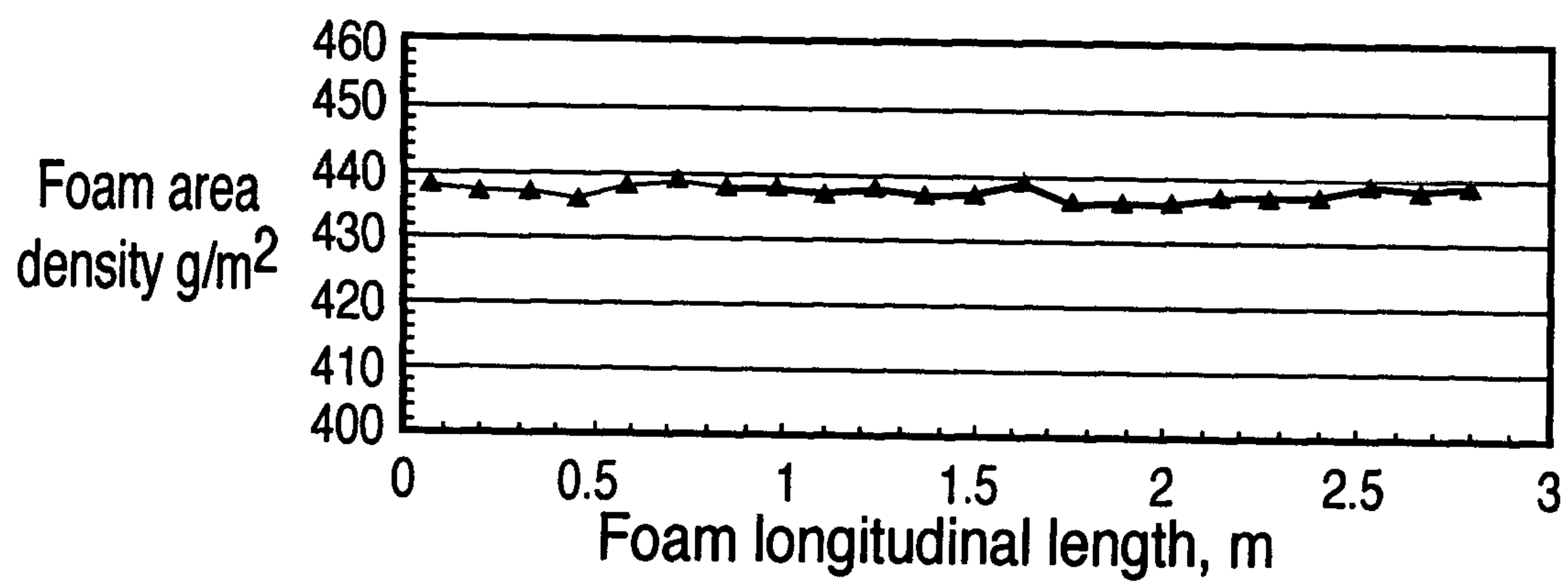


FIG. 6

