

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 412 137 B1

(12)

EUROPEAN PATENT SPECIFICATION(45) Date of publication of patent specification: **11.05.94** (51) Int. Cl.⁵: **H01F 41/26**, G08B 13/24(21) Application number: **90901612.3**(22) Date of filing: **09.01.90**(86) International application number:
PCT/GB90/00024(87) International publication number:
WO 90/07784 (12.07.90 90/16)(54) **MAGNETIC MATERIALS FOR SECURITY APPLICATIONS.**(30) Priority: **09.01.89 GB 8900398**(43) Date of publication of application:
13.02.91 Bulletin 91/07(45) Publication of the grant of the patent:
11.05.94 Bulletin 94/19(84) Designated Contracting States:
AT BE CH DE DK ES FR GB IT LI LU NL SE(56) References cited:
EP-A- 0 295 028 WO-A-80/2538
WO-A-80/9979 US-A- 4 484 184
US-A- 4 489 357 US-A- 4 661 216

Extended Abstracts/Electrochemical Society, Fall Meeting, 18-23 October 1987, Honolulu, Hawaii, volume 87-2, (Princeton, New Jersey, US), D.L. Grimmer et al.: "Electrodeposition of Fe-Ni alloys. I. Invar", page 800, abstract 569 see whole abstract

(73) Proprietor: **Esselte Meto International GmbH**
Postfach 550,
Westerwaldstrasse 3-13
D-64646 Heppenheim(DE)(72) Inventor: **DAVIES, Dafydd, Geraint**
19 Beche Road
Cambridge CB5 8HX(GB)(74) Representative: **Abrams, Michael John et al**
HASELTINE LAKE & CO.
Hazlitt House
28 Southampton Buildings
Chancery Lane
London WC2A 1AT (GB)

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

Description

This application relates to magnetic materials and their use in tags or markers in systems for security tagging, anti-pilferage, article location and article identification.

Anti-pilferage tags or markers are applied to articles of commerce in order to protect them from theft from the sale premises. Similar tags are applied to articles or persons for stock control or identification purposes, being detected when the articles or persons pass or attempt to pass preselected detection stations. The markers are also attached to fixed articles which may be concealed, encased or covered over by other structures or materials; in this case, the articles to which the markers are attached are located by the use of a portable marker detector.

In order to achieve the desired magnetic properties, and in order to minimise the overall size and manufacturing cost of the marker, it is advantageous to manufacture magnetic elements of the marker in the form of thin sheets, foils, or films. There are usually two components to such markers. One is an 'active' magnetic material which has soft magnetic properties, i.e. high permeability and low coercive force (under 100 Am^{-1}). It is known from EP-A-0 295 028 to use electrodeposited cobalt-nickel-based alloys as this 'active' magnetic material. The second component is a semi-hard or hard magnetic material, which is often referred to as a 'deactivation' material, and which has a medium permeability and a medium to hard coercive force (over 1000 Am^{-1}). The active material produces the detectable signal, and the semi-hard or hard component produces a switchable dc magnetic field which biases or suppresses the response of the active material under appropriate conditions. Both types of material are currently produced using comparatively expensive alloys and processes to achieve the special magnetic properties required. Examples of current alloys are Vacozet, Vitrovac and Crovac from Vacuumschmelze in Germany; and Arnokrome from Arnolds in the USA. We have identified materials and processes which may result in cheaper production of the magnetic components.

According to one aspect of the invention, there is provided a magnetically active tag or marker which comprises a substrate; an 'active' magnetic material which is a soft magnetic material having a high magnetic permeability and a low coercive force; and a deactivating material which is a hard or semi-hard magnetic material having a moderate or high coercive force and a moderate magnetic permeability, whereby the deactivating material, when subjected to a sufficiently high magnetising force, is able to clamp the magnetic properties of

the 'active' material so as to deactivate the 'active' material, characterised in that said deactivating material is electrodeposited nickel.

Thus the deactivating material is produced by a technique such as electrodeposition, electroforming or electroless chemical deposition. These processes are advantageous for producing thin foils of material with well-defined properties at low cost. They involve deposition of a metal or metallic alloy film from a liquid containing the metallic ions in solution, such as a nickel sulphamate solution; deposition being driven either by electric current or by chemical catalysis. With electroforming, the film is formed onto a mould, die, template, tool or mandrel, and may then be removed as a free-standing foil. The addition of small quantities of organic molecules to the working solution is used to control the stress in the electroformed film. In electrodeposition, the foil is usually deposited onto a metallic or conducting substrate or carrier from which it is not subsequently removed, while in electroless deposition the substrate need not be conducting. A further advantage of using such deposition processes is that the foil may also be formed as discontinuous elements (e.g. dots or islands) or as a sheet with holes, without material cutting or waste, since the area of deposition can be controlled by a simple masking technique. We have discovered that this masking can be achieved either by screen printing of a non-conducting ink or paint onto the metallic substrate, or by the use of an ink roller with a suitable pattern. Alternatively, a reusable mask may be pressed against the substrate during deposition, or photolithographic masking can be used. Another method is to fix non-conducting areas of material such as polymer or resin onto the former or mandrel in the electroforming process. A discontinuous film, or one containing a plurality of holes, is advantageous because the non-uniform shape enhances the magnetic effect of the semi-hard or deactivating component in the marking system. The ability to form a discontinuous or hole-permeated film or foil in one single process, without the need to subsequently cut or remove material, leads to considerable cost savings in the manufacturing process.

These deposition processes are attractive for forming thin films below about 100 microns, and in particular for films below about 40 microns, since the process costs are lower than for rolling or casting processes, and they are particularly cost-effective for films in the thickness range 5-25 microns. A further advantage of these processes is that the magnetic properties are usually isotropic or uniform in the film plane, so that the materials do not have to be specially oriented during manufacture of the markers. The magnetic performance of the components is thus also isotropic, leading to a

better performance of the marker. In contrast, rolled or cast materials tend to have a strong anisotropy - for example, the coercive force may vary by a factor of two for different directions in the film plane, requiring that the material be aligned along specific directions during manufacture of the marker.

The crystal grain structure produced by these deposition processes is often columnar in nature, i.e. long thin crystals with the long axis perpendicular to the foil plane. This gives the advantageous isotropic properties in the plane, as referred to above. For some applications, however, it is desirable to have anisotropic properties. We have discovered that this can be achieved by changing the additives to the electrolyte and changing the deposition conditions in order to achieve planar, rather than columnar, crystal growth. The conditions required to achieve planar grain growth (often referred to as a 'bright' deposition) would be known to a person skilled in these deposition techniques.

With columnar grains, the microscopic magnetic fields associated with the end faces of the columns may lead to unwanted magnetic effects, such as stray magnetic fields, when the material is nominally not magnetised. We have discovered that these effects may be diminished if a thin layer of planar-grain material is deposited on top of the isotropic, columnar material, to form a magnetic short-circuit for the unwanted microscopic magnetic fields.

A suitable material for the active or soft magnetic element is electrodeposited nickel-iron alloy with 60-100% Ni. Low magnetostriction is achieved with Ni at 75-80%. Some subsequent heat treatment may be necessary if it is required to reduce the coercive force of the foil to a value below about 20 Am^{-1} .

Formation of the semi-hard magnetic component by these deposition processes is particularly attractive since in general this is the largest component by volume in the markers. The requirement of this component is a well defined coercive force in the range $1000\text{-}15,000 \text{ Am}^{-1}$ (depending on the design of the marker). We have fabricated electrodeposited samples of Ni which display coercive forces in the desired range and with sufficiently high squareness of the magnetic hysteresis loop to give a magnetic remanence ratio ($M_{\text{remanent}}/M_{\text{saturation}}$) of over 0.5. In particular, electroformed Ni produced on a drum mandrel can be rapidly and cheaply manufactured without undesirable residual stresses at thicknesses between 2 microns and 100 microns, and with coercive force easily controllable in the range $5000\text{-}6000 \text{ Am}^{-1}$ without the need for heat treatment. Ni is also highly resistant to corrosion. We have found that electroformed Ni foil is also easily cut compared to currently used special

alloys, so that pieces or holes may be easily stamped from the foils mechanically.

According to another aspect of the invention, the electrodeposited material is rendered magnetically discontinuous or non-homogeneous by a selective cold-forming or deformation process such as stamping, rolling, processing or embossing. The deformation process changes the magnetic properties, in particular the permeability of the material in the plane of the foil. The purpose of this is that, as described previously, a pattern of changing magnetic properties enhances the structure and efficacy of the magnetic field of the material. The advantage of a deformation process is that it leaves a mechanically continuous foil, with little or no topographic variations, which is simpler and cheaper to handle in subsequent stages such as lamination, and which gives a more uniform surface finish in the final product. In addition, the deformation is simple to implement in comparison with foil masking, or cutting or removing pieces from the foil.

The invention will be illustrated by the following Examples, which are of non-limiting of the scope of the invention. Reference is made, in the following, to the accompanying drawings, in which:

Figure 1a illustrates a press tool used in one embodiment of the invention;

Figure 1b is an enlarged view of a part of the tool shown in Figure 1a;

Figure 2 illustrates the pattern resulting from the use of the tool of Figure 1 in the cold working of a metal foil;

Figure 3 shows a schematic view of a heated press used for selectively annealing predetermined areas of a metal foil; and

Figure 4 illustrates schematically the result of using the press of Figure 3.

Reference will be made to the drawings in the Examples which now follow.

EXAMPLE 1

This Example describes the manufacture of a deactivation material from electroformed nickel foil. A continuous roll of electroformed plain nickel foil having a thickness of 20 microns was purchased from INCO Alloys Ltd in the UK. The foil was then annealed for 24 hours at a temperature of 280°C , followed by a 24 hour cooling period to room temperature. This reduced the coercive force from 6000 A/m to 2000 A/m , which was the required value for this particular application. The finished material was in the form of a roll of width 50 cm. This roll was then slit to rolls of width 8 mm, and then used as the deactivator supply material for lamination with other components in an anti-pilferage label manufacturing process.

EXAMPLE 2

This Example describes the manufacture of a hole-permeated foil of deactivation material using an electroforming process. The same electrolytic process and conditions as in Example 1 were used, but the forming mandrel consisted of a titanium drum of width 50 cm, covered with a continuous array (based on a hexagonal lattice) of circular embedded epoxy resin islands of diameter 1.5 mm and centre to centre spacing of 3 mm. The resin was embedded in depressions of the appropriate size machined into the titanium drum to a depth of 1 mm, and the resin was then machined back to be flush with the drum surface. Electroforming the foil on this mandrel produced a 20 micron thick nickel foil which could be produced continuously and which had 1.5mm circular holes the pattern of which corresponded to the pattern of the epoxy resin islands. The foil was then annealed in the manner described in Example 1. Finally, the foil was laminated to a continuous foil-like 'active' magnetic material which had been deposited on a 25 micron polymer film. The advantage of this process is that the active material and the deactivation material may be handled as continuous webs for the lamination process, and thereby facilitated the production of a continuous web which could then be cut into deactivatable anti-pilferage markers of any required size.

EXAMPLE 3

This Example describes the manufacture of a structurally continuous deactivation foil which is rendered magnetically discontinuous by a selective cold working process. The same nickel foil as that employed in Example 1 was used in this Example. The foil, of width 50cm, was fed into a flatbed parallel press as illustrated in Figures 1a and 1b. The press tool consisted of a lower face 1 formed of a mild steel which was machined to be smooth and flat; and an upper face 2 which was formed with a mesh of lines 3 arranged in a square grid array, the side of the square being 2.5cm. The upper face 2 was formed of a tool grade steel, and the square grid pattern 3 was formed by machining the array of grid lines to a depth of 0.5mm. (see Figure 1b). The press tool 1, 2 covered an area of 50cm x 2cm, so that by feeding the nickel foil through the press in a direction normal to the long side of the tool, and advancing the foil in steps of 2cm after each pressing operation, the entire continuous roll of foil could be treated easily. The result of using this press tool was to form a roll of foil carrying a deformation pattern 4 (see Figure 2) throughout its width and length, the pattern conforming to that of the grid array of Fig. 1b. In order

to achieve the desired degree of plastic deformation in the lines 4 of the treated foil, without requiring cutting or significant bending of the foil, it was found that a press force in the range of 20 to 100 tons weight per stroke of the press tool was required. Advantageously, the force was about 50 tons force. Below the lower limit of 20 tons, the resultant plastic deformation was insufficient to cause an adequate disruption of any magnetic circuit in the plane of the foil. The resultant continuous foil roll of deactivating material was then laminated to an active magnetic material (in the form of a foil) in a continuous process as described above in Example 2.

EXAMPLE 4

A nickel foil was pressed with a deformation pattern, as described above in Example 3, but in this Example a rotary embossing-type process was used in place of the flatbed press of Figure 1. The cylindrical rotary roller tools were of similar materials and patterns to those described in Example 2, but lower forces, in the range 2-10 tons force, were necessary because the instantaneous contact area was smaller in this example. This produced a similar material to that described in Example 3 but the foil could be processed more quickly and there was less tool wear in the rotary process.

Claims

1. A magnetically active tag or marker which comprises a substrate; an 'active' magnetic material which is a soft magnetic material having a high magnetic permeability and a low coercive force; and a deactivating material which is a hard or semi-hard magnetic material having a moderate or high coercive force and a moderate magnetic permeability, whereby the deactivating material, when subjected to a sufficiently high magnetising force, is able to clamp the magnetic properties of the 'active' material so as to deactivate the 'active' material, characterised in that said deactivating material is electrodeposited nickel.
2. A tag or marker as claimed in claim 1, characterised in that said deactivating material is electroformed or electroless chemically deposited nickel.
3. A tag or marker as claimed in any preceding claim, characterised in that said deactivating material comprises an electrodeposited discontinuous foil or layer, or a plurality of electrodeposited islands carried by a substrate.

4. A tag or marker as claimed in any preceding claim, characterised in that said deactivating material has a columnar crystal grain structure and substantially isotropic magnetic properties in the plane of said material. 5
5. A tag or marker as claimed in claim 4, characterised in that said columnar crystal grain structure is coated with a thin layer of a planar crystal grain structure. 10
6. A tag or marker as claimed in any preceding claim, characterised in that said deactivating material has regions with anisotropic magnetic properties in the plane of said material, which regions are introduced by subjecting said material to a deformation process. 15
7. A tag or marker as claimed in any preceding claim, characterised in that said deactivating material has regions with anisotropic magnetic properties in the plane of said material, which regions are introduced by subjecting said material to a stamping, rolling, pressing or embossing process. 20 25
8. A tag or marker as claimed in any preceding claim, characterised in that said deactivating material has regions with anisotropic magnetic properties in the plane of said material, which regions are introduced by subjecting said material to mechanical deformation or cold working. 30

Patentansprüche 35

1. Magnetisch aktives Schild oder magnetisch aktive Marke, enthaltend ein Substrat;
ein "aktives" magnetisches Material, das weichmagnetisch ist und eine hohe magnetische Permeabilität und eine niedrige Koerzitivkraft hat; und
ein Deaktivierungsmaterial, das hartmagnetisch oder semihartmagnetisch ist und eine mittlere magnetische Permeabilität sowie eine mittlere oder hohe Koerzitivkraft hat;
wodurch das Deaktivierungsmaterial, wenn es einer ausreichend hohen Magnetisierungskraft ausgesetzt ist, die magnetischen Eigenschaften des "aktiven" Materials so festzuhalten vermag, daß das "aktive" Material deaktiviert wird; dadurch gekennzeichnet,
daß das Deaktivierungsmaterial galvanisch niedergeschlagenes Nickel ist. 40 45
2. Schild oder Marke nach Anspruch 1, dadurch gekennzeichnet, daß das Nickel für das Deaktivierungsmaterial durch Galvanoformen oder 50 55

stromloses chemisches Niederschlagen erhalten wurde.

3. Schild oder Marke nach irgendeinem vorhergehenden Anspruch, dadurch gekennzeichnet, daß das Deaktivierungsmaterial eine galvanisch niedergeschlagene, diskontinuierliche Folie oder Schicht ist oder eine Anzahl galvanisch niedergeschlagener Inseln, die von einem Substrat getragen werden.
4. Schild oder Marke nach irgendeinem vorhergehenden Anspruch, dadurch gekennzeichnet, daß das Deaktivierungsmaterial eine säulenartige Kristallkornstruktur hat und in der Fläche im wesentlichen isotrope, magnetische Eigenschaften.
5. Schild oder Marke nach Anspruch 4, dadurch gekennzeichnet, daß die säulenartige Kristallkornstruktur von einer dünnen Schicht mit planarer Kristallkornstruktur bedeckt ist.
6. Schild oder Marke nach irgendeinem vorhergehenden Anspruch, dadurch gekennzeichnet, daß das Deaktivierungsmaterial in der Materialfläche Bereiche mit anisotropen, magnetischen Eigenschaften hat und die Bereiche eingebracht wurden, indem das Material einem Verformungsprozeß unterzogen wurde.
7. Schild oder Marke nach irgendeinem vorhergehenden Anspruch, dadurch gekennzeichnet, daß das Deaktivierungsmaterial in der Materialfläche Bereiche mit anisotropen, magnetischen Eigenschaften hat und die Bereiche eingebracht wurden, indem das Material einem Stanz-, Walz-, Preß- oder Prägeverfahren unterzogen wurde.
8. Schild oder Marke nach irgendeinem vorhergehenden Anspruch, dadurch gekennzeichnet, daß das Deaktivierungsmaterial in der Materialfläche Bereiche mit anisotropen, magnetischen Eigenschaften hat und die Bereiche eingebracht wurden, indem das Material einer mechanischen Verformung oder Kaltbearbeitung unterzogen wurde.

Revendications 50

1. Etiquette ou marqueur magnétiquement actif qui comporte un substrat; un matériau magnétique 'actif' qui est un matériau magnétique doux ayant une perméabilité magnétique élevée et un champ coercitif faible; et un matériau de désactivation qui est un matériau magnétique dur ou semi-dur ayant un champ coercitif 55

modéré ou élevé et une perméabilité magnétique modérée, de telle sorte que le matériau de désactivation, lorsqu'il est soumis à une force de magnétisation suffisamment élevée, peut fixer les propriétés magnétiques du matériau 'actif' de manière à désactiver le matériau 'actif', caractérisé en ce que ledit matériau de désactivation est du nickel déposé par électrolyse.

5

10

2. Etiquette ou marqueur selon la revendication 1, caractérisé en ce que ledit matériau de désactivation est du nickel électroformé ou déposé chimiquement sans l'aide d'un courant.

15

3. Etiquette ou marqueur selon l'une quelconque des revendications précédentes, caractérisé en ce que ledit matériau de désactivation comporte une feuille ou une couche discontinue déposée par électrolyse, ou une pluralité d'îlots déposés par électrolyse portés par un substrat.

20

4. Etiquette ou marqueur selon l'une quelconque des revendications précédentes, caractérisé en ce que ledit matériau de désactivation a une structure à grains de cristaux colonnaires et des propriétés magnétiques sensiblement isotropes dans le plan dudit matériau.

25

5. Etiquette ou marqueur selon la revendication 4, caractérisé en ce que ladite structure granulaire à cristaux colonnaires est revêtue d'une couche mince d'une structure à grains de cristaux plans.

30

35

6. Etiquette ou marqueur selon l'une quelconque des revendications précédentes, caractérisé en ce que ledit matériau de désactivation comporte des régions avec des propriétés magnétiques anisotropes dans le plan dudit matériau, ces régions étant introduites en soumettant ledit matériau à un processus de déformation.

40

7. Etiquette ou marqueur selon l'une quelconque des revendications précédentes, caractérisé en ce que le matériau de désactivation comporte des régions avec des propriétés magnétiques anisotropes dans le plan dudit matériau, ces régions étant introduites en soumettant ledit matériau à un processus d'estampage, de laminage, de compression ou d'emboutissage.

45

50

8. Etiquette ou marqueur selon l'une quelconque des revendications précédentes, caractérisé en ce que ledit matériau de désactivation comporte des régions avec des propriétés magnétiques anisotropes dans le plan dudit matériau, ces régions étant introduites en soumettant

55

ledit matériau à une déformation mécanique ou à un façonnage à froid.

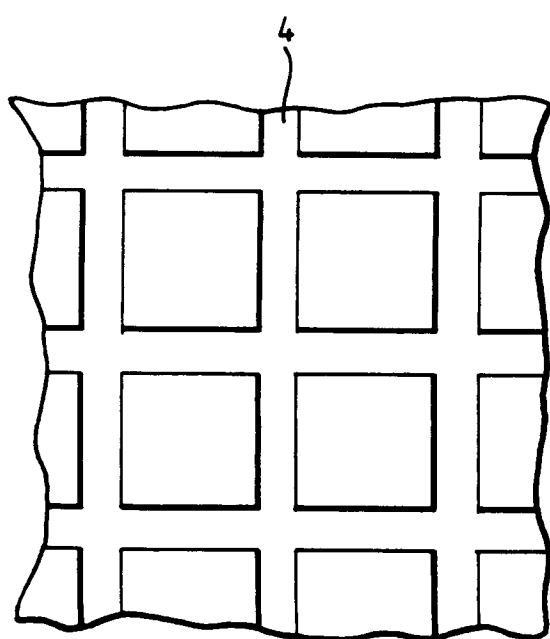
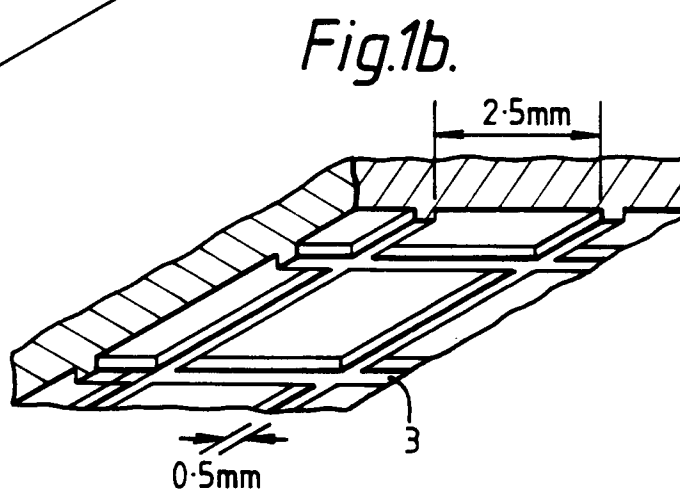
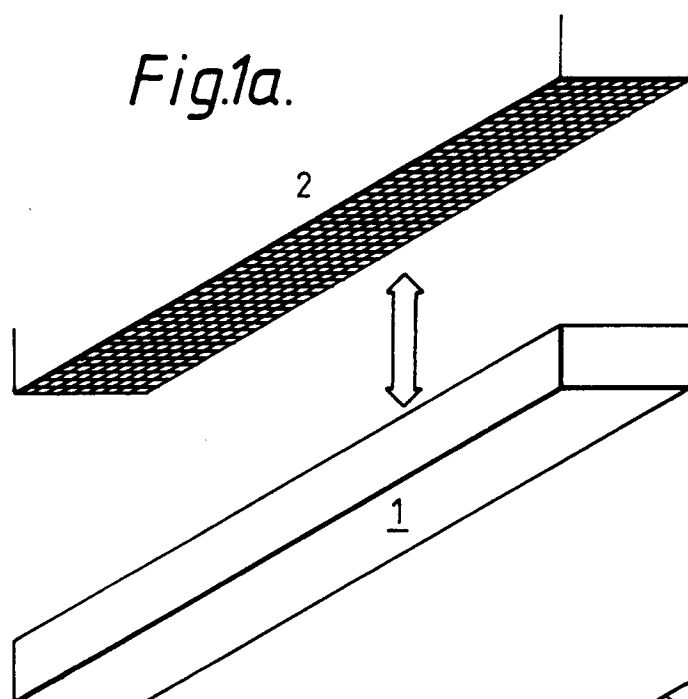


Fig.3.

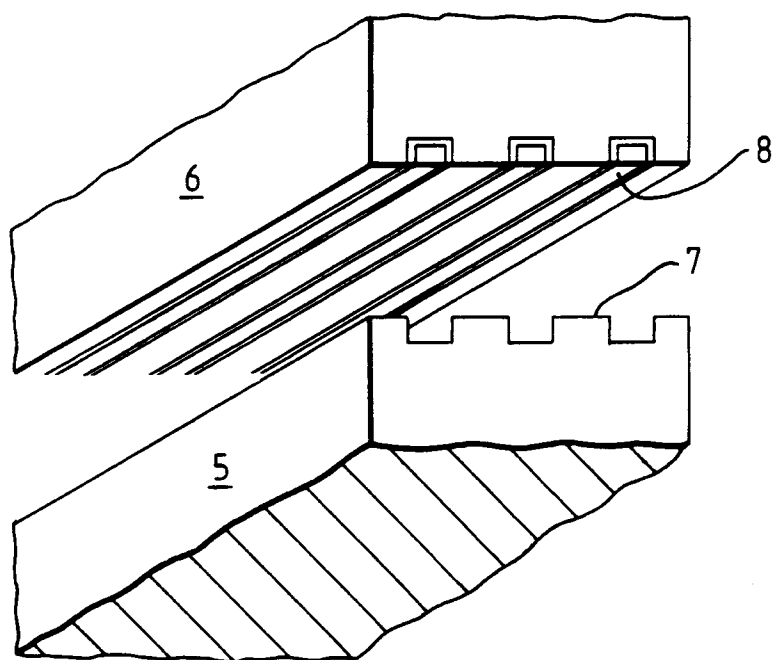


Fig.4.

