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(54) **Aluminium alloy cathode plates**

Kathodeplatten aus Aluminium-Legierung
Plaques cathodiques en alliage d'aluminium

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(56) References cited:
FR-A- 2 099 031 **US-A- 5 498 322**

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Description

[0001] The present invention relates to plates for use as the cathode in an electrolytic cell in which zinc is deposited onto the plates from an acidic solution of a zinc salt, wherein the plates are arranged to be supported vertically and partially immersed in the solution.

[0002] Frequently, such plates are composed of an aluminium alloy of the type AA1200, AA1050 or AA1070 because of the good strength and electrical conductivity of such alloys and their reasonable resistance to the corrosive effects of the acidic zinc salt solutions used in such electrolytic cells, but as explained in US-A-5498322, such conventional alloys without further treatment still suffer from unacceptably high levels of corrosive attack from the acidic solutions used. There is therefore a need to provide cathode plates with improved corrosion resistance, whilst at the same time not reducing significantly their mechanical strength or electrical conductivity.

[0003] The solution to this problem proposed in US-A-5498322 is to utilise a specially-formulated alloy of aluminium for the cathode plates, but inevitably the use of such a non-standard aluminium alloy will increase the cost of the cathode plates.

[0004] In the discussion of the problem of corrosion in US-A-5498322, there is reference to very pure aluminium, for instance 99.99% by weight pure aluminium, and whilst it is recognised that such a material has good corrosion resistance and electrical conductivity it is dismissed as unsatisfactory for cathode plates on the ground that it is very weak and soft and will have trouble standing up to the harsh mechanical handling to which cathode plates are subjected. Also very pure aluminium plates would be expensive.

[0005] In a 1933 patent, namely US-A-1925339, the problem of corrosive attack on cathodes is well explained, and the proposed solution is to provide each cathode plate with a substantially non-insulating coating of an acid resistant material extending from a point above the solution line to a point a short distance below the solution line. For this coating, it is proposed to employ an organic substance such as a rubber product. Such coating tends, however, to exfoliate in service. In a slightly later development described in US-A-2058259, a layer of zinc is proposed to be applied to the edge of the cathode plates.

[0006] It is noteworthy that in none of these prior art documents is it suggested the use of a coating on a cathode plate a metal other than zinc, since it is well known that where two different metals are immersed in electrical contact with each other in an aqueous solution a galvanic couple is set up which will cause substantially increased corrosion at the junction of the different metals. The use of zinc in US-A-2058259 does not give rise to any such junction effect because the material being deposited is zinc itself.

[0007] In the course of researching the electrochem-

ical deposition of zinc onto aluminium cathode plates, the Applicants examined the behaviour of an aluminium plate cathode partially coated with high purity aluminium. As anticipated, when such a coated cathode is immersed in the acidic electrolyte in laboratory tests preferential corrosion commenced immediately at the junction of the two materials, implying galvanic corrosion at the interface. Such corrosion was expected to hasten the failure of such a cathode plate in an electrolytic cell or at least make the stripping off of the deposited zinc difficult since the underlying surface would be pitted and would no longer be smooth. Surprisingly, however, when used as a full size cathode in a commercial production cell, the coated plate behaved well and did not in fact exhibit the enhanced and localised corrosion that had been predicted by the laboratory tests. Whilst not wishing to be bound by theory, it would appear that the initial deposition of zinc onto the coated cathode masks the junction of the different aluminium alloys, and thereafter normal deposition of zinc takes place uniformly, with the zinc layer itself protecting the underlying cathode from corrosive attack from the acidic solution in the cell.

[0008] In accordance with the present invention there is provided a plate for use as the cathode in an electrolytic cell in which zinc is deposited onto the plate from an acidic solution of a zinc salt, wherein the plate is arranged to be supported vertically and partially immersed in the solution, and wherein the plate is composed of an aluminium alloy of less than 99.85% by weight purity, characterised in that in the region of the plate where in use the level of the solution in the cell on the plate will lie the plate carries on each of its two faces a surface layer of aluminium having a higher purity of at least 99.80% by weight, and wherein the compositional difference between the plate and the surface layer is at least 0.2% by weight of aluminium.

[0009] Preferably the surface layer in the region of the solution level is composed of aluminium having a purity of about 99.99% by weight, the remainder being conventional impurities such as silicon and iron. Such material is commercially available.

[0010] The aluminium that forms the body of the plate preferably has a purity of from 99.0% to 99.7%, particularly about 99.50%, by weight, and suitable alloys are of the AA1XXX series of alloys, e.g. type AA1200-1080, preferably AA1200, AA1050, and AA1070, as well as the Applicants' unregistered alloys 1370 and 1235.

[0011] Generally in electrolytic cells the higher the purity of the aluminium alloy used the higher will be its resistance to corrosion. Because of the range of possible alloy specifications that can be used for the body of the plate and for the cladding layer, in theory there could be an overlap of compositions. In practice, the composition of the cladding alloy should be at least 0.2% by weight of aluminium higher than the composition of the alloy of the body of the plate.

[0012] As is known in the art, the corrosion of alumin-

ium cathode plates takes place not only exactly along the solution level on the plate, but to a certain extent above and below that level. Furthermore, there can be small variations in the solution level in electrolytic cells, and also the effect of bubbling and splashing broadens the region on cathode plates where corrosive attack preferentially takes place. Accordingly, it is preferred that the surface layer of higher purity aluminium extends on the plate to just below the lowest solution level likely to be encountered in the cell when the plate is in use, and preferably the layer extends substantially above the highest solution level likely to be encountered in the cell when the plate is in use. Although it is not necessary from a corrosion point of view, it is preferable for ease of manufacture for the high purity surface layer to extend to the top of the plate.

[0013] Because of the periodic mechanical or manual stripping from the faces of the cathode plates of the deposited zinc, the plates must be manufactured with close dimensional tolerances and high flatness standards for the two faces of the plates. Cladding of the higher purity aluminium layer onto the body of the plate can be done by the application of the cladding plate to the major faces of the rolling ingot. Accurate positioning and alignment of the cladding plates is difficult with this practice. Accurate positioning of the higher purity cladding is very important as incorrect positioning/alignment could have an adverse effect on the corrosion and zinc stripping performance of the plate. It is therefore preferred that the cathode plates of the present invention be prepared from a block of the lower purity aluminium alloy in which a groove or similar recess is formed across both faces, and into which the higher purity alloy is either inserted in the manner of a fillet or cast from the molten alloy. The composite block can then be reduced in thickness by rolling, preferably by hot rolling in excess of 400°C, optionally with cross-rolling, to achieve good bonding between the different alloys of the block and the desired hot rolled dimensions for the plate. These desired hot-rolled dimensions, particularly thickness, will depend upon the final dimensions and mechanical properties required of the finished cathode plate. The thickness will generally be either the final desired thickness or a thickness up to 80% greater than the required final thickness. Where additional reduction in thickness is required, this is generally performed using cold rolling, either with unidirectional rolling or with cross-rolling. Conventional heat treatments can be introduced into the production process in order to optimise the mechanical properties of the final cathode plate.

[0014] After the rolling stages, the plate can then be finished by levelling using a roller leveller and/or stretching optionally with shearing to the final size to ensure that when the plate is in use the interface between the higher and lower purity alloys will lie in the customers' electrolytic cells at the correct height relative to the solution level.

[0015] When the higher purity alloy is clad onto the

lower purity alloy by means of a groove in the alloy block, the top edge of the finished plate will usually be trimmed off so that the surface layer of higher purity alloy extends right to the top of the plate.

[0016] The thickness of the surface layer of higher purity aluminium alloy on the plate will depend upon the particular corrosion requirements of the plates when in use, but can be up to 30% of the total thickness of the plate for each of the surface layers of the two faces of the plate.

[0017] As an alternative to machining a pair of grooves into an already cast block of the lower purity alloy, the block can be DC cast with grooves or similar recesses therein. By introducing the higher purity alloy into grooves which are either machined or cast into the block, the location of the interface between the two alloys can be carefully controlled. Cladding of the block with the higher purity alloy either by the insertion of a fillet or by casting can be arranged to be flush with, or proud of, the block's surface, depending upon the cladding geometry and corrosion characteristics required of the finished plate.

[0018] Alternatively, it is possible to surface mount a cladding plate of the higher purity alloy onto a block of the lower purity alloy without using grooves or similar recesses, provided that the rolling operation can be carefully controlled so that correct alignment and positioning of the surface layer is achieved in the finished plate.

[0019] When using a surface mounted cladding plate on a cast billet, the cladding plate can be applied transverse to or in alignment with the casting direction. On the other hand where cladding is to be effected by the insertion of a fillet into a groove or similar recess which is cast into the billet, then generally the fillet will be applied in alignment with the casting direction.

[0020] Generally, edge beads or strips are applied to the cathode plate long edges in order to prevent "wrap around" of deposited zinc at the edges of the plate, which would result in stripping difficulties.

[0021] The present invention will now be described in more detail by way of example with reference to the accompanying drawings, in which:-

Fig. 1 is a perspective view of a block of an aluminium alloy ready for rolling to form a cathode plate, and

Fig. 2 is a perspective view of the cathode plate formed from the block of Fig. 1.

[0022] In Fig. 1 a DC cast block of an AA 1200 alloy is shown having faces 2, 3 onto which there are to be clad layers of 99.99% by weight purity aluminium. The casting direction is longitudinal.

[0023] The higher purity alloy is in the form of two parallel sided plates 4,5 which are arranged transversely on the block 1 with their longitudinal edges 6 lying parallel to the bottom edge 7 of the block 1.

[0024] Cladding plate 4 rests on the surface of block face 2, whilst cladding plate 5 lies in a groove 8 which is machined into face 3. The cladding plate 5 is arranged so that its exposed surface is flush with face 3. Cladding plate 5 is of the same thickness and is arranged parallel to and in the same orientation on face 3 as cladding plate 4 is on face 2.

[0025] Block 1 with cladding plates 4 and 5 in place is then subjected to hot rolling at above 400°C firstly, if desired, crosswise and in parallel to the longitudinal edges 6 of cladding plates 4 and 5, and then in the longitudinal direction, followed by cold rolling, so as to achieve the desired thickness of the plate to act as a cathode. Cladding plates 4 and 5 become integral with block 1 by high pressure welding through the hot rolling process.

[0026] After rolling, heat treatment, levelling, stretching, shearing and cleaning, the finished cathode plate is shown in Fig. 2. The lower purity alloy body of the plate 11 is now of the desired final dimensions with its faces 12 and 13 level and grease/oil free.

[0027] Surface layers 14 and 15 derived from the high purity cladding plates 4, 5 are of uniform thickness and run up to the top of the plate, the top edge 19 having a sheared surface such that the interface 16 between surface layer 14 and the body of the plate 11 lies parallel to the bottom edge 17 of the finished plate and just below the intended solution level (indicated by the irregular line 20) which will be experienced by the plate when in use. Surface layer 15 is of the same thickness and orientation on face 13 as surface layer 14 is on face 12.

EXAMPLE:

[0028] In order to assess the operability of the cathode plates of the present invention, a number of conventional AA1000-series aluminium cathodes were tested, typically in the gauge range 4 to 8 mm in the H14 to H18 tempers, as are currently used in the zinc extraction industry. Typically after immersion for 24 hours in a sulphuric acid solution into which the zinc ore has been leached the cathode plates are removed and the deposited zinc layer is mechanically stripped from the aluminium. Typical sizes for such currently used plates are:-

Width	600 - 1200 mm
Length	1000 - 2000 mm
Thickness	4 - 8 mm

[0029] For such conventional plates, corrosion of the faces was seen to occur in the region above the water line and this gave rise to a significant reduction in thickness of the aluminium plates in this region. The maximum rate of loss was seen to occur approximately 25-50mm above the solution level. This loss of material limits the life of such plates, and generally these plates have to be discarded as no longer useful when the thickness in this region is reduced to around 3 or 5mm. This

limited plate life can be as little as 12 months or can be as much as four years, although typically around 2 years, depending upon the precise composition of the cathode plate, the electrolyte composition and the extent of handling and mechanical damage resulting from the regular stripping operation.

[0030] In order to try to assess the likely service life of a cathode plate, samples of plate material were subjected to corrosion testing by total immersion in a simulated electrolyte acidic solution with no applied voltage. The rate of corrosion attack can then be determined by establishing a weight loss per unit area. Testing was performed by immersing the sample in the selected solution for three days at 38°C. Typical corrosion rates of between 0.9 and 1.4 mg/cm²/day were reported for samples of alloys AA1070, AA1370 and AA1235.

[0031] For comparison, samples of these conventional alloy plates were partially roll clad with a layer of 99.99% by weight high purity aluminium, either banding a sample of the plating material to the surface or machining a slot in the plate into which the higher purity aluminium is inserted. In all cases under the test conditions it was found that the interface between the higher and lower purity alloys eroded away at a faster rate than the surrounding material, implying galvanic corrosion along the interface. Not only was plate material found to be lost at a significantly higher rate for these samples than for the plain plate samples, but also significant depressions were formed in the surface by the preferential corrosion which, if encountered during electrolytic deposition would give rise to the deposited zinc being keyed to these depressions and lead to serious difficulties in stripping the deposited zinc off the cathode plate surface.

[0032] Samples of AA1200 plate of 7mm thickness were tested in a commercial zinc extraction plant, which plates carried thereon in the region of the waterline roll bonded cladding of 99.99% by weight aluminium of a thickness of 0.7mm on both faces in accordance with the present invention. This cladding extended from 10mm below the waterline to the top of each plate - a total distance of 150mm. Plastic strips covered the majority of the unclad vertical edges of the plates. For operational reasons the top 50/60mm of each plate edge were not plastic beaded. For comparison a number of unclad plates of the same alloy and of the same thickness were trialled alongside the clad plates under the same industrial conditions.

[0033] After 34 weeks of service with regular mechanical stripping in the same manner, the average loss of thickness for the unclad cathode plates was 1.72mm, as compared with the clad plates of the present invention where a loss of thickness of from 0.71 to 1.10mm was reported for the various test plates. No significant preferential corrosion at the interface between the higher purity and lower purity alloys was noticed, and the mechanical stripping of the plates of the present invention could be carried out with the same ease as with the

unclad plates. There was no signs of the cladding exfoliating.

[0034] Whilst it will be appreciated that the principle of cladding an aluminium alloy cathode plate with a surface layer of a more corrosion-resistant material in the region of the waterline could be applied to any material and not solely to an aluminium alloy having a purity of at least 99.80% by weight, from a commercial point of view the fact that such alloys are commercially available, possesses high corrosion resistance, have good electrical conductivity, and are compatible both electrically and mechanically with the lower purity aluminium alloy of the body of the plate, makes the choice of such a material the best at the present time.

Claims

1. A plate for use as the cathode in an electrolytic cell in which zinc is deposited onto the plate from an acidic solution of a zinc salt, wherein the plate is arranged to be supported vertically and partially immersed in the solution, and wherein the plate is composed of an aluminium alloy of less than 99.85% by weight purity, **characterised in that** in the region of the plate where in use the level of the solution in the cell on the plate will lie the plate carries on each of its two faces a surface layer of aluminium having a higher purity of at least 99.80% by weight and wherein the compositional difference between the plate and the surface layer is at least 0.2% by weight of aluminium.
2. A plate as claimed in claim 1 wherein the said surface layer is composed of aluminium having a purity of about 99.99% by weight.
3. A plate as claimed in claim 1 or claim 2 wherein the aluminium of the body of the plate has a purity of about 99.50% by weight.
4. A plate as claimed in claim 3 wherein the aluminium of the body of the plate is composed of the alloy AA1200, AA1050 or AA1070.
5. A plate as claimed in any one of the preceding claims wherein the said surface layer extends on both faces of the plate to just below the lowest solution level likely to be encountered in the cell when the plate is in use.
6. A plate as claimed in any one of the preceding claims wherein the said surface layer extends on both faces of the plate substantially above the highest solution level likely to be encountered in the cell when the plate is in use.
7. A plate as claimed in any one of the preceding

claims wherein the said surface layer extends to the top of the plate.

8. A plate as claimed in any one of the preceding claims wherein the said surface layer is formed on the plate by casting.
9. A plate as claimed in any one of the claims 1 to 7 wherein the said surface layer is formed on the plate by roll cladding.
10. A plate as claimed in any one of the preceding claims wherein the thickness of the said surface layer on each face of the plate is up to 30% of the total thickness of the plate in the said region.

Patentansprüche

1. Platte für die Verwendung als Kathode in einer Elektrolysezelle, in welcher Zink aus einer säurehaltigen Lösung eines Zinksalzes auf die Platte ausgeschieden wird, worin die Platte zur vertikalen Halterung angeordnet und teilweise in die Lösung eingetaucht ist, und worin die Platte aus einer Aluminiumlegierung von weniger als 99,85 Gewichts% Reinheit besteht, **dadurch gekennzeichnet, daß** in der Zone der Platte, wo sich in Betrieb der Spiegel der Lösung in der Zelle auf der Platte befinden wird, die Platte auf jeder ihrer beiden Seiten eine Oberflächenschicht aus Aluminium einer höheren Reinheit von mindestens 99,80 Gewichts% trägt, und worin der Zusammensetzungsunterschied zwischen der Platte und der Oberflächenschicht mindestens 0,2 Gewichts% an Aluminium beträgt.
2. Platte nach Anspruch 1, worin die Oberflächenschicht aus Aluminium mit einer Reinheit von etwa 99,99 Gewichts% besteht.
3. Platte nach Anspruch 1 oder 2, worin das Aluminium des Plattenkörpers eine Reinheit von etwa 99,50 Gewichts% hat.
4. Platte nach Anspruch 3, worin das Aluminium des Plattenkörpers aus den Legierungen AA1200, AA1050 oder AA1070 zusammengesetzt ist.
5. Platte nach einem der vorangehenden Ansprüche, worin sich die Oberflächenschicht auf beiden Flächen der Platte bis gerade unterhalb des niedrigsten Spiegels der Lösung erstreckt, der voraussichtlich in der Zelle auftritt, wenn sich die Platte in Betrieb befindet.
6. Platte nach einem der vorangehenden Ansprüche, worin sich die Oberflächenschicht auf beiden Flächen der Platte im wesentlichen oberhalb des höch-

sten Spiegels der Lösung erstreckt, der voraussichtlich in der Zelle auftritt, wenn sich die Platte in Betrieb befindet.

7. Platte nach einem der vorangehenden Ansprüche, worin sich die Oberflächenschicht bis zum Kopfen-
de der Platte erstreckt.
8. Platte nach einem der vorangehenden Ansprüche, worin die Oberflächenschicht durch Gießen auf der
Platte gebildet ist.
9. Platte nach einem der Ansprüche 1 bis 7, worin die
Oberflächenschicht durch Walzplattieren auf der
Platte gebildet ist.
10. Platte nach einem der vorangehenden Ansprüche, worin die Dicke der Oberflächenschicht auf jeder
Seite der Platte bis zu 30 % der Gesamtdicke der
Platte in dieser Zone beträgt.

Revendications

1. Une plaque destinée à servir de cathode dans une
cellule électrolytique dans laquelle du zinc est dé-
posé sur la plaque à partir d'une solution acide d'un
sel de zinc, tandis que la plaque est agencée pour
être supportée verticalement et partiellement im-
mergée dans la solution, et que la plaque est com-
posée d'un alliage d'aluminium ayant une pureté de
moins de 99,85% en poids, **caractérisé en ce que**,
dans la région de la plaque où se trouvera, en ser-
vice, le niveau de la solution dans la cellule, la pla-
que porte sur chacune de ses deux faces une cou-
che de surface en aluminium ayant une pureté su-
périeure, d'au moins 99,80% en poids, et **en ce que**
la différence de composition entre la plaque et la
couche de surface est d'au moins 0,2% en poids
d'aluminium.
2. Une plaque selon la revendication 1, **caractérisée
en ce que** la couche de surface est composée
d'aluminium ayant une pureté d'environ 99,99% en
poids.
3. Une plaque selon l'une des revendications 1 et 2,
caractérisée en ce que l'aluminium du corps de la
plaque possède une pureté d'environ 99,50% en
poids.
4. Une plaque selon la revendication 3, **caractérisée
en ce que** l'aluminium du corps de la plaque est
composé de l'alliage AA1200, AA1050 ou AA1070.
5. Une plaque selon l'une des revendications précé-
dentes, **caractérisée en ce que** la couche de sur-
face s'étend sur les faces de la plaque jusqu'à juste

au-dessous du niveau le plus bas de solution qui
soit susceptible d'être rencontré dans la cellule lors-
que la plaque est en service.

6. Une plaque selon l'une des revendications précé-
dentes, **caractérisée en ce que** la couche de sur-
face s'étend sur les deux faces de la plaque sensi-
blement au-dessus du niveau de solution le plus
haut que l'on est susceptible de rencontrer dans la
cellule lorsque la plaque est en service.
7. Une plaque selon l'une des revendications précé-
dentes, **caractérisée en ce que** la couche de sur-
face s'étend jusqu'au haut de la plaque.
8. Une plaque selon l'une des revendications précé-
dentes, **caractérisée en ce que** la couche de sur-
face est formée sur la plaque par coulée.
9. Une plaque selon l'une des revendications 1 à 7,
caractérisée en ce que la couche de surface est
formée sur la plaque par placage au rouleau.
10. Une plaque selon l'une des revendications précé-
dentes, **caractérisée en ce que** l'épaisseur de la
couche de surface sur chaque face de la plaque va
jusqu'à 30% de l'épaisseur totale de la plaque dans
ladite région.

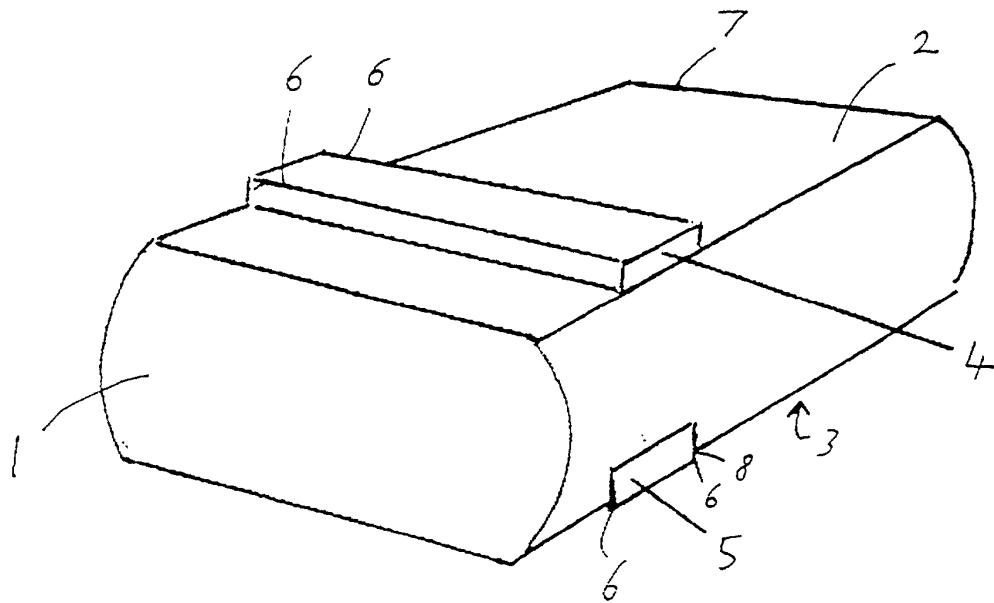


FIG. 1

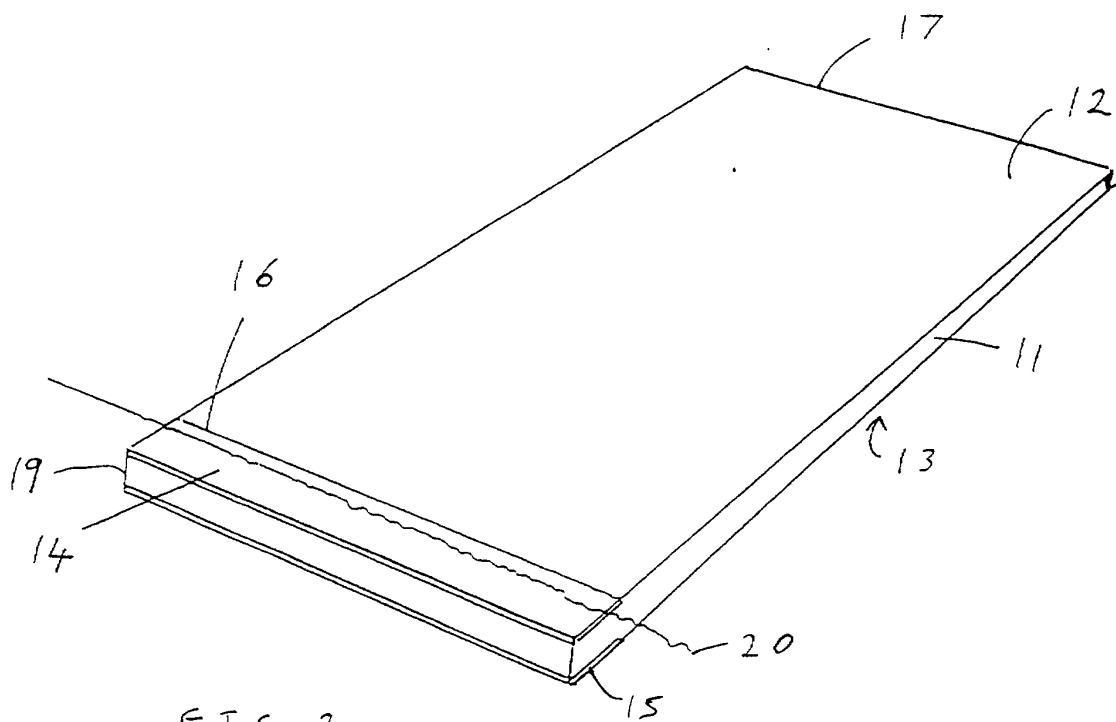


FIG. 2