(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 911 106 B9

(12) **CORRECTED EUROPEAN PATENT SPECIFICATION**

Note: Bibliography reflects the latest situation

(15) Correction information:
Corrected version no 1 (W1 B1)
Corrections, see page(s) 5, 6

(48) Corrigendum issued on:
26.01.2005 Bulletin 2005/04

(45) Date of publication and mention of the grant of the patent:
25.08.2004 Bulletin 2004/35

(21) Application number: **98118996.2**

(22) Date of filing: **08.10.1998**

(51) Int Cl.[7]: **B23K 9/04**, B32B 15/01

(54) **Protective lining for pressure equipment which can be used in processes for the synthesis of urea**

Schutzauskleidung für Druckeinrichtung insbesondere zum Verwenden im Harnstoffsyntheseverfahren

Garnissage de protection pour dispositf sous pression notamment à utiliser dans la synthèse d'urée

(84) Designated Contracting States:
AT CH DE ES LI NL

(30) Priority: **23.10.1997 IT MI972386**

(43) Date of publication of application:
28.04.1999 Bulletin 1999/17

(73) Proprietor: **SNAMPROGETTI S.p.A.**
20097 San Donato Milanese (Milano) (IT)

(72) Inventor: **Miola, Cesare**
Sannazzaro (Pavia) (IT)

(74) Representative: **De Gregori, Antonella et al**
Ing. Barzano' & Zanardo Milano S.p.A.
Via Borgonuovo 10
20121 Milano (IT)

(56) References cited:
EP-A- 0 114 893
EP-A- 0 511 084
WO-A-95/00674
WO-A-96/09136
US-A- 2 764 805
US-A- 3 066 402
US-A- 3 624 345
US-A- 4 431 447
US-A- 4 600 139
US-A- 5 362 937

EP 0 911 106 B9

Description

[0001] The present invention relates to a method for the production of a double layered stainless steel laminar element, a double layered laminar element, a method for the protection from corrosion of process fluids of equipment or elements resistant to high pressures of a plant for the production of urea and a chemical equipment in an industrial plant for the synthesis of urea, in particular a protective lining for pressure equipment which can be used in processes for the synthesis of urea.

[0002] More specifically, the present invention relates to a lining for equipment suitable for tolerating pressures of up to 100 MPa, capable of providing adequate protection of the relative pressure-resistant body, normally made of carbon steel, from the aggressive action of typical process fluids in industrial plants for the production of urea, particularly with reference to equipment included in the synthesis cycle.

[0003] The construction technique of high pressure chemical equipment, whether it be reactors, separators, boilers, etc., normally comprises the preparation of a compact body capable of tolerating the operating pressures, guaranteeing maximum safety and time duration of the mechanical specifications, equipped with necessary passages for external communication and the inlet and outlet of process fluids. The most widely used material for this construction is steel, owing to its excellent combination of high mechanical properties, its relatively low cost and commercial availability.

[0004] Processes for the production of urea normally used in industry comprise at least one section which operates at high temperatures and pressures (synthesis loop), at which the process fluids, i e. water, ammonia and especially saline solutions, become particularly aggressive. It has long been known that normal carbon steel is not capable of resisting the corrosion of these fluids at a high temperature and, when in contact with them, undergoes a progressive deterioration which weakens the structure causing external losses and even explosions.

[0005] In these processes, ammonia, generally in excess, and carbon dioxide are reacted in one or more reactors, at pressures normally ranging from 10 to 30 MPa and temperatures between 150 and 240°C, obtaining an aqueous solution containing urea, the non-transformed ammonium carbamate residue and the excess ammonia used in the synthesis. This aqueous solution is purified of the ammonium carbamate contained therein by its decomposition in decomposers operating, in succession, at gradually decreasing pressures. In most of the existing processes, the first of these decomposers operates at pressures which are substantially equal to the synthesis pressure or slightly lower, and basically consists of an evaporator-decomposer (more widely known as "stripper", used hereafter) in which the aqueous solution of urea is heated with external vapor in the presence of a vapor phase in countercurrent which favours the decomposition of the carbamate and at the same time acts as entrainment fluid of the decomposition products. Stripping agents can be inert gases, or ammonia or carbon dioxide, or mixtures of inert gases with ammonia and/or carbon dioxide; the stripping can also possibly be carried out by using the excess ammonia dissolved in the mixture coming from the reactor (autostripping), consequently without introducing another external agent.

[0006] The decomposition products of ammonium carbamate (NH_3 and CO_2), together with the possible stripping agents, inert gases included, are normally condensed in a suitable condenser obtaining a liquid mixture comprising water, ammonia and ammonium carbamate, which is recycled to the synthesis reactor. In technologically more advanced plants, this condensation step is carried out at pressures substantially equal to those of the reactor or slightly lower.

[0007] As reference, among the many existing patents, US patents 3.886.210, US 4.314.077, US 4.137.262 and published European patent application 504.966, can be mentioned, which describe processes for the production of urea with the above characteristics. A wide range of processes mainly used for the production of urea, is provided in "Encyclopedia of Chemical Technology", 3rd Edition (1983), Vol 23, pages 548-574, John Wiley & Sons Ed..

[0008] The most critical steps in carrying out the process are those in which the ammonium carbamate is at its highest concentration and highest temperature and consequently, in the processes mentioned above, these steps coincide with the equipment of the synthesis cycle, such as the reactor, the stripper and ammonium carbamate condenser, to mention the most important, all operating under analogous or similar conditions to those of the reactor. The problem to be solved in this equipment is that of corrosion and/or erosion particularly caused by contact with solutions of ammonium carbamate at the high temperatures and pressures necessary for the synthesis of urea.

[0009] This problem of corrosion has been confronted with various solutions in existing industrial plants and others have been proposed in literature. There are in fact numerous metals and alloys capable of withstanding for sufficiently long periods the potentially corrosive conditions arising inside a synthesis reactor of urea. Among these, lead, titanium, zirconium and several stainless steels such as, for example, AISI 316L (urea grade)steel, INOX 25/22/2 Cr/Ni/Mo steel, special austenitic-ferritic steels, etc can be mentioned. For economic reasons however, equipment of the above type cannont be entirely constructed with these corrosion-resistant alloys or metals. Usually containers or columns are used, made of normal carbon steel, possibly multilayered, with a thickness varying from 40 to 350 mm, depending on the geometry and pressure to be tolerated (pressure-resistant body), whose surface in contact with the corrosive or erosive fluids is uniformly covered with an anticorrosive metal lining from 2 to 30 mm thick.

[0010] In particular, the reactor normally consists of a vertical container with an inlet of the reagents from below and discharge of the reaction mixture from above. The pressure-resistant body usually comprises a cylinder from 0.5 to 4 m in diameter made with a multilayer or solid wall technique, of which the two ends are closed by caps adequately welded to it. Inside the reactor, an anticorrosive lining is applied to all the walls subject to corrosion, which can consist of for example, titanium, lead, zirconium, or preferably, stainless steels (urea grade) of the type mentioned above.

[0011] The subsequent carbamate stripper, especially if operating at the same pressure as the reactor, consists of a tube-bundle exchanger. Also in this case the pressure-resistant body is made of normal carbon steel, whereas titanium or urea-grade stainless steels are preferably used for the lining. In particular zones of the stripper there are conditions of extreme aggressivity of the fluids. This can be attributed to the high temperature, but also to the geometry of the equipment which does not allow a uniform distribution of the passivating agents, such as air, possibly combined with hydrogen peroxide, normally introduced in small quantities mixed with the process fluids.

[0012] Moreover, the injection of passivating air in the high pressure section of a urea plant can raise a risk of explosion, besides the advantage of improving the corrosion resistance of the linings most frequently used. In facts, most part of the oxigen introduced with the injected air is not consumed in the plant and is purged, mixed with the inert gas, usually from either the carbamate condenser or the top of the reactor. This gas stream contains also ammonia and hydrogen in such an amount as to produce an explosive mixture with the oxigen at the pressure and temperature conditions of the urea process, which may have catastrophic consequences in industry.

[0013] The gases leaving the stripper are usually recondensed in a carbamate condenser which is therefore in contact with a mixture similar to that of the decomposer (except for urea) and therefore extremely corrosive. Also in this case the internal lining preferably consists of the above special urea-grade stainless steels.

[0014] In the above equipment or plant units, the anticorrosive lining is obtained by the assembly of numerous elements having adequate resistance to corrosion, so as to form, at the end, a hermetically sealed structure at the high operating pressure. For the various junctions and weldings carried out for this purpose, it is frequently necessary to resort to particular techniques depending on the geometry and nature of the parts to be joined.

[0015] In the all of the above equipment, a certain number of "weep-holes" are effected to reveal any possible losses in the anticorrosive lining.

[0016] A weep-hole normally consists of a small tube of 8-15 mm in diameter made of corrosion-resistant material, which is inserted in the pressure-resistant body until it reaches the contact point between this and the corrosion-resistant alloy or metal lining. If there is a loss in the lining, owing to the high pressure, the internal fluid which is corrosive, immediately spreads to the interstitial zone between the lining and the pressure-resistant body and, if not discovered, causes rapid corrosion of the carbon steel of which the latter is made. The presence of weep-holes enables these losses to be revealed. For this purpose all the interstitial zones beneath the anticorrosion lining must communicate with at least one weep-hole. The number of weep-holes is normally from 2 to 4 for each ferrule which means, for example, that there are usually from 30 to 60 weep-holes in a reactor.

[0017] The material used for the protective lining is normally selected from metals or metal alloys capable of tolerating contact with the process fluids without undergoing corrosion or alterations for prolonged periods. Depending on the composition and thermal level (temperature) of the process fluids, the materials selected can differ greatly from each other, also taking into consideration their cost and specific chemical properties. Materials commonly used for the lining of equipment operating at high pressure in plants for the production of urea are, for example, stainless steel, titanium, zirconium, lead. "Urea-grade" stainless steels are particularly preferred, such as AISI 316L (urea-grade) steel, INOX 25/22/2 Cr/Ni/Mo steel, special austenite-ferrite steels, etc. owing to their relatively low cost and an operating performance which is sufficient to protect equipment for several years.

[0018] Inspite of their good performance, the duration of stainless steel linings however is limited and it would be preferable to have even more resistant steels. In addition, the formation of specific zones of preferential corrosion in particular plant equipment has been observed, making it necessary to resort to repair or substitution interventions of the lining more frequently than estimated on the basis of standard corrosion resistance tests. This occurs, for example, in the high pressure stripping section.

[0019] US patent No. 3,066,402 discloses a method for making a hard facing article, consisting of the deposition on a steel plate of a layer of hard solid material in discrete particles, by heating and welding a rod of suitable composition. The articles find application as hard anti-wear coatings, but are not suitable for lining equipments exposed to heavy chemical corrosion, as the deposited layer is not homogeneous.

[0020] According to the PCT publication WO 96/09136, the use of corrosion resistant metallic elements is disclosed for repairing an equipment which has undergone corrosion in a process for producing urea under heavy duty conditions. The metallic elements are obtained by suitably cutting and shaping standard laminates made of such materials as INOX stainless steel, austenitic-ferritic steels, titanium, zirconium and their alloys.

[0021] US 4431447 discloses discloses a welding alloy containing at least 5 % b.w. of Mo, and a weld deposit containing at least 4% Mo obtained in certain zones of a chemical equipment, but it does not disclose any expedient for the achievement of single double layer elements with high corrosion resistance even with a lower content of molibdenum.

[0022] EP 114893 discloses a lining of stainless steel over a base metal of carbon steel or a low alloy steel within a chemical equipment in order to improve its resistance to corrosion. However, it fails to address the problem of formation of defects in the base metal.

[0023] It would therefore be desirable to further improve the performance of the lining, especially in equipment operating under critical conditions, at the same time maintaining, for obvious reasons of convenience and availability, the use of stainless steels normally adopted for its construction.

[0024] It would be also desirable to have a lined equipment, particularly a urea stripper, of such a good corrosion resistance as to avoid any injection of passivating air in the plant, in order to not incur any danger of explosion

[0025] The Applicant has now observed that resistance to corrosion in stainless steel linings is better along weldings effected during their assembley At the same time, it has been found however that a welding deposit situated directly on the pressure-resistant body does not allow an efficient system of weep-holes to be effected owing to the lack of interstitial zones previously mentioned, and consequently the safety of the whole equipment is reduced.

[0026] On the other hand, the formation of an extensive welding deposit on a pre-existing anticorrosion lining in certain equipment, although allowing an effective weep-hole system to be maintained, causes deformation, and in certain cases damage, of the lining itself due to the great thermal and mechanical stress on a relatively thin plate subjected to tension.

[0027] The Applicant has now found a method which allows the corrosion resistance of linings to be improved also in the most critical points of a plant for the production of urea, at the same time maintaining a high safety margin, which consists in the preparation of a lining with double-layered plates

[0028] A first object of the present invention therefore relates to a method for the construction of a double-layered stainless steel laminar element according to claim 1.

[0029] A second object of the present invention relates to a double layered laminar element essentially according to claim 10.

[0030] Further objects of the present invention will be made evident in the following description and examples.

[0031] In step (i) of the manufacturing method of the present invention, the plate consists of a stainless steel or alloy of stainless steels, preferably of the type called "urea grade", such as, for example, AISI 316L steel (urea grade), INOX 25/22/2 Cr/Ni/Mo steel, special austenitic-ferritic steels, and others normally known to experts in the field. The selection of the most suitable material is left to the expert in the field, on the basis of the performances desired during operation. Typical examples of these steels are those commercially available under the following names: "2 RE 69" (®, SANDVIK), "724 L" (®, AVESTA), "725 LN" (®, AVESTA), "DP 12" (®, SUMITOMO).

[0032] It is not critical, at this stage in the method of the present invention, for the plate to be preformed or shaped according to the geometry and arrangement of the double-layered element, once positioned in the relative equipment. This is in fact one of the advantages of the present invention, that the end-form of this element can be obtained with the known methods, even after its construction. For obvious reasons of greater simplicity and practicality, the plate is normally square-shaped or rectangular, with a surface extension between 0.5 and 5 m^2. The plate more preferably has a width which is less than 1 m and up to 0.1 m, the length being selected each time according to necessity and in relation to the dimensions of the support used in carrying out step (ii).

[0033] The thickness of the plate is that normally used for the construction of a typical anticorrosive lining and is selected on the basis of criteria known to experts in the field. Thicknesses slightly less than the standard can be used owing to the contribution provided by the subsequent welding deposit to the resistance of the product. The thickness selected is normally greater than 2 mm to guarantee sufficient mechanical reliability, and less than 30 mm to facilitate the subsequent cutting and forming, as well as for obvious economic reasons. Preferred thicknesses are between 4 and 10 mm.

[0034] Plates of the above type are easily available and are produced with the usual methods of the iron and steel industry by lamination and cutting.

[0035] Step (ii) of the present manufacturing method comprises the consolidated fixing of the plate prepared according to step (i) on a suitable metal support. The term "consolidated" , as used in this context, refers to the fixing of the plate onto the support which allows a surface of the former to be put in substantial contact with the surface of the latter, so that efficient heat transmission is established during the subsequent depositing of the welding material.

[0036] The metal support normally consists of a plate of an adequate thickness, usually between 20 and 200 mm, and preferably between 40 and 100 mm, having at least one relatively smooth surface so as to allow adequate mechanical support of the above plate, and an efficient heat dissipation. It consists of a material which is preferably selected from metals or alloys which can be welded to the overlying steel plate, in particular, normal carbon steel or other ferrous alloys, thus allowing easy fixing by welding points. Other metal materials however can also be used for the purpose, such as, for example, aluminum, where it is possible to effect adequate fixing with different methods from welding, for example, by means of clamps, screws, screw threads, etc.

[0037] In the particular case of fixing by welding, this is carried out by points on the edge of the plate, preferably with a distance between adjacent points of 20 to 150 mm, depending on the geometry, dimensions and thickness of the plate. In this way an assembly between plate and support is obtained which is surprisingly sufficient to ensure the absence of significant deformations in the subsequent step (iii), even for plates of various square metres.

[0038] In a particular embodiment of the present invention, the support consists of a metal plate having at least one communicating hollow space with inlets to allow the circulation of a liquid inside the plate itself. This further increases the heat dissipation in the subsequent step (iii). Preferred cooling liquids are selected from oils with a low viscosity and water.

[0039] The welding deposit which is extended on the plate according to step (iii) of the present method consists of a metal or metal alloy evidently compatible with the metal or metal alloy of the plate itself, as it must adhere and amalgamate on the surface to form a continuous structure with the minimum quantity of defects possible, which is a characteristic of a proper welding between two metals.

[0040] The method for extending the welding deposit can be any of the methods known in the art, for example, welding with arc-electrodes, "T.I.G" (Tungsten Inert Gas) with wire rods, or by means of an automatic belt system. The operation can be indifferently carried out either manually or automatically (by belts), depending on the requirements of the case and dimensions and shape of the surface to be covered.

[0041] In a preferred embodiment of the present method, it is preferable to limit the thermal supply as much as possible during the extension of the welding deposit, in order to guarantee dimensional stability of the underlying metal plate and not to produce metal pick-ups between the two parts. This is achieved, for example, by limiting the power emitted by the welder so that no point of the surface of the plate opposite the welding welding surface (that leaning on the support) exceeds a temperature of 450°C. Thermal flows ranging from 8000 to 16000 J/cm^2 are advantageously used.

[0042] The metal or metal alloy used for the welding deposit is ***[deletion(s)]*** a urea-grade stainless steel of the type which is resistant to corrosion of the process fluids involved in the high pressure cycle of the synthesis of urea, particularly aqueous-ammonia solutions of carbamate and/or urea such as those present in the reactor, at the bottom of the stripper or in the chamber of the carbamate condenser. These steels are known in the art and are commercially available. They contain, in addition to iron, other metals compatible with this and resistant to oxidation in an acid environment, such as, for example, Ni, V, Cr, W, Mo, etc. in sufficient quantities and combinations to make the resulting alloy corrosion resistant under the normal operating conditions. Typical examples of these steels are those previously mentioned for forming the stainless steel plate on which the welding deposit of the present invention is effected. Particularly preferred are urea grade stainless steels for welding, which have a particularly low content of ferrite and other elements different from those listed above, and can comprise appropriate additives, such as flows and fluxes, suitable for favouring melting and adhesion on the surface to be welded. Typical examples of these stainless steels are those available on the market under the trade-names "P6"(®, AVESTA), "Batox F(U) M" (®, SECHERON), "Thermanit 19/15 H" (®, THYSSEN), "NC 316 MF" (®, KOBE STEEL), "16KCR" (®, ESAB), "CITOXID B 316 LM" (®, SIDEROTERMICA), "No. 4051" (®, KOBE STEEL), "Siderfil 316 LM" (®, SIDEROTERMICA), "20-16-3 L Mn" (®, SANDVIK) with flow "12 b 316 LFT 2" (®, SOUDOMETAL), "21.17.E" (®, THYSSEN) with flow "Rekord 13 BLFT" (®, SOUDOMETAL), "25-22-2 L Mn" (®, SANDVIK) with flow "12 b 316 LFT 2" (®, SOUDOMETAL), "25-22-2 L Mn" (®, SANDVIK) with flow "31 S (®, SANDVIK), "FOX EASN 25 M" (®. VEW), "Thermanit 25/22 H" (®, THYSSEN), "Soudinox LF" (®, SOUDOMETAL), "NC 310 MF" (®, KOBE STEEL), "FILARC BM 310 Mo L" (®, ESAB), "Grinox 67" (®, GRIESHEIM), "TGS 310 MF" (®, KOBE STEEL), "FOX EASN 25 MIG" (®, VEW), "Grinox T67" (®, GRIESHEIM), "25-22-2 L Mn" (®. SANDVIK) with flow "37 S (electroslag)" (®, SANDVIK), "25-22 H" (®, THYSSEN) with flow "EST 122 (electroslag)" (®, SOUDOMETAL). The selection of the most suitable welding material is left to experts in the field, depending on the composition of the plate on which the welding is carried out and the final characteristics desired.

[0043] The thickness of the stainless steel plate as per step (i) is preferably uniform, even though this requisite is not essential for the purposes of the present invention. It is also preferable for the plate to be flat as this simplifies the dispersion of the heat produced by the welding deposit in step (iii) and also facilitates the fixing of the plate to the support according to step (ii). The thickness of the welding deposit deposited on the plate according to step (iii) of the present method is preferably maintained at a value which is more or less equal on the whole surface of the deposit, to guarantee uniform performance of the end-product thus obtained. In quantitative terms this thickness can have at the most a deviation from the average value of ±20%, preferably ±10%.

[0044] In the subsequent step (iv), the double-layered laminar element obtained according to the procedure of step (iii) is removed from the support onto which it was fixed using normal operations. If the fixing was effected by welding, the removal must be carried out with due precautions to avoid distorsion of the plate.

[0045] A double-layered laminar element is obtained which is essentially without deformations, and which can be used for the production of anticorrosive linings of equipment used in plants for the production of urea, comprising a first layer consisting of a stainless steel metal plate having a thickness ranging from 2 to 30 mm, preferably between 2 and 15 mm, and a surface extension ***[deletion(s)]*** between 0.5 and 5 m^2, characterized in that the second layer has an almost uniform thickness, ranging from 0.5 to 6 mm, preferably between 1 and 4 mm, is uniformly welded to the first layer and consists of a stainless steel of the type called "urea grade" obtained by welding deposit.

[0046] This second layer preferably consists of a welding deposit of a urea-grade low ferrite stainless steel selected from AISI 316L (urea grade) steels, INOX 25/22/2 Cr/Ni/Mo steels, special austenite-ferrite steels.

[0047] The present invention also relates to a method for the protection from corrosion by process fluids of equipment or elements resistant to high pressures of a plant for the production of urea, particularly in the synthesis section according to claim 12.

[0048] The selection of the most suitable construction technology among the many known methods for the production of the protective lining of the present invention is left to experts in the field, comprising cutting and welding methods, as well as those for obtaining weep-holes in the most appropriate points, the annealing of the weldings on the pressure-resistant body, the application of welding deposits below the welding lines, and also additional protection in the case of accidental losses, the formation of communication points or slots between the various interstitial zones beneath the lining and among these weep-holes, the shaping methods of the laminar elements, such as calendering or moulding, and all the other known techniques which can be used for the purpose.

[0049] The above method of the present invention allows the corrosion resistance of equipment involved in the synthesis process of urea to be improved, maintaining all the elements necessary for guaranteeing the safety of the plant and also enables accidental losses to be revealed. In fact, this lining is produced with the known methods used for traditional linings, i.e. by placing the double-layered elements onto the underlying pressure-resistant body without extensive welding, but only welding the edges to each other and to the underlying pressure-resistant body, thus forming interstices between lining and pressure-resistant body which communicate with each other and with a system of weep-holes to reveal any possible losses.

[0050] On the contrary, an extensive welding deposit directly on the pressure-resistant body would not make it possible to maintain an efficient safety system based on weep-holes, as there would not be interstitial spaces suitable as outlets for the corrosive fluids in the case of losses of the lining. In these cases the corrosive process fluid would not be revealed and would remain in contact with the carbon steel of the pressure-resistant body causing its corrosion and jeopardizing the structure.

[0051] According to a particular aspect of the present invention, not all the surface of the equipment is lined with the above double-layered laminar elements having improved resistance to corrosion, but optionally, only the part attributed as being the most exposed to corrosion. For example, in the case of stripping equipment, a lining can be produced with double-layered elements in the lower section where the process temperature is higher, providing a traditional type lining, evidently less expensive, in the upper section which is less exposed to corrosive attack.

[0052] As previously specified, the method of the present invention can be particularly applied to the high or medium pressure section of a synthesis plant of urea. This substantially refers to synthesis reactors of urea, equipment for the decomposition of non-transformed carbamate (particularly strippers), and containers for the condensation of NH_3 and CO_2 with the formation of carbamate solutions.

[0053] This equipment operates at pressures normally ranging from 10 to 50 MPa and temperatures ranging from 70 to 300°C, in the presence of mixtures containing water, ammonia, carbon dioxide and ammonium carbamate which is the condensation product of these compounds according to the reaction:

$$[2\ NH_3 + CO_2 + nH_2O \dashrightarrow NK_4OCONH_2 \times nH_2O]$$

[0054] The operating conditions are preferably a pressure of 12-25 MPa and a temperature of 120 to 240°C.

[0055] In normal industrial plants for the production of urea, to which the present invention particularly relates, the above equipment included in the high or medium pressure section normally contains volumes ranging from 2000 to 400000 litres.

[0056] The production of the anticorrosive lining of the present invention comprises the positioning, on the surface of the pressure-resistant body of the above double-layered laminar elements, suitably cut and shaped to adapt themselves to the curvature of the surface to be lined As they can become easily deformed however, suitable curvature can be obtained with normal instruments availabe to experts in the field.

[0057] The double-layered elements are arranged side by side to facilitate their subsequent welding. Slots, supports, connecting elements and other interventions or products are arranged, especially along the edges to be welded, according to common practice known to experts in the field.

[0058] The welding of the double-layered laminar elements arranged as described above, is usually carried out with one of the methods previously listed with reference to the welding deposit procedure. The production of the weep-hole system is also left to the experts in the field.

[0059] The improved anticorrosive lining of the present invention is also suitable for the functional restoration of pre-existing equipment whose original lining requires substitution or repair owing to the presence of significant corrosion zones which jeopardize its functionality and safety. In particular, it is possible in this way to completely re-establish the original functionality of the equipment and guarantee, owing to the improved performance of the new lining, greater duration and operating safety than the original.

[0060] The various aspects of the present invention are further illustrated by referring to the drawing of figure 1 enclosed, which schematically represents a perspective view of the longitudinal section of the wall of a high pressure stripper in a plant for the synthesis of urea, and also the example described below, without limiting or restricting the overall scope of the present invention in any way.

[0061] Figure 1 essentially illustrates the section of the pressure-resistant body **1**, made of stainless steel, on whose surface the lining **2** is placed, which consists of a lower layer **3**, in direct contact with the pressure-resistant body and made up of a traditional stainless steel plate, and an upper layer **4** welded to the previous layer and consisting of a welding deposit according to the present invention. It is also possible to observe the weep-holes **5** below the welding **6** between two double-layered laminar elements **7a** and **7b** which locally form the above lining. The weep-holes are situated below the lining **2**, near the welding line **6**, below which is a welding deposit **8**, also in stainless steel, which has the purpose of stably and homogeneously anchoring the welding to the pressure-resistant body to prevent the latter from being damaged by possible losses (normally due to accidental defects in the welding itself). Figure 1 also schematically represents, with the dashed line, the flow of the process fluid deriving from a possible loss due to a welding defect, which runs above the deposit **8** until it reaches the nearest weep-hole **5**.

[0062] The above description of the present invention in general lines and details, is followed by a practical example for its application.

EXAMPLE

[0063] The lower head of a stripper used in the high pressure synthesis cycle of a plant for the production of urea was equipped with an anticorrosive lining according to the present invention, whereas the remaining part of the equipment was equipped with a traditional lining made of 25/22/2 Cr/Ni/Mo steel.

[0064] The head, consisting of a cylindrical stainless steel body having a diameter of 840 mm and a length of 2000 mm and equipped with a manhole of 600 mm in diameter, was completely lined with the new double-layered lining in accordance with the following procedure.

[0065] An adequate number of rectangular steel plates of 25/22/2 Cr/Ni/Mo having a thickness of 6 mm and dimensions of about 600 mm x 1200 mm, were prepared. Each plate was fixed onto a support consisting of a carbon steel plate 80 mm thick and equipped with a hollow space for the continuous circulation of cooling water, by means of welding points on the edge at a distance of about 100 mm from each other.

[0066] A welding deposit having a thickness of about 3 mm was deposited on the exposed face of the plate thus fixed, by means of a plunged arc and an automatic procedure, using a "25/22/2 L Mn" (®, SANDVIK) tape 30 mm wide and 0.5 mm thick with a "Rekord 13 BLFT" (®, SOUDOMETAL) flow, with a shift of 180 mm/minute and a thermal flow of 38,000 J/cm (12,670 J/cm^2). Adjacent strips were deposited having a width of about 30 mm until the whole plate was covered. Water was circulated in the hollow space of the support during the entire procedure so that the temperature of the underlying face of the plate was maintained below 350°C.

[0067] With reference to the section represented in figure 1, the pressure-resistant body **2** of the head was prepared for the lining with the usual method, by making slots having a width of about 60 mm and a depth of about 4 mm in correspondence with the estimated welding lines of the lining, and then filling these with the welding deposit **8** made of 25/22/2 Cr/Ni/Mo steel. Weep-holes **5** were made through the welding deposit and pressure-resistant body in an adequate quantity and position to guarantee the revealing of any possible losses at any point in the equipment. Each weep-hole is lined with 25/22/2 Cr/Ni/Mo steel and the edge is hermetically sealed with the above welding deposit **8**. The double-layered laminar elements obtained as described above were subjected to calendering to provide a curvature in conformance with the geometry of the head, and were then positioned on the pressure-resistant body and fixed with welding lines **6** to each other and to the underlying deposit **8**, thus forming the desired lining (**7a** and **7b**). The welding was carried out with the T.I.G. method with "Thermanit 25/22 H" (®, THYSSEN) rods.

[0068] At the end of the operation, the stripper was subjected to the usual verifications to ensure satisfactory functioning. In particular, the following tests were carried out:

- Welding control with penetrating liquids according to regulation "ASME VIII, div. 1. appendix 8";
- Gas seal test according to regulation "ASME V, article 10", carried out with helium;
- Pressure seal test, carried out by bringing the internal pressure of the reactor to the value specified by the project regulations (320 bars). All of the above tests gave satisfactory results.

[0069] The stripper thus obtained was subsequently started up at plant regime and was left functioning for at least two years, except for interruption periods for ordinary maintenance, without there being, on careful examination, any specific losses or significant thinning out due to corrosion of the lining. Analogous equipment, operating under the same conditions and equipped with a traditional lining showed, after the same period, significant deterioration zones and thinning out of the lining in the lower head.

[0070] A further test made with no injection of passivating air also showed very low or absence of corrosion of the stripper lined according to the present invention.

Claims

1. A method for the production of a double-layered stainless steel laminar element, comprising the following operations in succession:

i) preparation of a stainless steel plate, having a thickness ranging from 2 to 30 mm, and a surface of between 0.5 and 5 m^2.
ii) consolidated fixing of this plate to a metal support with a flat surface and a thickness ranging between 20 and 200 mm, to obtain a substantial contact between a surface of the plate and a surface of the support;
iii) depositing of a welding deposit of urea-grad of stainless steel onto the surface of the plate, with a thickness ranging from 0.5 to 6 mm;
iv) removal of the double-layered laminar element thus obtained, from the support.

2. The method according to claim 1, wherein the plate consists of a stainless steel selected from AISI 316L urea grade steels, INOX 25/22/2 Cr/Ni/Mo steels and special austenitic-ferritic steels, and has a thickness ranging from 4 to 10 mm.

3. The method according to any of the previous claims 1 or 2, wherein, in step (ii) the support is made of carbon steel, has an extension equal to or greater than the stainless steel plate and a thickness ranging from 40 to 100 mm.

4. The method according to any of the claims from 1 to 3, wherein the support in step (ii) is equipped with a hollow space for the circulation of a cooling fluid.

5. The method according to any of claims 3 or 4, wherein the fixing of the plate to the support in step (ii) is carried out by welding with points at a distance of 4 to 15 cm from each other.

6. The method according to any of the previous claims, wherein the welding deposit in step (iii) has an almost uniform thickness ranging from 1 to 4 mm.

7. The method according to any of the previous claims, wherein the welding deposit is deposited by limiting the thermal flow supplied by the welder to a value ranging from 8000 to 16000 J/cm^2.

8. The method according to claims 4 to 7, wherein, in step (iii), cooling water is circulated in the hollow space of the support so that no point of the surface of the plate opposite to that of deposit exceeds a temperature of 450°C.

9. The method according to any of the previous claims, wherein the welding deposit is obtained starting from a urea grade stainless steel with a low contrent of ferrite.

10. A double-layered laminar element essentially without deformations, which can be used for the production of anticorrosive linings of equipment used in plants for the production of urea, comprising a first layer consisting of a stainless steel metal plate having a thickness ranging from 2 to 30 mm and a surface extension of from 0.5 to 5 m^2, **characterized in that** the second layer has a thickness ranging from 0.5 to 6 mm, is uniformly welded onto the first layer, consists of a welding deposit of a metal or metal alloy selected from urea grade low ferrite stainless steels, and obtainable by a process according to claim 9.

11. The double-layered laminar element according to claim 10, wherein the second layer is obtained by the welding deposit of a steel selected from AISI 316L (urea grade) steel, INOX 25/22/2 Cr/Ni/Mo steel, special austenitic-ferritic steels, and has an almost uniform thickness whose average value is between 1 and 4 mm.

12. A method for the protection from the corrosion of process fluids of equipment or elements resistant to high pressures of a plant for the production of urea, particularly included in the synthesis cycle, comprising the production of a hermetically sealed lining of at least a part of the surface of said equipment in contact with the process fluids, by one or more double-layered laminar elements according to any of the claims from 10 to 11, suitably shaped and welded to each other.

13. The method according to claim 12, wherein said equipment is a reactor or a stripper operating at pressures ranging from 10 to 50 MPa and temperatures ranging from 70 to 300°C.

14. A method for the functional restoration of chemical equipment in a plant for the production of urea by reaction of ammonia and carbon dioxide at high temperatures and pressures, in which at least one extensive zone has been subjected to corrosion, wherein the functioning of this equipment is re-established by repair comprising the production of a hermetically sealed lining on the zone subject to corrosion by one or more double-layered elements according to any of the claims from 10 to 11, suitably shaped and welded to each other.

15. Chemical equipment for normally operating at high or medium pressure in an industrial plant, for the synthesis of urea in contact with potentially corrosive process fluids in a plant for the production of urea, comprising internally, an anticorrosive metal lining which comprises one or more double-layered laminar elements according to any claims 10 or 11.

16. The chemical equipment according to claims 15, consisting of a stripper or a reactor.

Patentansprüche

1. Verfahren zur Herstellung eines zweilagigen laminaren Elements aus rostfreiem Stahl mit den folgenden aufeinanderfolgenden Schritten:

i) Herstellung einer Platte aus rostfreiem Stahl, die eine Dicke im Bereich von 2 bis 30 mm und eine Oberfläche zwischen 0,5 und 5 m^2 aufweist;
ii) festes Anbringen dieser Platte an einem Metallträger mit einer flachen Oberfläche und einer Dicke im Bereich zwischen 20 und 200 mm, um einen wesentlichen Kontakt zwischen einer Oberfläche der Platte und einer Oberfläche des Trägers zu erhalten;
iii) Aufbringen eines Schweißguts aus rostfreiem Stahl der Karbamid-Güteklasse auf die Oberfläche der Platte mit einer Dicke im Bereich von 0,5 bis 6 mm;
iv) Entfernen des so erhaltenen zweilagigen laminaren Elements von dem Träger.

2. Verfahren nach Anspruch 1, bei dem die Platte aus rostfreiem Stahl besteht, der aus AISI 316L-Stählen der Karbamid-Güteklasse, INOX 25/22/2 Cr/Ni/Mo-Stählen und speziellen austenitisch-ferritischen Stählen ausgewählt ist, und eine Dicke im Bereich von 4 bis 10 mm aufweist.

3. Verfahren nach einem der vorgehenden Ansprüche 1 oder 2, bei dem im Schritt (ii) der Träger aus einem Kohlenstoffstahl besteht, eine Ausdehnung die gleich oder größer ist als die Platte aus rostfreiem Stahl und eine Dicke im Bereich von 40 bis 100 mm aufweist.

4. Verfahren nach einem der Ansprüche 1 bis 3, bei dem der Träger im Schritt (ii) mit einem Hohlraum zur Zirkulation eines Kühlfluids ausgestattet ist.

5. Verfahren nach einem der Ansprüche 3 oder 4, bei dem die Befestigung der Platte an dem Träger im Schritt (ii) durch Schweißen mit Punkten in einem Abstand von 4 bis 15 cm voneinander erfolgt.

6. Verfahren nach einem der vorhergehenden Ansprüche, bei dem das Schweißgut im Schritt (iii) eine nahezu gleichmäßige Dicke im Bereich von 1 bis 4 mm aufweist.

7. Verfahren nach einem der vorhergehenden Ansprüche, bei dem das Schweißgut aufgebracht wird, indem der durch den Schweißer zugeführte Wärmefluss auf einen Wert im Bereich von 8000 bis 16000 J/cm^2 begrenzt wird.

8. Verfahren nach den Ansprüchen 4 bis 7, bei dem im Schritt (iii) Kühlwasser in dem Hohlraum des Trägers im Kreislauf geführt wird, so dass kein Punkt der Oberfläche der Platte gegenüber der des aufgebrachten Guts eine Temperatur von 450 °C überschreitet.

9. Verfahren nach einem der vorhergehenden Ansprüche, bei dem das Schweißgut durch Ausgehen von einem rostfreien Stahl der Karbamid-Güteklasse mit einem geringen Ferritgehalt erhalten wird.

10. Zweilagiges laminares Element, im Wesentlichen ohne Verformungen, das zur Herstellung korrosionsschützender Verkleidungen einer in Anlagen zur Herstellung von Karbamid verwendeten Einrichtung eingesetzt werden kann, mit einer ersten Schicht, die aus einer Metallplatte aus rostfreiem Stahl mit einer Dicke im Bereich von **2** bis 30 mm und einer Oberflächenausdehnung von 0,5 bis 5 m^2 besteht, **dadurch gekennzeichnet, dass** die zweite Schicht eine Dicke im Bereich von 0,5 bis 6 mm aufweist, gleichmäßig auf die erste Schicht geschweißt ist und aus einem Schweißgut aus einem Metall oder einer Metalllegierung, ausgewählt aus rostfreien Stählen der Karbamid-Güteklasse mit einem geringen Ferritgehalt, besteht und durch ein Verfahren nach dem vorhergehenden Anspruch 9 erhältlich ist.

11. Zweilagiges laminares Element nach Anspruch 10, bei dem die zweite Schicht durch das Schweißgut aus einem Stahl, ausgewählt aus AISI 316L (Karbamid-Güteklasse)-Stahl, INOX 25/22/2 Cr/Ni/Mo-Stahl und speziellen austenitisch-ferritischen Stählen, erhalten wird und eine nahezu gleichmäßige Dicke aufweist, deren Durchschnittswert zwischen 1 und 4 mm liegt.

12. Verfahren zum Schutz einer hochdruckbeständigen Einrichtung oder von hochdruckbeständigen Elementen einer Anlage zur Herstellung von Karbamid, die insbesondere in dem Synthesezyklus enthalten sind, vor der Korrosion durch Prozessfluide, umfassend die Herstellung einer luftdicht abgeschlossenen Verkleidung von zumindest einem Teil der Oberfläche der Einrichtung, die sich in Kontakt mit den Prozessfluiden befindet, durch ein zweilagiges laminares Element oder mehrere zweilagige laminare Elemente nach einem der Ansprüche 10 bis 11, die geeignet geformt und miteinander verschweißt sind.

13. Verfahren nach Anspruch 12, bei dem die Einrichtung ein Reaktor oder ein Abscheider ist, der bei Drücken im Bereich von 10 bis 50 MPa and bei Temperaturen im Bereich von 70 bis 300 °C betrieben wird.

14. Verfahren zur funktionellen Wiederherstellung einer chemischen Einrichtung in einer Anlage zur Herstellung von Karbamid durch die Reaktion von Ammoniak und Kohlendioxid bei hohen Temperaturen und Drücken, in der wenigstens eine ausgedehnte Zone korrodiert ist, wobei die Funktion dieser Einrichtung durch eine Reparatur wiederhergestellt wird, die die Herstellung einer luftdicht abgeschlossenen Verkleidung auf der korrodierten Zone durch ein zweilagiges Element oder mehrere zweilagige Elemente nach einem der Ansprüche 10 bis 11 umfasst, die geeignet geformt und miteinander verschweißt sind.

15. Chemische Einrichtung, die normalerweise bei einem hohen oder einem mittleren Druck in einer Industrieanlage für die Synthese von Karbamid in Kotakt mit potenziell korrosiven Prozessfluiden in einer Anlage zur Herstellung von Karbamid betrieben wird und die in ihrem Inneren eine korrosionsschützende Metallverkleidung umfasst, die ein zweilagiges laminares Element oder mehrere zweilagige laminare Elemente nach einem der Ansprüche 10 oder 11 umfasst.

16. Chemische Einrichtung nach Anspruch 15, die aus einem Abscheider oder einem Reaktor besteht.

Revendications

1. Procédé de production d'un élément laminaire en acier inoxydable à double couche, comprenant les opérations suivantes en succession :

i) préparation d'une plaque d'acier inoxydable, ayant une épaisseur comprise dans l'intervalle de 2 à 30 mm, et une surface comprise dans l'intervalle de 0,5 à 5 m^2 ;

ii) fixation consolidée de cette plaque sur un support métallique ayant une surface plate et une épaisseur comprise dans l'intervalle de 20 à 200 mm, pour obtenir un contact substantiel entre une surface de la plaque et une surface du support ;

iii) dépôt d'un métal d'apport de soudage en acier inoxydable de qualité urée sur la surface de la plaque, avec une épaisseur comprise dans l'intervalle de 0,5 à 6 mm ;

iv) retrait du support de l'élément laminaire à double couche ainsi obtenu.

2. Procédé selon la revendication 1, dans lequel la plaque est constituée d'un acier inoxydable choisi parmi les aciers AISI 316L, les aciers INOX 25/22/2 Cr/Ni/Mo et les aciers spéciaux austénitique-ferritique, et a une épaisseur comprise dans l'intervalle de 4 à 10 mm.

3. Procédé selon la revendication 1 ou 2, dans lequel, à l'étape (ii), le support est en acier au carbone, a une étendue supérieure ou égale à celle de la plaque en acier inoxydable et une épaisseur comprise dans l'intervalle de 40 à 100 mm.

4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel, à l'étape (ii), le support est muni d'un espace creux pour la circulation d'un fluide de refroidissement.

5. Procédé selon l'une quelconque des revendications 3 et 4, dans lequel la fixation de la plaque sur le support à l'étape (ii) est exécutée par un soudage par points à une distance de 4 à 15 cm les uns des autres.

6. Procédé selon l'une quelconque des revendications précédentes, dans lequel le dépôt de l'étape (iii) a une épaisseur presque uniforme comprise entre 1 et 4 mm.

7. Procédé selon l'une quelconque des revendications précédentes, dans lequel le dépôt est déposé en limitant le flux thermique fourni par le soudeur à une valeur comprise dans l'intervalle de 8 000 à 16 000 J/cm^2.

8. Procédé selon les revendications 4 à 7, dans lequel, à l'étape (iii), on fait circuler de l'eau de refroidissement dans l'espace creux du support de sorte qu'aucun point de la surface de la plaque en regard de celle du dépôt ne dépasse une température de 450 °C.

9. Procédé selon l'une quelconque des revendications précédentes, dans lequel le dépôt est obtenu à partir d'un acier inoxydable de qualité urée à faible teneur en ferrite.

10. Elément laminaire à double couche essentiellement exempt de déformations, qui peut être utilisé pour la production de garnitures anticorrosion d'équipements utilisés dans la production d'urée, comprenant une première couche constituée d'une plaque métallique en acier inoxydable ayant une épaisseur comprise dans l'intervalle de 2 à 30 mm et une étendue surfacique comprise dans l'intervalle de 0,5 à 5 m^2, **caractérisé en ce que** la deuxième couche a une épaisseur comprise dans l'intervalle de 0,5 à 6 mm, est soudée uniformément sur la première couche, consiste en un métal d'apport de soudage fait d'un métal ou d'un alliage de métaux choisi parmi les aciers inoxydables de qualité urée à faible teneur en ferrite, et pouvant être obtenue au moyen d'un procédé selon la revendication 9.

11. Elément laminaire à double couche selon la revendication 10, dans lequel la deuxième couche est obtenue par le dépôt de soudage d'un acier choisi parmi l'acier AISI 316L (qualité urée), l'acier INOX 25/22/2 Cr/Ni/Mo, les aciers spéciaux austénitique-ferritique, et a une épaisseur presque uniforme dont la valeur moyenne est comprise entre 1 et 4 mm.

12. Procédé de protection contre la corrosion de fluides de processus d'un équipement ou d'éléments résistants aux hautes pressions d'une usine de production d'urée, en particulier inclus dans le cycle de synthèse, comprenant la production d'une garniture scellée hermétiquement d'au moins une partie de la surface dudit équipement en contact avec les fluides de processus, par un ou plusieurs élément(s) laminaire(s) à double couche conforme(s) à l'une quelconque des revendications 10 et 11, mis en forme de manière appropriée et soudés entre eux.

13. Procédé selon la revendication 12, dans lequel ledit équipement est un réacteur ou une colonne de fractionnement fonctionnant à des pressions comprises dans l'intervalle de 10 à 50 MPa et à des températures comprises dans l'intervalle de 70 à 300 °C.

14. Procédé de restauration fonctionnelle d'un équipement chimique dans une usine de production d'urée par réaction d'ammoniac et de dioxyde de carbone à des températures et pressions élevées, dans lequel au moins une zone extensive a été soumise à une corrosion, le fonctionnement de cet équipement étant rétabli par une réparation comprenant la production d'une garniture scellée hermétiquement sur la zone soumise à la corrosion par un ou plusieurs élément(s) à double couche conforme(s) à l'une quelconque des revendications 10 et 11, mis en forme de manière appropriée et soudés entre eux.

15. Equipement chimique destiné à fonctionner normalement à une pression élevée ou moyenne dans une usine industrielle pour la synthèse d'urée, en contact avec des fluides de processus potentiellement corrosifs dans une usine de production d'urée, comprenant, à l'intérieur, une garniture métallique anticorrosion qui comprend un ou plusieurs élément(s) laminaire(s) à double couche conforme(s) à l'une quelconque des revendications 10 et 11.

16. Equipement chimique selon la revendication 15, consistant en une colonne de fractionnement ou un réacteur.

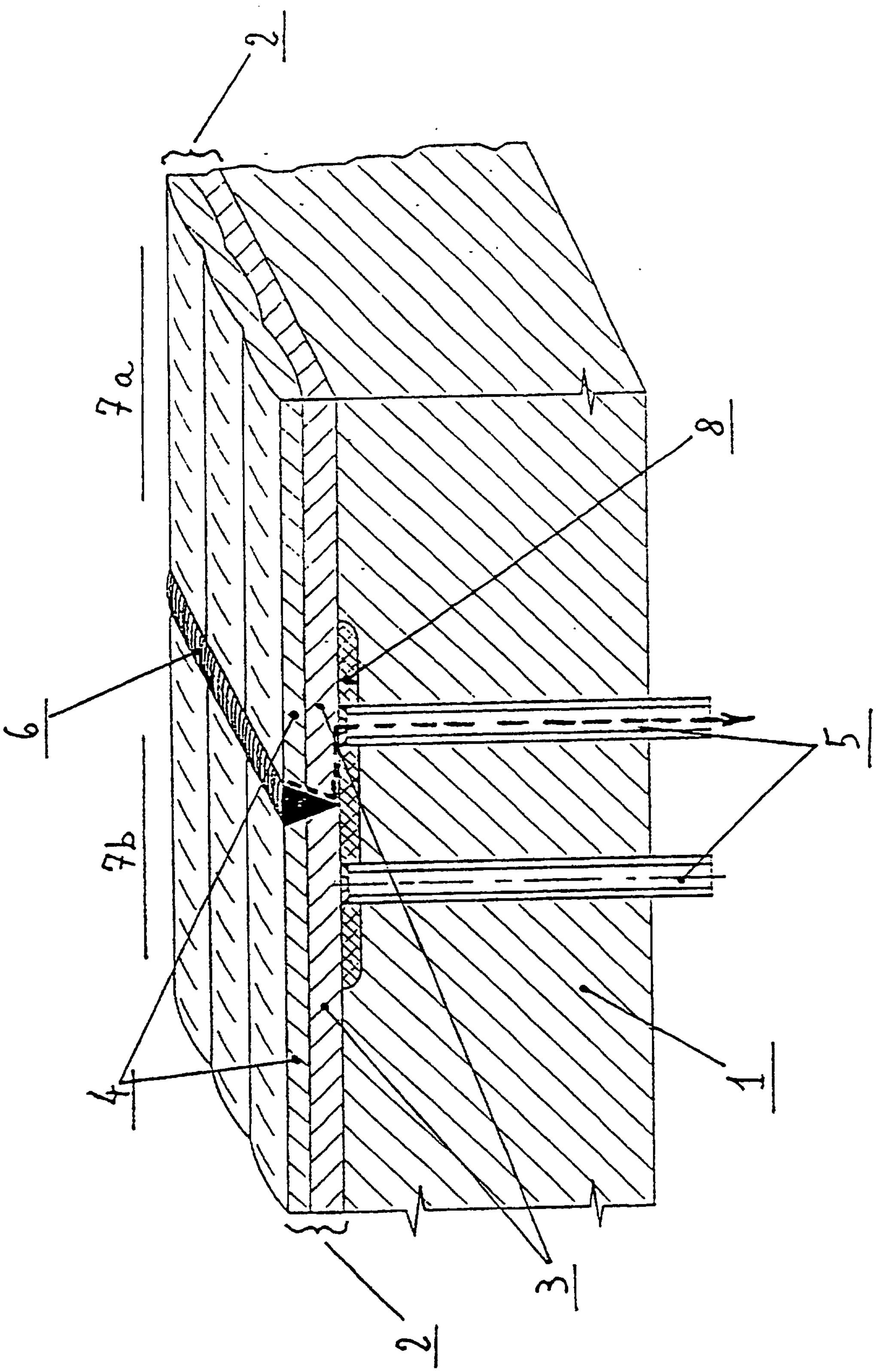

Fig. 1