July 26, 1966 J. H. OLSON 3,262,490

PROCESS FOR JOINING METALLIC SURFACES AND PRODUCTS MADE THEREBY

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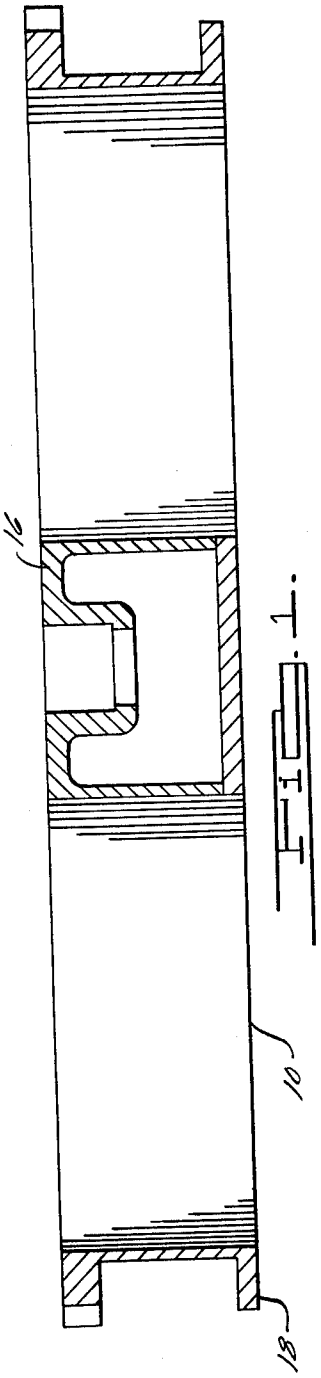


Fig. 1.

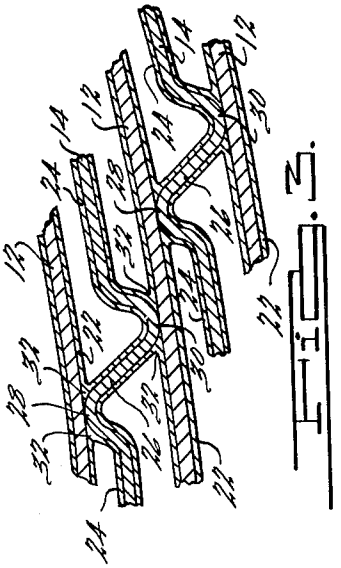


Fig. 3.

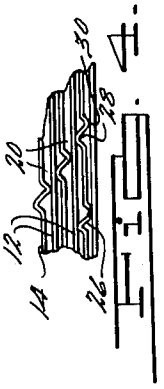


Fig. 4.

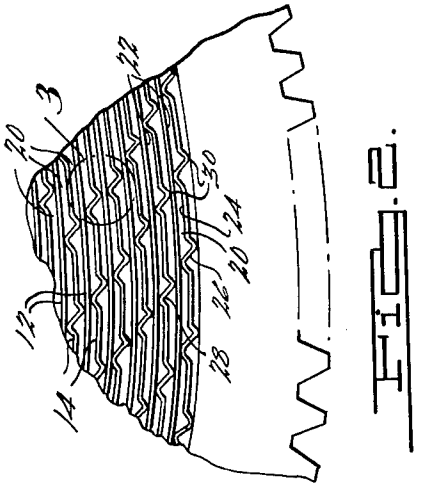


Fig. 2.

INVENTOR.
John H. Olson
BY Harness & Harris
ATTORNEYS

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PROCESS FOR JOINING METALLIC SURFACES AND PRODUCTS MADE THEREBY

John H. Olson, Westfield, N.J., assignor to Chrysler Corporation, Highland Park, Mich., a corporation of Delaware

Original application Apr. 21, 1954, Ser. No. 424,680, now Patent No. 3,129,502, dated Apr. 21, 1964. Divided and this application Sept. 20, 1963, Ser. No. 310,256

2 Claims. (Cl. 165—10)

The present application is a division of my copending application Serial No. 424,680, filed April 21, 1954, now Patent 3,129,502, granted April 21, 1964.

This invention relates to methods for securely, firmly, and intimately joining or uniting metallic parts of a single or plurality of members by a metal bond. It is especially concerned with an electroless plate bond of such parts; and with the heat treatment of parts so bonded. Also with the simultaneous electroless plating and bonding of metallic parts. It has particular application to parts of a ferrous character. Moreover, it relates to novel structures such as heat exchangers, and rotary regenerators for gas turbines comprising a composite of thin sheets of irregular or other shaped character, in the making of which these bonding methods are employed to provide a metal bond substantially impervious to the passage of gas and which also may be hard.

It is known to join metallic surfaces by soft soldering, hard soldering, (silver brazing) or copper brazing. These procedures require the use of a flux and/or an inert atmosphere and a metal or alloy of lead, tin, brass, copper, silver, phosphorous. Moreover, since the brazing must take place at high temperatures (over 2000° F. in the case of copper brazing) distortion, buckling and grain growth in the iron structure can easily occur at such high temperatures when joining metals such as low carbon steels.

My invention avoids these difficulties in that neither high heat nor melting of the bonding metal is essential to effect a bond. However, these steps may be employed as supplemental procedures in my invention for further advantages that will flow therefrom but in such cases one or more of the difficulties of distortion and grain growth are inhibited because of the basic steps which precede such heating and/or melting and because lower temperatures are then feasible. Moreover, in my invention the resulting product has an oxidation resisting plate protecting all iron surfaces.

Broadly stated, my invention comprises bringing the portions of the parts to be bonded into juxtaposition, preferably into contact with each other, better yet pressure contact, and electroless plating these parts contiguous with these portions, while maintaining the parts in their juxtaposed relationship, for a sufficient time to form an adherent connecting web of fillet of deposited alloy metal between the portions to be bonded. The plating is carried out by immersing the portions to be bonded, while maintained as stated above, in an electroless plating bath or fluid whereby under the catalytic action of the metal of which the parts are made or of some other metal applied thereto, the bonding metal is deposited out of the bath and onto the portions of the parts to be bonded. The action is one of chemical reduction. Not only are the immersed parts plated with the metal given up by the bath, but where the action is continued for a sufficient time, tying webs of fillets are formed contiguous with the portions to be bonded which adequately join and hold the parts together.

By "electroless plating" I mean a chemical plating process, examples of which are hereinafter given wherein an alloy metal comprising nickel and phosphorus is deposited from a plating bath without the use of electric current and by reason of a catalytic metal present in or on the structure to be plated.

Electroless plating is further advantageous in that the alloy deposits obtained have a melting point facilitating fusion of the plate bond.

In actual practice I have found that a plate of at least about 0.0003 inch thickness is necessary to produce a satisfactory mechanical bond. By a satisfactory mechanical bond I mean one which will permit ordinary handling of the bonded structure and its subjection to reasonable vibration and/or shock without failure of the bond or stated otherwise, I mean a bond which permits use of the bonded part for its intended purposes. For example, where the bonded parts are to be used for heat exchangers, the bond should provide a seal for the passage of air and combustion gases and be good enough to prevent the gases from diffusing through the joint. It will be understood that the thickness will be influenced somewhat by how well the parts are held together during plating, that is to say, whether or not there is pressure contact between the parts.

Heat treatment of the bonded part at a temperature below the melting point of the plate will improve the strength and hardness of the joint and may in certain cases permit the use of plates of lesser thickness than that above. In fact, a plate of even about 0.0002 inch thickness will give a satisfactory mechanical bond if the surfaces joined by the plate are thereafter heated to the fusion temperature of the bonding metal plate, this being preferably carried out in a non-oxidizing atmosphere. This will also render the bond substantially non-porous. It may also be noted that although the plate will flow, the parts will not shift during holding since there is a substantially parent metal-to-metal contact. This is of importance where a large number of parts must be bonded together within a limited space.

The combination plating and heating is also of especial significance where a strong metal bond is required in a structure employing readily oxidized parts such as mild or low carbon steel and with a minimum plate. The plating operation renders the surfaces of the bonded structure resistant to oxidation during subsequent heating and the plate bond holds the parts together during heating. Moreover, by obtaining an alloy plate bond, a sufficiently low melting point may be available such that the structure, especially where of a low carbon steel, may be plated and heated without deleterious buckling, distortion or grain growth on the steel during heating. Tensile readings on two sheet test specimens indicate a joint strength in tension of 20,000 to 23,200 lbs. per sq. in.

Where the heating procedure is employed, the bond may be effected by either first bonding the parts by plating and then heating or by first separately plating the parts and then heating the parts while held together. The latter procedure requires good pressure contact between the surfaces to be bonded and cannot be used, for example, where the plated parts would have to be shaped after plating as the plate deposit does not permit of sharp bending. Moreover, where the parts are separately plated before joining, the heating step should be carried out in an atmosphere which will not oxidize the metal, that is to say, a neutral atmosphere, for instance in an atmosphere of hydrogen or cracked gas. Where the parts are however bonded by plating, heating in a neutral atmosphere preferred is not always necessary.

The plating process I use and which is generally known in its broad aspects involves the reducing action of hy-

pophosphites in a solution of nickel salts at 180° F. or higher preferably 180–200° F. or above in the presence of certain catalytic metals. The reaction may be expressed generally by the following equations:

$$NiCl_2+NaH_2PO_2+H_2O\rightarrow Ni+2HCl+NaH_2PO_3$$

or

$$NaH_2PO_2+H_2O\rightarrow NaH_2PO_3+H_2$$

The hypophosphite undergoes oxidation and the nickel is reduced. No electric current is involved in the deposition. The nickel plating process may be carried out with acid or alkaline solutions. The deposition of nickel may be carried out in conjunction with any catalytic material which will initiate at its surface the above reaction. Iron, nickel, gold, cobalt, aluminum are especially good catalysts. Other metals which are non-catalytic or which are temporarily passivated catalytic metals, such as brass, copper, and platinum, may be nickel plated by special methods, such as by using particular alkaine plating solutions, omitting ammonium salts for brass and copper; making momentary contact of the surface of the parts with a more electronegative metal such as aluminum, iron or steel or by depositing minute amounts of catalytic metal such as palladium or rhodium on the non-catalytic one by dipping the parts after cleaning, into a solution containing one of these metals. Once the plating starts, the reduction continues on the phosphorous-nickel first deposited. Zinc gives poor deposits and lead and cadmium are not favorably affected. It has been found, however, that the commonly used zinc immersion pre-treatment if applied to aluminum or alloys such as 3S and 24S alloys (aluminum-manganese and aluminum-copper respectively) provides a good base for securely bonding electroless nickel-phosphorous.

Although similar plating procedures using alkaline baths may be followed with respect to obtaining a cobalt plate, these deposits have been found to be porous and of poor physical character not suitable for the physical bonds required in this invention.

An object of my invention is to join or unite metallic parts of a single or plurality of members by a metal bond produced by electroless plating.

Another object is to join or unite metallic parts as aforesaid and to subsequently subject the plated composite structure to heat treatment to increase the strength of the bond.

Still another object is to simultaneously electroless plate and bond metallic parts by a metal bond.

A specific object is to bond metallic parts by first electroless plating the same and then heating the parts to the melting point of the plate while holding the parts in face-to-face contact to effect the bond.

A further object is to join or unite metallic parts in accordance with any of the preceding objects, and to subsequently subject the plated structure to heat treatment at or above the fusion temperature of the bonding metal of the plate but below the fusion temperature of the bonded parts.

Still a further object is to join or unite parts composed of mild or low carbon steel or of which one of these is a member, by a strong solid bond or joint of metal impermeable to the passage of gas, by electroless plating the parts to bond the same and provide a corrosion and oxidation resisting metal protective layer for the steel and then heating the parts to the melting point of the bonding metal but below that of the steel parts.

Another object is to provide a rotatable regenerator structure for a gas turbine power plant or the like comprising a cellular core having a multiplicity of elongated cells defined by wall portions abutting each other along seams closed to the passage of gas by a metallic bond or layer comprising an electroless plate.

A further object is to provide a regenerator structure as in the preceding object wherein the abutting parts are bonded by a fused electroless metal plate.

These and other objects of my invention will be apparent from the following description and the accompanying drawings wherein I have exemplified my invention as applied to a regenerator or heat exchange structure such as disclosed in the copending application of George Huebner et al. Serial No. 389,094, filed October 29, 1953.

In the drawings:

FIGURE 1 is a sectional view of a rotatable regenerator unit for the power plant of a gas turbine engine;

FIGURE 2 is a detail sectional view of a portion of the core of the regenerator of FIGURE 1;

FIGURE 3 is an enlarged sectional view of the circled portion in FIGURE 2 showing the manner of bonding adjacent layers of the regenerator core; and

FIGURE 4 is a detail sectional view of a composite core made up of substantially flat elements.

As seen in FIGURES 1 and 2, the regenerator core **10** smooth sheet metal stock which may be of a mild or low may consist, for example, of a plurality of layers **12** of smooth sheet metal stock which may be of a mild or low carbon steel composition and a plurality of layers **14** of corrugated metal sheets which also may be of a mild or low carbon steel composition, which layers **14** alternate with the layers **12**. These layers **12** and **14** are arranged concentric to or in a spiral about a hub **16** and surrounded by a confining rim member **18**. The layers **12** and **14** in the core structure **10** may be constituted of concentric rings, or the core may be made up by a spiral winding of a pair of continuous sheets forming the layer **12** and **14**.

As seen in FIGURE 2, the alternate arrangement of corrugated and flat layers **14** and **12** respectively form passages or recesses **20** extending axially of the core adjacent the joints **28**, **30** formed at the contacting portions there shown these layers. Each of these passages **20** is defined by spaced wall portions **22** and **24**, respectively, of the layers **12** and **14**, respectively, and by spaced corrugations **26** of the layer **14**. The corrugations **26**, as shown, have offset peak portions at the joints **28**, **30** in contact with adjacent layers **12** of the core, these peak portions defining apices of the passages or recesses **20** with the layers **12**. When this core is treated in accordance with the present invention, each of the contacting peaks of the corrugations **26** will be bonded to the adjacent layer **12**, as seen in FIGURE 3, by webs or fillets **32** of metal in said apices of the passages **20** which securely hold these layers together and provide a gas-impervious joint between the adjacent passages **20**.

The following examples will serve to illustrate the manner of carrying out my invention:

Example I

A rectangular core section 1" x 2.2" x 3" of the layer character shown in FIGURE 4 and consisting of **93** plates was suitably held in a fixture to obtain pressure contact between the adjacent sheets at the peak of the corrugations and immersed in an electroless chemical solution of 4.7 liters capacity for 12½ hours. The section was made up of alternate layers of corrugated and flat sheets of low carbon steel of 0.002" thickness and contained 1230 sq. in. of surface area disregarding the corrugations.

The bath was of the acid type and contained the following ingredients:

10 grams per liter of nickel chloride ($NiCl_2\cdot 6H_2O$);

10 grams per liter of sodium hypophosphite

$(NaH_2PO_2\cdot H_2O)$

8.9 grams per liter of citric acid ($C_6H_8O_7\cdot H_2O$);

15 grams per liter of dibasic sodium phosphate (Na_2HPO_4).

The dibasic sodium phosphate in this bath serves as a buffer maintaining the pH at 4 to 6. The amount of citric acid employed is sufficient to make a new acid bath having a pH of about 6. The nickel chloride and sodium hypophosphite react upon immersing the steel structure in the bath to give a catalytic deposit of nickel-phos-

phorous on the steel. This plating bath has the ability to plate at the rate of about 0.0002 inch per hour where the area plated does not exceed about 20 sq. inches per liter of solution.

The section was maintained in the bath for twelve hours after which it was removed and found to have a plate layer of nickel-phosphorous of about 0.0005 inch thick. Based on chemical tests the amount of phosphorous in the plate was about 14.15 to 14.75 percent.

An examination of the section showed the adjacent layers to have their faces plated and the peaks of the corrugations bonded to the adjacent layers by fillets of the plating metal. These fillets were continuous throughout the length of the core and the plating was substantially uniform. There was a good physical bond between the plates and the assembly was free of distortions. A structure of this character is suitable for heat exchange purposes.

Example II

A core section plated as in Example I was heated for twenty minutes at 1650° F. in a neutral atmosphere (cracked gas). At this temperature the metal of the plate was molten and flowed towards the joints between the corrugations of the layers **14** of the section and the contacting faces of the layers **12**. There was a tendency for the plate between the corrugations to become somewhat thinner than the original deposit, some of the plate at these points shifting to the joints between the adjacent layers. The resulting structure showed improved structural strength due to the flow of plate metal to the joints to produce fillets of increased section. The hardness of the plate was reduced from about 480 Vickers to about 250 Vickers, this also being believed to enhance joint strength and to improve ductility.

Example III

A regenerator unit core, as seen in FIGURES 1 and 2, suitably held in a fixture which may be the rim **18**, was immersed in an electroless chemical plating solution of 86-gallon capacity. The unit was 20½" in diameter and 3" thick. It was made up of alternate layers of corrugated and flat sheets of low carbon steel of 0.002" thickness and contained 725 sq. ft. of surface area disregarding the corrugations.

The bath which was of the acid type, contained the following ingredients:

10 grams per liter of nickel chloride ($NiCl_2 \cdot 6H_2O$);
10 grams per liter of sodium hypophosphite

($NaH_2PO_2 \cdot H_2O$)

8.9 grams per liter of citric acid ($C_6H_8O_7 \cdot H_2O$);
37.5 grams per liter of dibasic sodium phosphate (Na_2HPO_4).

The dibasic sodium phosphate in this bath serves as a buffer maintaining the pH at 4 to 6. The amount of citric acid employed is sufficient to make a new acid bath having a pH of about 6. The nickel chloride and sodium hypophosphite react upon immersing the steel structure in the bath to give a catalytic deposit of nickel-phosphorous on the steel. This plating bath has the ability to plate at the rate of about 0.0002 inch per hour where the area plated does not exceed about 20 sq. in. per liter of solution.

The regenerator unit was maintained in the bath for twelve hours after which it was removed and found to have a plate layer of nickel-phosphorous at least 0.0004 inch thick. The adjacent layers had their faces completely plated and the peaks of the corrugations were strongly bonded to the adjacent layers by fillets of the plating metal which fillets were continuous throughout the length of the core. The physical bond was good and the structure was free of distortion.

Example IV

A composite structure of alternate flat and corrugated sheets, five in number, 1" x 3" and having a surface area of 30 sq. in. excluding the corrugations, were held together by a wire and immersed in a nickel-phosphorous plating bath of alkaline character for four hours and upon removal was found to have a plate thickness of 0.0008".

The solution contained the following ingredients:
30 grams per liter nickel sulphate ($NiSO_4 \cdot 6H_2O$);
50 grams per liter of ammonium chloride (NH_4Cl);
100 grams per liter of sodium citrate

($Na_3C_6H_5O_7 \cdot 5H_2O$)

10 grams per liter of sodium hypophosphite

($NaH_2PO_2 \cdot H_2O$)

To the above was added enough ammonium hydroxide (NH_4OH) to bring the pH value of the solution to about 9.0. The bond was satisfactory.

Example V

A composite structure as in Example IV but made up of four alternating flat and corrugated low carbon steel sheets 1" x 1" held together by a wire, was plated in a solution of the same character as that of Example IV but wherein 30 grams of nickel chloride ($NiCl_2 \cdot 6H_2O$) was substituted for the nickel sulphate. This structure was maintained immersed in the solution for one hour. The plates were bonded together by a nickel phosphorous plating of 0.00031" thickness.

Example VI

A structure as in Example V was immersed in the solution for one-half hour instead of one hour and upon removal was found to have a plate thickness of 0.00021". Although this plate bonded the layers together, it was insufficient to provide a satisfactory mechanical bond. However, upon heating the bonded and wired structure to 1850° F. in an inert atmosphere of dry hydrogen for a short time, the character of the bond was sufficiently improved to be mechanically satisfactory.

Example VII

A composite structure as shown in FIGURE 4 comprising a plurality of .038" thick mild steel flat sheets alternating with .002" thick corrugated sheets were held in a fixture and immersed for six hours in an acid solution consisting of 30 grams per liter of nickel chloride, 10 grams per liter of sodium hypophosphite, and 50 grams of sodium glycolate (also known as sodium hydroxa acetate) produced from 70% glycolic acid and a diluted sodium hydroxide solution containing 24 grams per 100 cc. of sodium hydroxide. The plates were bonded together by 0.0005" thick plate.

Example VIII

Two pieces of 1/16" diameter drill rod were wired together to form a 1" lap joint with a third piece 1" long. This was immersed in a solution as in Example I for 3½ hours. The plating thickness was 0.0003" on the sections of rod beyond the lap joint. After heating for one hour at 750° F. the wire was removed and the structure tested in tension. It was found that a weight of 417 grams could be supported before the joint failed. This would appear to correspond to an appreciable tensile strength.

Example IX

A heat exchange unit for the oil cooler of an automatic transmission had its heat exchange element plated by electroless nickel on its outer sides only and the halves of its split steel water housing plated by electroless nickel on all faces, by immersing in an acid solution according to

Example I. The nickel-phosphorous plate deposit was 0.001" thick. After plating, the parts were assembled and the casing parts held between clamps with their joint faces in abutment and the assembly heated to 1800° F., which is above the fusion temperature of the nickel-phosphorus plate. Heating was carried on in a non-oxidizing atmosphere such as cracked gas for one-half hour during which period the parts of the casing became securely bonded by the plate. This unit and a similar one which had been electroless plated after the housing parts had been bonded by copper brazing and not heated to the fusion temperature of the plate, were then tested for anti-corrosive properties by circulating a hot corrosive solution of salt through the units for 500 hours. This solution consisted of 30% alcohol, 70% water, and 522 parts per million of sodium chloride.

The two units were then cut open and examined. The copper brazed unit was found to contain numerous areas of rust whereas the plate-fused unit was free of any rust and in excellent condition. This indicates that heating of the nickel-phosphorus plate renders the treated structure highly resistant to corrosion. This improvement is believed due to the fact that heating of the plate eliminates any pre-existing porosity of microscopic cracks in the plate and such prevents penetration of the corrosive material to the under ferrous layer.

In the above processing, the baths were made up by heating the nickel hypophosphite and buffer salts to 190° F. but at all times remaining below the boiling point of this solution. The articles to be plated were then brought into contact with the solution as by immersing in the bath while preferably maintaining the bath at a temperature above 180° F. but below the boiling point of the solution (about 205° F.).

In operation of the bath it is desirable to replace the hypophosphite, nickel and the dibasic sodium phosphate after long periods of operation. The thickness of the ferrous sheets or structure plated is not important. They may be thin or thick. In the acid solutions the dibasic sodium phosphate may be replaced with the corresponding potassium or ammonium salt. The ammonium salt produces the highest plating rate but the deposit has larger crystals. Moreover, the potassium salt appears to give a somewhat faster plating rate than the sodium salt. In all cases a substantially uniform plate is obtained. It is found that the alkaline-type bath usually boils off ammonia and therefore is not as good as the acid bath from the practical operational standpoint.

In connection with the above examples, it has been found that the plate of Example I will contain about 14% phosphorous; that the plate of Example III will contain about 10 to 12% phosphorous; the plate of Example IV will contain about 2.9% phosphorous, and that the plate of Example VII will contain about 6½% phosphorous. Thus the amount of phosphorous in the nickel-phosphorous plate obtained by any invention may be varied between the amounts given by a proper selection of the solution and its contents.

From the foregoing description of my invention, it will be apparent that I have provided a novel and efficient method for joining metal parts by a metal bond and provide a metal bond whose composition is particularly adapted for the purposes described. The above description and examples are intended as illustrative only. Hence any modification of or variation therefrom or equivalent thereof which conforms to the spirit and intent of my invention and comes within the scope of the appended claims are contemplated.

I claim:

1. A metallic structure comprising a plurality of metallic parts arranged in a joint forming relationship whereby an elongated recess is formed between said parts having its apex in said joint, a substantially uniform and continuous layer of nickel phosphorous alloy having between 85 to 97.5% nickel and 2½ to 15% phosphorous produced by electroless plating over said parts contiguous said joint and providing a continuous substantially uniform fillet-like web in the apex of said recess, said layer bonding said parts together and providing a highly corrosion resistant and gas tight joint between said parts in said joint, said layer having a thickness of at least about 0.0002".

2. A metallic structure comprising a plurality of thin metal layers at least alternate ones of which are of undulated form providing adjacent elongated peaks and valleys, said layers being arranged with the valley portions of the undulated layers in substantial contact with portions of the immediately adjacent layers, the said layers forming adjacent elongated passages spaced by said substantially contacting portions, and an adherent connecting fillet-like web of metal between said layers adjacent said substantially contacting portions in said passages tenaciously bonding said layers together and providing a highly corrosion resistant and gaseous seal between said adjacent passages at said portions, said web consisting essentially of nickel phosphorous alloy having between 85 to 97.5% nickel and 2½ to 15% phosphorous produced by electroless plating, said web having a thickness of at least about 0.0002".

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ROBERT A. O'LEARY, *Primary Examiner.*

CHARLES SUKALO, *Examiner.*

A. W. DAVIS, *Assiistant Examiner.*