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3,455,014

METHOD OF JOINING BY PLATING ALUMINUM AND ALLOYS THEREOF

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FIG. 1

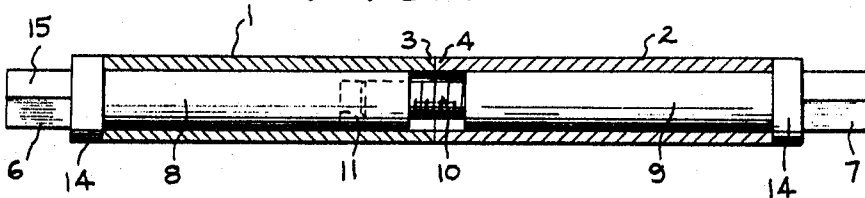


FIG. 2

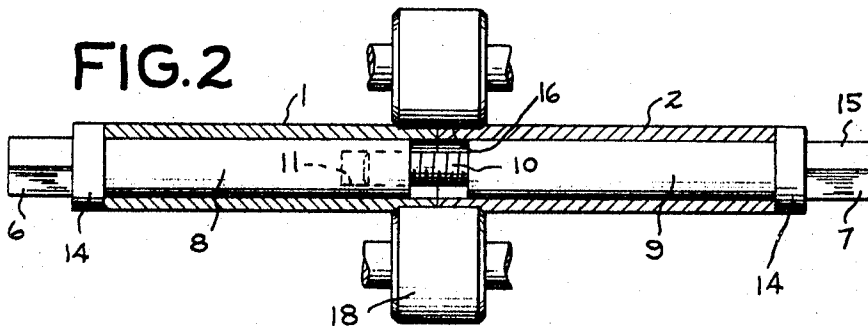


FIG. 3

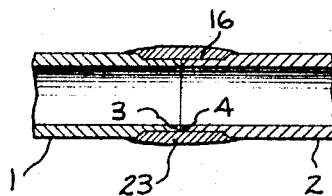
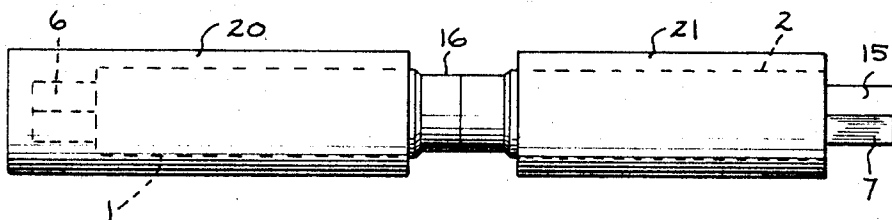


FIG. 4

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METHOD OF JOINING BY PLATING ALUMINUM AND ALLOYS THEREOF

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Continuation-in-part of application Ser. No. 479,450,

Aug. 13, 1965. This application Jan. 11, 1968, Ser.

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U.S. Cl. 29—460

8 Claims

ABSTRACT OF THE DISCLOSURE

The method of joining by deforming the abutting edges of two articles of aluminum, or alloys thereof, and uniting the articles by plating in the deformed area including the initial electrodeposition of an electro-tin strike from a plating bath consisting essentially of an aqueous solution of potassium stannate.

Cross reference to related application

This application is a continuation-in-part of my copending application Ser. No. 479,450 filed Aug. 13, 1965, now abandoned and assigned to the same assignee as the present invention.

Background of the invention

There are two basic commercial pre-treatments generally used in providing adherence of electrodeposited metallic coatings on aluminum. One involves immersion zinc coating and the second immersion tin coating. Both pre-treatments depend on obtaining an initial adherent immersion coating on the aluminum. One pre-treatment is based on obtaining an immersion zinc coating. The quality of the adherence of subsequent electrodeposits and the resistance to corrosion of aluminum articles finished by the zinc immersion process leaves much to be desired. In fact, to be successfully applied, the immersion zinc process requires close control of a large number of treating and plating steps and even under the best control conditions the resultant zinc coatings are generally not as adherent as the immersion tin coating.

The immersion tin plating of aluminum also results from the fact that aluminum is above tin in the electromotive force series of metals and therefore will displace tin from its solution. Although some aluminum alloys, particularly the copper containing aluminum alloys, are tinned readily by immersion in an alkali stannate bath, other alloys and pure aluminum tend to yield blistered coatings. The "tinning" of pure aluminum and such other alloys has required the use of special immersion baths containing copper ions added for example in the form of copper cyanide. This immersion tin deposit is believed to contain some copper as is more fully described in Patent 3,108,006 Kenedi.

The selectivity of the immersion tin treatment is due to the fact that as aluminum is alloyed with various other metals in various quantities, the single electrode potential of the aluminum in the bath, which is the driving force for the tin immersion deposit, changes. Thus the potential for immersion tin deposition is different for each aluminum alloy and therefore at least some of the conditions of alkali concentration, free copper cyanide concentration, temperature, time of immersion, etc., must vary with each alloy. Processing alloys with different potentials together through the same process cycle at the same time becomes most difficult or impossible. Further, the use of

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copper, copper alloy or other metal rack fixtures (other than aluminum, that is) commonly desired for subsequent electrodeposition of copper and other metals results in poor adhesion adjacent to the rack contact with the aluminum being processed by any immersion process.

Summary of the invention

The present invention is broadly directed to the provision of an aluminum plating process which is equally effective for plating articles of pure aluminum, articles of aluminum alloys containing copper or other alloying ingredients as well as aluminum or aluminum alloy surfaces adjacent or in electrical contact with other metal surfaces such as a copper surface.

The process is characterized by an initial *electrodeposit* of tin from a potassium stannate electrolyte in such a way as to positively exclude an immersion deposit of tin. This step is effected either by introducing the aluminum or aluminum alloy articles into the tin electrolyte electrically "hot" or by making electrical connection very soon, i.e., within a few seconds, after entering the tin electrolyte. The initial electrodeposit of tin is followed immediately by application of an electrodeposit of copper effected by transferring the article directly from the potassium stannate electrolyte, without an intervening rinse, to a cuprous cyanide bath with the article entering the cuprous cyanide electrolyte electrically "hot."

The plating process of the present invention is particularly applicable to the plating of an aluminum surface in electrical contact with another metal surface, such as a copper surface, and thus can be advantageously used in the production of an electroplated joint between the copper and aluminum tubular components of a copper-aluminum connector for use in a refrigeration system employing the procedure illustrated in the accompanying drawing.

Brief description of drawing

FIGURE 1 illustrates an initial step for assembling the tubular copper and aluminum components in end-to-end relationship in the manufacture of a copper-aluminum connector;

FIGURE 2 illustrates a means for carrying out the reduction of the assembled tubes in the joint area;

FIGURE 3 illustrates the preparation of the assembly for plating of the joint area; and

FIGURE 4 is a cross-sectional view of a portion of the finished connector.

Description of preferred embodiments

In the application of the present invention to the plating of aluminum articles or aluminum articles in electrical contact with copper or other metal surfaces, the surfaces to be plated are first cleaned to remove oxides and other materials which may interfere with the adhesion of subsequent electrodeposits. These cleaning procedures are well known and generally include treatment with a solution of any of a number of metal cleaning mixtures containing sodium hydroxide, sodium carbonate, sodium silicate, sodium phosphate or other alkalies plus surface active agents.

After a cold water rinse to remove the alkaline cleaning compound, the surfaces to be plated are preferably also treated with an acid for the purpose of neutralizing the residual alkali and slightly etching the surfaces. A mixture of nitric acid and hydrofluoric acid or other ionizable fluoride compound has been found to be particularly suited to operate on both the aluminum or its alloys and other metals such as copper simultaneously. While a wide range of proportions and concentrations may be employed, an example of a suitable acid treatment is immersion for 10 to 60 seconds at room temperature in

a bath containing one part concentrated nitric acid, two parts water plus about 45 grams per liter of sodium bifluoride. Also in accordance with the usual plating practices the residual acid is thereafter removed by rinsing with cold running water before proceeding with the subsequent electroplating steps.

A tin strike is then applied by electrodeposition thereby obtaining an adherent electrodeposit on aluminum and a variety of aluminum alloys having no tendency to blister or peel. The tin strike or deposit is prepared by the use of a solution of potassium stannate and insoluble stainless steel or equivalent anodes. Successful tin deposits have been obtained employing plating solutions containing at least 35 grams per liter and up to 500 grams per liter of more of potassium stannate in water at room temperature, current densities of from 1.5 to 5.0 amps per square decimeter, pH of from 10 to 14 and plating times from 10 to 55 seconds. However, other conditions of concentration, temperature, time and current density may also be used. Also copper, for example copper cyanide, can be present in this bath but it is not required or desired.

In the next step, the tin coated article is transferred directly from the tin bath, that is without rinsing, into a copper plating bath to apply over the tin deposit a copper layer of sufficient thickness to completely cover or mask the aluminum surfaces. For satisfactory results, it is essential that parts enter the copper plating bath "hot," that is already connected to a negative electrical potential before immersion into the plating bath. Copper plating baths suitable for this deposition are preferably of the cyanide type well known in the art. One example of a suitable bath is an aqueous solution of about 15 grams per liter of copper cyanide, 15 grams per liter of free sodium or potassium hydroxide. Drag over of tin salts from the tin bath will in time convert the copper bath to a copper-tin alloy plating bath so that during use the copper plating bath may reach an equilibrium tin content at no more than the concentration of alkali stannate in the electro-tin strike bath. A copper deposit from an alloy bath also containing 100 grams per liter of $K_2SnO_3 \cdot 3H_2O$ has the appearance of copper. Alternatively some sodium or potassium stannate may initially be added to the copper plating bath although in general it appears preferable to start without any tin salt addition and make no direct addition of tin salts to the copper bath in use.

Copper anodes are preferably employed in the copper plating bath and the copper deposition is continued at a current density of 1.5 to 5.0 amps per square decimeter until there is obtained an electrodeposit which completely covers and seals the aluminum surfaces from attack by subsequent alkaline or acid plating solutions. Four to eight minutes plating time is usually required for this purpose.

The copper layer forms the base for the successful electrodeposition of any of a number of other metals such as nickel, tin-nickel, chromium, etc. deposited from suitable plating baths employing the usual plating conditions.

In addition to pure aluminum, a large number of wrought and extruded aluminum alloys containing one or more of the alloying elements; copper silicon, manganese, magnesium, chromium and zinc have been successfully plated using the subject process without regard to the alloying elements. For example, employing tin plating baths of the same composition, that is baths containing about 100/liter of $K_2SnO_3 \cdot 3H_2O$ and adjusted to a pH between 11.5 to 12.5 by appropriate additions of potassium acid carbonate or potassium hydroxide and operating at room temperature and at current densities of from 1.5 to 5 amperes per square decimeter for a plating time of from 10 to 30 seconds, aluminum alloys 1100, 3003, 2024, 5052, 5357, 5457 and 6061, 6063 and 7075 all behave or react in similar manners. All accept deposits of a triplex copper-nickel-chromium coating over the copper layers which showed no evidence of blistering when heated to 500° C. and quenched in water. In fact, no commonly

available aluminum alloy has been found which cannot be plated successfully by this procedure.

As has been indicated previously, the wide range of usefulness of the subject process is best illustrated in its application to the manufacture of tubular copper-aluminum connectors for refrigeration systems.

The fact that two metal components or parts such as two tube segments may be joined or bonded together by an electrodeposited or plated layer of metal is well known. However, the practical use thereof has been restricted to the joining of parts composed of the same metal or parts composed of different metals which can be readily plated. For the joining of an aluminum segment to a second metal segment, it has been proposed that the aluminum to be pre-coated, as by plating with a copper layer, and the joining be accomplished either by soldering, brazing or the application of a joining or bonding layer of electrodeposited metal to the two surfaces one of which is the copper-coated aluminum surface. However, such joints have involved the additional step of pre-coating the aluminum surface which increases the cost of the final product.

In accordance with a specific aspect of the present invention, a copper-aluminum connector is made as follows. An aluminum tube and a copper tube are assembled on a fixture adapted to position the two tubes in end-to-end butting relationship and to maintain the abutting ends of the tube in firm mechanical engagement. Thereafter the assembled tubes are subjected to a series of operations, the first of which is a mechanical working, preferably a rolling and/or burnishing, of the joint area, that is the portions of the two tubes adjacent to and including their contacting ends, to reduce and equate their exterior diameters in the joint area and to provide in this area a smooth and substantially continuous exterior surface to which there is then applied an electrodeposited metal layer including an electrodeposited tin strike, providing the sole mechanical bond between the two tube components. This copper layer forms the base for the subsequent electrodeposition of a metal layer of sufficient thickness and strength to join the two tubular components. To this end, there may be deposited on the copper coating a layer of any relatively strong metal such as a thicker layer of copper or a layer of nickel. Best results have been obtained by employing a nickel layer of sufficient thickness to provide a joint area having a greater tensile strength than the aluminum tube.

The detailed procedure of making such a connector is illustrated in the accompanying drawing in which FIGURE 1 illustrates an initial step which comprises assembly of an aluminum tube segment 1 and a copper tube segment 2 on a fixture adapted to maintain the two tubes in coaxial alignment with their adjacent or contacting ends 3 and 4 held in firm mechanical engagement with one another. The simple fixture illustrated comprises cooperating metal members 6 and 7 respectively including shaft portions 8 and 9 adapted to be inserted in the aluminum tube 1 and the copper tube 2. The adjacent or inner ends of these shafts 8 and 9 are provided with means such as a threaded portion 10 on one of the two members adapted to be threadably received in a bore 11 in the end of the other member. Each of the members also include a shoulder 14 adapted to engage the free or outer end of one of the tubes 1 and 2 so that when the threaded portion 10 is screwed into the stud receiving bore 11, the shoulders 14 bearing against the outer ends of the two tubes cause the inner or contacting ends 3 and 4 to be brought into firm mechanical engagement. Squared ends 15 on each of the members 6 and 7 are provided for tightening the fixture and thus provide the desired mechanical engagement between the contacting ends of the two tubes.

A rolling tool or similar means is then employed to reduce the exterior diameter of the tubes in the joint area which is generally indicated by the numeral 16 and

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which includes the contacting ends 3 and 4 and the adjacent portions of both tubes to a diameter equal to or preferably slightly less than the original diameter of either of the tubes. In the embodiment of this step shown in FIGURE 2 of the drawing, a plurality of rollers 18, preferably three rollers are employed and these rollers are slowly brought together as the assembly is rotated. The results of the operation are the reduction of the exterior portions of both tubes in the joint area to the same diameter to provide a smooth continuous surface throughout the joint area. During this mechanical reduction of the joint area, the softer aluminum also tends to fill any voids or spaces between the two contacting ends 3 and 5.

While this reduction of the joint area is essential, the amount of reduction is not particularly critical provided there is sufficient reduction to provide a void-free, smooth continuous surface within this area. For example, in joining of copper and aluminum tubing of $\frac{5}{16}$ inch nominal outside diameters, excellent results are obtained when the exterior diameter in the joint area is reduced to 0.310 inch.

The assembly, with the tube segments supported on the fixture, is then ready for the application to the joint area of a bonding electrodeposited layer of metal. Prior to the actual plating, the portions of the tubes and fixture on which no plating is desired are first shielded by suitable non-conducting shields. For example, the portion of the assembly including the aluminum tube 1 is covered with a cup-shaped shield 20 which completely encloses the exposed outer end of the fixture member 8 and all of the aluminum tube 1 with the exception of the portion thereof forming the joint area 16. Similarly a tubular shield 21 is positioned over the copper tube 2 leaving exposed only the copper component of the joint area 16 and the extreme end 15 of the fixture member 9 which is thereafter employed to make electrical contact with the assembly during the plating operations.

The shielded assembly, or a plurality of such assemblies held on a common plating rack, is then processed through a cycle of cleaning and plating operations to create an electroformed or electrodeposited metal coupling 23 which separately joins the aluminum and copper tubes.

A satisfactory bonding of the aluminum tube to the copper tube by an electrodeposited metal layer depends primarily upon the preparation of a satisfactory bond between the aluminum surface component of the joint and the electrodeposited metal layer due to the plating problems which are substantially unique to an aluminum surface and which result from the presence of the adherent oxide coating present on this metal and the activity of the aluminum in many plating solutions.

Numerous tests have indicated that neither a preliminary immersion zinc coating of the aluminum nor an immersion tinning of the aluminum prior to the application thereto of a copper or similar electrodeposit can be employed for the preparation of an electroplated copper-aluminum joint. More specifically, it has been found that in order to prepare a strong, heat resistant joint between the aluminum and copper components of the assembly, it is necessary to apply to the joint area a relatively thin electro-tin coating or in other words a tin strike by electrodepositing the tin from an alkali stannate solution and to follow this tin coating by the immediate application of a copper layer of a sufficient thickness to mask or completely cover the tin-coated aluminum surface. More specifically, it has been found that unless the initial metal coating of the joint area involves the application of an electrodeposited tin coating, acceptable adhesion of the final plated layer to the aluminum surface is not obtained. For example, attempts to employ immersion zinc coatings in the joining of the tubes have resulted in a complete lack of adhesion to the aluminum of any subsequent coating even in the absence of heat. Apparently the presence of copper adjacent to the aluminum does not permit the production of an adherent immersion zinc coating on the aluminum.

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Similar results were obtained in attempts to use immersion tin coatings using the accepted commercial procedures which work well on aluminum and aluminum alloys by themselves. With copper adjacent to the aluminum, it was impossible to proceed beyond the initial deposition of immersion tin because of a complete lack of adhesion of the tin layer to the aluminum.

Successful results are obtained employing the subject electrodeposited tin strike. As has been indicated heretofore, there can be used a solution of 35 or more grams per liter of potassium stannate, insoluble stainless steel anodes, current densities of from 1.5 to 5.0 amps per square decimeter and plating times of from 10 to 55 seconds.

To provide a joint having sufficient strength, a layer of copper of sufficient thickness to provide this strength may be plated onto the masking copper layer thereon either from the same copper plating bath or a different copper plating bath.

Preferably however the copper plated assembly is rinsed with cold running water to remove the cyanide solution, immersed in a suitable acid solution such as a 5 to 10% solution of fluoboric, sulfuric or hydrochloric acid to neutralize the remaining alkalis, rinsed with clear water to remove excess acid and thereafter provided with a nickel plate capable of producing a strong ductile electroformed coupling between the aluminum and copper copper components of the connector.

A suitable nickel plating bath is the nickel sulfamate bath widely used commercially for providing a nickel plate over a copper base. For example, preferably the nickel sulfamate bath contains, per liter of aqueous solution, nickel sulfamate equivalent to about 90 grams of nickel (as metal), about 30 grams of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and about 50 grams of boric acid. The bath is preferably operated at a pH of from 3.5 to 5.0 and a temperature of about 50° C. The current density and hence the rate of deposition of nickel will depend upon the method of operating the nickel plating bath. For example, with air agitation of the bath, current densities, such as a current density not over 25 amperes per square decimeter of surface being plated should be used in order to obtain a relatively smooth ductile nickel deposit. By rotating the cathode during the plating operation, higher current densities up to about 50 amperes per square decimeter may be employed to obtain a faster deposition of nickel. Using solution circulation involving the directing of submerged streams of solution through one or more jet nozzles positioned within the bath permits the use of even higher current densities of up to about 60 amperes per square decimeter for the production of smooth ductile nickel layers. The nickel layer should of course be of a thickness sufficient to provide a strong joint having a strength at least equal to or greater than the aluminum component of the connector. To this end, a nickel layer of about 0.010 inch has been found to be ample for tubing having a diameter of about $\frac{5}{16}$ inch and a wall thickness of 0.040 inch.

Copper-aluminum connectors produced by the electroforming technique described herein are cheaper to produce than butt welded connectors. Since the electroformed connector is one integral piece of metal and all of the bonds between dissimilar metals are inherently stronger than the individual metals used to make up the joints, the strength of the connector is determined only by the strength of the aluminum which is the weakest component thereof. Furthermore, the electroformed connector is completely free of any of brittle eutectic alloy present in some butt welded joints so that the joints are of more uniform strength and are inherently non-porous.

The electroformed connectors can also be heated to well over 500° C. for short periods of time without destroying the joint area since there is no brittle alloy formed during the fabrication thereof or by heat diffusion. Thus the joints are much more heat resistant than many butt welded joints in which any eutectic alloy

present melts at a much lower temperature, i.e., about 345° C. Furthermore, the electroformed connectors of the present invention do not require any subsequent machining or other treatment to remove unwanted flash or the like. Plated joints including tubes of $\frac{5}{16}$ inch diameter joined by a nickel layer of about 0.01 inch have been found to completely pass all of the usual tests which copper-aluminum joints for use in refrigeration systems are expected to meet. Such tests include a high pressure leak test of 3000 p.s.i., a thermal shock test involving 10 cycles of transfer directly from boiling water to liquid nitrogen, heating at 500° C. for ten minutes followed by water quenching and pressure cycling between 0 and 600 p.s.i.

From the above description, it will be seen that the subject process using an initial coating of *electrodeposited* tin rather than an immersion deposit affords a number of advantages. Far broader operating limits, particularly with respect to time and alkali concentration in obtaining the first adherent coating of tin are available. Also there is little or no solution contamination by aluminum in the tin bath. Electrons required for deposition are supplied from an external electrical source in place of a transfer of electrons internally by the solution of aluminum into the operating bath as is the case in immersion coating.

The process also uses a copper plating bath wherein the tin content is to be kept to a minimum approaching that of a regular copper cyanide bath. Only such tin as is required for the initial coating plus the tin carried out from this solution on the work being processed is consumed. No tin is added either as a tin salt or as tin in bronze anodes. Obviously, such a process is cheaper than a process which prescribes the use of tin salts in a bronze bath and the use of bronze anodes in place of copper anodes.

Thus, the major advantages include using exactly the same conditions for all aluminum alloys, being able to process different alloys at one and the same time, obtaining adhesion adjacent to copper surfaces, and the simplicity of the make-up and control of the electro-tin bath.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. The method of plating an aluminum surface which comprises the steps of:

electrodepositing a tin strike on said surface as a cathode from a potassium stannate bath under conditions preventing the immersion deposit of tin, and transferring the surface directly from the potassium stannate bath to a copper cyanide bath and introducing it into said cyanide bath electrically "hot" for electrodeposition of a copper layer.

2. The method of claim 1 in which said aluminum surface is in electrical contact with a copper surface.

3. The method of making a copper-aluminum connector including an electroplate copper-aluminum joint which comprises the steps of:

positioning one end of an aluminum tube in firm mechanical contact with one end of a copper tube, while maintaining said ends in firm mechanical contact, mechanically reducing the exterior diameter of the contacting end portions of both of said tubes to provide a joint area including portions of both tubes of uniform diameter, electrodepositing on said joint area an electro-tin strike layer, and electroplating onto said tin layer a layer of metal adapted to form a strong metallurgical bond between said tubes.

4. The method of making a copper-aluminum connector which comprises the steps of:

positioning one end of an aluminum tube in firm mechanical contact with one end of a copper tube, mechanically reducing the exterior diameter of the contacting end portions of both of said tubes to pro-

vide a joint area including portions of both tubes of uniform diameter, electrodepositing on said joint area an electro-tin strike layer,

electroplating onto said tin layer a layer of copper, and applying to said copper layer an electrodeposited layer of nickel.

5. The method of making a copper-aluminum connector which comprises:

assembling a copper tube and an aluminum tube on a fixture adapted to position said tubes in end-to-end abutting relationship to apply a force thereto to maintain said ends in firm mechanical engagement and, while said tubes are assembled on said fixture, subjecting the area of said assembled tubes adjacent to and including said ends to a sequence of operations including:

rolling said area to reduce the exterior diameter of both tubes,

electrodepositing on said area an electro-tin strike layer from a potassium stannate bath and a copper layer from a copper cyanide bath, said assembly being immersed in said copper cyanide bath electrically "hot" and said area copper plated to a thickness sufficient to completely coat the aluminum surface component of said area,

and finally electrodepositing onto said copper plated area a layer of metal selected from the group consisting of copper and nickel of sufficient thickness to provide a fluid tight joint between said tubes in which said electrodeposited metal layer forms the sole means for joining said tubes.

6. The method of making a copper-aluminum connector which comprises:

assembling a copper tube and an aluminum tube on a fixture adapted to position said tubes in end-to-end abutting relationship and maintain said ends in firm mechanical engagement and, while said tubes are assembled on said fixture, subjecting the area of said assembled tubes encompassing said ends to a sequence of operations including:

mechanically working said area to reduce the exterior diameter thereof to a diameter less than the smaller diameter tube,

masking all of the surfaces of said tubes except at least a portion of said joint area including the abutting tube ends,

immersing said assembly as the cathode in a potassium stannate plating bath to electrodeposit on said area a tin strike layer and then in a copper cyanide bath to electrodeposit on said tin strike layer a copper coating of a thickness sufficient to completely coat the aluminum surface component of said area,

rinsing said area to remove traces of said copper cyanide bath,

and electrodepositing onto said copper plated area a layer of nickel of sufficient thickness to provide a fluid tight joint between said tubes in which said electrodeposited metal layers forms the sole means for joining said tubes.

7. The method of making a copper-aluminum connector which comprises:

assembling a copper tube and an aluminum tube on a fixture adapted to position said tubes in end-to-end abutting relationship to apply a force thereto to maintain said ends in firm mechanical engagement and, while said tubes are assembled on said fixture, subjecting the area of said assembled tubes adjacent to and including said ends to a sequence of operations including:

rolling said area to reduce the exterior diameter thereof to a diameter less than the smaller diameter tube,

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masking all of the surfaces of said tubes except at least a portion of said joint area including the abutting tube ends,

connecting said assembly to a negative direct current potential and thereafter first immersing said assembly as the cathode in a potassium stannate plating bath to electrodeposit on said area a tin strike layer and then in a copper cyanide bath to electrodeposit on said tin strike layer a copper coating of a thickness sufficient to completely coat the aluminum surface component of said area,

and thereafter electrodepositing onto said copper plated area a layer of a strong metal of sufficient thickness to provide a fluid tight joint between said tubes in which said electrodeposited metal layer forms the sole means for joining said tubes.

8. The method of electroplating aluminum which comprises the initial application thereto of an electrodeposit of tin from a bath consisting essentially of an aqueous

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solution of at least 35 g./l. of potassium stannate under conditions excluding an immersion deposit of tin in which the pH of said bath is maintained between about 10 and 14, followed immediately by the electrodeposition on said tin strike of a layer of electrodeposited copper.

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