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PROCESS OF FORMING A METALLIC COPPER LAYER ON THE SURFACE OF WORKPIECE OF ALUMINUM OR ALUMINUM BASE ALLOY

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FIG. 2

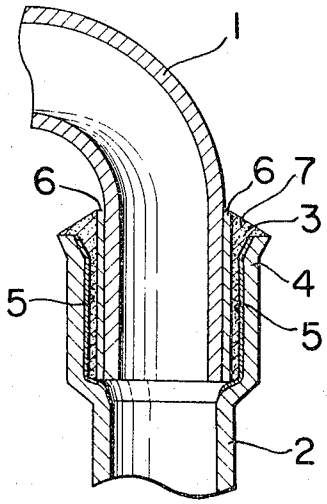
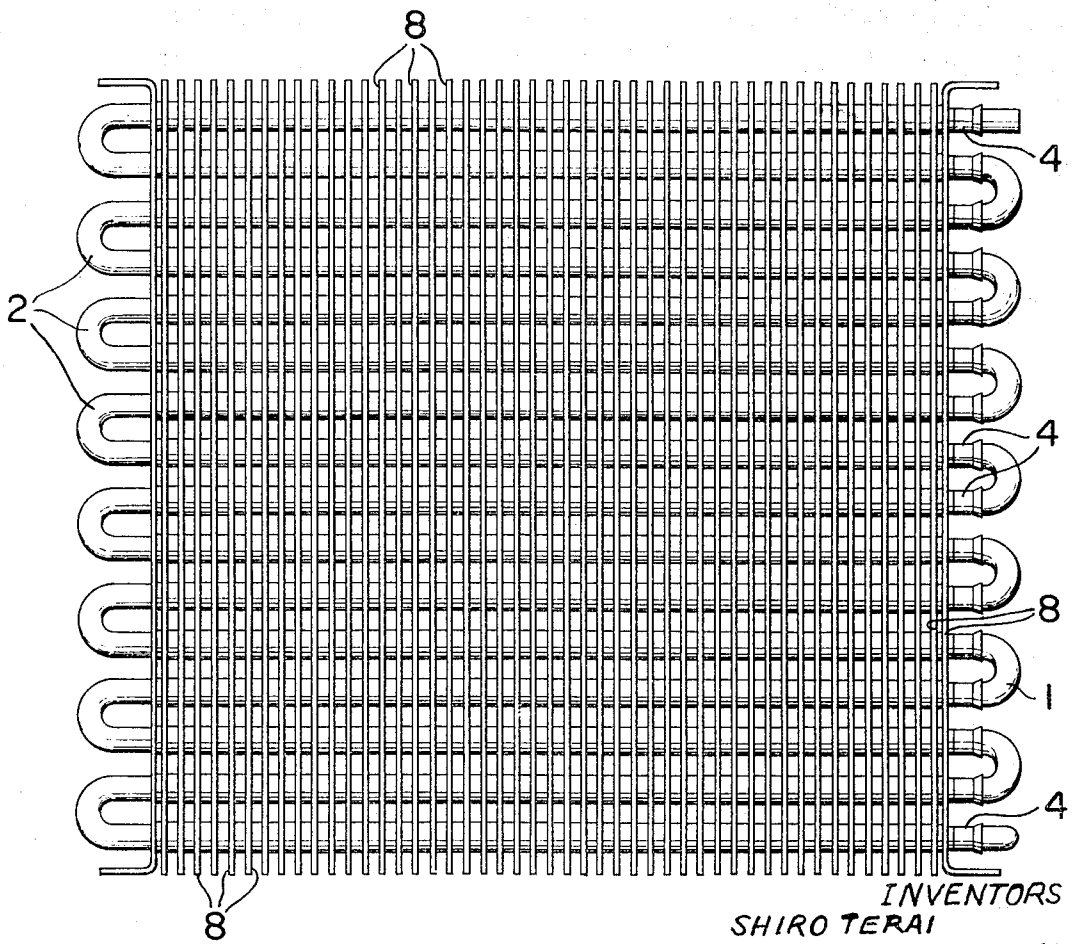



FIG. 1




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# PROCESS OF FORMING A METALLIC COPPER LAYER ON THE SURFACE OF WORKPIECE OF ALUMINUM OR ALUMINUM BASE ALLOY

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## ABSTRACT OF THE DISCLOSURE

This invention relates to a process of forming a metallic copper layer of a uniform thickness on the surface of workpiece made of aluminum or aluminum base alloy by applying finely divided copper halide particles on said surface uniformly with aid of a higher aliphtic mono-hydric alcohol containing 6–12 carbon atoms or a cyclo-aliphatic mono-hydric alcohol containing 6–8 carbon atoms as the adhesive medium, and then heating said surface to a sufficient temperature to react the copper halide with the aluminum material of the workpiece at the surface of the workpiece, whereby metallic copper is liberated, deposited on and partly diffused into the surface of the workpiece and a firmly adhered copper layer of a uniform thickness may be formed on the surface of the aluminum or aluminum base alloy material and, if desired, within a sharply limited area of the surface of the workpiece.

This invention relates to a process of forming a continuous and firmly adhered metallic copper layer of a small and uniform thickness on the surface of a workpiece of aluminum or aluminum base alloy and, if desired, limitedly within a bounded area of said surface.

Among the prior art methods of forming a metallic copper layer on the surface of aluminum or aluminum base alloy materials, so-called Betts process and the process of Japanese Patent No. 527,777 (Japanese patent publication No. 8161/68) are known. The known Betts process usually comprises the steps of (a) applying a paste-like mixture of cuprous chloride with a lacquer onto the surface of an aluminum material within a limited area intended to be coated with the metallic copper, and (b) heating the so-coated aluminum material to a temperature sufficient to react the cuprous chloride with aluminum whereby metallic copper is liberated from the copper chloride and deposited on the surface of the aluminum material within said area.

The Betts process, however, can suffer from the following various drawbacks. Thus, when the lacquer used to prepare the above-mentioned paste-like mixture comprising cuprous chloride is such type of lacquer as containing nitro-cellulose, a composition comprising liquid hydrocarbons and containing added amounts of an ester, ketone or alcohol is used as the solvent for the nitro-cellulose in the lacquer. This solvent composition is very much volatile, and the lacquers containing this solvent composition are of a lower pot-life. Accordingly, the paste comprising this type of the lacquers normally exhibits a poor workability for application and is very much difficult to be applied uniformly on the surface of aluminum material. Besides, even if the paste of this kind may have been applied uniformly on the substrate, the coating layer of the paste can partly inflate or rise during the subsequent step



of rapidly heating the substrate which is necessary to react the cuprous chloride with the aluminum material. Since the inflated part of the coating paste layer is then detached from the top surface of the aluminum material, the metallic copper layer cannot be produced on the surface within the area which corresponds to the inflated part of the coating paste layer.

When the known Betts process is carried out by applying the paste containing a mixture of cuprous chloride with the lacquer onto the surface of aluminum material and then heating the surface to a temperature sufficient to react cuprous chloride with aluminum, generally the lacquer components are burnt out at first and the cuprous chloride is then fused and reacted with aluminum in the surface of the aluminum material. In case the lacquer used to prepare the paste-like mixture of cuprous chloride contains any resinous composition in addition to the nitro-cellulose ingredient, or in case the lacquer used contains any film-former other than the nitro-cellulose ingredient, the resinous and other components of the lacquer present in the paste applied can only incompletely and nonuniformly be decomposed and burnt during the heating step of the process, so that the solid decomposition products can remain as the carbonaceous residue or "char" which would hinder the reaction of cuprous chloride with aluminum at the surface of the aluminum material and would be necessary to be removed subsequently through an extra troublesome processing.

The known process of the above-mentioned Japanese Patent No. 527,777 usually comprises the first step of applying a thin coating of sticky hydrocarbons, particularly Vaseline onto the surface of aluminum material, the second step of sprinkling a fine powder of a metal halide such as cuprous chloride to deposit on the coating of the sticky hydrocarbons, and the third step of heating the so coated aluminum material in a furnace or oven to at least such a temperature that the metal halide can sublimate, followed by cooling to room temperature. However, the known process of this Japenese patent exclusively employs Vaseline in practice and suffers from many difficulties, too. Thus, it is very difficult to coat on the surface of aluminum material Vaseline thinly and uniformly owing to high sticky and viscous nature of Vaseline and hence to form the liberated metal layer of a uniform depth deposited on said surface. Besides, the coating of Vaseline which has been applied on the surface of aluminum material in the first step of the process has a higher tendency to fuse, flow and spread out during the third heating step of the process, so that some of the fused Vaseline can readily run out beyond the boundary of an area of the surface of aluminum material in which the Vaseline has initially been applied to. The fused and run-out part of the Vaseline can entrain a portion of the fine powder of the metal halide which has been applied thereon in the second step of the process, so that an extra metal layer can additionally be formed outside of such bounded area of the surface in which the metal layer is desired to be formed limitedly in the final product. For this reason, when the sticky hydrocarbons and particularly Vaseline are used as the adhesive medium to apply a fine powder of copper halide on the surface of aluminum material, it is difficult to form the metallic copper layer on the surface of aluminum material limitedly as desired within a bounded area of the surface of aluminum material. This is lethally disadvantageous, because, the methods of forming the metallic copper layer on the surface of aluminum or aluminum base alloy material are generally utilized for the purpose to enable workpieces of aluminum or aluminum base alloy to be soldered together as much easily and strongly as when workpieces

made of copper are bonded together by soldering and because for this purpose, the copper layer formed should naturally be necessary to exist on the surface of the workpieces limitedly within the area on which the soldering joints are intended to be produced between the workpieces of aluminum material to be bonded together. Further, the use of vaseline can give on the surface of the deposited metal layer a carbonaceous residue or "char" which strongly adheres to said surface and which is necessary to be removed through an extra cleaning operation.

Through our research, we, the inventors, have found that a satisfactory adhesive medium used to apply a fine powder of a copper halide and to form the metallic copper layer on the surface of aluminum or aluminum base alloy material should possess in combination the following properties:

(1) The medium is difficult to evaporate at ambient temperatures.

(2) The medium is chemically inert to any copper halide at ambient and higher temperatures and exhibits suitable values of viscosity and adhesiveness to be applied thinly and uniformly onto the surface of aluminum or aluminum base alloy material and to carry and retain or support stably the finely divided particles of the copper halide on the surface of the layer and/or in the layer of the medium applied.

(3) The medium does not run out or migrate over the surface of the aluminum material beyond the boundary of the area within which the medium has initially been applied as a thin layer thereonto, even when the medium is heated to high temperatures sufficient to fuse and react the copper halide with aluminum or aluminum base alloy.

(4) The medium can evaporate or vaporise off completely at the temperatures sufficient to fuse and react the copper halide with aluminum or aluminum base alloy.

(5) The medium has a high wettability to the surface of aluminum or aluminum base alloy.

(6) The medium and its vapor are non-toxic to operators.

We have now found that higher aliphatic monohydric alcohols containing 6–12 carbon atoms and cyclo-aliphatic mono-hydric alcohols containing 6–8 carbon atoms are effective and satisfactory as the adhesive medium for the above-mentioned purpose, because these kinds of the alcohols exhibit all the above-mentioned properties in combination. Our invention is based on this discovery.

An object of the present invention is to provide an improved process of forming a metallic copper layer on the surface of workpiece of aluminum or an aluminum base alloy which is free from the drawbacks of the above-mentioned prior art methods and by which the copper layer of a small and uniform thickness and of a better grade and higher adhesiveness can be formed through easy and simple operations using new adhesive media and by which the copper layer formed may be limited as desired within the boundary of a local area on the surface of the workpiece. Other objects of the present invention will be clear from the following descriptions.

According to a generic aspect of the present invention, there is provided a process of forming a metallic copper layer on the surface of workpiece made of one of aluminum and aluminum base alloys, which comprises the step (a) of applying onto the surface of the workpiece a thin layer consisting essentially of one of aliphatic mono-hydric alcohols of 6–12 carbon atoms and cyclo-aliphatic mono-hydric alcohols of 6–8 carbon atoms which is carrying finely divided particles of a copper halide uniformly distributed on and over the surface of said workpiece at least within an area of said surface, and the step (b) of then heating the surface of said workpiece together with the thin layer applied thereon at a high temperature sufficient to fuse and react the copper halide with the aluminum material of the workpiece for a sufficient time to insure that metallic copper is liberated, deposited on and partly diffused into the surface of the workpiece with the formation of a metallic copper layer adhered on said surface of the workpiece.

The process of the present invention may be carried out as follows: The step (a) of applying onto the surface of the workpiece a thin layer consisting essentially of one of the aforesaid alcohols which is carrying finely divided particles of a copper halide uniformly distributed on and over the surface of said workpiece at least within an area of said surface may be performed either by applying at first a thin layer consisting essentially of one of the aforesaid alcohols alone onto the surface of the workpiece within a predetermined area or over the whole of said surface and then sprinkling a fine powder of the copper halide over said thin alcohol layer to cause to adhere thereto the particles of the copper halide distributed uniformly on the top surface of said thin alcohol layer, or by applying onto the surface of the workpiece at least within an area of said surface a paste-like and uniform mixture of the copper halide with one of the aforesaid alcohols which was previously prepared by blending the components together uniformly, so that a thin and uniform layer of the paste containing the uniformly distributed copper halide particles therein coats the surface of the workpiece at least within a predetermined area of said surface.

Before carrying out the step (a) of the process, it is generally preferred to clean the surface of the workpiece at least within the area in which the metallic copper layer is desired to be applied thereonto. The surface of the workpiece made of aluminum material is usually contaminated with oils, greases, hydrocarbons and other foreign matters which have occasionally been attached thereonto, so that it can hardly be wetted well by the aliphatic and cycloalphatic mono-hydric alcohols as defined above. Thus, it is usually not easy to apply the aliphatic or cyclo-aliphatic mono-hydric alcohol or its paste-like mixture with the copper halide uniformly onto the surface of aluminum workpiece if the workpiece has not been cleaned preparatorily to remove the contaminating matters from its surface.

In order to remove the contaminating foreign matters and improve the wettability of the surface of aluminum workpiece to be coated with the copper layer, therefore, it is generally perferred to subject the surface of the workpiece to a preparatory cleaning step which may be worked out in a known manner, either chemically or electro-chemically or mechanically. The cleaning step may desirably be carried out to such an extent as to remove further the oxide film which normally covers and strongly adheres to the surface of the aluminum workpiece, since the presence of the oxide film can give a poor wettability to the surface of the aluminum workpiece.

For carrying out the preparatory cleaning step chemically, the workpiece may preferably be immersed at first in an aqueous alkaline bath containing a well-known alkaline cleaning agent, for example, in a bath of an aqueous solution of 5% sodium hydroxide optionally containing an added amount of a surface-active agent at 70° C. and then treated in a bath of dilute nitric acid, for example, an aqueous solution of 10% nitric acid for neutralisation and finally be rinsed with water.

For carrying out the cleaning step electro-chemically, for example, the workpiece may conveniently be arranged as a cathode in a bath of an aqueous solution of 1–2% sodium hydroxide at room temperature, a direct electric current is passed at a current density of 4–8 A./dm.$^2$ for 30 seconds between the cathode and an anode oppositely placed thereto, and the workpiece is then removed from the bath, washed with water and then treated in an aqueous solution of 10–50% nitric acid for neutralisation and finally rinsed with water. To clean the surface of the workpiece mechanically, the surface may be subjected to a grinding with wire-brush or a surface-cutting with any cutting tool.

The step (a) of the process according to the present invention may be performed subsequently to the preparatory cleaning step, and this step (a) may be worked

out as mentioned before either by applying one of the aforesaid aliphatic and cyclo-aliphatic mono-hydric alcohols in the form of a thin layer onto the surface of the workpiece at least within a pre-determined bounded area thereof in which the copper layer is intended to be formed, and then sprinkling and adhering onto the applied thin layer of the alcohol uniformly the finely divided particles of the copper halide used, or by applying in the form of a thin layer of a uniform thickness the paste-like mixture which has been prepared by blending uniformly one of the aforesaid alcohols with a fine powder of the copper halide. All of the above-mentioned aliphatic and cyclo-aliphatic mono-hydric alcohols used according to the present invention are very much easy to be applied in the form of a thin and a uniform layer onto the surface of the aluminum workpiece, because all of them are substantially not or little volatile at ambient temperatures so that the operation of applying them cannot be hindered by the occasional evaporation of the adhesive medium which would take place with the lacquers as used in the prior Betts process, and because all of them are liquid and exhibit appropriate values of viscosity and adhesiveness at ambient temperatures. Moreover, the alcohol applied in the form of the thin layer on the surface of the workpiece according to the present invention does not chemically attack the copper halide which is either subsequently applied on the thin layer made of the alcohol alone or contained within the thin layer composed of the paste-like mixture of the alcohol and the copper halide. The thin layer made of the above-mentioned alcohol or of its paste-like mixture with the copper halide which has been applied on the surface of the workpiece can well adhere or stick to the surface of the workpiece and can carry or support adhesively and stably the fine particles of the copper halide uniformly distributed on the surface of or within said thin layer, so that the fine particles of the copper halide thus supported may be kept distributed uniformly at their initially applied places on and over the surface of the workpiece and may further be prevented from dropping down out of the thin alcohol layer, even when the workpiece is inclined, moved or transported and when the workpiece is heated to a higher temperature.

Furthermore, all of the aliphatic and cycloaliphatic mono-hydric alcohols used in accordance with the present invention may readily be mixed with a fine powder of the copper halide in proportions suitable to give a paste-like uniform mixture of them which may have viscosity and adhesion suitable to be applied by conventional means of application such as brushing, dipping, roller and doctor-knife etc. The thin layer of the paste so prepared which has been applied onto the surface of the workpiece is also able to adhere well to the surface so that it may be retained stably by said surface without flowing down from said surface even when the workpiece is inclined, moved or transported. The alcohol may be conveniently and economically applied at a rate of about 0.1–2.0 mg./cm.$^2$ and the paste-like mixture of the alcohol with the copper halide may be applied at a rate of about 35.0–45.0 mg./cm.$^2$.

Workpiece of aluminum or aluminum base alloy on the surface of which the copper layer is formed according to the process of the present invention includes workpieces made of pure aluminum such as Aluminum 1100, Aluminum 1060 and those made of aluminum base alloys such as aluminum-copper alloys, for example, aluminum alloy 2024; aluminum-manganese alloys, for example, aluminum alloys 3003 and 3004; aluminum-magnesium alloys, for example, aluminum alloy 5052; aluminum-magnesium-silicon alloys, for example, aluminum alloys 6061 and 6063; and aluminum-zinc-magnesium alloys as well as other types of aluminum alloys. The workpiece of aluminum or aluminum base alloy treated by the process of the present invention may be of any shape such as sheet, plate, panel, pipe, tube, extruded shapes, castings or forgings. It may be in the form of finished products such as heat-exchanger etc.

The aliphatic mono-hydric alcohols which may be used in the process of the present invention may contain 6–12 carbon atoms and a single hydroxyl group and may contain a straight chain or branched chain of carbon atoms. Examples of the available aliphatic mono-hydric alcohols include n-hexyl alcohol, methyl-amyl alcohol, ethyl-butyl alcohol, heptyl alcohol, methyl-amyl carbinol, 3-heptanol, dimethyl pentanol, n-octyl alcohol, sec-octyl alcohol, ethyl-hexyl alcohol, iso-octyl alcohol, n-nonyl alcohol, diisobutyl carbinol, n-decyl alcohol and lauryl alcohol. Among of them, n-octyl alcohol, n-nonyl alcohol and n-decyl alcohol are most preferred. The cycloaliphatic mono-hydric alcohols which may be used in the process of the present invention contain 6–8 carbon atoms and a single hydroxyl group and may carry a lower alkyl substituent such as methyl and ethyl on its cyclic ring. Examples of the available cyclo-aliphatic mono-hydric alcohols include cyclohexanol, methyl cyclohexanol, trimethyl cyclohexanol and cyclo-octanol. Among these, cyclohexanol is most preferred.

Poly-hydric aliphatic and cyclo-aliphatic alcohols containing two or more hydroxyl groups are more reactive to the copper halide in the form of a fine powder and hence are not suitable for use as the adhesive medium to apply the finely divided particles of the copper halide on the surface of the workpiece of the aluminum material for the purpose of forming the metallic copper layer thereon.

The copper halide which may be employed in the process of the present invention includes cuprous chloride, cupric chloride, cupric ammonium chloride. Among these, cuprous chloride is most preferred.

After the alcohol layer carrying the finely divided particles of the copper halide thereon and/or therein has been applied onto the surface of the workpiece in the step (a) of the present process, the surface of the workpiece which bears thereon the thin layer comprising the alcohol and finely divided copper halide is then heated according to the step (b) of the present process at a temperature sufficient to react the copper halide with the aluminum material of the workpiece. This heating step may be carried out by placing the workpiece in a furnace or oven at a sufficiently high temperature or by heating the surface of the workpiece by means of torch. The heating temperature may preferably be in a range of about 430–450° C. when the copper halide used is cuprous chloride. The heating time may suitably be 2 to 6 minutes. If the heating temperature is below 430° C., the time required to complete the reaction is too long to finish the process in a reasonable time. On the other hand, if the heating temperature is above 450° C., the metallic copper once liberated and deposited on the surface of the workpiece can again react with the aluminum material of the workpiece with production of a certain intermetallic compound, so that the copper layer former is likely to fade away or otherwise can be darkened due to the oxidation of the metallic copper. In order to prevent the deposited copper layer and the exposed aluminum surface of the workpiece from being oxidised by air, it is preferable to carry out the heating of the workpiece under an inert atmosphere such as nitrogen, argon etc.

During the heating step (b) of the present process, the alcohol can initially be evaporated or vaporised out of the thin layer applied on the surface of the workpiece, and the fine particles of the copper halide are then settled down on the surface of the workpiece and fused there and reacted with the aluminum of the workpiece material to liberate the metallic copper and aluminum halide. The aluminum halide can then be vaporised and the vapor removed out of the surface of the workpiece, so that it does not exert any influence on the metallic copper liberated. The metallic copper liberated is deposited on and covers the surface of the aluminum workpiece within the area in

which the finely divided particles of the copper halide have initially been applied together with the adhesive medium, and a portion of the liberated metallic copper is diffused into the interior of the surface layer of the aluminum workpiece to produce an intermediate layer made of an aluminum-copper alloy between the deposited top metallic copper layer and the aluminum matrix of the workpiece. The presence of the intermediate layer of aluminum-copper alloy so produced serves to improve the adhesiveness of the top metallic copper layer to the matrix of the workpiece.

Subsequent to the heating step (b) of the present process, the aluminum workpiece may be cooled down to room temperature. It is preferred to force the hot workpiece to be cooled down rapidly by blowing a flow of e.g. compressed air or carbon dioxide gas or other inert gases thereonto. It is permitted to quench the hot workpiece by dipping into a water bath or subjecting to a shower of water, if the workpiece cannot be strained detrimentally thereby.

All of the aliphatic and cyclo-aliphatic mono-hydric alcohols which are defined above and may be used according to the present invention are so very much excellent in their nature that they are able to support and retain adhesively and stably the finely divided particles of the copper halide limitedly within the area in which they have initially been applied as the adhesive medium for the copper halide particles, substantially without running or flowing out beyond the boundary of said area even when they have been heated to higher temperatures necesary to bring about the reaction of the copper halide with the aluminum material of the workpiece. This nature is most important for the adhesive medium because the finely divided particles of the copper halide which are applied for the purpose of forming the metallic copper layer on the surface of an aluminum workpiece are confined within a predetermined area thereof.

In order to demonstrate this excellent ability of the aliphatic and cyclo-aliphatic mono-hydric alcohols used according to the present invention, as compared to that of the Vaseline which is exclusively used as one of sticky hydrocarbons in the prior art practice of the method of Japanese Patent No. 527,777, a series of tests was carried out as follows:

Different alcohols as specified in Table 1 below were each applied at a rate of about 0.1–12.5 mg./cm.$^2$ within a rectangular-shaped area of about 3 cm. x 5 cm., on the surface of a panel of aluminum. A fine powder of cuprous chloride was then applied at a rate of about 23.3 mg./cm.$^2$ onto the thin layer of the alcohol by sprinkling carefully in such a manner that the finely divided particles of cuprous chloride were uniformly distributed over and deposited on thin layer of the alcohol. The aluminum panels so prepared were then placed inclined at angle of 90° in an oven and heated at 450° C. for 10 minutes. The panels were then removed from the oven, and it was observed that the metallic copper layer was formed showing the rectangular contour substantially same as that of the initially applied alcohol layer on the surface of each aluminum panel and that the rectangular-shaped metallic copper layer had its running down part (about 2–8 mm. wide) projecting a little from the lower side thereof. The length of the running down part of the copper layer on the surface of each aluminum panel was determined and the determined values are tabulated in Table 1 below. For comparison, Vaseline was also tested in the same manner. The length of the running down part of the copper layer projecting from the lower side of the main rectangular shaped area of the copper layer may be considered to give a reliable measure by which it can be estimated how effectively the adhesive medium (the alcohol or Vaseline) used is able to support and retain the finely divided particles of the copper chloride limitedly within the area in which the copper chloride has initially been applied with aid of the adhesive medium.

TABLE 1

| Adhesive medium materials tested | Rate of applied medium materials (mg./cm.$^2$) | Rate of applied cuprous chloride (mg./cm.$^2$) | Length (mm.) [1] |
|---|---|---|---|
| n-Hexyl alcohol | 0.1–2.3 | 23.3 | 8 |
| n-Octyl alcohol | 0.3–2.0 | 23.3 | 5 |
| Lauryl alcohol | 0.5–2.0 | 23.3 | 8 |
| Cyclohexanol | 0.4–12.5 | 23.3 | 3 |
| Cyclo-octanol | 0.3–2.3 | 23.3 | 2 |
| Vaseline (comparative) | 0.2–10.0 | 23.3 | 26 |

[1] Mean length (mm.) of the running down part of the copper layer at angle (90°) of inclination of aluminum panel.

From the results as shown in Table 1, it is clear that the running-down part of the copper layer formed using the alcohols according to the present invention as the adhesive medium generally showed a length of only about one-third to one-thirteenth of that of the running-down part of the copper layer obtained when the Vaseline was used as the adhesive medium, and therefore that surprisingly higher is the ability of the alcohols according to the present invention to support and retain the finely divided particles of the copper halide only within the pre-determined area or region on the surface of aluminum workpiece.

In carrying out the process of the present invention, the thickness or depth of the metallic copper layer finally formed on the surface of the aluminum workpiece may be varied largely dependent on the rate of the copper halide applied onto the surface together with the adhesive medium used. A series of tests was carried out to estimate the relationship between the rate of the copper halide applied and the thickness of the metallic copper layer finally formed on the surface of the aluminum workpiece. It has been found that the depth of the metallic copper layer finally formed generally increases as the rate of the copper halide powder applied is increased and that the depth of the metallic copper layer substantially reaches an approximately constant maximum value of about 6 microns or more when the copper halide is applied at a rate of 40–60 mg./cm.$^2$ of the surface of the aluminum workpiece, though the heating time and temperature and other operating factors can naturally have some influences on the thickness of the metallic copper layer formed. It has been found that an application of the copper halide at a rate of 20–50 mg./cm.$^2$ will generally suffice to give a metallic copper layer which has a depth of about 3 to 6 microns and an adhesive strength sufficiently high to engage the subsequently applied layer of the soldering alloy. The rate of application of the adhesive medium used may be adjusted to support and retain the amount of the copper halide particles which is needed to give a desired thickness of the metallic copper layer to be formed. Optimum rates of application of the adhesive medium and the copper halide to give a desired thickness of the metallic copper layer may readily be determined through simple preparatory experiments. In normal cases, it is enough to apply the adhesive medium at a rate of 0.1–2.0 mg. per cm.$^2$ of the surface of the aluminum workpiece.

The process of the present invention may be applied to with advantage in various fields or arts. For instance, it may effectively and advantgeously be applied to the manufacture of heat-exchangers made of aluminum or aluminum base alloy where hermetically sealed joints must be formed between aluminum pipes or between aluminum pipes and copper pipes, because the process of the present invention is able to facilitate and insure the formation of such joints with a reliably high adhesive strength.

Usually, jointing between an aluminum pipe and an aluminum pipe is made by a conventional soldering work wherein any corrosive flux such as the chloride-type flux is commonly used to remove the oxide film which is normally present on and strongly adheres to the surface of the aluminum material and which would prevent a

strong adhesion from being made between the soldering metal layer and the matrix of the aluminum material. The use of the corrosive flux can bring about a danger that a corrosion takes place later in the joints owing to the presence of the residue of the flux. In contrast to this, it is well known that hermetical jointing between metallic copper materials may be achieved much more easily by soldering without resorting to such corrosive flux. When it is desired to joint an aluminum pipe to another aluminum pipe, the process of the present invention may be utilised to form the copper layer deposited on the surface of the aluminum pipes within the areas in which the joints are to be made. When the deposited copper layer-carrying areas or regions of the aluminum pipes are then jointed together by a usual soldering method known for the metallic copper materials, the soldered joints can easily be formed as much hermetically and strongly as that joints obtained between the copper materials. When it is desired to joint an aluminum pipe to a copper pipe, it will suffice to use the process of the present invention so as to form the copper layer only on the area or region of the aluminum pipe to be jointed.

Referring to the accompanying drawings:

FIG. 1 shows a lateral view of a heat-exchanger composed of aluminum pipes during the manufacture of which the process of the present invention has been employed to form the hermetically sealed joints between the aluminum pipe units.

FIG. 2 shows a diagrammatical view of a cross-section of a joint part between the aluminum pipe units of the heat-exchanger of FIG. 1.

The invention is now described with reference to FIGS. 1and 2. The heat-exchanger as shown in FIG. 1 has a conventional arrangement and comprises a succession of aluminum pipes **1** and **2** which have been jointed together to form a zigzag shape; and a number of radiating fine **8** which are arranged in parallel to each other but attached transversely to a row of the aluminum pipes **2**. Each longer U-shaped aluminum pipe **2** is connected with the shorter U-shaped bent pipe of aluminum **1** in such a way that each of the ends of the shorter aluminum pipe **1** is engaged and contained by the ends **4** of the longer aluminum pipe **2** which have been widened into a bell-form in a known manner, leaving an annular space **3** therebetween (see FIG. 2). The inner surface of the bell-shaped ends of the aluminum pipe **2** and the outer surface of the engaged ends of the aluminum pipe **1** are provided with the metallic copper layers **5** and **6**, respectively, which have been formed according to the process of the present invention. It has been found necessary that the copper layers **5** and **6** have a thickness of at least 3 mircons, as otherwise the copper layers are likely to be stripped from the matrix material of the aluminum pipes and are insufficient to give a satisfactorily oily strong adhesion of the soldering metal.

The annular space **3** is filled with a solid mass of the soldering metal **7** which strongly has adhered to both the copper layers **5** and **6** and hence firmly jointed both the aluminum pipes **1** and **2** together. In jointing the ends of the aluminum pipes **1** and **2** by soldering, the surfaces of the copper layers **5** and **6** may be firstly coated with a non-corrosive soldering flux, preferably a flux composition of rosin type, for example, such one comprising 40% by weight of water white rosin (containing 75% ethanol and 25% rosin), 4% by weight of stearic acid and the balance ethanol, or a flux composition of amine type, for example, such one comprising ethylene diamine. The end of the aluminum pipe **1** is then inserted into and engaged by the bell-shaped widened end **4** of the aluminum pipe **2**, leaving the annular space **3** which is subsequently filled by casting thereinto a molten mass of e.g. of a soldering alloy of Sn-Pb type by means of a torch. Alternatively, the annular space **3** may be filled with solid pieces of a soldering alloy of Sn-Pb type, at least the ends to be jointed of the aluminum pipes are then placed into a hot oven or heated externally by means of torch to fuse the pieces of the soldering alloy and fill hermetically the annular space **3**, and the molten soldering alloy is subsequently solidified by cooling to give the soldered joints at the ends of the aluminum pipes **1** and **2**.

The above-mentioned annular space **3** is preferred to have a width of 0.1 to 0.3 mm. so as to facilitate the soldering operation. Available soldering alloys of Sn-Pb type include, for example, an alloy containing 50% Sn-50% Pb and an alloy containing 60% Sn-40% Pb or alloys of these kinds further containing minor amounts of Ag, Cd, Zn and other modifying agents. The other soft and hard soldering alloys which are known to be suitable for soldering to joint copper materials may be used to make the soldered joints on the metallic copper layer which has been formed by the process of the present invention. The soldering operation may be performed much more easily when a cream-like soldering composition comprising a blend of a soldering alloy and a flux. By soldering in a known manner on the copper layers which have been formed by the process of the present invention. the aluminum pipes may be connected in succession by the soldered joints which are hermetically sealed and entirely free from pin-hole and other defects.

The process of the present invention is now illustrated with reference to the following examples to which the present invention is not limited in any way.

## EXAMPLE 1

A panel made of a pure aluminum of a grade 1100 and of a size 150 mm. x 200 mm. was subjected to a cleaning treatment by immersing for 1 minute in a bath of an aqueous solution of 5% sodium hydroxide at 70° C. to remove the greases and other contaminating matters which adhered to the surface of the panel. The panel was then removed from said bath, washed with water and dipped in a bath of an aqueous solution of 15% nitric acid at room temperature for neutralisation. The panel was further rinsed with water and dried in air.

The dry panel was lightly rubbed on its one surface with a mass of absorbent cotton which had impregnated with cyclohexanol, so that cyclohexanol was applied at the rate of 1.0 mg./cm.$^2$ uniformly within a region in the form of a square of about 10 cm. in its one side on the surface of the panel in the middle thereof. A fine powder of cuprous chloride was then applied by sprinkling onto the thin layer of cyclohexanol to deposit the finely divided particles of cuprous chloride uniformly thereon. The panel was then inclined so that an extra portion of the cuprous chloride particles which was not well adhered by the cyclohexanol layer was permitted to drop down from the panel. Consequently, the cuprous chloride particles were firmly deposited on and adhered by on the cyclohexanol layer at a rate of 25 mg./cm.$^2$. The panel was placed horizontally in an electrically heated oven and heated at 440° C. for 3 minutes. The panel was then removed from the oven and forcibly cooled down by blowing a flow of compressed air to the hot panel. In order to eliminate the residue of the reaction product mainly comprising aluminum chloride which still remained on the surface of the copper layer formed on the panel, the panel was well washed with water. The aluminum panel had a metallic copper layer which was formed firmly adhered onto the one side of the panel, and the metallic copper layer had a uniform depth of about 3 microns and its contour was exactly the same as that of the thin layer of cyclohexanol initially applied.

## EXAMPLE 2

A panel made of aluminum alloy 3003 and of a size 150 mm. x 200 mm. was subjected to a chemical cleaning treatment in a similar way to Example 1.

One surface of the dry panel was then lightly rubbed with a mass of absorbent cotton which was impregnated

with n-octyl alcohol, so that n-octyl alcohol was applied at a rate of 0.5 mg./cm.$^2$ uniformly in an area of an about 5 cm.-diametered circle shape on the surface of the panel in the middle thereof. A fine powder of cuprous chloride was sprinkled down onto the top surface of the thin layer of n-octyl alcohol to deposit the fine particles of cuprous chloride uniformly thereon. The panel was then inclined so that an extra portion of the cuprous chloride particles which was not well adhered by the n-octyl alcohol layer was permitted to fall down from the surface of the panel. In consequence, the cuprous chloride particles were deposited on and firmly adhered by the n-octyl alcohol layer at a rate of about 25 mg./cm.$^2$. The panel was subsequently placed horizontally in an electrically heated oven, heated at 440° C. for 3 minutes therein and removed therefrom.

The panel was then forcibly cooled down by blowing a flow of compressed air to the hot panel. In order to eliminate the aluminum chloride residue of the reaction products still remaining on the surface of the copper layer formed, the panel was well washed with water. The aluminum panel carried thereon a metallic copper layer which was formed, deposited and firmly adhered onto the surface of the panel, and the metallic copper layer had a uniform depth of about 3 microns and a contour exactly same as that of the initially applied n-octyl alcohol layer.

## EXAMPLE 3

A panel made of pure aluminum of a grade 1100 and of a size 150 mm. x 200 mm. was subjected to an electrochemical cleaning treatment by placing as a cathode in a bath of an aqueous solution of 1% sodium hydroxide at 50° C. and then passing a direct electric current at a current density of 6 A./dm.$^2$ for 30 minutes between the cathode and the anode which was the wall of the vessel containing the cleaning bath. The panel was then removed from the bath, washed with water and dipped into a bath of an aqueous solution of 15% nitric acid for neutralisation, followed by repeated rinsing with water.

Pulverised cuprous chloride was mixed with n-octyl alcohol at a ratio of 5 g. of the fomrer to 10 cc. of the latter, and the mixture was kneaded to give a paste. This paste was then applied by means of brush onto a surface of the dry panel, so that the paste was applied at a rate of about 41.5 mg./cm.$^2$ uniformly on said surface within an area of rectangular shape (about 5 cm. x 10 cm.). The rate of application of cuprous chloride was then about 40 mg./cm.$^2$. The panel was then inserted in an electrically heated oven, heated at 440° C. for 3 minutes therein and removed therefrom. The pannel was subsequently forcibly cooled down by means of a blowing flow of compressed air and washed with water to remove the aluminum chloride residue of the reaction products which still remained on the surface of the metallic copper layer formed. The metallic copper layer deposited adhesively on the surface of the aluminum panel had a uniform thickness of about 3 microns and a contour exactly same as that of the initially applied paste layer.

## EXAMPLE 4

A panel made of pure aluminum of a grade 1100 and a size of 150 mm. x 20 mm. was chemically cleaned and rinsed in a similar way to Example 1.

A fine powder of cupric chloride was mixed with cyclohexanol at a ratio of 5 g. of the former to 10 cc. of the latter, and the mixture was completely kneaded to give a uniform paste. This paste was applied by means of a brush onto one surface of the dry panel in such a manner that the paste was applied at a rate of about 41.5 mg./cm.$^2$ uniformly on the whole of said surface. The rate of application of cupric chloride was then about 39 mg. per cm.$^2$ of the surface. The panel was placed horizontally in an electrically heated oven, heated at 440° C. for 3 minutes therein and then removed therefrom. The panel was then forcibly cooled down by means of a blowing flow of compressed air and further washed with water to remove the aluminum chloride residue of the reaction products which still remained on the metallic copper layer formed. The metallic copper layer was firmly adhered by the matrix material of the panel and had a uniform thickness of about 3 microns.

## EXAMPLE 5

Two pipes made of a pure aluminum of a grade 1060 and of dimensions 10 mm. in external diameter and 1 mm. in wall thickness, respectively were subjected to a chemical cleaning treatment by dipping in a bath of an aqueous solution of 10% sodium hydroxide at 70° C. for 3 minutes for de-greasing, removing from the bath, washing with water, neutralising in a bath of an aqueous solution of 15% nitric acid at room temperature and then again rising with water.

An end of one of the above-mentioned two aluminum pipes was widened into a bell-shape as shown in FIG. 2. The internal surface of the bell-shaped end of the one aluminum pipe and the external surface of an end of the other aluminum pipe were both ground by means of wire-brush for further mechanical cleaning treatment. The ground surfaces of both the ends of the aluminum pipes were each provided with a thin coating layer of a paste which had been prepared by mixing cuprous chloride powder with cyclohexanol at a ratio of 5 g. of the former to 10 cc. of the latter and kneading the resulting mixture. The coating was made by means of a spatula. The pipes were placed in an electrically heated oven, maintained at 450° C. for 5 minutes therein, removed therefrom and then quenched by dipping into a bath of water. A metallic copper layer was formed adhesively on the internal surface of the bell-shaped end of the one aluminum pipe and on the external surface of the end of the other aluminum pipe, respectively. The copper layers formed had a uniform thickness of about 3 microns and a contour same as that of the initially applied paste, respectively. A fluxing composition of rosin type comprising 40 parts by weight of water white rosin (75% ethanol, 25% rosin), 4 parts by weight of stearic acid and the balance ethanol was applied to coat uniformly over both the metallic copper layers. Both the two aluminum pipes were connected together by introducing the copper-coated end of the one pipe into the copper-coated, bell-shaped end of the other pipe while leaving the annular space of about 0.2 mm. wide between the external and internal surface of the ends so engaged. An amount of a soldering alloy comprising 50% Sn–50% Pb was fused by means of a torch, filled into said annular space and then solidified therein. As result, a hermetically sealed joint entirely free from defects such as pin-hole was produced at the connected ends of the two aluminum pipes. The jointed part of the aluminum pipes so connected was then examined by tensile tests, and it was then observed that the main length of the connected aluminum pipes was burst during the hydraulic pressure test without giving any damage in the jointed part of the pipes, which revealed that the jointed part exhibited an excellent and high bonding strength.

What we claim is:

1. A process of forming a metallic copper layer on the surface of workpiece made of one of aluminum and aluminum base alloys, which comprises the step (a) of applying onto the surface of the workpiece a thin layer consisting essentially of one of aliphatic mono-hydric alcohols of 6–12 carbon atoms and cyclo-aliphatic mono-hydric alcohols of 6–8 carbon atoms which is carrying finely divided particles of a copper halide uniformly distributed on and over the surface of said workpiece at least within an area of said surface, and the step (b) of then heating the surface of the workpiece together with the thin layer applied thereon at a high temperature sufficient to fuse and react the copper halide with the aluminum material of the workpiece for a sufficient time to insure that metallic copper is liberated, deposited on and

partly diffused into the surface of the workpiece with the formation of a metallic copper layer adhered on said surface of the workpiece.

2. A process as claimed in claim 1 wherein a thin layer made of one of the aliphatic and cycloaliphatic mono-hydric alcohols as defined above which is carrying the finely divided particles of a copper halide uniformly distributed on and over the surface of the workpiece is applied onto the surface of the workpiece by applying firstly a thin layer consisting essentially of one of the aforesaid alcohols on the surface of the workpiece, and then sprinkling down a fine powder of a copper halide over the surface of said thin alcohol layer to adhere the finely divided particles of the copper halide uniformly distributed on the top surface of the said thin alcohol layer.

3. A process as claimed in claim 1 wherein a thin layer consisting essentially of one of the aliphatic and cycloaliphatic mono-hydric alcohols as defined above which is carrying the finely divided particles uniformly distributed on and over the surface of the workpiece is applied onto the surface of the workpiece by applying thereonto in the form of a thin layer of a uniform thickness a paste-like and uniform mixture which has been prepared by blending completely one of the aforesaid alcohols with a fine powder of the copper halide.

4. A process as claimed in claim 1 wherein the thin layer of the alcohol which is carrying the finely divided particles of a copper halide is applied onto the surface of the workpiece limitedly within predetermined area of said surface.

5. A process as claimed in claim 1 wherein the thin layer of the alcohol which is carrying the finely divided particles of a copper halide is applied onto the whole surface of the workpiece.

6. A process as claimed in claim 1 wherein one of n-octyl alcohol, decyl alcohol and nonyl alcohol is used to apply the thin layer consisting essentially of one of the aliphatic mono-hydric alcohols as defined above.

7. A process as claimed in claim 1 wherein cyclohexanol is used to apply the thin layer consisting essentially of one of the cyclo-aliphatic mono-hydric alcohols as defined above.

8. A process as claimed in claim 1 wherein a copper halide used is cuprous chloride, and the step of heating the surface of the workpiece is carried out at a temperature of 430 to 450° C. for a period of 2 to 6 minutes.

9. A process of forming a metallic copper layer on the surface of workpiece made of one of aluminum and aluminum base alloys, which comprises the steps of applying onto the surface of the workpiece at least within a pre-determined area of said surface a thin layer consisting essentially of one of aliphatic mono-hydric alcohols of 6–12 carbon atoms and cyclo-aliphatic mono-hydric alcohols of 6–8 carbon atoms alone, then sprinkling down a fine powder of a copper halide over the surface of said thin alcohol layer to deposit the finely divided particles of the copper halide distributed uniformly on the top surface of said thin alcohol layer, and subsequently heating the surface of the workpiece together with the copper halide particle-carrying thin layer of the alcohol applied thereon at a high temperature sufficient to fuse and react the copper halide with the aluminum material of the workpiece for a sufficient time to insure that metallic copper is liberated, deposited on and partly diffused into the surface of the workpiece with the formation of a metallic copper layer adhered on said surface of the workpiece.



10. A process of forming a metallic copper layer on the surface of workpiece made of one of aluminum and aluminum base alloys, which comprises the steps of applying onto the surface of the workpiece at least within a pre-determined area of said surface in the form of a thin layer of a uniform thickness a paste-like and uniform mixture which has been prepared by blending completely one of aliphatic mono-hydric alcohols of 6–12 carbon atoms and cyclo-aliphatic mono-hydric alcohols of 6–8 carbon atoms with a fine powder of a copper halide, and subsequently heating the surface of the workpiece together with the thin layer of the paste applied thereon at a high temperature sufficient to fuse and react the copper halide with the aluminum material of the workpiece for a sufficient time to insure that metallic copper is liberated, deposited on and partly diffused into the surface of the workpiece with the formation of a metallic copper layer adhered on said surface of the workpiece.

**References Cited**

UNITED STATES PATENTS

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| 2,737,463 | 3/1956 | Lawton et al. | 117—46 CA X |
| 3,096,567 | 7/1963 | Ross et al. | 117—46 CA X |
| 3,305,369 | 2/1967 | Cuhra et al. | 117—46 CA X |


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