2,782,156

PURIFICATION OF FUSED SALT ELECTROLYTES

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5 Claims. (Cl. 204—64)

This invention relates to the electrolytic deposition of certain transition metals in fused salt baths. More particularly, it relates to a method for purifying the fused salt baths in which these transition metals are electrodeposited.

The usefulness of the so-called transition metals titanium, zirconium, hafnium, vanadium, thorium, tantalum and niobium is, for most purposes, greatly impaired if these metals contain even small amounts of such impurities as oxygen, nitrogen and other metals that tend to embrittle or otherwise adversely affect the quality of the metals produced. The transition metals are commonly prepared by the electrolytic decomposition of a transition metal compound in a fused salt diluent bath with the resulting deposition of the metal on a cathode immersed in the bath. It has been found, however, that the fused salt bath must be substantially completely free of impurities which would react with or become incorporated in the transition metal deposited in the cathode in the course of the electrolysis. It is particularly important that the salt bath be free of moisture and of contaminant elements whose oxides or salts are more electropositive than those of the transition metal deposited at the cathode. The presence of water or of the aforesaid oxides and salts in the fused salt bath will result in the incorporation of oxygen or other contaminant elements in the transition metal cathode deposit thus impairing the quality and usefulness of the ultimate metal product.

The best commercial grades of transition metal and diluent salt constituents of the fused salt baths employed in the electrolytic production of the aforesaid transition metals contain small but significant amounts of moisture and other deleterious impurities. In particular, the double fluorides of the transition metals, which are a common constituent of these fused salt baths, are prone to contain metallic impurities that would contaminate the cathode deposit unless removed from the double fluoride electrolytic cell feed material. Therefore, to avoid the inclusion of oxygen and other impurities in the cathode deposit, it has heretofore been the practice to subject commercial grade cell feed material to extensive and costly purification prior to the electrolysis of the fused salt bath. The purification procedure commonly employed involves wet chemical treatment of the cell feed material to remove therefrom substantially all of the elements that would otherwise contaminate the cathode deposit, followed by careful drying of the purified bath constituents, advantageously by means of a vacuum drying treatment.

To insure that the fused salt bath is completely anhydrous before the electrolytic deposition of the transition metal is initiated, a preliminary electrolysis of the bath is commonly carried out. The preliminary electrolysis is conducted at voltages and current densities below those at which any appreciable amount of the transition metal constituents of the bath will deposit at the cathode, and is continued until all of the moisture in the bath has been

electrolytically decomposed and removed therefrom. At the relatively low voltages and current densities at which the preliminary electrolysis is carried out, the fused bath is substantially completely dehydrated. However, this relatively mild pre-electrolysis does not remove from the bath any of the contaminant elements whose oxides or salts are more electropositive than those of the transition metal constituent of the bath, necessitating, therefore, the use as cell feed materials of transition metal compounds and diluents salts of substantially absolute chemical purity. In accordance with accepted usage in this art, the term "more electropositive" hereinafter employed is intended to mean that the voltage required for electrodepositing the impurity ions is higher than or greater than the voltage at which the transition metal is electrodeposited.

I have now found it possible to use as cell feed material transition metal compounds and diluent salts of commercial grade by purifying these materials in situ in an electrolytic cell. The purification of the cell feed material is accomplished by means of a novel electrolytic procedure by which water and contaminant elements whose salts and oxides are more electropositive than those of the transition metal are removed from the fused cell feed material as a preliminary to the subsequent electrodeposition of substantially pure transition metal at the cell cathode. Accordingly, my novel preliminary electrolytic procedure for the purification of cell feed material constitutes an important improvement in known processes for the electrolytic preparation of the transition metals titanium, zirconium, hafnium, thorium, vanadium, niobium and tantalum. The preliminary purification electrolysis of my invention is carried out at a voltage and current density in excess of that required to effect deposition of some of the transition metal at the cathode, and sufficient to effect decomposition of the water and the salts and oxides of the aforesaid contaminant elements and deposition of these contaminant elements at the cell cathode. This so-called rapid pre-electrolysis is continued for a period of time sufficient to insure that substantially all of the water and the contaminant elements are removed from the fused salt bath, together with a small amount of the transition metal component of the bath.

When the purification electrolysis is a preliminary step to the subsequent electrolytic deposition of substantially pure transition metal at the cell cathode, I have found that the voltage employed for the pre-electrolysis should be about equal to that employed for the subsequent electrolysis, and that the current density should be at least about one half that employed for the subsequent electrolysis. Moreover, the passage of about 2 to 5% of the total ampere hours required for substantially complete reduction of the transition metal contents of the fused salt bath will be sufficient to purify fused salt baths composed of cell feed materials of commercial grade or better. Fused salt baths purified by my rapid pre-electrolysis procedure can then be electrolyzed in the same electrolytic cell to produce a cathodic transition metal deposit of high purity. Alternatively, the purified bath can be removed from the cell in which the preliminary electrolysis is carried out for subsequent introduction into one or more other electrolytic cells adapted to carry out the electrolysis by which the desired pure transition metal product is produced.

The fused salt baths to which the process of my invention is particularly applicable are those containing double fluorides of the transition metal as the primary source of the transition metal electrodeposited at the cathode, such as those of the tye described in the copending application of Topinka, McKenna and Carlton, Serial No. 297,158, filed July 3, 1952, which issued

January 17, 1956, as United States Patent 2,731,402 of Steinberg and Topinka, Serial No. 262,886, filed December 21, 1951, and of Young and Somerville, Serial Nos. 332,327 and 332,328, filed January 21, 1953, which issued as United States Patents 2,731,405 and 2,731,406 respectively on January 17, 1956. Fused salt baths advantageously purified by my process also include those of the type described in the copending applications of Steinberg, Sibert and Topinka, Serial No. 202,806, filed December 26, 1950, which issued April 26, 1955, as United States Patent 2,707,169 of Wainer, Serial No. 313,795, filed October 8, 1952, which issued April 26, 1955, as United States Patent 2,707,170, Serial No. 320,113, filed November 12, 1952, which issued as United States Patent 2,722,509 and Serial No. 320,345, filed November 13, 1952, and of Sibert and Burwell, Serial No. 358,194, filed May 28, 1953.

A typical fused salt bath that can be purified by my novel procedure comprises an alkali metal double fluoride of the transition metal, such as potassium fluotitanate, in admixture with one or more diluent alkali metal or alkaline earth metal halides, such as sodium chloride. The alkali metal double fluorides can be obtained commercially in a reasonably pure condition. However, even the best commercial grades of these salts ordinarily contain appreciable amounts of contaminating metallic oxides and salts, such as the oxides or halides of iron, chromium, aluminum and the like, which must be removed if a pure transition metal deposit is to be produced therefrom. The alkali metal and alkaline earth metal halides can be obtained commercially in substantially pure condition. However, for economic reasons the grades of these salts usually employed contain minor amounts of contaminants that would adversely affect the quality of the transition metal product. These contaminants can be removed by extensive wet chemical purification techniques, as described in certain of the aforementioned copending patent applications, to obtain a feed material of a purity satisfactory for fused salt baths used in electrolytic processes for the preparation of pure transition metal deposits. However, by employing the purifying pre-electrolysis procedure of my invention, it is possible to introduce commercial grade salts directly into the fused salt bath without such prior wet chemical treatment designed to remove impurities which can now be removed from the fused salt bath itself pursuant to my process.

In the practice of my invention, the mixture of salts comprising the salt bath is introduced into an electrolytic cell in which an inert atmosphere can be established. Inert atmosphere cells of the type suitable for use in my processes are described in the aforementioned copending applications. In general, such cells comprise a container for the fused salt bath, such as a graphite crucible, disposed in a gastight furnace provided with means for maintaining the fused bath in the crucible at its operating temperature and with means for introducing cell electrodes into the fused bath so that the desired electrolysis can be carried out. It is essential that the electrolysis be conducted under an inert atmosphere. Such an atmosphere may be established by evacuating all of the air and other gases from the interior of the furnace and operating the cell under a vacuum, or by replacing the air in the furnace with an atmosphere composed of an inert gas such as argon.

On establishing an inert atmosphere in the furnace, the mixture of salts in the cell is fused by heating the furnace to above the melting point of these salts. The operating temperature of the cell depends upon the composition of the fused salt bath and upon the requirements of the particular electrolytic procedure employed. Electrodes of a material inert with respect to the molten bath are then inserted in the bath. The cathode is advantageously a graphite rod and the anode may be a similar rod of graphite or, advantageously, it may be the graphite crucible itself.

The electrolysis is carried out at a voltage and current density above that at which the product transition metal will electrodeposit on the cathode. Thus, the preelectrolysis voltage should be about the same magnitude as that at which the subsequent metal deposition electrolysis is carried out, while the current density should be at least about one half that employed for the subsequent electrolysis. For example, when, as in a typical case, the electrolytic production of a transition metal cathode deposit from a fused salt bath requires a voltage in the range of about 5 to 6 volts and a current density in the range of about 450 to 500 amps./dm.^{2}, the pre-electrolysis should be carried at a voltage of about 5 to 6 volts, with a current density of about 200 to 225 amps./dm.^{2}. The passage of about 2 to 5% of the total anticipated ampere hours required for the substantially complete reduction of the initial transition metal content of the fused salt bath is ordinarily sufficient to rid the bath of moisture and all contaminant elements whose oxides and salts are more electropositive than the transition metal constituent of the bath.

The rapid preliminary electrolysis of my invention results in the electrodeposition on the cathode of a small amount of the product transition metal. The transition metal deposited on the cathode during the pre-electrolysis is, of course, contaminated with the metallic elements being removed from the bath therewith and is of little value as a transition metal product per se. However, the loss of this amount of transition metal on the pre-electrolysis cathode is not sufficient to seriously adversely affect the economies of the overall procedure. Moreover, if desired this preliminary cathode deposit can be recovered and the transition metal component thereof converted into a form suitable for reintroduction into the electrolytic cell.

After the rapid pre-electrolysis has been carried out, the graphite electrode is removed from the bath together with any of the metallic bath impurities and product transition metal that have deposited on the cathode. The purified fused salt bath is then subjected to electrolysis, either in the pre-electrolysis cell or in one or more other electrolytic cells, to recover therefrom the major portion of the transition metal constituent of the salt bath. The product metal recovered from a salt bath purified pursuant to my invention is itself substantially pure and, therefore, is relatively soft and ductile.

The following examples, which compare the transition metal product obtained pursuant to my invention with that obtained when my procedure is not followed, are illustrative but not limitative of the method of my invention:

Example I

A mixture of 340 parts by weight of potassium fluotitanate and 1800 parts by weight of sodium chloride were charged to a graphite crucible disposed within an electric furnace. The furnace was equipped with means for establishing an inert atmosphere therein, and with gas-locks for introducing electrodes into the graphite crucible. The potassium fluotitanate and sodium chloride were of commercial grade and contained small but significant amounts of moisture and metallic contaminants more electropositive than titanium. An inert atmosphere of dry argon gas was established within the furnace and the furnace heated to a temperature of about 800° C. to melt the salts contained in the crucible. After fusion of the salt charge, the temperature of the furnace was maintained at about 800° C. and a ¾ inch graphite rod cathode was inserted into the fused salt bath. Employing the graphite crucible as the anode, a direct current was passed through the molten bath to rid the bath of water and metallic contaminants. During the rapid pre-electrolysis, over-all cell voltage was maintained within the range of about 4 to 4.5 volts and the current was about 100 amperes. After one-half hour, the electrolysis was stopped and the graphite cathode removed from the bath. The cathode was coated with a thin layer of fine particles of electrodeposited metal. A 1 inch steel rod cathode was then inserted into the bath and electrolysis carried out at substantially the same voltage as previously used and at a current of about 200 amperes. After about 5 hours the bath had become extensively depleted in titanium content, the titanium being electrodeposited on the cathode in the form of adherent crystals of titanium. The titanium metal deposited on the steel cathode, after consolidation by melting under an insert atmosphere, had a Rockwell B hardness of 69 and a Brinell hardness number of about 140.

Example II

A bath identical in its constituents, proportions and grade as that employed in Example I was prepared and was melted in an inert atmosphere furnace as in Example I. A steel cathode was inserted into the molten bath and a preliminary electrolysis at a voltage of about 1.5 to 2 volts was performed to dehydrate the bath. There was no preliminary electrolysis performed to rid the bath of contaminating metal constituents pursuant to my invention. The metal deposition electrolysis was then performed at about 4 to 4.5 volts and with a current of about 200 amperes. The titanium metal product recovered at the cathode had, after consolidation, a Rockwell B hardness of 89 and a Brinell hardness number of about 180.

Example III

A mixture of 600 grams of commercial grade potassium fluozirconate and 1800 grams of commercial grade sodium chloride was introduced into a graphite crucible disposed within the electric furnace employed in Example I. The salt charge was melted under an inert atmosphere and the temperature of the molten bath maintained at 750° C. A ½ inch graphite rod was introduced into the molten bath and electrolysis initiated by passing a direct current from the graphite crucible to the graphite rod. The over-all cell voltage was within the range of 5 to 6 volts and the current density was about 200 amps./dm.^{2}. After 45 ampere hours of direct current had been passed through the bath, the graphite rod was removed therefrom and a steel rod was inserted in its place. Electrolysis of the bath was continued at a voltage within the range of 5 to 6 volts, with a current density of about 450 amps./dm.^{2}. The metallic deposit adhering to the graphite rod was found to have a Rockwell A hardness of 62 while the cast zirconium ingot prepared from the zirconium metal electrodeposited on the steel rod had a Rockwell B hardness of 76.

Example IV

A bath identical in composition, proportion and grade to that employed in Example III was prepared and the bath melted under an inert atmosphere in the furnace of Example I. No preliminary electrolysis was carried out to rid the bath of metallic contaminants. A steel cathode was inserted into the bath and electrolysis was carried out at a voltage and current density of about 5 to 6 volts and 450 amps./dm.^{2}, respectively. On completion of the electrolysis, the steel rod was removed with its adhering deposit of zirconium metal. The zirconium metal was consolidated under an inert atmosphere and found to have a Rockwell A hardness of 56.

I claim:

1. In the electrolytic deposition of a transition metal of the group consisting of titanium, zirconium, hafnium, thorium, vanadium, niobium and tantalum in a fused salt bath, the improvement which comprises removing water and contaminant elements whose salts and oxides are more electropositive than those of said transition metal from the fused salt bath by subjecting said bath to a preliminary electrolysis at a cell voltage in excess of that required to effect deposition of the transition metal at the cathode and sufficient to effect decomposition of said water and said salts and oxides of said contaminant elements and deposition of said contaminant elements at the cathode, and continuing said preliminary electrolysis for a period of time sufficient to insure substantially complete removal of all of said water and said contaminant elements from said bath thereby removing said contaminant elements from the bath and subsequently electrolyzing the purified bath to obtain the transition metal in substantially pure form as an electrodeposit.

2. In the electrolytic deposition of a transition metal of the group consisting of titanium, zirconium, hafnium, thorium, vanadium, niobium and tantalum in a fused salt bath containing a transition metal compound and at least one diluent salt of the group consisting of alkali metal and alkaline earth metal halides, the improvement which comprises removing water and contaminant elements whose salts and oxides are more electropositive than those of said transition metal from the fused salt bath by subjecting said bath to a preliminary electrolysis at a cell voltage in excess of that required to effect deposition of the transition metal at the cathode and sufficient to effect decomposition of said water and said salts and oxides of said contaminant elements and to effect deposition of said contaminant elements at the cathode, and continuing said preliminary electrolysis for a period of time sufficient to insure substantally complete removal of all of said water and said contaminant elements from said bath thereby removing said contaminant elements from the bath and subsequently electrolyzing the purified bath to obtain the transition metal in substantially pure form as an electrodeposit.

3. In the electrolytic deposition of a transition metal of the group consisting of titanium, zirconium, hafnium, thorium, vanadium, niobium and tantalum in a fused salt bath comprising a halide of the transition metal and at least one diluent metal salt of the group consisting of alkali metal and alkaline earth metal halides, the improvement which comprises removing water and contaminant elements whose salts and oxides are more electropositive than those of said transition metal from the fused salt bath by subjecting said bath to a preliminary electrolysis at a cell voltage in excess of that required to effect deposition of said contaminant elements at the cath- and sufficient to effect decomposition of said water and said salts and oxides of said contaminant elements and to effect deposition of said contaminant elements at the cathode, and continuing said preliminary electrolysis for a period of time sufficient to insure that substantially all of said water and said contaminant elements are removed from said bath thereby removing said contaminant elements from the bath and subsequently electrolyzing the purified bath to obtain the transition metal in substantially pure form as an electrodeposit.

4. In the electrolytic deposition of titanium metal in a fused salt bath containing a titanium compound and at least one diluent metal salt of the group consisting of alkali metal and alkaline earth metal halides, the improvement which comprises removing water and contaminant elements whose salts and oxides are more electropositive than those of titanium from the fused salt bath by subjecting said bath to a preliminary electrolysis at a cell voltage in excess of that required to effect deposition of titanium metal at the cathode and sufficient to effect decomposition of said water and said salts and oxides of said contaminant elements and to effect deposition of said contaminant elements at the cathode, and continuing said preliminary electrolysis for a period of time sufficient to insure that substantially all of said water and said contaminant elements are removed from said bath thereby removing said contaminant elements from

the bath and subsequently electrolyzing the purified bath to obtain the titanium in substantially pure form as an electrodeposit.

5. In the electrolytic deposition of a transition metal of the group consisting of titanium, zirconium, hafnium, thorium, vanadium, niobium and tantalum in a fused salt bath, the improvement which comprises removing water and contaminant elements whose salts and oxides are more electropositive than those of said transition metal from the fused salt bath by subjecting said bath to a preliminary electrolysis at a cell voltage in excess of that required to effect deposition of the transition metal at the cathode and sufficient to effect decomposition of said water and said salts and oxides of said contaminant elements and deposition of said contaminant elements at the cathode, continuing said preliminary electrolysis for a period of time sufficient to insure susbtantially complete removal of all of said water and said contaminant elements from said bath for at least a time sufficient to provide between about 2% and about 5% of the total

ampere hours required for substantially complete deposition of the transition metal content of the fused salt bath, and thereby removing said impurity-containing cathode deposit from the fused bath and subsequently electrolyzing the purified bath to obtain the transition metal in substantially pure form.

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Feb. 26, 1957 B. C. RAYNES ET AL 2,783,195

CONTROL OF CORROSION IN REACTION VESSELS

Filed April 29, 1955

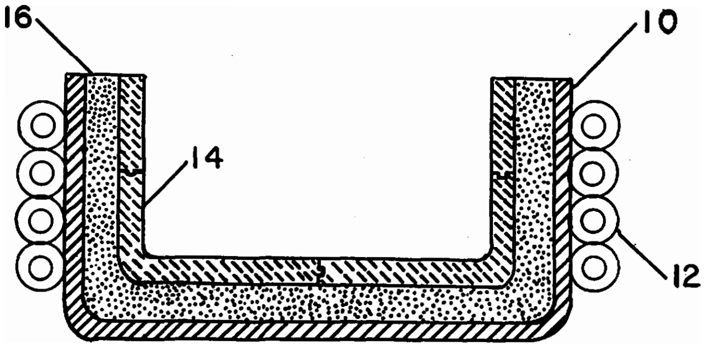

FIG. 1.

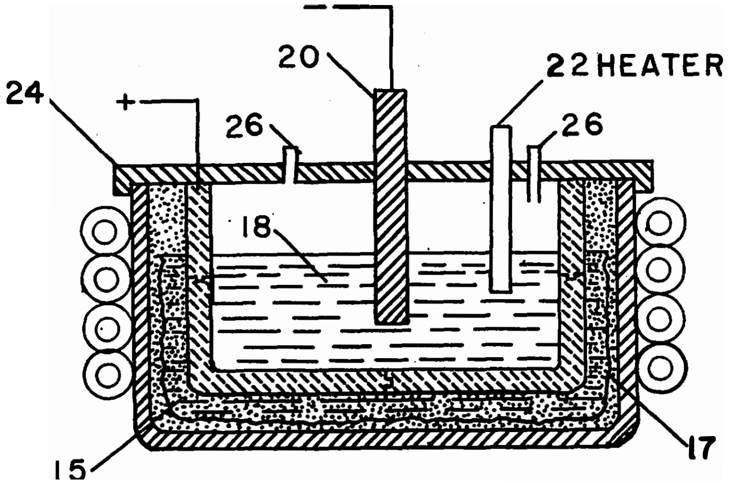

FIG. 2.

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CONTROL OF CORROSION IN REACTION VESSELS

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This invention relates to an improved design for vessels in which highly corrosive materials are to be processed or reacted at elevated temperatures. The principles herein disclosed may be readily adapted to the design of the containers for highly heated corrosive liquids generally. More particularly, this invention may be utilized to advantage in the construction of cells intended to be employed in the electrolytic recovery of metals by a fused salt electrolysis.

For the purpose of illustration, this invention will be described as applied to the recovery of transition metals, but it will be appreciated that this is not to be taken as a limitation thereon since similar considerations will apply to other specific processes for the recovery of other products by fused salt electrolysis or by fused salt reactions.

In the recovery of transition metals, one of the more promising procedures which has been intensively investigated is electrolysis of molten salts. It has been found that most of the ordinary materials of construction are rapidly attacked by the corrosive molten salts constituting the fused bath, or by such other products of the electrolysis as elemental or combined fluorine or chlorine. The attack is particularly severe since the operating temperatures are often as high as 900° C. The choice of a material of construction has often been found therefore to be limited to commercial graphite or carbon. Because of the highly corrosive nature of the fused salt and because of the porosity of commercial carbon crucibles, particularly in large sizes, a definite limit is thus placed upon cell size, and therefore cell capacity.

The prior art has long been aware of the possibility of increasing the life of furnace refractories by permitting some of the contents of the furnace to freeze and to form a protective frozen shell which thereafter serves as a container for the corrosive molten contents of the furnace. In applying such a teaching to an electrolytic cell, it is necessary to sacrifice the advantages attendant on the use of the container or crucible as one of the electrodes, since the frozen salt shell generally does not conduct electricity. Thus, in prior art electrolytic cells, additional electrodes of relatively limited area must be provided to replace the container as an electrode.

By the practice of this invention, it now becomes possible to conduct the electrolysis in a frozen salt shell, while at the same time utilizing the container or crucible as one electrode. As a result, it becomes possible to conduct the desired electrolysis of a fused bath in a container which is nowise limited as to size or capacity, except for the strength of the materials employed in its construction, while at the same time preserving the purity of the electrolytic product obtained. Furthermore, because of the virtually limitless size of the electrolytic cell, much higher electrical charges may be used in the electrolysis.

These and other advantages will become apparent from the following specifications and claims in which:

Figure 1 is a schematic representation of an electrolytic cell constructed in accordance with this invention seen in section with the cover removed and before the charge is present.

Figure 2 is a schematic representation of a similar section of the vessel containing a molten charge.

As shown in Figure 1, an electrolytic cell constructed in accordance with this invention includes an outer shell 10 of any suitable structural material, the principal function of which is to support and contain the materials within its confines. Generally, shell 10 is of metal such as steel. Surrounding shell 10 is a heat exchange means 12 for controlling the temperature of shell 10 within any desired range. The heat exchange means may comprise a plurality of perforated pipes by means of which heated or cooled fluid is continuously sprayed on shell 10. or it may comprise a coil disposed in intimate contact with shell 10, through which a heated or cooled fluid is caused to circulate. Any suitable means may be provided as the heat exchanger.

Within shell 10 there is disposed a container 14 constructed of carbon or graphite or other suitably inert, electrically conductive material. The container 14 serves as one of the electrodes in the preferred use of the cell shown. Where the vessel constructed in accordance with the invention herein disclosed is to be employed as a reaction vessel, not involving any electrolysis, the inner container 14 may be constructed of an electrically nonconductive material such as a ceramic, without sacrificing certain other benefits obtained in the practice of our invention.

Because, in accordance with this invention, a certain amount of leakage may be tolerated without a failure of the cell, the inner crucible 14 may be constructed of pieces of graphite or carbon or other material. These pieces need only fit reasonably closely together as they are not required to form a leakproof impervious vessel. In this way vessels of any size may be fabricated from relatively small, standard shapes much in the same manner that carbon shells have been installed in the lower portions of blast furnaces. Common sizes for present day carbon blocks are pieces slightly larger than 1 foot by 2 feet in section by three to five feet in length.

Between the inner crucible 14 and the outer metallic shell 10, there is disposed a thermally insulating material 16 such as carbon black, lamp black, or powdered carbon or graphite, or even powdered metal, or other material having the required inertness toward the contents of crucible 14 and the desired relatively poor thermal conductivity.

Crucible 14 is adapted to contain a melt 18 composed essentially of one or more molten salts. In the electrolytic production of a transition metal one such bath migh contain one or more alkali metal halides or alkaline earth metal halides in combination with various transition metal compounds as described in U. S. Patents 1,815,654; 1,835,025 and 1,861,625 among others. Suspended in the bath are one or more cathodes 20 and one or more immersion type heaters 22 for maintaining the bath molten.

The above cell is constructed in the following manner:

After the volume required of vessel 14 and the temperatures at which bath 18 and outer shell 10 are to operate have been ascertained, the thickness of thermal insulation is computed to provide a zone intermediate of shell 10 and crucible 14 in which a temperature will be obtained corresponding to the temperature at which the molten material in vessel 14 becomes a solid.

To assemble the apparatus, shell 10 is positioned on a suitable support and a layer of thermal insulation of the desired thickness is provided in the bottom of shell 10. The thermal insulation may be disposed in the form of a loose powdery or granular material, or it may be tamped in place, or formed into a plastic mixture with a temporary plasticizer such as water or methylcellulose and poured in place and baked. Next a bottom is constructed for vessel **14** from standard flat shapes of carbon, graphite or other suitably inert materials which may be interlocked if desired. Gradually, the sides of vessel **14** are built up and the space between vessel **14** and shell **10** is gradually filled with insulation. Heat exchanger **12** is then positioned adjacent shell **10** and, as shown in Figure 2, a heating means **22** and one or more electrodes **20** are positioned within the vessel **14**. Means are provided to connect electrodes **20** and vessel **14** to a source of potential, in the event that it is desired to conduct an electrolysis in the vessel.

In operation, once the components have been assembled, the bath or reaction mixture is melted by means of heaters **22** positioned within the vessel. When molten as shown in Figure 2, the contents of vessel **14** tend to leak either through any pores or discontinuities in the walls of the vessel into the thermal insulation **16**. Heat exchanger means **12** is operated so as to restrict the leakage to a region corresponding to a zone **15** therein by adjusting the heat transfer so that a portion of the liquid becomes solid in a zone **17** after leaking through crucible **14**. In this manner, the entire contents of vessel **14** remains molten throughout the vessel and the vessel may properly function as one electrode in any electrolysis conducted therein.

The above described cell is in marked contrast with prior art cells operated heretofore with a lining formed of frozen salts. Since the solidified salt is non-conductive, it is necessary to insert an anode and a cathode in the bath, in order to conduct an electrolysis. As shown in the figure, the frozen lining and the anode and cathode occupy a considerable fraction of the volume of crucible and thus diminishes the efficiency of the operation. Furthermore, the area of both the anode and cathode is but a small fraction of the area of crucible **14** of Figure 1 and hence, the electrical capacity of such cells is substantially less than that of the cell of Figure 1, of equal volume.

A further precaution concerning the construction and operation of vessels as described above should be mentioned. When operating at temperatures at which the carbonaceous materials employed tend to oxidize, or in instances in which the contents of the vessel tend to react detrimentally with the normal atmosphere, it will be appreciated by those skilled in the art that precautions must be taken to prevent such undesirable developments. Usually it suffices to provide a cover **24** extending over the vessel, whereby a controlled atmosphere of any desired composition may be maintained above the contents of the vessel and in contact with the exposed portions of the inner vessel **14**. Cover **24** may be provided with openings through which heating means **22**, electrodes **20**, connections **26** to a source of a suitable atmosphere and the like, may be positioned.

We claim:

1. An electrolytic cell comprising: an outer supporting shell, an inner electrically conductive slightly porous shell spaced at least a predetermined minimum distance from the outer shell and adapted to contain a body of electrolyte, heating means positioned in the electrolyte contained in the inner shell, thermal insulation filling the volume between the outer shell and the inner shell, at least one electrode positioned within the inner shell in contact with the electrolyte, a source of potential, leads connecting the source of potential with the inner shell and with the said electrode whereby an electrolysis may be conducted in the inner shell and means to maintain the outer supporting shell at a temperature sufficiently below the melting temperature of the electrolyte that there are provided three zones in the thermal insulation between the inner shell and the outer shell as follows: a first zone adjacent the inner shell and containing some electrolyte in liquid form, a second zone adjacent the outer shell containing only thermal insulation and a third zone between the two in which any electrolyte present is in solid form.

2. An electrolytic cell comprising: an outer supporting shell, an inner electrically conductive slightly porous shell spaced at least a predetermined minimum distance from the outer shell and adapted to contain a body of molten salt, heating means positioned in the molten salt contained in the inner shell for maintaining the salt in molten condition, thermal insulation filling the volume between the outer shell and the inner shell, at least one electrode positioned within the inner shell in contact with the molten electrolyte, a source of potential, leads connecting the source of potential with the inner shell and with the said electrode whereby an electrolysis may be conducted in the inner shell, and means to maintain the outer supporting shell at a temperature sufficiently below the melting temperature of the electrolyte that there are provided three zones in the thermal insulation between the inner shell and the outer shell as follows: a first zone adjacent the inner shell and containing some electrolyte in liquid form, a second zone adjacent the outer shell containing only thermal insulation and a third zone between the two in which any electrolyte present is in solid form.

3. An electrolytic cell comprising: an outer supporting shell, an inner electrically conductive slightly porous shell of carbonaceous material spaced at least a predetermined minimum from the outer shell and adapted to contain a fused salt electrolyte, heating means positioned within the fused salt for maintaining said salt in molten condition, thermal insulation filling the volume between the outer shell and the inner shell, at least one electrode positioned within the inner shell in contact with the electrolyte, a source of potential, leads connecting the source of potential with the inner shell and with the said electrode whereby an electrolysis may be conducted in the inner shell and means to maintain the outer supporting shell at a temperature sufficiently below the melting temperature of the electrolyte that there are provided three zones in the thermal insulation between the inner shell and the outer shell as follows: a first zone adjacent the inner shell and containing some electrolyte in liquid form, a second zone adjacent the outer shell containing only thermal insulation and a third zone between the two in which any electrolyte present is in solid form.

4. A method of containing corrosive liquid materials which comprises: providing a porous inert container for corrosive liquid, establishing therein a body of liquid corrosive material, maintaining the body of liquid at an elevated temperature by a heating means positioned within the body of liquid, disposing an outer support shell spaced from the inner container, introducing a comminuted thermally insulating material into the space between the outer shell and the container and maintaining the temperature of the outer shell so as to establish three zones in the thermal insulation as follows: a first zone adjacent the inner container in which the corrosive material is present in liquid form in the thermal insulation, a second zone adjacent the outer shell in which the thermal insulation alone is present, and an intermediate zone between the first zone and the second zone in which the corrosive material is present in the form of a solid.

5. A method of electrolyzing a corrosive fused electrolytic salt bath which comprises: providing a porous inert electrically conductive container for the salt bath, establishing therein a fused salt bath of the corrosive electrolyte, maintaining the fused salt bath in fused condition by heating means positioned within the bath, disposing an outer support shell spaced from the inner container, introducing a comminuted thermally insulated material into the space between the outer shell and the container, immersing at least one electrode in the fused salt bath, impressing a potential through the salt bath by suitably connecting the immersed electrode and the container to a source of potential whereby the fused electrolyte is

electrolyzed and maintaining the temperature of the outer shell during the electrolysis of the fused salt electrolyte so as to establish three zones in the thermal insulation as follows: a first zone adjacent the inner conductive container in which the electrolyte is present in liquid form, a second zone adjacent the outer shell in which thermal insulation alone is present and an intermediate zone between the first zone and the second zone in which the electrolyte salts are present in solid form.

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ELECTROLYTIC CLADDING

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Serial No. 383,402

6 Claims. (Cl. 204—39)

This invention relates to the cladding of base metals with corrosion-resistant metals and, more particularly, to such cladding by electrolysis in a fused salt bath.

The quest for an effective and economical method of producing transition elements such as titanium and zirconium in pure metallic form has been spurred by their mechanical properties as well as by their corrosion-resistant properties. Where the advantage in constructing a device of such a transition element is predicated primarily upon the corrosion-resistance of the transition element, this objective could be attained by forming the device from a less expensive and more readily available base metal having a surface coating of the corrosion-resistant transition element. A similar coating arrangement would be effective where the strength versus weight characteristics of titanium and the corrosion-resistance of zirconium are desired. It will be apparent, accordingly, that many of the contemplated applications of the corrosion-resistant transition elements to structural devices can be substantially completely satisfied if only the surface of the device possesses the corrosion-resistant characteristic of the transition element.

Although a number of metals can be readily electrodeposited on a base metal in the form of an adherent thin film by aqueous electrolytic methods, such aqueous electro-deposition of the transition elements including titanium, zirconium, hafnium, vanadium, niobium and tantalum has not been successfully achieved. The classic method of electro-depositing these transition elements is through the medium of a fused halide salt bath, but it is characteristic of such electrodeposition from a fused bath that the deposited transition element is obtained on the cathode in the form of a relatively loosely adhering granular deposit.

In the copending application of Merle E. Sibert and John T. Burwell, Jr., Serial Number 383,401 filed simultaneously herewith, there is described a method of cladding base metals with the aforementioned transition elements in the form of a firmly adherent layer of the deposited metal joined to the base metal by a metal-to-metal bond. The aforesaid method depends upon a combination of a specific range of relatively high temperatures for the fused salt bath and a specific range of cathode current densities in conjunction with the supplying of the metal to be deposited by means of a consumable anode comprising a solid metalliferous form of the transition element. Although this method is effective, it requires relatively high bath temperatures with consequent complications including volatilization of bath constituents.

I have now found that a base metal may be clad with a corrosion-resistant metal such as the aforementioned transition elements at considerably lower temperatures by supplying the corrosion-resistant metal component of the fused salt bath in the form of its alkali metal double fluoride and by further incorporating in the bath from about ¼ to 10% by weight of water. Thus, my method of cladding a base metal with a corrosion-resistant metal by electrolysis in a fused salt bath comprises establishing and maintaining a fused salt bath comprising (*a*) a major amount of a halide of one or more of the alkali metal and alkaline earth metal halides, (*b*) about 15 to 50% by weight of a double fluoride of an alkali metal and the corrosion-resistant metal, and (*c*) about ¼ to 10% by weight of water. The bath is maintained at an elevated temperature above its melting point, and electrolysis of the molten bath is carried out between a solid anode and a solid cathode composed of a base metal having a melting point substantially above the melting point of the bath. The base metal cathode is thus clad with the corrosion-resistant metal by a metal-to-metal bond, and the clad base metal may be then further fabricated if necessary to shape it for its intended use.

The base metals which may be clad by the practice of my invention are all metals having a melting point at least as high as 600° C. and include, but are not limited to, iron, steel, stainless steels, molybdenum-iron alloys, molybdenum-nickel alloys, nickel-chromium alloys, nickel-copper alloys, nickel, chromium and copper, and further include one of the corrosion-resistant metals other than that which is to be deposited, to wit, one of the corrosion-resistant metals titanium, zirconium, hafnium, tantalum, vanadium, niobium, chromium, molybdenum and tungsten. All of the aforementioned base metals have melting points substantially above the melting points of the fused halide salt baths which are used in the practice of my invention. The base metal is clad with the electrodeposited metal by providing the former in the form of a cathode having any suitable shape compatible with the geometry of the electrolytic cell in which it is clad with the corrosion-resistant metal.

The corrosion-resistant metals which may be deposited on the aforementioned base metals in the form of a firmly adherent layer include not only the transition elements titaium, zirconium, hafnium, tantalum, vanadium and niobium but also chromium, molybdenum and tungsten. Each of these corrosion-resistant metals may be readily electrodeposited from an alkali metal double fluoride of the metal in a fused halide salt bath.

The fused salt baths useful in practicing my invention comprise fused halide salts composed primarily of one or more of the alkali metal halides and alkaline earth metal halides, and mixtures thereof. The useful halides include the chlorides, bromides, iodides and fluorides, and the choice of specific salt or mixture of salts is wholly dependent upon the desired melting point for the bath. For example, if sodium chloride is used as the sole constituent of the carrier bath other than the alkali metal double fluodide of the corrosion-resistant metal and the water, the resulting mixture of the sodium chloride with the double fluoride will have a melting point within the range of about 700° C. On the other hand, if a eutectic mixture of potassium and sodium chlorides is used, the double fluoride-containing bath will have a melting point below 550° C. Similarly, other bath melting points may be achieved by using mixtures of the halides of potassium, sodium and lithium and the halides of calcium, magnesium, strontium and barium. For example, mixtures of calcium and sodium chlorides and mixtures of calcium, sodium and potassium chlorides have been used satisfactorily as the carrier components of the fused salt baths wherein my inventon is practiced. The aforementioned halide components of the bath comprise a major constituent of the bath, the other constituents being generally restricted to the double fluoride of the corrosion-resistant metal to be electrodeposited and a small but significant amount of water.

The alkali metal double fluoride of the corrosion-resistant metal comprises the source of the corrosion-resistant metal which is electrodeposited. Although this double fluoride can be produced in situ in the bath by electrolysis of a solid metalliferous anode composed of the corrosion-resistant metal, I presently prefer to establish the corrosion-resistant component of the bath by the direct addition thereto of the alkali metal double fluoride. In general, I prefer to use the sodium and potassium double fluorides of the aforementioned corrosion-resistant metals, and I have found that amounts of these double fluorides ranging from about 15 to 50% by weight of the total bath constituents are satisfactory in practicing the method of my invention.

The effective cladding of the corrosion resistant metal on the surface of the base metal cathode at fused salt bath temperatures below the melting point of any alloy of the corrosion-resistant metal and the base metal of the cathode, pursuant to my invention, is predicated upon the presence in the bath of a small but significant amount of water. In general, I have found that from ¼% to 10% of water by weight of the total bath constituents is effective for this purpose, and within this range I presently prefer to use from ½% to 5% of water by weight of the bath. The water may be incorporated in the bath either in an indigenous form, such as the water of hydration of one of the bath constituents, or it may be added from an extraneous source.

The effectiveness of the water component of the bath in promoting cladding pursuant to my invention appears to be a result of its presence as water and not by virtue of any oxide or oxides which may be formed in the bath as a result of the presence of the water in the hot halides. The presence of such oxides, in the absence of a significant amount of water pursuant to my present invention, appears to be wholly ineffective in promoting the formation of a metal-to-metal bond between the electrodeposited corrosion-resistant metal and the base metal cathode. However, the presence of such an extraneous oxide in a bath containing a significant amount of water in accordance with the invention does not adversely affect the quality of the cladding bond nor does it appear to have any pronounced advantageous effect upon the cladding.

The cladding operation is performed simply by electrolyzing the aforementioned bath composition between a solid anode and a solid cathode composed of the base metal to be clad. This electrolysis takes place readily at cell voltages of at least 4.5 volts and preferably at cell voltages within the range of about 5 to 8 volts. The choice of cell voltage within this range is based upon the cell geometry and upon the shape and size of the cathode, the voltage being such as to establish and maintain a cathode current density within the range of about 100 to 500 amperes per square decimeter. The cell atmosphere above the bath should be maintained free of oxygen, nitrogen and carbon, and for this purpose I have found it suitable to maintain either vacuum conditions above the molten bath or to sweep the cell with an inert gas such as argon. In general, the cell operation may be continued without interruption for a period sufficient to effect the desired cladding of the base metal cathode with an impervious layer of corrosion-resistant metal, but when the amount of water initially present in the bath mixture is low it has been found to be advantageous in some instances to replenish the water component of the bath either continuously or intermittently during the electrolysis. The electrolytic cell design and structure are not critical, although due care should be taken to use cell components which are not attacked by the fused salt bath during electrolysis. Graphite is wholly satisfactory as a cell wall material, and the graphite cell either may be used as the anode or it may remain electrically neutral whereupon a graphite rod or plate (or other solid material not attacked by chlorine at the prevailing cell temperature) is used as the anode.

After cladding of the cathode base metal has been effected, the cathode is withdrawn from the bath and into a cooling chamber associated with the cell where it is permitted to cool to room temperature in an inert atmosphere without being exposed during the interim to the ambient atmosphere. The cooled cathode is then removed from the cooling chamber and the salt cake which has frozen around the metal is leached by conventional means so as to expose the clad layer.

The following specific examples are illustrative of the practice of my invention:

Example I

Six hundred parts by weight of potassium fluozirconate and 12 parts by weight of water were mixed with 1800 parts by weight of sodium chloride. The resulting mixture was then placed in a graphite crucible and was heated and maintained at a temperature of 750° to 850° C. in an atmosphere of argon. After fusion of the salt mixture occured an iron base metal shape was completely immersed in the fused bath. A voltage of about 6 volts was applied between the praphite crucible as the anode and the base metal shape as the cathode in order to maintain a cathode current density of about 420 amperes per square decimeter. The electrolysis was continued for 20 minutes, at the end of which period a deposit of metallic zirconium 1/16 inch thick was obtained on the base metal shape. Upon completion of the electrolysis, the cathode shape was withdrawn from the bath and cooled in an argon atmosphere to room temperature. The clad piece was removed from the cooling chamber and was leached free of residual salts. Metallographic examination of the resulting product showed that the zirconium-base metal bond was continuous and not intermittent, the base metal adjacent the bond exhibiting an intermediate region approximately equal in thickness to that of the zirconium layer.

Example II

The fused salt bath of sodium chloride and potassium fluozirconate described in Example I but with no addition of water failed to produce a clad layer of zirconium at bath temperatures of 770°–800° C. when attempts were made to deposit the zirconium on cathodes of steel, ingot iron, molybdenum, nickel and copper in the same cell and under the same electrolysis conditions prevailing in Example I.

Example III

A fused salt bath consisting of carefully purified and pre-electrolyzed mixture of sodium chloride (1800 parts by weight) and potassium fluotitanate (345 parts by weight) was electrolyzed at a cathode current density of 380 amperes per square decimeter on a steel cathode at 885° C. under the cell conditions reported in Example I. No addition of water was made. There was no evidence of a cladding layer of titanium, the titanium deposit being granular and loosely adhering to the cathode.

Example IV

A fused bath consisting of 1800 parts by weight of sodium chloride and 400 parts by weight of potassium fluotitanate, the latter containing 20% water of crystallization, was electrolyzed at 770° C. under the cell conditions set forth in Example I and resulted in a clad layer of titanium adhering to an ingot iron cathode by a metal-to-metal bond.

It will be seen, accordingly, that the method of my invention effectively clads a wide variety of base metals with a firmly adherent layer of a corrosion-resistant metal. Inasmuch as the resulting product may frequently be used without further deformation during subsequent fabrication, the ductility of the clad layer is not important. As a matter of fact, the tendency of the electrodeposited metal to exhibit a hardness greater than that compatible with cold rollability, as is generally exhibited by these metals in their electrodeposited form, becomes a virtue inasmuch as it enhances the durability of the corrosion-resistant surface on the basic metal object. Thus, the purity of the clad layer is relatively unimportant except for any influence which such impurities may have on the corrosion-resistance of the cladding metal. Nevertheless, clad layers produced in the manner of my invention have exhibited fabrication properties which permit the clad specimens to be deformed readily in subsequent fabrication.

I claim:

1. The method of cladding a base metal with a corrosion-resistant metal of the group consisting of titanium, zirconium, hafnium, vanadium, tantalum, niobium, chromium, molybdenum and tungsten by electrolysis in a fused salt bath which comprises establishing a fused salt bath consisting essentially of (*a*) a major amount of a halide of the group consisting of alkali metal and alkaline earth metal halides, (*b*) about 15 to 50% by weight of a double fluoride of an alkali metal and the corrosion-resistant metal and (*c*) about ¼ to 10% by weight of water, maintaining said bath at an elevated temperature above its melting point, and then electrolyzing the bath at said elevated temperature between a solid anode and a solid cathode composed of a base metal having a melting point substantially above the melting point of the bath, and recovering the resulting base metal cathode clad by a metal-to-metal bond with the corrosion-resistant metal.

2. The method of cladding a base metal with a corrosion-resistant metal of the group consisting of titanium, zirconium, hafnium, vanadium, tantalum, niobium, chromium, molybdenum and tungsten by electrolysis in a fused salt bath which comprises establishing a fused salt bath consisting essentially of (*a*) a major amount of a halide of the group consisting of alkali metal and alkaline earth metal halides, (*b*) about 15 to 50% by weigh of a double fluoride of an alkali metal and the corrosion-resistant metal and (*c*) about ½ to 5% by weight of water, maintaining said bath at an elevated temperature above its melting point, and then electrolyzing the bath at said elevated temperature between a solid anode and a solid cathode composed of a base metal having a melting point substantially above the melting point of the bath, and recovering the resulting base metal cathode clad by a metal-to-metal bond with the corrosion-resistant metal.

3. The method of cladding a base metal with a corrosion-resistant metal of the group consisting of titanium, zirconium, hafnium, vanadium, tantalum, niobium, chromium, molybdenum and tungsten by electrolysis in a fused salt bath which comprises establishing a fused salt bath consisting essentially of (*a*) a major amount of a halide of the group consisting of alkali metal and alkaline earth metal halides, (*b*) about 15 to 50% by weight of a double fluoride of an alkali metal and the corrosion-resistant metal and (*c*) about ¼ to 10% by weight of water, maintaining said bath at an elevated temperature above its melting point but below the melting point of any alloy of the corrosion-resistant metal with the base metal, and then electrolyzing the bath at said elevated temperature between a solid anode and a solid cathode composed of a base metal having a melting point substantially above the melting point of the bath, and recovering the resulting base metal cathode clad by a metal-to-metal bond with the corrosion-resistant metal.

4. The method of cladding a base metal with a corrosion-resistant metal of the group consisting of titanium, zirconium, hafnium, vanadium, tantalum, niobium, chromium, molybdenum and tungsten by electrolysis in a fused salt bath which comprises establishing a fused salt bath consisting essentially of (*a*) a major amount of a halide of the group consisting of alkali metal and alkaline earth metal halides, (*b*) about 15 to 50% by weight of a double fluoride of an alkali metal and the corrosion-resistant metal and (*c*) about ¼ to 10% by weight of water, maintaining said bath at an elevated temperature above its melting point, and then electrolyzing the bath at said elevated temperature between a solid anode and a solid cathode composed of a base metal having a melting point substantially above the melting point of the bath and with a cathode current density within the range of about 100 to 500 amperes per square decimeter, and recovering the resulting base metal cathode clad by a metal-to-metal bond with the corrosion-resistant metal.

5. The method of cladding a base metal of the group consisting of titanium, zirconium, hafnium, vanadium, tantalum, niobium, chromium, molybdenum and tungsten with another metal of said group by electrolysis in a fused salt bath which comprises establishing a fused salt bath consisting essentially of (*a*) a major amount of a halide of the group consisting of alkali metal and alkaline earth metal halides, (*b*) about 15 to 50% by weight of a double fluoride of an alkali metal and of the metal with which the base metal is to be clad, and (*c*) about ¼ to 10% by weight of water, maintaining said bath at an elevated temperature above its melting point, and then electrolyzing the bath at said elevated temperature between a solid anode and a solid cathode composed of a base metal having a melting point substantially above the melting point of the bath, and recovering the resulting base metal cathode clad by a metal-to-metal bond with the corrosion-resistant metal.

6. The method of cladding a base metal with a corrosion-resistant metal of the group consisting of titanium, zirconium, hafnium, vanadium, tantalum, niobium, chromium, molybdenum and tungsten by electrolysis in a fused salt bath which comprises establishing a fused salt bath consisting essentially of (*a*) a major amount of a halide of the group consisting of alkali metal and alkaline earth metal halides, (*b*) about 15 to 50% by weight of a double fluoride of an alkali metal and the corrosion-resistant metal and (*c*) about ¼ to 10% by weight of water, maintaining said bath at an elevated temperature above its melting point under a cell atmosphere substantially free of oxygen-, nitrogen- and carbon-containing gases, electrolyzing the bath at said elevated temperature between a solid anode and a solid cathode composed of a base metal having a melting point substantially above the melting point of the bath, and recovering the resulting base metal cathode clad by a metal-to-metal bond with the corrosion-resistant metal.

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POROUS ANODE

Bertram C. Raynes and Merle E. Sibert, Euclid, and John T. Burwell, Jr., Gates Mills, Ohio, assignors to Horizons Titanium Corporation, Princeton, N. J., a corporation of New Jersey

No Drawing. Application December 14, 1953, Serial No. 398,191

4 Claims. (Cl. 204—64)

This invention relates to the electrolytic deposition of certain transition metals and, more particularly, to the electrolytic deposition of titanium, zirconium, hafnium, vanadium, tantalum and niobium.

In the copending application of two of us, Merle E. Sibert and John T. Burwell, Serial No. 358,194, filed May 28, 1953, there is described and claimed the electrolytic deposition of the aforementioned transition metals by electrolyzing, as the anode of a cell, a substantially 100% density carbide of the transition metal in a fused halide bath under a cell voltage below that at which any bath component, including a halide of the transition metal, decomposes with evolution of a significant amount of free halogen. In the course of this electrolysis of the transition metal carbide, the metal component of the carbide is anodically dissolved in the bath and is transported through the bath for deposition at the cathode under conditions which are virtually the same as those prevailing at conventional aqueous electroplating operations. As the carbide anode becomes depleted in its metal component, and this depletion begins at the surface of the anode structure and develops inwardly, there remains behind a coherent carbonaceous structure substantially free of the metal. However, because of the dense and non-porous structure of the anode material used in the practice of invention of the aforementioned application, the coherent carbonaceous structure developed at the surface of the anode as a result of decomposition of the carbide has a correspondingly dense and non-porous structure and therefore tends to isolate the inner residual mass of metal carbide in the anode from the fused salt electrolyte. As a result, it has been found that only about 20% of the metal constituent of such a dense anode material can be anodically dissolved and deposited at the cathode before the resistance of the anode to further anodic dissolution becomes so high as to require a cell voltage which causes the unwanted and undesirable decomposition of some of the bath components. Consequently, after a minor amount of the metal carbide of the anode structure has been consumed by electrolysis, the aforementioned dense carbide anodes have had to be disintegrated and reprocessed into fresh anode structures.

We have now found that it is possible to produce the aforementioned transition metal carbide anodes having only about one-half the density of the aforementioned carbide anode structures, and we have further found that these relatively low density carbide anodes are amenable to over 90% utilization in continuous electrolytic operation at cell voltages below that at which a significant amount of any fused salt bath component is electrolytically decomposed. Accordingly, our present invention resides in the use of a transition metal carbide anode having an apparent density of approximately 50% of the carbide itself in an electrolytic operation such as that described in the aforementioned Sibert and Burwell application Serial No. 358,194 and in the Sibert and Burwell application Serial No. 383,401, filed September 30, 1953, in both of which the anode is electrolyzed in a fused halide bath under a cell voltage below that at which any bath component decomposes with the evolution of a significant amount of free halogen.

We have found that the aforementioned transition metal carbide anodes having a relatively low apparent density may be obtained by substantially the same procedure as that described in the aforementioned application with the exception of particular control over the nature of the carbonaceous component of the carbide and over the sintering conditions under which this anode structure is formed.

Our invention will be more fully understood from the following discussion of the preparation of a low-density high-porosity titanium carbide anode, and the electrolytic decomposition of this titanium carbide anode in a fused salt diluent bath with the resultant deposition of metallic titanium at the cathode of the electrolytic cell. It must be understood, however, that this discussion is directed to titanium carbide merely in the interest of simplicity and that what is said here with regard to titanium applies generally to each of the other transition metals, zirconium, hafnium, vanadium, tantalum and niobium.

The essential chemical characteristic of the titanium carbide which may be used as the titaniferous anode material in practicing our invention, in addition to its being substantially free of impurities other than uncombined carbon, is that it contains no oxygen in the form of incompletely reduced titanium oxides or in any other form. When produced in the presence of carbon monoxide or carbon dioxide, titanium carbide, which is formed by a high temperature reaction between titanium oxide and carbon, tends to retain in the residual carbide product enough oxygen to disqualify it for use in the practice of the invention. Thus, the mere presence of a stoichiometric excess of carbon during reduction of a titanium oxide at a temperature below that at which fusion occurs is not by itself sufficient to produce such oxygen-free carbide and must be supplemented by carrying out the reduction under vacuum conditions so as to remove from the reaction zone any carbon dioxide or carbon monoxide, or both, as rapidly as formed. Therefore, the titanium carbide which is useful in practicing our invention will generally, but not necessarily, contain a small amount, usually about 0.5 to 2% by weight, of free carbon. This free carbon, it will be understood, is a deliberate and extraneous contaminant when it is present in the titanium carbide anode material.

The physical characteristic of the titanium carbide anode material required for the practice of our invention is that the small crystals of titanium carbide forming the anode be firmly sintered into a rigid, relatively strong mass having a porous structure and an apparent density approximately one-half that of the titanium carbide itself. It is important that the adjoining crystals of titanium carbide in the anode be firmly sintered together while at the same time the essential porous structure of the titanium carbide mass is preserved. Thus, because of the porosity of the carbide anode material, relatively free movement of electrolyte and dissolved titanium metal is permitted throughout the carbide mass, and, because of the firmly sintered nature of the anode material, more than 90% of the titanium component of the titanium carbide anode material may be electrolytically removed therefrom without significant destruction of the residual carbide-carbon structure. The electrolytic decomposition of such a porous titanium carbide anode under the conditions set forth herein results in the transference of the titanium component of the carbide anode to the cell cathode while leaving the carbon component of the carbide as a black, solid, self-coherent mass in the physical shape of the original anode.

A titanium carbide anode having the aforementioned chemical and physical characteristics can be readily produced from raw materials either directly in a single operation or less directly in an operation involving first the production of titanium carbide and then the formation of an anode from this carbide material. Irrespective of the method employed to form the titanium carbide anode material, however, the raw materials that must be used are purified titanium dioxide (or other oxide of titanium) having a particle size of about 20 microns or smaller and purified carbon in the form of graphite having a particle size of 44 microns or less (i. e. minus 325 mesh Tyler Standard). These purified and finely divided raw materials comprising a mixture of stoichiometric proportions of the titanium oxide and graphite, together with about 1% to 2% excess graphite to insure a minimum of oxygen in the final product, are brought into intimate contact with one another by means of a ball mill or other grinding device. The resulting mixture of titanium oxide and graphite is then treated in either of the following alternative procedures to manufacture a carbide anode material suitable for the practice of our invention.

In the more direct procedure for the manufacture of the anode material, the mixture of titanium oxide and graphite is mixed with about 2% of a binder such as methyl cellulose and with sufficient water to form a plastic moldable mass. The plastic mixture is then extruded, pressed or otherwise formed into the rectangular slabs, cylindrical rods, coarse lumps or other shapes required of the anode. The formed anodes are dried and then are heated in a controlled atmosphere furnace to convert the raw materials into the desired titanium carbide anode material. Care must be taken to remove the carbon monoxide evolved during the conversion of titanium oxide to titanium carbide from the zone of the reaction substantially as rapidly as it is formed in order to prevent the inclusion of oxygen in the final carbide anode material. Moreover, the temperature should be closely controlled to insure firm sintering of the crystals of titanium carbide formed by the reaction while at the same time avoiding such drastic sintering or fusion of these crystals which would destroy the essential porosity of the anode material. The atmosphere of the furnace is evacuated until the pressure therein is reduced to about 20 microns of mercury, and the temperature of the furnace is raised to within the range of about 2100° to 2200° C. and is maintained within this range throughout the reaction period while continuing active vacuum pumping. This sintering operation, it will be noted, is carried out in the complete absence of any sintering aid, such as the alkali and alkaline earth metal halides, which are used in practicing the method of the aforementioned Sibert and Burwell application, Serial No. 358,194 to produce a high density carbide with this relatively low sintering temperature range. After the conversion of the raw materials to the desired porous titanium carbide anode is complete (as indicated by the cessation of evolution of carbon monoxide from the anode) the furnace is allowed to cool while maintaining the vacuum. After reaching room temperature, the vacuum is broken and the resulting sintered anode material is removed from the furnace.

Alternatively, a titanium carbide powder may be prepared from the mixture of titanium oxide and graphite, and this powder may then be formed into the desired low density carbide anode material. In this alternative procedure, the mixture of titanium oxide and graphite is placed in a controlled atmosphere furnace and the air within the furnace is evacuated by means of a high speed vacuum pump until the pressure therein is reduced to about 20 microns. The mix is thereupon heated to a temperature within the range of about 1500° to 2000° C. for about 2 hours while continuing active vacuum pumping in order to remove the evolved carbon monoxide from the zone of reaction. On completion of the reaction the furnace is cooled, the vacuum is broken, and the carbide material is removed. The resulting titanium carbide material is then crushed to minus 40 mesh (Tyler Standard) and is mixed with about 2% of a binder such as methyl cellulose and with sufficient water to form a plastic mass. The plastic carbide mass is formed into the desired anode shape, is dried to remove excess water, and then is fired in a controlled atmosphere furnace to sinter the carbide and form the desired porous anode material. The firing should be conducted under a vacuum of about 20 microns in order to avoid the occlusion of oxygen (from carbon oxides) in the titanium carbide product, and the temperature at which the firing is conducted should be closely controlled so that the carbide mass is firmly sintered without drastic sintering or fusion in order to preserve the porosity and low density of the anode material. The temperature of the furnace should therefore be maintained within the range of about 2100° to 2200° C. throughout the firing period and in the absence of any mineralizer or other sintering aid such as is used in forming a high density carbide pursuant to the method described in the aforementioned Sibert and Burwell application. On completion of the sintering operation, the furnace is cooled, the vacuum is broken, and the carbide anode material is removed for use in the electrolytic process.

As hereinbefore noted, the titanium carbide anode material produced according to either of the foregoing procedures is a rigid, self-supporting material having an apparent density of approximately 50% that of the titanium carbide of which it is formed. That is, the apparent density of the anode material is approximately 2.2 gm./cc. as compared to the actual density of titanium carbide, which is about 4.25 gm./cc. The low density and porous structure of the anode material is due to the use of highly purified and finely divided raw materials, the graphitic form of the carbon constituent of the anode, and the close control of the sintering temperatures employed. An average analysis of a titanium carbide anode produced in accordance with our procedure shows less than .02% oxygen, less than .02% nitrogen, less than .005% hydrogen, and substantially theoretical amounts of titanium and carbon.

The high purity carbide anode material is electrolytically decomposed in a fused salt diluent bath composed of a mixture of alkali metal halides and a halide of the transition metal, the bath composition and the electrolytic condition being those described in the first mentioned Sibert and Burwell application. The cell voltage, as noted hereinbefore, is maintained below about 3 volts in order to prevent the electrolytic decomposition of any of the fused salt components of the bath. The anodic decomposition of the carbide anode results in the dissolution in the fused salt bath of the transition metal component of the carbide anode. This transition metal is transferred through the bath and is deposited on the cathode in the form of firmly adhering crystals. The cathode, which may be formed from a metal such as iron that is unaffected by the fused salt bath, is periodically removed from the bath and a new cathode is substituted therefor. The electrolysis may be continued without interruption, except for the substitution of fresh cathodes, until at least 90% of the transition metal component of the carbide anode material has been anodically dissolved in the fused salt bath and (except for mechanical losses) has been deposited at the cathode.

The fused salt baths which may be used in the practice of our invention may vary considerably in composition. For example, the fused salt bath may be composed, in addition to the transition metal halide, of one or a mixture of the chlorides, bromides, iodides and fluorides of alkali metals such as sodium and potassium. The titanium (or other transition metal) halide may be a chloride, bromide, iodide or fluoride and may be a simple halide or a complex halide such as a double fluoride of titanium and an alkali metal (also known as an alkali metal fluotitanate). The titanium halide should be present in the bath in the amount of at least about 5% by weight and generally up to about 25% by weight. The presence of fluorine in the bath in the form of such an alkali metal-titanium double fluoride, or of a simple alkali metal fluoride, promotes the formation of larger particles of cathodically deposited titanium than that which is obtained by any one or a mixture of the other halides. Except for this special effect of an added fluoride, the specific composition of the bath appears to have no effect upon the quality of the titanium metal deposited. Illustrative bath compositions which are useful in the practice of our invention are set forth in the following table, the numerical values under each salt heading representing the parts by weight or percentage of each component in the bath:

K_2TiF_6	NaCl	KCl	NaBr	KBr	NaI	KI
5	95	--	--	--	--	--
10	90	--	--	--	--	--
10	45	45	--	--	--	--
5	30	20	20	15	10	--
10	20	--	30	--	30	10

Decomposition of a titanium carbide anode during electrolysis proceeds with the deposition of metallic titanium on the cathode and the development of a residual carbon structure or regulus at the anode. When the titanium carbide anode has been formed under optimum temperature conditions, there is a negligible tendency for this carbide-carbon residue to become detached from the anode and enter into the bath. However, it is possible to guard against possible contamination of the titanium deposit with liberated particles of carbon or titanium carbide by interposing an inert mechanical barrier between the anode and the cathode as mentioned hereinbefore. Such a barrier may comprise, for example, a graphite partition pierced with a number of very fine holes with the top of the partition positioned below the surface of the fused salt bath so as to insure the presence of a low resistance electrical path through the bath. In general, however, the provision of a trough-shaped well or the like in the lower portion of the cell structure is sufficient to collect any particles of the carbon residue which become detached from the anode. Such a collector of carbon particles may be provided in conjunction with a mechanical barrier by mounting a graphite cylinder, pierced with a number of fine holes, concentrically about the anode with the upper end of the cylinder positioned below the surface of the fused salt bath and with the lower end of the cylinder either embedded in the cell bottom or in a layer of solid bath composition maintained in the solid state by water cooling of the lower portion of the cell.

The electrolysis is carried out under purified argon in which all oxygen, hydrogen, water vapor, nitrogen, and the like have been eliminated by conventional cleaning techniques well known in the technical arts. When titanium carbide anodes are properly made the electrolytic reaction proceeds quietly as long as a significant amount of titanium carbide remains in the anode structure. Most efficient utilization of the titanium carbide dictates a physical shape such as to provide a relatively large surface area-to-volume ratio. With these conditions properly observed, at least 90% of the titanium content of the titanium carbide immersed in the fused salt bath may be deposited on the cathode without interrupting the electrolysis or raising the cell voltage above about 3 volts.

The cathodically deposited titanium metal is formed as a tightly adhering, densely deposited and well-crystallized metal. The cathode with the deposited titanium metal and adhering fused salt is periodically withdrawn into a separate cell chamber so that it may be cooled out of contact with air, whereupon a fresh cathode is immediately

inserted in its place. After cooling of the withdrawn cathode is completed, the cathode deposit is knocked off and is disintegrated by treatment with hot water. The disintegrated cathode deposit is washed several times until substantially all of the salt has been removed, after which the powdered metal is dried under vacuum. It may then be compressed and fused either under a vacuum or under a controlled atmosphere of argon or helium to form a massive ingot.

The following examples are illustrative but not limitative to the practice of our invention.

Example I

Titanium carbide anode material was prepared by mixing pure titanium dioxide with an amount of finely divided graphite about 1% in excess of that required to convert all of the titanium dioxide to titanium carbide. The particle size of the titanium dioxide in the mixture was less than 20 microns and the particle size of the graphite was less than 44 microns. The mixture of titanium dioxide and graphite was ground together in a ball mill and then was mixed with about 1% of methyl cellulose binder and with enough water to wet the mixture. The resulting plastic mass was then formed into a rectangular anode shape approximately 3 x 4 x 1 inch. The anode shape was placed in a controlled atmosphere furnace connected to a high speed vacuum pump and the pressure within the furnace was reduced to below about 20 microns. The furnace was heated to a temperature of about 2100° C. and this temperature was maintained for about 2 hours. Continuous active vacuum pumping removed carbon monoxide from the furnace substantially as rapidly as it was evolved from the reaction mass. At the end of the reaction period, the titanium dioxide and graphite had been converted to a sintered mass of fine titanium carbide crystals. The apparent density of the titanium-carbide anode material was 2.2 gms./cc., or approximately 50% of the density of titanium carbide itself. The sintered carbide anode weighed 330 grams of which 263 grams comprised the available titanium constituent thereof.

The sintered carbide anode was placed into a previously prepared fused salt diluent bath. The composition of the fused salt diluent bath comprised 60 parts by weight of reagent grade sodium chloride and 9 parts by weight of pure anhydrous potassium fluotitanate. The fused salt bath, the temperature of which was maintained at about 850° C., had previously been subjected to a purification electrolysis to remove therefrom all traces of oxygen and water. The electrolysis of the titanium carbide anode material was carried out at the aforesaid temperature at a cell voltage of between 2.5 and 3.0 volts. The titanium metal anodically dissolved at the anode was deposited on a cathode formed of a one-inch diameter steel rod. During the course of the electrolysis the steel cathode became heavily coated with a layer of deposited titanium metal necessitating replacement of the cathode with a fresh cathode at frequent intervals. The cathodic deposit of titanium metal on each of the cathodes was removed therefrom under conditions that prevented the contamination of the metallic deposit with atmospheric oxygen.

Of the total of 263 grams of titanium available in the titanium carbide anode, 248 grams of crystallized titanium metal was deposited at the cathode. This amount of titanium deposited at the cathode represented a 94% recovery of the titanium content of the carbide anode. The final weight of the carbide anode was 78 grams, of which 66 grams was graphitic carbon. The average overall current efficiency was approximately 60%. The metallic titanium recovered from the anode was washed to remove adhering salts and the resulting metal crystals were melted under an inert atmosphere to form an ingot weighing 218 grams. The loss of 30 grams in weight of metal deposited at the cathode was due to metal fines washed away and other mechanical losses. The titanium metal had a Brinell hardness of 140–180.

Example II

The operation described in Example 1 was repeated for each of the other transition elements, zirconium, hafnium, vanadium, tantalum and niobium, the only variations being that the carbide of the transition element was substituted for titanium carbide and that the potassium double fluoride of the respective transition element was substituted for the potassium titanium fluoride referred to in Example 1. Electrochemical efficiencies and metal recovery efficiencies were substantially the same for each of these transition elements as they were in the case of titanium.

We claim:

1. In a method of electrolytically depositing a metal of the group consisting of titanium, zirconium, hafnium, vanadium, tantalum and niobium, which comprises the steps of preparing an anhydrous fused salt bath consisting essentially of at least one alkali metal halide and at least about 5% by weight of a halide of said metal, introducing into said bath a carbide of said metal to be electrodeposited, passing an electrolyzing current through the fused bath between said carbide and a cathode in electrical contact with said bath, and recovering the resultant cathodically deposited metal; the improvement which comprises: providing said carbide as a sintered porous rigid mass having a density after sintering of approximately one-half that of the solid metal carbide and having a self-coherent carbon skeleton which remains after removal of metal from the mass during said electrolysis.

2. In a method of electrolytically depositing titanium, which comprises the steps of preparing an anhydrous fused salt bath consisting essentially of at least one alkali metal halide and at least about 5% by weight of a halide of titanium, introducing into said bath a titanium carbide, passing an electrolyzing current through the fused bath between said carbide and a cathode in electrical contact with said bath, and recovering the resultant cathodically deposited titanium; the improvement which comprises: providing said carbide as a sintered porous rigid mass having a density after sintering of approximately one-half that of the solid metal carbide and having a self-coherent carbon skeleton which remains after removal of titanium from the mass during said electrolysis.

3. In a method of electrolytically depositing titanium, which comprises the steps of preparing an anhydrous fused salt bath consisting essentially of at least one alkali metal halide and at least about 5% by weight of a halide of titanium, introducing into said bath a titanium carbide, passing an electrolyzing current through the fused bath between said carbide and a cathode in electrical contact with said bath, and recovering the resultant cathodically deposited titanium, the improvement which comprises: providing said carbide as a sintered porous rigid mass having a density after sintering of approximately 2.2 grams/cubic centimeter and having a self-coherent carbon skeleton which remains after removal of the titanium from the mass during said electrolysis.

4. In a method of electrolytically depositing zirconium, which comprises the steps of preparing an anhydrous fused salt bath consisting essentially of at least one alkali metal halide and at least about 5% by weight of a halide of zirconium, introducing into said bath a carbide of said metal to be electrodeposited, passing an electrolyzing current through the fused bath between said carbide and a cathode in electrical contact with said bath, and recovering the resultant cathodically deposited zirconium; the improvement which comprises: providing said carbide as a sintered porous rigid mass having a density after sintering of approximately one-half that of the solid metal carbide and having a self-coherent carbon skeleton which remains after removal of zirconium from the mass during said electrolysis.

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ELECTROLYTIC PROCESS

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No Drawing. Application July 9, 1956
Serial No. 596,450

12 Claims. (Cl. 204—64)

This invention relates to the refining of impure titanium metal and its alloys by an electrolytic procedure. More particularly, it relates to a method of electrolytically refining impure titanium material in a fused salt medium by passing a direct current between a cathode on which a refined titanium product is deposited and solid impure titanium immersed in the fused salt and in electrical contact with an anode.

Titanium metal and titanium alloys have recently achieved considerable prominence as materials of construction possessing a peculiarly advantageous combination of properties. The relatively low weight and excellent corrosion resistance to particular environments have caused this metal and its alloys to be employed in a number of applications with outstanding results.

Most of the titanium presently produced is obtained by the reduction of titanium tetrachloride by means of magnesium as in the Kroll process, described in U.S. Patent 2,205,854 or by means of sodium or other reducing agents. The resulting product, after treatment to remove various contaminants, is then consolidated by arc melting or other techniques.

In another approach to the production of this metal, the metal is recovered from various titanium compounds by electrolysis of fused salt baths containing titanium compounds. Thus, the production of titanium metal in the from of a cathode deposit from a fused bath by the electrolytic decomposition of titanium monoxide is described in U.S. Patent 2,707,168. Electrolytic decomposition of a mutual solid solution of titanium monoxide and titanium carbide is disclosed in U.S. Patent 2,722,509. The decomposition of purified alkali metal fluotitanates is taught in U.S. Patent 2,731,402. The production of titanium from various other titanium compounds, principally titanium halides, is disclosed in a number of other U.S. patents, but except for metal produced by the De Boer-Van Arkel (iodide) process, it has been found necessary to separate the metal produced by pyrometallurgical processes from other contaminating reaction constituents. In addition, titanium produced by pyrometallurgical process always contains a proportion, sometimes large, of off-grade impure metal unsuitable as primary metal.

Furthermore, in the fabrication of the titanium metal and its alloys, a high percentage of scrap material is generated in the form of bar, sheet and ingot croppings; turnings and shavings; and material of even finer particle size from grinding, drilling and boring operations. Because of the high affinity of the metal for oxygen and nitrogen, the reclamation of the scrap material by simple melting procedures has been found to be difficult. Furthermore, much of the scrap already contains substantial proportions of tenaciously held impurities acquired either during the initial winning of the metal or during the subsequent conversion of the metal to various finished products.

Unfortunately, in many of the foregoing procedures the metal scrap or the crude virgin metal obtained after removal of adhering salts is contaminated with oxygen and/or other impurities which severely restrict its utility and cause its properties to be noticeably impaired.

In British Patent 728,523 which appears to correspond to United States Patent 2,734,856 there is described a method of refining impure titanium metal in which impure titanium metal forms the anode in a fused salt electrolyte comprising titanium dichloride and titanium trichloride in stated concentrations. When proceeding in the manner described in the British patent the metal product obtained as a cathode deposit usually had a Brinell hardness of 200 or more which greatly exceeded the hardness which was acceptable to the trade. By suitably modifying the process it has now been discovered that when crude titanium metal or titanium scrap, both alloyed and unalloyed, is electrolyzed in a fused salt bath in the manner about to be described, the metal obtained as a cathode deposit has a Brinell hardness lower than 120 and often as low as 80–90, and is substantially free from the major portion of these undesirable contaminants. This metal has a usefulness greatly exceeding that of the unrefined metal and it has been found that the metal may be consolidated directly into solid stock material by suitable powder metallurgical technique, thus avoiding the necessity for melting the product metal to obtain useful product, as has been heretofore necessary in the utilization of titanium produced by electrochemical or pyrometallurgical techniques.

Briefly, the method comprises electrolysis of a fused alkali metal halide salt bath containing an alkali metal fluotitanate as a carrier salt in which there is immersed titanium metal or titanium alloy scrap which is in electrical contact with an anode, the electrolysis being carried out under certain conditions about to be described, which have been found to be determinative of the quality of the metal produced. It has been found that the electrorefining of the impure metal produces, after a short time, dependent upon the impurity and alloy content of the metal, a sludge containing substantially all of the nonmetallic contaminants and a portion of the metallic contaminants in addition to some of the titanium metal content of the material to be refined.

By maintaining the over-all cell voltage and the anode current density at values below those at which the sludge exhibits any appreciable tendency to go into solution in the fused bath, particularly when in contact with a supply of available metal and maintaining a fresh supply of available titanuim scrap in the cell at at times and in electrical contact with the anode and with the fused salt bath and particularly with the sludge, it has been found that oxygen, hydrogen, nitrogen, carbon and other nonmetallic impurities are not transported to the cathode or deposited thereon. As a result, the cathode deposited metal is considerably purer than the material to be refined.

While we do not wish to be bound by any specific theory as to the reasons for the much lower hardness of the metal obtained by the changes introduced by us in the process described in British Patent 728,523, we believe that in the vicinity of the anode the metallic titanium, in the form of the impure material to be refined, at the elevated temperatures at which the electrolysis is to be carried out, appears to function as a "getter" or sequestering agent for the impurities in the bath and in or on the scrap and in the atmosphere above the bath and that the sludge which forms contains the highly impure product of the reaction between the heated titanium metal and the oxygen, carbon, and similar impurities in the system.

In carrying out the process, a melt is prepared by fusing a mixture of alkali metal halide salt and alkali metal-titanium double fluoride. To the fused melt, there is then added the impure titanium metal. One or more of several possible reactions is then believed to take place, whereby a titanium carrier in which the titanium is trivalent or possibly divalent forms. The formation of such a material may follow from either a chemical reaction (e.g. $3Ti^{+4}+Ti^{0}\rightarrow 4Ti^{+3}$) or an electrochemical reaction (e.g. $Ti^{+4}+e\rightarrow Ti^{+3}$), or both; that is, it may occur before any electrical current is passed through the cell or as a result of the passage of such current, or partially from both causes. In any event, in order to electrodeposit pure titanium metal at the cathode, a carrier ion in which the titanium has a valence less than four is required to be present in the fused salt bath.

Regardless of the actual explanation, we have found that in continuous cell operation the purity of the cathode deposited metal, as evidenced by the diminished hardness and increased purity of such metal, and the efficiency of the electrolysis, were both noticeably increased whenever an excess of metal was present in the region of the anode, and when an excess of such metal was in electrical contact with any sludge present, as would be the case, for example, immediately after compacting the charge and immediately after charging a fresh supply of metal to be refined, into the cell.

The fused salt bath in which the present electrorefining is effected is preferably formed of a solvent comprising one or more alkali metal halides and one or more of the normal double fluorides of titanium and an alkali metal. The alkali metal halides are available commercialy of a purity sufficient for the present process. For reasons of economy, the akali metal chlorides, particularly sodium chloride, are preferred, but any of the other alkali metal halides may be used, either alone or as mixtures of one or more of said halides. Preferably the alkali metal halide is in the anhydrous condition. Double fluorides of the alkali metals and titanium are also available commercially, particularly K_2TiF_6 and Na_2TiF_6. As has been indicated in U.S. Patent 2,731,402, it is desirable to subject these double fluorides to at least a simple recrystallization, to remove most of the extraneous impurity content and thereby to improve the quality of the metal obtained. It should be understood that such a treatment is optional, and is preferred because it tends to diminish the total amount of sludge formed during the electrolysis.

A preferred anhydrous salt bath electrolyte composition useful at the start of a refining operation is one containing about 16% by weight of K_2TiF_6 and about 84% by weight of NaCl. The process may, however, be operated with as little as 3% or as much as 30% by weight of the double fluoride in the initial fused electrolyte. To lower the cost of the bath ingredients, it is preferred to operate with no more than 18% of the double fluoride in the fused salt electrolyte. Under the usual conditions of operation, the bath composition remains virtually unchanged during the operation, and it merely becomes necessary to add make-up salts from time to time to compensate for the mechanical losses or for salt removed with the cathode deposit. The make-up salt addition is preferably in the form of a mixture of NaCl and K_2TiF_6 in the ratio of 84:16 by weight.

The other major raw material in the process is the impure titanium metal. As has been indicated above, this may be either virgin metal, such as that obtainable by the Kroll process or other processes, or scrap metal produced as a result of normal fabrication of the metal and its alloys. When the metal is grossly contaminated with dirt, grease, or other undesirable material (e.g. masking tape) it is cleaned by any of the conventional methods common in the treatment of scrap, e.g., by tumbling the scrap in contact with a solvent such as trichlorethylene. Depending on the configuration of the cell, it may be found to be necessary to reduce the titanium scrap in size or to consolidate by bundling, pressing, etc., before any refining is performed in the electrolytic cell.

The electrolytic cell employed in the process consists of a container of any suitably refractory material. Graphite, nickel, iron, stainless steel and other alloys have been found suitable as the crucible or container. In the manner now well known in this art, the cell should be provided with means to heat the contents and to maintain the contents molten; means for maintaining an inert atmosphere in the cell; and a diaphragm or baffle for confining the scrap charge to a region adjacent the anode. The container itself may advantageously serve as the anode.

The electrolytic cell thus consists of a container, means to heat the container, means for maintaining any desired inert atmosphere therein, at least one cathode suspended in an electroylte contained in the cell, at least one anode in the cell, and means whereby the impure charge is confined, within the melt, to a region closely adjacent the anode.

The metal added to the melt is added adjacent to the anode and remote from the cathode. Preferably it is confined to the regions of the cell which are farthest removed from the cathode. For instance, in a cell in which the bath is contained in a square or rectangular crucible, and with the cathode suspended at the intersection of the diagonals, the scrap is confined to the corners of the anodic crucible by means of perforated baffles of graphite or other suitable metallic or ceramic material.

When graphite is used as one of the materials of construction of the cell or baffles, or when pieces of graphite or of titanium carbide are added to the charge, we have found that the sludge formed during the refining operation consists principally of a compound having the formula Ti_2OC.

When the anode (crucible) has a circular cross section, e.g. when it is cylindrical, with the cathode suspended along the axis of the cylinder, the scrap-confining means may conveniently comprise a perforated cylinder of smaller diameter, nested in the larger cylinder. For other cell geometries, other arrangements will be readily apparent to those skilled in the art.

Before the cell is heated, an argon, helium or other suitable inert atmosphere is provided. Thereafter the electrolyte and scrap charge are heated and electrolysis is initiated following the charging of the scrap. Electrolysis proceeds smoothly at cathode current densities of between 50 and 600 amperes per square decimeter, and at bath temperatures between about 875° C. and 950° C. No significant evolution of gas occurs once the cell is operating properly. From the wide range of cathode current densities at which the process has been operated satisfactorily, it will be readily apparent that the cathode current density is not a critical operating limitation. Rather, we have found that in the present process, the anode current density is of much greater significance in determining the quality of the refining achieved. Since the cathode dimensions are continually increasing during electrolysis, it would be difficult to maintain any exact current density, but this situation does not obtain at the anode, which retains its original average geometric dimensions throughout the process. Hence operation at a specific anode current density is relatively easier to accomplish. In our process, anode current densities of 7–75 amp./sq. dm. have been found to produce satisfactory metal while densities in the range 35–40 amperes per square decimeter, have been found to produce optimum refining of the impure metal.

The following examples will serve to further illustrate our invention but are not to be taken as limitative thereof.

EXAMPLE I

After an electrolytic cell with a dry argon atmosphere was heated to a temperature of about 850° C., commercially pure sodium chloride was charged into the cell and heating was continued under the argon atmosphere until the sodium chloride was fused. Recrystallized potassium fluotitanate was charged into the fused sodium chloride in the proportion of 6 parts of K_2TiF_6 to 84 parts of NaCl (by weight). Pieces of degreased metallic titanium scrap in the form of small clippings approximately ½ inch x ¼ inch in area and $\frac{1}{16}$ inch thick were charged between a perforated graphite barrier which served as the anode, and the crucible wall, which was also anodic. The scrap was tamped with a tamping rod to insure that it would remain in physical contact with the anode and with any sludge formed during the electrolysis. An iron cathode was then inserted into the bath to a depth of 9 inches. The cathode was about 3⅜ inches from the anode. The cell temperature was maintained between about 910° C. and 935° C. and electrolysis of the charge was carried out at this temperature under the argon atmosphere while maintaining the cell voltage within the range of 2.8 and 2.9 volts. The cathode current density during the electrolysis period of 110 minutes varied between 225 and 450 amperes per square decimeter, and the anode current density varied between 34 and 39 amperes per square decimeter. After 1710 ampere hours had been passed through the cell, the deposit was withdrawn, stripped from the cathode and separated from adhering salts. To initiate further runs, the cathode was reinserted into the melt, and additional scrap and bath salts were added at intervals. The following table indicates the oxygen, hydrogen, nitrogen, and carbon contents of the original scrap and of the refined metal, and also the Brinel hardness of an arc melted button of the refined metal products for a series of other runs made under similar operating conditions.

Table I

Metal	Brinell Hardness	Percent O	Percent H	Percent N	Percent C
Charge	218	0.233	0.032	0.016	0.114
Run:					
VII-3	83	0.026	0.006	0.009	--------
VIII-1	107	0.075	0.002	0.002	0.023
VIII-5	86	0.031	0.001	0.006	0.009
VIII-14	95	0.050	0.001	0.005	0.009
VIII-39	130	0.077	0.004	0.002	0.005
IX-23	94	0.043	0.002	0.005	0.014
X-1	110	0.053	0.002	0.005	0.027
X-10	127	0.092	--------	0.003	0.014
X-26	116	0.073	--------	0.009	0.014
X-74	103	0.050	--------	0.009	--------
X-75	86	0.031	--------	0.004	--------
X-94	107	0.069	--------	0.003	0.024

A spectrographic analysis of the original scrap showed the following in addition to titanium:

	Percent
Si	0.01
Mn	0.25
Mg	0.03
Al	0.005
Mo	<0.001
V	<0.001
Cu	0.001
Zr	<0.05
Ni	0.002
Sn	<0.001
Ca	<0.005
Cr	0.002

Not detected—Cd, Sb, B, Pb, Co.

EXAMPLE II

Example I was repeated using a scrap comprising chips about ½ inch x 1 inch in size, produced in a machining operation. The scrap was a uniform golden color and was charged into the cell in the as received condition, it having been degreased before shipment.

The unrefined scrap analyzed, in addition to titanium:

	Percent by weight
Oxygen	0.338
Hydrogen	0.010
Nitrogen	0.029
Carbon	0.089
Si	0.01
Mn	0.15
Mg	0.02
Al	0.01
Mo	<0.001
V	<0.001
Cu	0.001
Zr	<0.05
Ni	0.005
Sn	<0.001
Ca	<0.005
Cr	0.008

Not detected—Cd, Sb, B, Pb, Co.

Results of refining this scrap by electrolysis under an argon atmosphere, in a K_2TiF_6—NaCl fused salt bath, at temperatures between 890° C. and 930° C. and anode current densities within the range of 35 amperes per square decimeter and 40 amperes per square decimeter of anode area are shown in Table II.

Table II

Metal	Brinell Hardness	Percent O	Percent H	Percent N	Percent C
Original Charge	260	0.338	0.010	0.029	0.089
Run:					
XI-1	110	0.066	--------	0.014	0.014
XI-3	90	0.025	--------	0.010	0.010
XI-14	107	0.047	--------	0.005	--------

A more complete spectrographic analysis of the products of some of the runs in Example I and Example II is given below.

	Run VII-3	Run VIII-5	Run X-75	Run XI-14
Hardness	83	86	83	107
Mn	0.17	0.17	0.20	0.20
Zr	<0.05	0.05	0.05	0.05
Mg	0.007	0.009	0.01	0.01
Al	0.005	0.007	0.006	0.007
Si	0.003	0.003	0.004	0.003
Cr	0.005	0.003	0.004	0.004
Ca	<0.005	<0.005	<0.005	<0.005

<0.001 each Mo, V, Ni, Sn, Cu
Not detected—Cd, Sb, B, P, Co.

EXAMPLE III

A synthetic titanium scrap was made by heating forty pounds of the scrap of Example I to temperatures between 1200 and 1400° C. in the presence of controlled amounts of air. The resulting product was separated into a silvery-gold fraction (I) and a blue to violet fraction (II). Both fractions were electrolyzed in the same manner as in the previous examples in a fused

$$NaCl—K_2TiF_6$$

(84:16) melt at about 900° C. and at 1.5–2.8 volts, and 35–40 amperes per square decimeter of anode area.

The results are given below.

Table III

Metal	Brinell Hardness	Percent O	Percent H	Percent N	Percent C
Charge (I)	>350	0.570	0.061	0.182	0.061
Run XI-22	145	0.133	--------	0.019	--------
Charge (II)	>350	5.22	0.066	3.53	0.426
Run:					
XI-23	210	0.069	--------	0.010	0.024
XI-25	188	0.227	--------	0.017	0.014

EXAMPLE IV

Efforts made to refine the scrap of Example I by repeating the procedure of that Example except that the scrap was not tamped to squeeze out the sludge formed in the main body of the anode and to maintain the bottom part of the scrap in contact with the sludge which formed, resulted in products with Brinell hardness considerably in excess of 120, and often as high as 250 or higher. It was found that immediately after tamping the scrap, the hardness and purity of the titanium product were greatly improved as compared with the hardness and purity of metal produced just previously thereto. The following consecutive runs, made under process conditions which were substantially identical except for the disposition of the scrap, illustrate this point.

Table IV

	Brinell Hardness	Remarks
Scrap	218	
Run:		
VII-17	238	Tamped, 20 pounds of scrap added.
18	180	
19	159	
Run:		
VII-25	205	Scrap tamped, 12 pounds of scrap added.
26	160	
Run:		
VII-46	250	
47	235	Tamped, 12 pounds added.
48	195	Tampod, 12 pounds added.
49	180	

As seen from the preceding description, impure titanium metal has been refined to a product which is a high purity ductile titanium, by passing a direct electric current through a fused salt bath consisting essentially of at least one alkali metal halide and at least one double fluoride of titanium and of an alkali metal, maintained at a temperature of about 920° C., and under an inert atmosphere, and by maintaining the impure metal disposed in a manner in which dissolution of the sludge formed was not favored.

An X-ray diffraction analysis was performed on the water insoluble part of two sludges recovered after 73 electrolytic runs and 94 electrolytic runs respectively. The results indicated the presence of carbon and of titanium oxycarbide, a solid solution of TiO and TiC approximating the formula: Ti_2OC. Neither free titanium metal nor titanium oxides could be identified. Petrographic examinations indicated the existence of only two phases: carbon and titanium oxycarbide. For the later series of runs, the proportion of $Ti_2OC:C$ was much higher than for the earlier series, showing that the compacting or tamping of the loose scrap tended to force the sludge out of the scrap material, whereby fresh scrap surfaces were presented for electrorefining.

Metal powder recovered from the cathode deposits of typical runs was mixed, briquetted and arc-melted into cast buttons. Each of the buttons was cold rolled 40% from an original thickness of 0.475 inch. The cold rolled product was annealed at 700° C. and reduced another 40% by cold rolling. The strips were again annealed at 700° C. and cold rolled to 0.063 inch thickness. The product strip was ductile with a good surface and very little edge cracking. The total reduction was 87%.

Samples of the 0.063" strip were tested for tensile properties. The tensile strength was found to be 115,000 p.s.i., the elongation 12% and the hardness of the as rolled strip was 245 Brinell. When annealed at 750° C. for one hour the hardness of the strip fell to 125, the percent elongation increased to 34% and the tensile strength was 52,000 p.s.i. Furnace cooling after the anneal at 750° C. produced a product with a 64,000 p.s.i. tensile strength and a 30% elongation, properties comparable with those of commercial titanium. The annealed strip had a fine grained equiaxed alpha structure, characteristic of pure titanium.

Other metal powder recovered from the cathode deposits of typical runs was cold briquetted into compacts 1 inch in diameter and about 2 inches in thickness. The compacts were made by pressing at about 25,500 p.s.i. and had green densities of between about 2.6 and 3.2. After heating in an argon atmosphere the compacts were extruded to ¼" and ⅜" diameter rods, at reduction ratios of 16/1 and 7/1 respectively, at a temperature of about 1400° F. Tensile tests were performed on two of the extruded rods with the following results, after annealing for one hour at 750° C.

Table V

Diameter	BHN	Density	Percent Theoretical Density	Tensile Strength, p. s. i.	Elongation, percent
¼ inch	121	4.52	99.6	85,600	48
⅜ inch	136	4.51	99.6	68,600	36

The extruded rods were cold reduced from 0.250 inch to 0.010 inch by cold rolling with annealing at 700° C. between intermediate reductions. The resulting strip had a good surface and was ductile.

While the foregoing description describes the refining of titanium scrap, it will be evident to those skilled in this art that other titanium bearing materials, for example, both impure titanium metal containing undesirable amounts of oxygen, carbon, sulfur, nitrogen, or more than one of these elements, and metallic compounds of titanium, e.g. ferrotitanium are suitable raw materials in our process to recover titanium in the form of a cathode deposited pure metal. Furthermore, although for the sake of brevity the description has been confined to a discussion of the refining of titanium bearing material, we have found our process to be equally applicable to the treatment of materials containing other elements in Group IV–A, particularly zirconium and hafnium, to produce said elements substantially pure metals, in the form of cathode deposits from a fused salt electrolysis as above described.

We claim:

1. The method of electrolytically refining impure titanium metal to produce a refined ductile metal having a Brinell hardness number less than 120 which comprises: providing an electrolytic cell having an anode and a cathode with an inert atmosphere, and a molten salt electrolyte consisting essentially of at least one alkali metal halide and at least one alkali metal fluotitanate; maintaining said atmosphere inert and said salt molten; charging impure titanium metal into said molten salt so that it is in physical contact with said anode; passing an electrolyzing direct current through said cell thereby depositing titanium on said cathode and forming a sludge containing the impurities in said impure metal; maintaining said sludge in physical contact with the unrefined impure titanium metal; maintaining an anode current density and voltage during the passage of said current sufficient to deposit purified titanium metal at the cathode but insufficient to liberate any halogen gas at the anode and insufficient to electrolytically dissociate any of the sludge formed during said refining; thereby separating impurities from the titanium metal and depositing refined titanium at the cathode.

2. The method of electrolytically refining impure titanium metal to produce a refined ductile metal having a Brinell hardness number less than 120 which comprises: providing an electrolytic cell having an anode and a cathode and a molten salt electrolyte consisting essentially of at least one alkali metal halide and at least one alkali metal fluotitanate; maintaining an inert atmosphere in said cell; charging impure titanium metal into said cell so that it is in physical contact with said anode; passing an

electrolyzing D.C. current through said cell to deposit titanium on said cathode and to form a sludge adjacent the anode containing non-metallic impurities in said scrap; maintaining an anode current density and voltage during the passing of said current sufficient to deposit purified titanium metal at the cathode but insufficient to liberate any halogen gas at the anode; maintaining the sludge of titanium and non-metallic impurities in physical contact with said scrap; thereby separating impurities from the titanium metal and depositing refined titanium at the cathode.

3. The method of electrolytically refining impure titanium metal to produce a refined ductile metal having a Brinell hardness number less than 120 which comprises: providing an electrolytic cell having an anode and a cathode and a perforated barrier dividing said cell into an anode compartment and a cathode compartment, while permitting the circulation of a molten salt electrolyte; introducing and maintaining an inert atmosphere in said cell; forming a molten electrolyte in said cell consisting essentially of at least one alkali metal chloride and at least one alkali metal fluotitanate; charging impure titanium metal into said cell on the anode side of said barrier so that it is in physical contact with said anode; passing a D.C. electrolyzing current between said anode and cathode and through said melt, thereby depositing titanium metal at the cathode and forming a sludge containing the impurities in said metal adjacent the anode; maintaining said sludge in physical contact with the impure titanium metal charge and adjacent the anode; maintaining an anode current density and voltage during the passage of said current sufficient to deposit purified titanium metal at the cathode but insufficient to liberate any halogen gas at the anode and insufficient to electrolytically dissociate any of the sludge formed during said refining; thereby separating impurities from the titanium metal and depositing refined titanium at the cathode.

4. The method of electrolytically refining impure titanium metal to produce a refined ductile metal having a Brinell hardness number less than 120 which comprises: passing an electric current through an electrolytic cell having an anode and a cathode and a molten salt electrolyte consisting essentially of at least one alkali metal chloride and at least one alkali metal fluotitanate and maintained under an inert atmosphere; charging impure titanium metal in the form of small pieces in electrical and physical contact with said anode; forming a sludge containing the impurities in said metal, by passage of said current; maintaining an anode current density and voltage during the passage of said current sufficient to deposit purified titanium metal at the cathode but insufficient to liberate any halogen gas at the anode and insufficient to electrolytically dissociate any of the sludge formed during said refining; intermittently compacting said metal to be refined, to cause the sludge formed during said refining to become detached from said metal and to collect on the bottom of the cell while remaining in physical contact with said impure metal; thereby separating impurities from the titanium metal and depositing refined titanium at the cathode.

5. The method of electrolytically refining impure titanium metal to produce a refined ductile metal having a Brinell hardness number less than 120 which comprises: passing an electric current through an electrolytic cell having an anode and a cathode and a molten salt electrolyte consisting essentially of sodium chloride and potassium fluotitanate (K_2TiF_6); disposing said impure titanium metal so that it is in physical contact with said anode and remains in physical contact with a sludge formed by the impurities during said refining; maintaining a current density and voltage during the passage of said current sufficient to deposit purified titanium metal at the cathode but insufficient to liberate any halogen gas at the anode, thereby depositing refined titanium at the cathode.

6. The method of producing a pure group IV–A metal of the group consisting of titanium, zirconium and hafnium which comprises: passing a direct electric current between an anode in electrical contact with a source material containing said metal associated with a substantial impurity content and a cathode immersed in a fused salt electrolyte; maintaining an anode current density and a cell voltage during the passage of said current density and a cell voltage during the passage of said current which are sufficient to deposit said group IV metal on said cathode, but insufficient to liberate any free halogen gas at the anode and insufficient to electrolytically dissociate any of the sludge formed with the impurities during said passage of current; maintaining said sludge in physical contact with said impure metal to prevent the transfer of sludge containing impurities to the cathode deposit; thereby separating the impurities from the group IV–A metal, and recovering said group IV–A metal from said cathode deposit.

7. The method of electrolytically refining an impure metal of the group consisting of impure titanium, impure zirconium and impure hafnium, to produce an electrorefined, ductile metal which comprises: passing an electrolyzing current through an electrolytic cell having an anode and a cathode and means dividing said cell into an anode compartment and a cathode compartment while permitting the circulation of a molten salt electrolyte between said compartments; introducing and maintaining an inert atmosphere in said cell; forming a molten electrolyte in said cell consisting essentially of at least one alkali metal chloride and at least one fluoride of an alkali metal and the impure metal to be refined; providing a charge comprising said impure metal and at least one additive of the group consisting of graphite and a carbide of said metal in the anode compartment of said cell and in physical contact with the anode; forming a sludge containing the impurities in said metal by passage of said current; maintaining an anode current density and voltage during the passage of said current sufficient to deposit refined metal at the cathode but insufficient to liberate any halogen gas at the anode and insufficient to electrolytically dissociate the sludge formed during said refining; and intermittently applying pressure to said metal to be refined to urge it into more intimate physical contact with the anode and to maintain it in physical contact with the sludge, while separating the sludge from a large portion of the surface of the small pieces constituting the charge.

8. The process of claim 7 in which the pressure is applied by tamping the pieces of charged material.

9. The process of claim 7 in which the metal recovered is titanium and the charge comprises pieces of impure titanium and pieces of graphite.

10. The process of claim 7 in which the metal to be recovered is zirconium and the charge comprises a mixture of pieces of impure zirconium and pieces of graphite.

11. In a method of electrorefining an impure metal of the group consisting of titanium, zirconium and hafnium which includes: (1) passing an electrolyzing current through an electrolytic cell circuit including an anodic portion, a cathodic portion and a molten salt electrolyte which consists essentially of at least one alkali metal halide and at least one double fluoride of an alkali metal and the metal to be electrorefined, and which connects said anodic portion to said cathodic portion; (2) disposing said impure metal so that it is in physical and electrical contact with the anodic portion of the circuit; thereby causing said impure metal to be separated into metal deposited at the cathode portion of said circuit and impurities contained in a sludge formed at the anode portion of said circuit; the improvement comprising maintaining said sludge in contact with said charge by intermittently physically urging said charge into more intimate contact with such sludge.

12. The process of claim 11 further improved by the incorporation of graphite into the impure charge to be refined.

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May 17, 1960 B. C. RAYNES ET AL 2,937,128

ELECTROLYTIC APPARATUS

Filed July 25, 1956 4 Sheets-Sheet 1

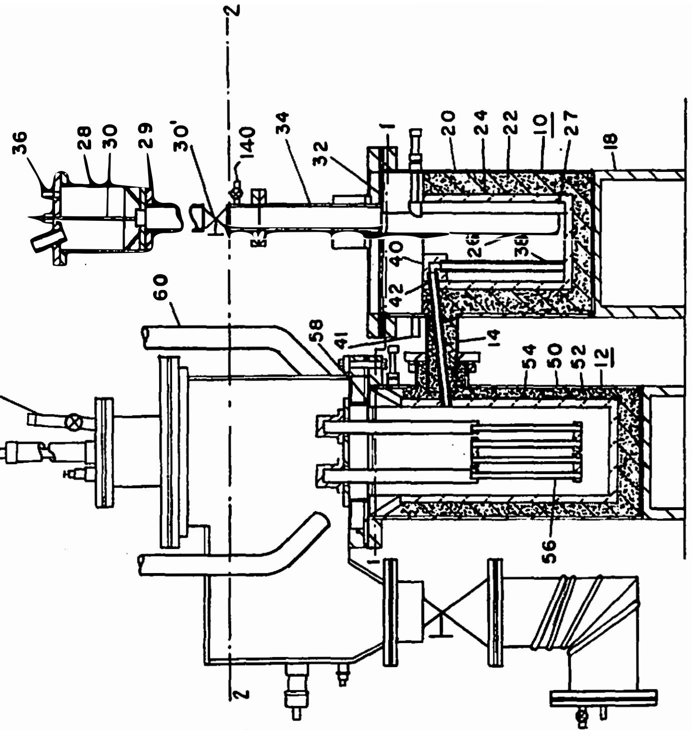

FIG. 3

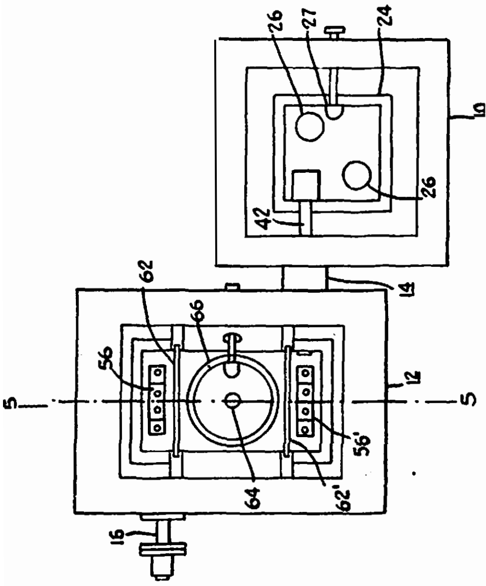

FIG. 1

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ELECTROLYTIC APPARATUS

Filed July 25, 1956 4 Sheets-Sheet 2

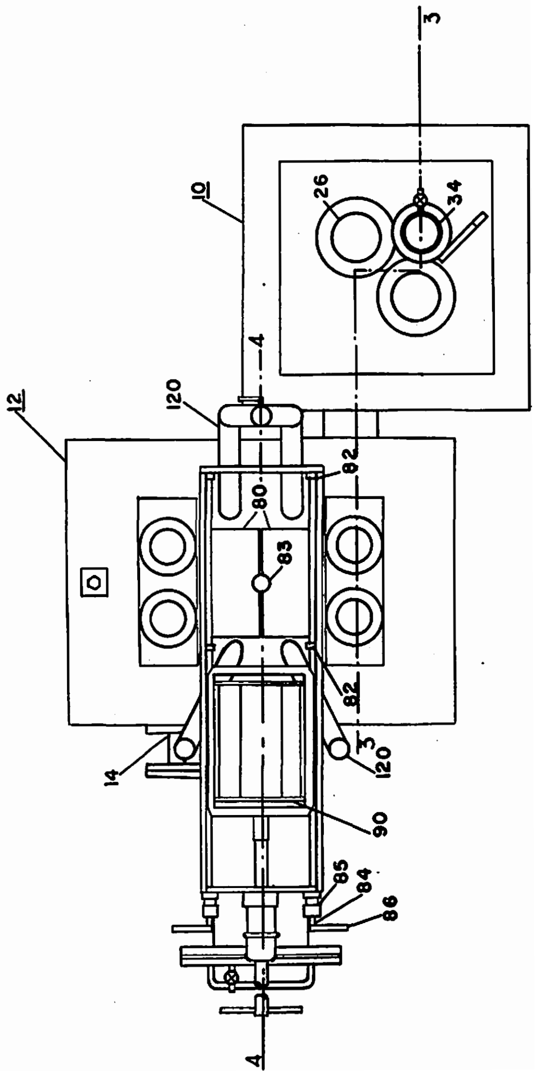

FIG. 2

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ELECTROLYTIC APPARATUS

Filed July 25, 1956 4 Sheets-Sheet 3

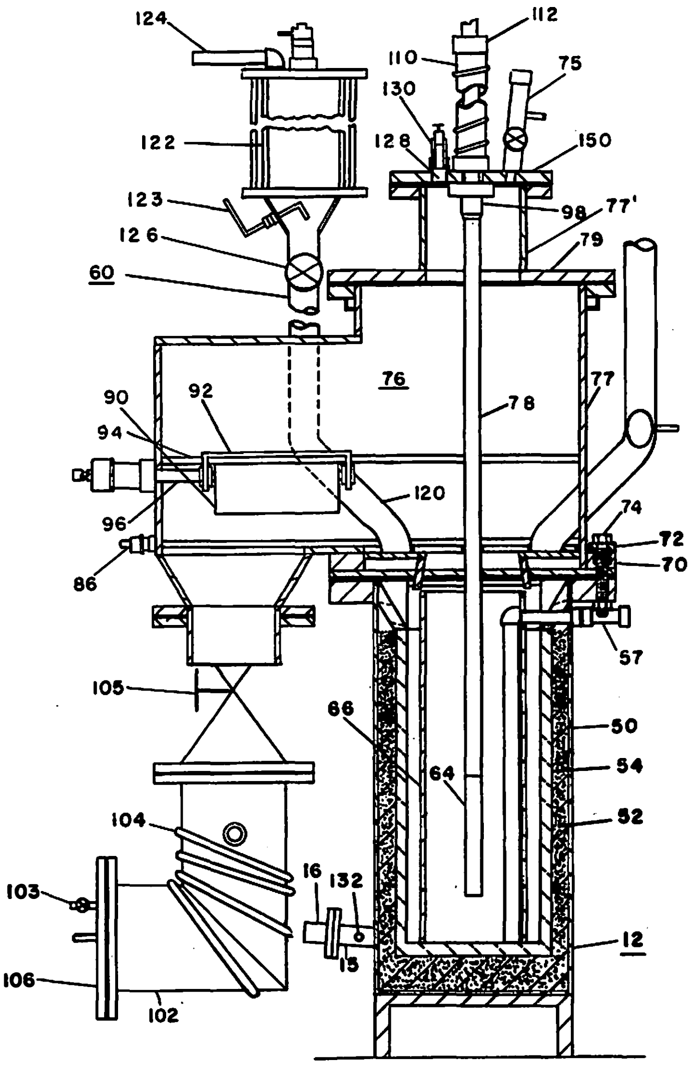

FIG. 4

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ELECTROLYTIC APPARATUS

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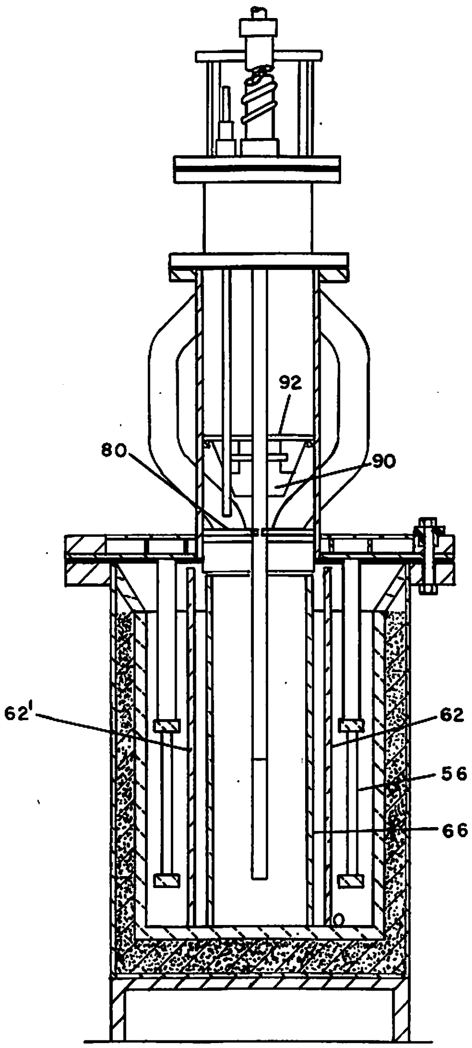

FIG. 5

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ELECTROLYTIC APPARATUS

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Application July 25, 1956, Serial No. 600,093

4 Claims. (Cl. 204—244)

This invention relates to the electrolytic preparation of metals. More particularly, it relates to an improved apparatus wherein the electrolysis of a fused salt bath may be accomplished to produce the desired metal as a cathode deposit.

The metals titanium, zirconium, niobium, tantalum, uranium and other metals of groups IVA, VA and VIA of the periodic table have recently come into prominence because they possess properties found to be extremely desirable in the construction of equipment for use in processes operating at high temperatures or at high levels of radioactivity. Considerable effort has, therefore, been devoted to the development of means for producing the desired metals by continuous electrolytic methods offering advantages over the older pyrometallurgical processes.

One object of this invention is to provide an apparatus for continuously producing said metals as cathode deposits in a fused salt electrolytic process.

Another object of this invention is the provision of an apparatus within which the preparation of a purified electrolyte, the fused salt electrolysis by which the desired metal is recovered as a cathode deposit, and the recovery of the cathode deposit in a form in which and at a temperature at which it is no longer reactive with the ordinary atmosphere, are all carried out in a manner designed to avoid the contamination of the ultimate metal product.

Another object of this invention is the provision of an improved means for preparing the electrolyte for said electrolysis.

Another object of this invention is the provision of an improved means for recovering the cathode deposited metal without impairing its quality and without materially reducing the continuity of operation of the cell.

These and other objects will become more apparent from the following specification and drawings in which:

Figure 1 is a top view of the portion of the apparatus below plane 1—1 of Figure 3;

Figure 2 is a top view of the apparatus as seen on plane 2—2 of Figure 3;

Figure 3 is a side view taken on plane 3—3 of Figure 2;

Figure 4 is a view taken on plane 4—4 of Figure 2; and

Figure 5 is a view taken on plane 5—5 of Figure 1.

Figure 1 shows a plan view of the general arrangement of the lower portion of the apparatus with the upper portion removed. As may be seen, the lower portion of the apparatus comprises a first vessel 10 in which the electrolyte is melted and purified and from which the molten electrolyte is transferred, and a second vessel 12 in which the electrolysis for recovering the desired metal is performed. The two vessels may be placed in communication with one another by means 14 comprising a conduit and associated structure. A drain 16 is provided to empty the second vessel 12. In addition to the lower portion of the apparatus shown in Figure 1, the other portions of the apparatus include means for charging the two vessels and for recovering the cathode deposited metal, means for supporting the means for heating the vessels and for ascertaining the temperatures of their contents, and means

for maintaining a desired atmosphere in the apparatus, shown more completely in the remaining figures.

As shown in Figures 1 and 3, the melting and purifying vessel 10 comprises a base 18 on which there is supported a metallic shell 20 of steel, nickel or other suitable material of construction. Shell 20 may assume any convenient shape, a square, rectangle or any equilateral polygon being generally preferred for ease and simplicity of fabrication, although circular or elliptical shells or shells whose shapes are a combination of curved and straight sides may be employed in our apparatus. Within the shell 20 is a packing 22 of lampblack, carbon, or other suitable powdered or granular heat insulating material on which there is supported an inner vessel 24 prefabricated from structural elements of any suitable material of construction, such as graphite or ceramic. In a preferred embodiment, shown in the drawings, the inner vessel serves as the anode. It will, of course, be understood that a separate anode may be substituted if an electrically neutral vessel is employed. Between the inner vessel and the outer shell the packing of granular material provides a zone into which the contents of the inner vessel may leak in a controlled manner as described in a copending application Serial No. 504,952, which issued February 26, 1957, as United States Patent 2,783,195 and which was filed jointly by one of the present applicants. Heating means 26, which may be one or more suitable immersion type heaters, is suspended in the inner vessel and serves to melt the salt, thus forming the electrolyte. Means 27 for suspending a thermocouple in the melt may be provided for control purposes. A charge hopper 28 controlled by valves 30 and 30′ permits the charging of weighed amounts of the ingredients constituting the electrolyte into the inner vessel. Hopper 28 is detachably supported on a flanged plate 29. A conduit 34 connects hopper 28 with a cover 32 through which it enters vessel 10. Cover 32 seals off and provides an air-tight shield for the top of the vessel 10. A connection 36 is provided to manifolds (not shown) for maintaining a vacuum or admitting argon or other inert atmosphere into the hopper 28 and conduit 34.

An exhaust vent 140 is provided to vent any gases evolved during the preconditioning of the electrolyte. Projecting through one side wall of the first vessel 10 and extending into the second vessel 12 is a means which serves to pass the salt charge, when molten, from the first vessel to the second vessel without exposure to the influence of a reactive environment likely to contaminate the charge of molten salts. This means, generally designated as 14, includes a conduit comprised of an impervious graphite riser 38 connected through a threaded elbow 40 to an inclined tube 42 which passes into the second vessel, together with inlet means 41, through a side wall of vessel 10, through which inert gas under pressure is admitted to cause the molten contents of vessel 10 to flow through riser 38 and tube 42 and into vessel 12. When it is desired to subject the contents of vessel 10 to electrolysis for the purpose of removing various impurities, a cathode (not shown) may be supported by the superstructure, e.g. by plate 29 in place of charging hopper 28.

The second vessel 12 constitutes the main electrolysis unit and is similar in many respects to the first vessel 10. It comprises a supporting shell 50, granular packing 52, an inner container 54, heaters 56 and 56′, thermocouple support 57, cover 58, and charging means 60 for introducing the material to be refined into the vessel. Vessel 12 is divided into three compartments by means of two partitions 62 and 62′ (Figure 1) which are formed of graphite or any other suitable material of construction. These partitions are pierced with a plurality of holes to permit the electrolyte to circulate freely. At least one heater is suspended in each of the end compartments, Preferably centrally disposed in the middle compartment is a cathode 64 which is suspended from above through means which electrically insulate it from the structure supporting it. Surrounding the cathode is a perforated barrier 66 formed of graphite or other suitably inert material. Barrier 66 is pierced with a large number of small holes to permit the molten salt to circulate freely. Barrier 66, which is preferably but not necessarily cylindrical, separates the middle compartment into a region surrounding the cathode within the inner confines of barrier 66 and a zone defined by partitions 62 and 62′, the walls of the inner container 54 and the outer surface of barrier 66. Both barrier 66 and container 54 are electrically anodic in the cell shown, but the barrier may be electrically neutral and either the charge or an electrode provided for the purpose may serve as the anode.

As best seen in Figure 4, the upper assembly of vessel 12 is mounted on a water-cooled flanged head 70 bolted to a flange on the shell 50. Most of the mechanical operations of the cell are performed within the confines of chamber 76 defined by sidewalls 77 and 77′ and upper plate 79 and a cover 150. A fitting 75 with a connection to the inert atmosphere and vacuum manifolds is provided in cover 150. Fitting 75 may accommodate a sight glass, or permit the insertion and removal of a bath sampling device. To simplify construction, the upper assembly is cathodic and is electrically insulated from the lower (anodic) portion of the cell by means of insulating bushings 72 provided on the connecting bolts 74 joining the superstructure to the lower portion of vessel 50. The cathode 64 is supported on a rod 78 which is of hollow construction to permit the temperature of the cathode to be controlled by means of fluids during deposition and during removal of the deposit. When the cell dimensions permit, several cathodes may be supported in like fashion. The lowermost portion of chamber 76 is closed by two baffles 80 to diminish the loss of heat from the cell, or from inner container 54. The baffles are hinged (Figure 2) at 82 and are cut away at the center of the vessel to provide an opening 83 for the rod 78 supporting the cathode, to permit the cathode to be inserted and withdrawn from the inner container 54. The baffles are operated by small steel rods 84 which pass through stuffing boxes 85 to external handles 86. Instead of pivoting, the baffles may be supported so as to permit their insertion into operating position by sliding in grooved trackways, or in any appropriate fashion.

Means are provided within the chamber 76 to recover the cathode deposit without exposure of said deposit to any contaminating influences, particularly while it is still at an elevated temperature. As best shown in Figure 4, there is a scraper 98 ground to a knife edge and secured to the cover plate 150 on the upper assembly, to detach the deposit from the cathode. Other means may, however, be employed to effect the separation of the cathode deposit from the cathode. A water-cooled receiving stack 110, to which a stuffing box 112 is attached, is positioned above the chamber 76 to accommodate the heated portion of the cathode in the scraping position. To recover the deposit after it has been scraped from the cathode, there is, in the embodiment shown, a tray 90 which is retractably mounted on a steel carriage 92 which rides on narrow steel rails 94 welded to the walls of the upper assembly chamber; a metal push rod 96 which advances and retracts tray 90 and which also rotates to permit the dumping of the deposit from tray 90, and the scraper 98. To protect the deposit from oxidation or other contaminating influence, a receiver 102, having a connection 103 to the inert gas manifold is provided. The receiver may be cooled either by the surrounding atmosphere or by a cooling coil 104 or by other means. A gate valve 105 or similar type of closure connects chamber 76 with the receiver 102 and a manhole 106 is provided for removing the deposit from the receiver after the deposit has cooled sufficiently.

A means for charging solid material into vessel 12 is shown in Figures 2, 4 and 5. As shown, separate tubes 120 leading to each of the four corners of the middle compartment of vessel 12, conduct the solid material from a feed hopper 122 through a valve 126 to the portion of the middle compartment between the cylinder 66 and each of the partitions 62 and 62′. A stirrer 123 may be provided to assist in the discharge of the contents of hopper 122 and to prevent clogging of the charge material, although such means is entirely optional. Feed hopper 122 is also provided with a connection 124 to the vacuum and to the inert gas manifolds. Inlet openings 128 in cover 150 are closed by valves 130 located above the four corners of the middle compartment. Openings 128 provide access to the charge, to permit the insertion of suitable means to tamp or compact the charge; to measure the height of the materials in the vessel; to ascertain the physical condition and disposition of the charge in the vessel and to permit samples to be taken for control purposes.

A salt drain 16 is provided at the bottom of vessel 12, through which the molten electrolyte may be tapped off at any time. Drain 16 is essentially a nickel pipe 15 lined with graphite and extending through the crucible and cell walls, and shaped or inclined so that the drain opening 132 is above the bottom of the inside of container 54, so that a liquid seal is formed in the drain means. As shown, pipe 15 is preferably inclined upwardly as it leaves vessel 12. The outer end of pipe 15 is water-cooled and an electrically insulated graphite electrode extends through the center of the pipe into the salt bath. An outlet 132, leading to a removable drain pan, is provided near the outer end of the pipe. On addition of the first charge of molten electrolyte to the cell or on melting a solid charge, a small quantity of the salt enters the pipe and freezes to form a plug in the tube. When it is desired to drain the cell a cathode lead is attached to the electrode, completing a circuit through the electrolyte to the anode. The electrode then serves as a resistance heater which quickly melts out the salt plug, permitting the contents of the cell to drain. The drain hole is so positioned as to retain at all times a liquid seal against air entering the cell at completion of draining.

In order to prevent contamination of the molten salts or heated solid materials, it is necessary to provide an inert environment in the free spaces of the apparatus. As is customary in this art, an "inert" atmosphere, that is, one which does not react appreciably with the contents of the apparatus, is required. The usual atmospheres are composed of one or more of the noble gases. Such means for evacuating or flushing the several portions of the apparatus and means for maintaining any desired atmosphere therein have been previously described. Any suitable arrangement of valves and manifolds may be provided so that either vacuum or a noble gas such as argon or helium may be selectively maintained in vessel 10, vessel 12, and the charging and discharging means associated with these vessels.

Thus the vessel 10 is connected by means 41 to the inert atmosphere manifold and when it is charged from hopper 28, the desired atmosphere is maintained by means of a connection 36 to vacuum or to the inert atmosphere manifold. Furthermore, a vent 140 permits the removal of extraneous gases from vessel 10.

The main electrolysis vessel 12 is charged with solid materials by means of a feeder 122 provided with a connection 124 to the vacuum and to the inert gas manifolds, and is connected through manhole 106 and valve 105 to a connection 103 to the inert atmosphere manifold.

For purposes of illustration, the operation of our apparatus will be described in connection with the electrolysis of a fused salt bath to recover metallic titanium as the metal deposited on the cathode, but the apparatus has been found equally suited to the production of other metals and hence the temperatures and specific conditions of operation are to be taken as illustrative rather than limitative.

Operation

The entire system is flushed with argon or other noble gas, to provide an inert atmosphere in the system before heating any of the apparatus. Vessel 10 is then heated to any convenient temperature above the melting point of the salt charge while under the inert atmosphere. The individual salts or a weighed proportioned charge of a diluent salt such as sodium chloride (NaCl) and a carrier salt providing a simple or complex ion of the metal to be refined is charged into the charging hopper. The hopper is evacuated through line 36 and flushed with argon several times to remove entrained air. Valve 30 is opened and the salt charge is dropped into the inner vessel, where it melts rapidly. If salts of low purity are used, it may be found desirable to pre-electrolyze the melt, but this step is optional. Pre-electrolysis is effected by removing the salt feeder-charge hopper 28 with valve 30 closed. A flange in which a cathode is retractibly mounted is substituted in its stead and connected to flange 29. The top of the stack is evacuated and then flushed with argon. With the salt charge at operating temperature, e.g. about 900° C., the cathode is lowered into the bath, while impressing a slight polarizing voltage on the cathode. After the cathode has been lowered into the bath, the current is increased to provide a voltage and current density just sufficient for a small amount of free halogen gas (chlorine) to form at the anode. At the same time, oxides and water in the melt are decomposed and impurity metals in the salts are plated out onto the cathode. During this period, small amounts of argon are passed through vessel 10 in order to remove the chlorine and any other gaseous products evolved from the melt. After a sufficient quantity of electrolyzing current has been passed, depending on the extent of purification required or desired, the electrolyzing current is reduced and the cathode is raised out of the melt. After the cathode has cooled, the cathode and the flange in which it is mounted are removed and replaced by the salt charge hopper, in preparation for the next salt charge to be processed.

While the salt melt is being prepared in vessel 10, vessel 12, filled with argon or other inert gas, is slowly heated to operating temperature of about 900° C. When both vessels are at the operating temperature, a pressure equalizer between them is closed, the vent 140 is closed and flow of the inert gas through line 41 into vessel 10 is increased. The molten salt is thereby caused to flow up riser 38 and through the inclined tube 42 into the larger vessel 12. The transfer of about 50 pounds of molten salt has been effected readily in about 30 seconds. The operation is completed, after the melt has been blown over, by closing inlet 41 and by opening the vent 140.

Since, with continuous operation, the main function of vessel 10 is to provide molten salt melts of suitable purity to vessel 12 and since the loss of salts from vessel 12 is usually only a small fraction of the total contents of vessel 12, the capacity of vessel 10 is preferably but a fraction of the capacity of vessel 12 desired for the electrolytic refining operation. While not in use, the vessel 10 may be maintained at a temperature lower than operating temperatures in order to reduce the heat-up time required for subsequent operation. Make-up salt additions may be melted and purified at any time and either blown into the cell immediately after preparation, or held molten at temperature until transferred, or cooled and held in reserve after pre-electrolysis and purification.

Material to be refined, for instance small pieces or titanium scrap as described in our copending application Serial No. 596,450, filed July 9, 1956, is placed in each feeder 120 and the feeder is evacuated and flushed with argon. Baffles 80 are opened, and a steel rod is inserted in the cell through the opening 128, in the corner into which the material is to be charged. The valve 126 in the feeder is opened and a full charge of material is added and tamped into place if necessary by means of the rod. Generally the material to be refined is charged in all four corners to a height of about 2 to 4 inches below the height of the melt in vessel 12.

Once the cell is in operation, both molten salt and the scrap, sponge, or other material to be refined may be charged without interrupting the electrolysis.

Electrolysis is effected by lowering the cathode into the melt. On initial insertion a small polarizing voltage is maintained on the cathode to prevent the cathode from dissolving in the bath. The electrolyzing current and voltage are increased to the operating level. When the cathode temperature rises above a predetermined upper level, cooling of the cathode is initiated and regulated to maintain an indicated internal cathode temperature well below the melting point of the cathode. About 10 minutes before the termination of the run, the cooling of the cathode is discontinued, in preparation for the removal of the deposit. The maximum size of deposit is determined principally by the size of perforated cylinder 66 which serves as the anode. Cathode deposits representing between 1500 and 2400 ampere hours of electrolytic current have been successfuly produced in our apparatus. With the cathode temperature increased to about 800° C., the hinged heat shields are opened and the cathode is raised to a level just below the scraper 98. Tray 90 is moved directly under the cathode deposit by means of rod 96. The cathode is then pulled up against the knife-edge of scraper 98, to scrape the deposit onto the tray. When the deposit has been removed, cathode motion is stopped; the tray is retracted and the deposit is dumped through the gate valve 105 into the receiver. Following this, the cathode is lowered into the bath for a repetition of the process. Raising, scraping and lowering of the cathode may be accomplished in less than 60 seconds with the apparatus shown. The cathode deposit is permitted to cool and after it has reached a temperature below that at which it reacts with the atmosphere, manhole door 106 is opened and the deposit is removed. The door is replaced and the receiver is evacuated, flushed with argon, and is then ready for another run.

From time to time additional material to be refined is added to the corners of the middle compartment of vessel 12 to maintain it between 2 and 4 inches below the surface of the fused salt electrolyte.

It will be seen that we have provided a simple and efficient apparatus for the electrolytic refining of impure charge material, characterized by the provision of an improved means for conditioning the electrolyte and for avoiding contamination of both the intermediate and final products by oxygen or oxygen-containing compounds during the refining operation and for permitting essentially continuous electrolyses to be carried out without interruption for making additions of solid material to be refined and of makeup salts. Furthermore, the apparatus may be used to produce primary metals in which only fused salt charges are processed in the electrolyzing vessel 12, for example by conditioning salts in vessel 10 and transferring the conditioned salt to vessel 12 for electrolytic processing as described in U.S. Patent 2,731,402, of which one of the present inventors is a joint patentee.

We claim:

1. In an electrolytic apparatus, the combination including a first vessel provided with an airtight cover; means to charge said vessel with a salt; heating means to melt said salt form a molten electrolyte; conduit means to admit and means to maintain an inert atmosphere in said first vessel, above said charge of salt; a source of inert atmosphere, maintained under pressure; a valved connection between said source of inert atmosphere under pressure and said conduit; means to admit said inert atmosphere to said vessel; anode and cathode means positioned in said first vessel, means to impress a potential

across said anode and cathode means to effect an electrolytic purification of said molten salt; a second vessel adapted to serve as the main electrolytic cell; anode and cathode means in said second vessel; a source of potential connected to impress a potential between said anode and cathode means; a conduit connecting said first vessel with said second vessel whereby purified molten salt from said first vessel may be transferred to said second vessel under the influence of the pressure of inert gas on said molten salt in said first vessel; means to recover the cathode deposited metal from said second vessel, and means to maintain an inert atmosphere in said second vessel.

2. The apparatus of claim 1 including a means for draining the second vessel and said means provides a liquid seal between an outlet in said drain means and the molten contents of the second vessel.

3. The apparatus of claim 1 wherein the second vessel includes means to introduce a charge of solid material to be electrorefined into said second vessel, adjacent to the anode region.

4. The apparatus of claim 3 in which the second vessel serves as an anode and the region adjacent said anode for receiving a charge to be refined includes a perforated graphite member separating the cathode from the anode and defining with the anode, a charge confining zone adjacent the anode.

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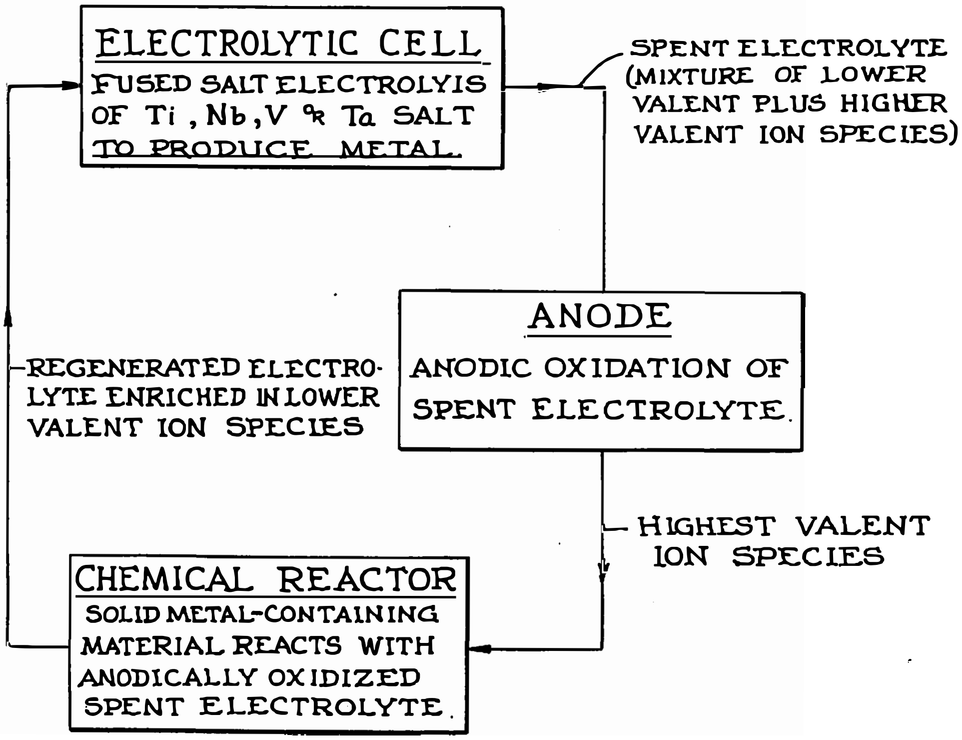
ELECTROLYTIC PROCESS

Filed Oct. 16, 1956



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2,955,078

ELECTROLYTIC PROCESS

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This invention relates to the production of transition metals such as titanium. More particularly, it relates to a fused salt electrolysis in which the metal is cathodically deposited and to an improved manner and means of carrying out said electrolysis.

In a copending application of John T. Burwell, Jr. and Quentin H. McKenna, Serial Number 398,193 filed December 14, 1953, which issued March 3, 1959 as United States Patent 2,876,180, there is described a method for producing cathode deposits of certain transition metals by electrolysis in fused salt baths wherein the source of the deposited metal is a fused salt electrolyte composition prepared by introducing a solid product composed of the carbide of the transition metal, or a mutual solid solution of the carbide and the monoxide of the transition metal or the transition metal itself in relatively impure form into a fused melt comprising at least one alkali metal halide or alkaline earth metal halide, or both, in further admixture with between 5 and 50% by weight of a halide of the transition metal. As further described, this melt may be the spent electrolyte of a previous electrolysis with consequent economy in the use of materials.

It has recently been observed that the system proposed in the earlier filed application suffers from one fundamental disadvantage which materially diminishes the efficiency of the operation when carried out in the cyclic manner contemplated. When "spent" electrolyte is withdrawn from the cell for reaction with a fresh supply of the solid material providing the transition metal, the reaction proceeds effectively between that portion of the spent electrolyte in which the transition metal is present in its highest valence state, e.g. +4 for titanium, but does not proceed to any appreciable extent between the transition-metal-providing-solid-material and the portion of the electrolyte in which the transition metal is present in its relatively lower valence states, e.g. +3 or +2 for titanium. It is evident, then, that it is necessary that the transition metal be present as an ion species in which it is in its highest valence form when it is brought into contact with the solid source material in order to efficiently convert the source of the transition metal, whether it be the carbide, mutual solid solution of carbide and monoxide or impure scrap metal, into the desired electrolyte from which the metal is later recovered as a cathode deposit.

From a study of the decomposition potentials in fused salt electrolytes, it seems probable that the transition metal ions present in the electrolyte comprise both higher valent ion species and lower valent ion species in proportions which vary. Hence when portions of the electrolyte are transferred from the cathode region to a region in which the transferred electrolyte is brought into contact with solid transition metal-providing material, it has been found that some lower valent ions inevitably accompany the desired higher valent transition metal ions.

It is a principal object of the invention to insure that the transition metal values in the recycled electrolyte be present in the highest valence form when recycled electrolyte is brought into contact with the solid transition metal-supplying material.

The method of the present invention is concerned with a cyclic process in which means are provided for insuring the presence of the transition metal ion species in the electrolyte is in the highest valent form when the electrolyte is brought into contact with the transition metal-supplying material. Furthermore, the method of this invention can be carried out in the electrolytic cell itself, if desired, thereby dispensing with the additional vessel required in the aforesaid Burwell, Jr. and McKenna application.

The method of the present invention is equally applicable to the production of any of the polyvalent transition metals which can be processed by the method of the aforementioned Burwell and McKenna application. That is, the present method is capable of producing any of the transition metals which, as impure metal, or as carbide, or as nitride, or as mutual solid solution of carbide and monoxide, or as carbide and/or monoxide and/or nitride dissolved in the metal, is capable of reacting with the higher valent ion species of the transition metal with consequent formation of the lower valent ion species of the transition metal. Titanium, niobium, tantalum and vanadium are presently known to participate in the stated reactions in the desired manner. In the case of zirconium and hafnium, there are presently indications that as chlorides these transition metals may exist in several valence states and hence it is entirely possible that these metals may be prepared by the presently proposed method.

In the drawings, the figure schematically depicts a suitable form of apparatus which may be utilized in the practice of this invention.

In accordance with the present invention, the fused electrolyte, hereinafter referred to as "spent" electrolyte, is withdrawn from the vicinity of the cathode for regeneration of the lower valent ion species whereby it will be rendered amenable to a repetition of the electrolysis. During regeneration of the electrolyte, the lower valent ions in the fused salt become reoxidized to the desired higher valence by contact with an anode provided for the purpose. To insure that substantially all of the transition metal ions ultimately present are in this higher valence state, in one embodiment of this invention, shown in the drawings an anodic means is provided between the cell and a reactor. One such anodic means, for example, is a packed anodic tube containing fragments of graphite through which the electrolyte salts are pumped or recycled en route to the reactor in which the higher valent ion species is to be reacted with the solid refractory metal-containing source material. Another suitable means for assuring the complete reoxidation of the polyvalent metal ions in the withdrawn electrolyte, is a perforated barrier or porous anode through which the spent electrolyte is forced to pass prior to entry into the reactor, thus effecting excellent contact between anode and electrolyte over a large surface area of anode with consequent completion of the conversion to the higher valent species of the transition metal ion in the electrolyte after it has been so processed.

Inasmuch as the production of titanium is representative of the production of the other aforementioned transition metals, the following description will be directed simply to the titanium aspect of the invention in the interest of simplicity. However, it must be understood that what is said with respect to the production of titanium applies with equal force and effect to the production of each of the other transition metals and particularly niobium, tantalum and vanadium.

The fused electrolyte from which a cathode deposit of titanium is formed pursuant to this invention may comprise one or more of the alkali metal halides, such as sodium and potassium chlorides, bromides, iodides and fluorides, or one or more of the alkaline earth metal halides such as calcium, barium, strontium and magnesium chlorides, bromides, iodides and fluorides or mixtures of one or more of each of these alkali metal halides and alkaline earth metal halides in further combination with a titanium halide, or with a lower valent titanium ion species whether or not it is considered as being derived from a halide.

The components of the electrolyte should be of high purity and should be substantially completely anhydrous in order to minimize the introduction of extraneous impurities, including oxygen, into the deposit of titanium produced by the electrolysis of the fused salt bath. The alkali metal halides and alkaline earth metal halides are commercially available in a state of purity adequate for use in the practice of the present invention. It is particularly desirable to have a resulting bath which is stable at temperatures up to 1200° C., and which has a relatively low melting point well below 800° C., and from which very little in the way of volatile fumes are lost within the temperature range between the melting point and 1200° C.

Fusion of the components of the electrolyte is carried out under conditions which will assure the absence of atmospheric oxygen and moisture. Thus, it has been found advantageous to carry out this fusion in a separate vessel in which an inert atmosphere of argon or other noble gas may be maintained. The salt in the melting vessel may be heated by any means which will not introduce impurities thereinto. For example, the heat may be supplied by electrical or burning means positioned outside the vessel. Alternatively, the salt may be heated by electric resistance elements within the melting vessel itself. The salts should be heated to a temperature at least 50° C., and advantageously about 100° C., above the fusion point in order to insure adequate reactivity of the ions in the fused mass. In general, the requisite bath reactivity is insured by heating to temperatures of at least about 850° C., or above. Temperatures of from about 850 to 1300° C., and preferably within the range of 900 to 1200° C. are effective in promoting the reaction between the solid titaniferous material and the higher valent titanium ion species present in the system, higher temperatures within this range promoting more rapid and more efficient reaction.

The introduction of the titanium component of the solid titaniferous material into the electrolyte is assured by simply immersing the solid titaniferous material in the bath and preferably in the preferred embodiment in the vicinity of the anode. The solid titaniferous materials useful for this purpose are those in which the titanium is present as an interstitial rather than a substitutional element. These titaniferous materials include titanium carbide, titanium nitride, a mutual solid solution of titanium carbide and titanium monoxide, and metallic titanium in relatively impure form, e.g. metallic titanium containing titanium carbide and/or titanium monoxide and/or titanium nitride dissolved therein. The metallic titanium may be, for example, the product of a pyrometallurgical reduction process, such as the Kroll process, as described in Patent 2,205,854, or it may be titanium alloy scrap or metallic titanium in the form of powder or pieces produced incidentally with the manufacturing and fabrication of titanium articles from sheet, bar, or powder materials. In each of these titaniferous materials, the titanium appears to exist as the elemental metal and in this form it reacts with the higher valent, titanium ion species to produce a lower valent ion species which is capable of electrolytic deposition on the cathode.

The solid titaniferous material may be introduced into the electrolytic cell either in the form of relatively large lumps or in the form of smaller pieces of about ¼ inch in the maximum dimensions, or even in the form of finely divided particles. When it is to be put directly into the cell, then it may be confined to a region adjacent to the anode by a graphite basket or by means of perforated baffles, or by any other suitable means. It is, of course, often advantageous to make the confining means, if suitably designed, anodic so that regeneration of the electrolyte for reaction with the solid metal supplying material prior to contact between the unregenerated electrolyte and the solid titaniferous material is further assured.

Extraction of the titanium component of the solid titaniferous material, and its resulting dissolution in the fused salt bath, is effected by reaction between the titanium halide component of the bath and the titanium component of the aforementioned type of solid titaniferous material. In this reaction the metalliferous titanium component of the solid material is oxidized to a titanium compound and the titanium halide component of the bath is correspondingly reduced to a lower valence titanium halide. For this reason, then, the practice of the invention is restricted to the refractory metals capable of existing in at least two different valence states in the form of halide salts, and this requirement is satisfied by titanium, niobium (columbium), tantalum and vanadium, and is probably satisfied by other metals of groups IV–A and V–A of the periodic table. With each of these elements, its halide which is incorporated in the fused salt is the higher or highest valence form, and the final bath composition contains the transition element in the form of one of its lower valence halides. It will be readily understood, therefore, that the amount of the transition metal which is extracted from the solid transition metal material is a function of the amount of the transition metal higher valence halide which is incorporated in the initial salt mixture and the difference in valence of the transition metal in the two forms of its halide which predominate in the bath before and after the aforementioned reaction. In the case of titanium each mol of alkali fluotitanate (in which the titanium has a valence of four) will extract one-third mol of titanium from the solid titaniferous material.

The resulting fused salt bath containing the extracted titanium component of the solid titaniferous material is capable of being electrolyzed in the fused state with the resulting electrodeposition of the extracted titanium component in the form of titanium metal. In transferring the fused salt bath to an electrolytic cell, unless the bath is formed in situ in the cell, it may be advantageous to filter the bath to remove any residual solid such as carbon or unreacted titaniferous material. The transfer of the fused salt may be carried out through pipes of graphite or other inert material communicating between the thermal reactor and the electrolytic cell.

The electrolytic cell equipment and the electrolytic conditions, such as cell voltage and cathode density, are well known in this art and need not be further described. Reference may be had to United States Patent 2,731,402, which describes the electrolysis of a fused salt titanium halide-containing bath for suitable operating conditions. As described therein, the product of the electrolysis is titanium metal, which is deposited on the cell cathode as a recoverable titanium deposit. The resulting spent cell bath, after completion of this electrolytic decomposition of the extracted titanium component of the bath, is caused to circulate into intimate contact with an anodic member provided to reoxidize the lower valent species of titanium ion present to its tetravalent state so that it may then be returned directly to the fused salt-solid material reactor for a completely cyclic operation. If desired, however, the production of the titanium-containing bath and its subsequent electrolysis may take place successively and repeatedly in a single vessel which thus serves both as the reactor and as the electrolytic cell.

When, as shown in the drawings, separate vessels are provided for effecting the reaction and the electrolysis; the reactor comprises a graphite vessel preferably, although other materials of construction may be used. As indicated above, the vessel should be provided with means for maintaining any desired inert atmosphere above the contents of the vessel and with means for maintaining the contents at any desired elevated temperature. Such means should be capable of maintaining the contents molten at the preferred reaction temperatures of between 900 and 1200° C. Reconstituted electrolyte may be discharged from the vessel through a separating means, such as a filter of graphite, to insure that impurities and any unreacted solid titaniferous material are not carried into the electrolytic cell. The reconstituted electrolyte in which the titanium is now present in the form of the lower ion species and particularly in the form of trivalent titanium, is now returned to the cell for a repetition or continuation of the electrolysis. Preferably, it is introduced into the cell in the vicinity of the cathode upon which the ion is to be electrodeposited.

The practice of the invention is illustrated by the following specific examples.

In order to illustrate the effect of repetitively reacting a suitable source of titanium, for example titanium carbide (TiC), with a fused melt of sodium chloride (NaCl) and potassium fluotitanate (K_2TiF_6) and then electrolyzing the reaction product and then regenerating the spent electrolyte by further reaction with titanium carbide, the following series of experiments were performed.

A graphite crucible was placed in a laboratory inert atmosphere furnace and charged with 630 parts by weight of titanium carbide in the form of rods, 276 parts by weight of recrystallized potassium fluotitanate (K_2TiF_6) and 1400 parts by weight of sodium chloride (NaCl). Before reaction the titanium content of the water soluble portion of the charge was 3.2%. The charge was held at a temperature of 850° C. for five hours to permit complete reaction to take place between the TiC and molten K_2TiF_6. The resulting salt cake thermal reaction product was permitted to cool and then was removed from the cell. The titanium carbide and solid carbon were separated from the salt. The salt had a deep red-brownish color. The salt was analyzed and found to contain approximately 5.3% water soluble Ti. This indicated that a considerable amount of the TiC and K_2TiF_6 had reacted to form the lower valent species further evidenced by the red-brown color of the salt. The salt cake was crushed and recharged into an electrolytic cell equipped with means to control the atmosphere therein. The salt was melted and then maintained at about 850° C. by application of heat. Electrolysis was carried out at between 1.5 and 2.3 volts, cell voltage. No evolution of free halogen was observed. A cathode deposit containing 8 parts by weight of titanium metal of a commercial quality was obtained. The salt bath turned deep lavender as a result of the electrolysis. The molten bath was permitted to cool and solidify and was then analyzed again for titanium. The salt analyzed approximately 3.2% Ti. After removal of the unreacted titanium carbide, the spent electrolyte was charged into a clean graphite crucible similar to that in which the first thermal reaction was effected. Titanium carbide rods were added thereto in the proportion of 140 parts by weight of titanium carbide to 1188 parts by weight of the lavender-colored spent electrolyte. The mixture was then maintained at a temperature of 850° C. for about five hours, resulting in a deep red salt product analyzing approximately 3.7% water soluble Ti. A steel cathode was inserted into the regenerated electrolyte and electrolysis was conducted at bath temperatures between 843 and 850° C. with a cell voltage of between 2.05 and 2.7 volts. A cathode deposit containing 6.5 parts by weight of titanium metal of commercial quality was obtained. Only a slight reaction could be achieved when it was attempted to regenerate the spent electrolyte by further reaction with TiC and the salt remained lavender when in contact with TiC for about four hours at above 850° C. The product analysis indicated that only a slight reaction occurred.

This series of runs illustrated that the regeneration was not fully effective in reconstituting the electrolyte. It appeared that this might be due to the presence of large amounts of titanium in the form of an ion species not readily susceptible to reaction with the titanium carbide.

Another series of runs was made in which titanium carbide served as the anode and the electrolysis and thermal reaction were carried out simultaneously, as disclosed in other copending applications, namely Serial No. 320,345 filed by Eugene Wainer on November 13, 1952 and Serial No. 358,194 filed by John T. Burwell, Jr. and Merle E. Sibert on May 28, 1953. In these experiments it was found that while the process could be continued more or less indefinitely, that is, if titanium carbide was added to the cell, titanium could be obtained as a cathode deposit as long as titanium carbide was available at the cathode; nevertheless, the process again exhibited a decreasing efficiency of operation. When, however, fresh tetravalent titanium ion was made available to the electrolyte, the efficiency of the process increased until it approached the original efficiency. In this case, then, tetravalent titanium ion was found to be essential to the process efficiency as before and was made available from sources outside of the electrolytic cell.

A third series of runs was made, employing the principle disclosed in the instant application. In these runs a single vessel served as both reaction chamber for the thermal reaction and cell for the electrolysis. The vessel actually employed was a crucible provided with an anodic barrier formed from a graphite member which had been perforated with a multiplicity of fine holes to permit the electrolyte to circulate freely between the two portions of the vessel but which prevented the zero valent titanium source material from circulating from the one region in which it was confined into the other region of the vessel. The barrier was connected to the positive terminal of a battery and the circuit was completed by a connection from the negative terminal of the battery to a cathode suspended in the region of the cell not containing the titanium supplying material. Of course, the electrolyte itself completed the circuit between cathode and anode. By maintaining the barrier anodic and by insuring that the titanium-containing material being refined was in electrical contact with the anodic barrier, it was found that the circulation of the electrolyte through the multiplicity of fine holes continually regenerated the necessary +4 ion species essential to a continuity of operation at high efficiencies, both process efficiency and current efficiency. Specifically, over a period of 388 hours a charge of impure titanium scrap was electrolyzed at the current density of between 145 and 450 amperes per square decimeter of cathode surface and a cell voltage of about between 2.2 volts and 7.1 volts in a fused electrolyte comprising 16% by weight of K_2TiF_6 and 84% by weight of NaCl maintained under an inert atmosphere of argon. The electrolyte was heated to a temperature between 750° C. and 900° C. throughout the electrolysis. Under these conditions no chlorine or other free halogen was evolved at the anode and a soft ductile titanium deposit was obtained at the cathode. Ninety-four cathodes were removed from the cell as a result of an input of 160,360 ampere hours of current. The titanium content of the water soluble portion of the electrolyte was 3.2% at the beginning of the run and was checked throughout the run and found to vary between 3.09% and 3.79%. The current efficiency for the first cathode deposit based on a conversion $Ti^{+3} \rightarrow Ti^0$ was 96% while at the end of the run it was 93%. Thus it will be seen that the efficiency of operation was maintained at substantially the original level. It should be noted that in the run described, small amounts of make-up salt (NaCl and K_2TiF_6) were added from time to time to the bath to replenish the salts lost mechanically or removed with the cathode deposit. Since the current efficiency did not appreciably change during the runs in which no salt addition was made, it was concluded that the high current efficiency was not the result of these intermittent salt additions but rather was characteristic of the process carried out in the manner described in which the electrolyte is regenerated by intimate forced contact with an anode so that the dissolved titanium carrier ions were re-converted to a +4 valence for a repetition of the thermal portion of the process in which the tetravalent titanium was converted to an ion species readily electrodeposited, i.e., either trivalent or possibly divalent titanium.

It will be appreciated, accordingly, that the method of my invention makes possible a highly efficient recovery of the aforementioned transition elements by a combination of chemical reaction and electrolysis. This combination is particularly amenable to commercial scale operation because the reaction and electrolysis may be carried out simultaneously in separate and independently controlled reaction zones. My method is also characterized by the fact that the fused salt or salt mixtures used in practicing the invention may be recycled between the thermal reaction and electrolysis operations. Therefore, the only consumable reactant is the solid titaniferous material. Any solid titaniferous material remaining unconsumed at the end of each extraction period, may be readily separated from the salt bath in the reaction zone and recovered for reuse. Such recovery is advantageously effected by mechanically agitating the unused solid titaniferous material, together with any residual carbon particles, e.g. from titanium carbide, when this material furnishes the titanium to the system, in order to separate from the useful titaniferous component any residual non-usable material such as carbon. The solid titaniferous component of this mechanically agitated mixture may then be separated by any conventional means so that it may be returned to the thermal reaction stage. Thus, except for relatively small make-up quantities of the salt component of the fused bath to compensate for mechanical losses, the only consumable raw material comprises the solid titaniferous material which is used as one of the reaction components. This economy of raw materials, coupled with the continuity of operation at continuing high efficiencies, and the high degree of purity of its primary product (the transition metal such as titanium), characterizes my method as one pre-eminently suitable for commercial scale operation.

To further illustrate my invention, a fourth series of electrolyses was performed in which the source of titanium was contaminated metallic titanium scrap having an average Brinell hardness of over 350 and containing 5.22% oxygen by weight and 3.53% nitrogen by weight and 0.452% carbon by weight. As in the previous runs, the electrolyte consisted of between 84% and 90% by weight NaCl and between 16% and 10% by weight of K_2TiF_6. The anode current density varied between 7 and 58 amperes per square decimeter and the cathode current density varied between 75 and 520 amperes per square decimeter, based on the original cathode area. The over-all cell voltage, that is, the IR drop between anode and cathode, was between 0.5 and 5 volts and was usually maintained between 3.5 and 5 volts. With bath temperatures between 850 and 965° C., a series of electrolyses were made in which the scrap was charged into the cell adjacent the anode and behind a perforated graphite member. The electrolyte passing into contact with the impure metal to be refined, thus necessarily passed through the perforations of the anodic graphite member which insured that a supply of tetravalent titanium ions would be provided for reaction with the impure metal charge. The process was shown to be capable of operation for an indefinite period, on impure metal containing 90–95% titanium and of yielding as product, refined titanium metal at current efficiencies of up to 97%. The product contained less than 0.10% total of oxygen, nitrogen and carbon and was the equivalent of virgin metal.

Having now described my invention in accordance with the patent statutes, I claim:

1. In the method of producing a polyvalent metal of the group consisting of titanium, niobium, vanadium and tantalum which includes: (1) electrolyzing a fused salt bath containing said metal in the form of a lower valent ion species, thereby depositing said metal at a cathode in said bath by reducing lower-valent ion species at the cathode and concurrently therewith, oxidizing another portion of said lower-valent ion species at an anode, and thereby producing a spent electrolyte containing a mixture of lower-valent ion species and higher-valent ion species of said metal; (2) transferring a portion of spent electrolyte from the electrolytic cell to a vessel in which it physically contacts solid material containing the metal to be electrolytically deposited and regenerating the so-transferred electrolyte by permitting it to chemically react with said solid metal-containing material selected from the group consisting of the carbide of said metal, the nitride of said metal, a mutual solid solution of the carbide and the monoxide of said metal and the said metal in impure form; and (3) returning the regenerated electrolyte to the electrolytic operation; the improvement in said process which consists in continuously withdrawing spent electrolyte from said fused salt bath; bringing the withdrawn spent electrolyte into physical and electrical contact with an electrically energized anode whereby the lower-valent ion species of said metal present in the withdrawn spent electrolyte is oxidized to the highest-valent ion species of said metal; thereby maintaining a high efficiency in the subsequent chemical reaction between said fused salt and said solid metal-containing material; transferring said anodically oxidized electrolyte to a zone wherein it physically contacts said solid metal-containing material and continuously returning the resultant regenerated electrolyte, enriched in lower-valent ion species of said metal, to the fused salt bath for electrolysis.

2. The method of claim 1 wherein the fused salt bath consists essentially of at least one alkali metal halide and at least one alkali metal double fluoride of said metal.

3. The method of claim 1 wherein the metal is titanium.

4. The method of claim 1 wherein the metal is niobium.

5. The method of claim 1 wherein the solid is impure metal.

6. The method of claim 1 wherein the solid is the carbide of the metal.

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LIQUID POLYMERS, SOLID ARTICLES MADE THEREFROM AND METHODS OF PREPARING SAME

Eugene Wainer, Shaker Heights, and Bertram C. Raynes and Andrew L. Cunningham, Cleveland, Ohio, assignors to Horizons Incorporated, a corporation of New Jersey

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This invention relates to inorganic polymers and more particularly, it relates to novel polymers in liquid forms, their preparation and to solid products prepared from such liquids. Specifically, it relates to high molecular weight polymeric liquids in single phase in which the major portion of such liquid is an inorganic moiety from which sheets, small diameter fibers in the form of continuous monofilaments and other solid shapes may be produced, preferably as transparent products.

Various techniques are known for producing solid products from inorganic melts, e.g. in the manufacture of glass and such products include not only sheets and shapes but also continuous filaments. As is known, the products are characterized by a fragility and brittleness which impairs their utility in many fields. Furthermore glass technology involves the preparation of melts at relatively high temperatures with attendant refractory and apparatus requirements.

In contrast thereto the solid products produced in accordance with the present invention are microcrystalline, flexible and may be prepared from liquids which operate as liquids at temperatures below 100° C.

One object of this invention is the preparation of high polymeric substances in liquid form wherein the liquid consists of a single and continuous phase in which the major portion of the polymer comprises a hydrous complex of a suitable inorganic oxide.

Materials which are effective in the practice of this invention are metals or combinations of metals whose salts produce hydrated oxides, more properly designated as hydrous oxides or hydrous oxide derivatives, as precipitates formed on neutralization of water solutions of such salts with alkalies. These precipitates form at a pH more acid than 7 and are not hydroxides. One distinguishing characteristic of hydrous oxides of the metals to which the present invention is applicable is that if the precipitate is thoroughly washed and is then dispersed in distilled water a pH of less than 7 will also be obtained. It is therefore proper to consider those hydrous oxides suitable for the preparation of the polymeric materials to which the present specification is addressed as weakly acidic hydrous materials.

Hydrous oxides which require alkaline conditions or a pH higher than 7 for their precipitation, or which in freshly precipitated and washed form and dispersed in water yield a pH higher than 7 are not effective by themselves in the practice of this invention. The acidic condition is the important limiting factor which thus enables combinations of materials to be utilized so that the sum total is acid in character, even though one of the ingredients forms an alkaline hydrate. For example, the alkaline earths by themselves will not fit the requirements, but when combined with acid hydroxides or hydrous oxides, the combination may be made to fit the requirement, providing there is sufficient excess of the acidic hydrous oxide. Specifically, zirconium fits the description very well, whereas calcium does not, but a combination comprising a mixture of the two in which the hydrous oxide of zirconium is a major constituent will meet the requirement and thus enable a fiber to be produced containing significant proportions of calcium oxide in its makeup by virtue of recognition of the limitation with regard to pH. The most acid of the elements to which the invention is applicable is titanium, and this will then accommodate substantially larger proportions of basic materials than the other elements listed below. Thorium is the least acid of the hydrous oxides in the list, and as a mattter of fact, it is a borderline case. One would have to operate with exceptional care in order to make thorium fully effective by itself. Additions of even small amounts of titania or zirconia will rectify this situation with regard to thoria.

The inorganic oxides constituting the principal portion of the polymeric products of this invention are therefore selected from the group consisting of the oxides of aluminum, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, yttrium, zirconium, the lanthanide rare earths hafnium, and thorium, or in other words the oxides of aluminum, yttrium and the lanthanides, the Group IV–A metals (Ti, Zr, Hf and Th) and the metals having atomic numbers 23–28 inclusive, in other words, those metals and combinations of metals whose hydrous oxides are capable of being precipitated at a pH less than 7 on treatment with alkalies, and whose hydrous oxides or combinations of hydrous oxides when freshly washed and dispersed in pure water will yield a pH of 7 or less.

A further object of the invention is the preparation of stable polymers wherein the degree of polymerization is controlled.

Still another object of the invention is to provide means for converting the liquid polymeric materials described above into solid products of definite shapes such as sheets, slabs, and continuous monofilaments suitable for weaving to produce tough strong fabric products.

Still another object is to provide a means for producing fibers in the form of continuous monofilaments having a circular cross section, and which in the raw state may contain a minor proportion of an organic (carboxylic acid) salt and which, after firing at temperatures greater than those required to fully eliminate all such organic material, consists entirely of inorganic material of crystalline character in which the size of the individual crystallites is less than one micron.

It is a further object of the invention to provide high viscosity polymeric liquids starting from dilute water solutions of water-soluble metal salts of suitable carboxylic acids, and to produce solid products from such solutions by suitable heat treatment thereof, in a controlled atmosphere, said products being free from organic materials and glass formers and being characterized by a high degree of strength and flexibility.

These and other objects are accomplished in the manner and by the means more fully described below.

Briefly the method of this invention comprises the following sequence of operations:

(1) Preparation of a dilute aqueous solution of a water-soluble organic salt, i.e. a metal salt of a mono- or di-carboxylic acid including filtration or other clarification.

(2) Concentration of the dilute aqueous solution, preferably by vacuum evaporation, to a concentrate of which at least 50% by weight comprises an oxygen-containing derivative of the metal, such as a metal oxide, hydroxide or complex.

(3) Polymerization of the concentrate by suitable heat treatment.

(4) Formation of solid shapes from the polymer.
  (*a*) Continuous monofilaments
  (*b*) Sheets or slabs
  (*c*) Other shapes (short fibers, etc.) and

(5) Final firing of the solid shapes to effect elimination of any organic material therein and to yield microcrystalline metal oxide products of high strength and flexibility. Each of these steps in the procedure will now be described more fully.

(1) PREPARATION OF DILUTE SOLUTION OF METAL SALT

The process of the present invention begins with the preparation of a dilute solution of a salt of a suitable carboxylic acid. Polyvalent metals to which the present invention is applicable are: aluminum, titanium, vanadium, chromium, manganese, iron cobalt, nickel, yttrium, zirconium, the lanthanide rare earths, hafnium and thorium. The metal is provided as a metal salt of an aliphatic monocarboxylic acid or aliphatic polycarboxylic acid, the dissociation constant of such acids being at least 1.5×10^{-5}. Salts of a single acid or of a mixture of acids may be used, provided the compounds are completely water soluble or are rendered soluble if sufficient acid is present.

Acetic acid and formic acid are preferred as the carboxylic acids to be used in the present invention, but the other acids which have been satisfactorily utilized with one or more of the above metals include oxalic, citric, adipic, itaconic, lactic and other mono- or polycarboxylic acids. Adipic acid is the preferred polycarboxylic acid. Each of these acids may be used alone or in admixtures with other members of the group.

Salts of substituted acids, e.g. ethoxyacetic, chloroacetic, etc. may also be used. The preparation of the dilute solution is readily effected by adding the water soluble salt to a sufficient volume of water, preferably at room temperature. Occasionally the addition of some of the carboxylic acid will be found useful in facilitating dissolution of the salt.

After the solution has been formed, it is freed of foreign solids and gases occluded therein by filtration or other known separation techniques to yield the completely clarified liquid solution required for the subsequent processing described below.

(2) PREPARATION OF CONCENTRATE TO BE POLYMERIZED

In order to produce the transparent solid products whether they are in the form of sheets, slabs, fibers or in the form of continuous monofilaments it is necessary to have available a clear polymeric liquid consisting entirely of a single phase containing a major proportion of a derivative of an oxide of the indicated metals. Furthermore it has been found that the liquid must still exhibit all the characteristics of a true liquid and particularly that it must be capable of being deformed through the application of even a minute applied force, and this must persist irrespective of the concentration of the hydroxyl-ion derivative or other metal oxide derivative present.

Novel polymeric liquids with the requisite properties are produced by concentration and heat treatment of the clarified dilute water solutions prepared as indicated above.

In order that the solution be readily polymerizable when subjected to a suitable heat treatment, it is necessary that such solutions contain at least 50% and up to about 90% of equivalent oxide by weight. Owing to the fact that this exceeds the solubility of the salt it is generally impossible to obtain compositions of this concentration consisting entirely of a single liquid phase by merely adding the required amount of salt to water. Instead, it is necessary to prepare a dilute solution in which the salt concentration does not exceed the solubility and thereafter to concentrate the solution by suitable techniques. A preferred method of concentrating the initial dilute solution prepared by dissolving the salt in water is to subject the solution to a vacuum at temperatures not exceeding 25° C. and preferably between 15° C. and 25° C. and to thereby effect evaporation and removal of the more volatile constituents, and simultaneously therewith concentration of the remaining liquid.

A less preferred technique which may be utilized comprises simultaneous concentration and heat treatment to completely eliminate any free water from the system while maintaining the polymeric character of the resulting solution.

Still a further technique which may be followed in the preparation of these polymeric materials comprises the addition of a freshly precipitated hydrous oxide derivative to an anhydrous solution of a carboxylic acid, whereby a metal carboxylate salt is precipitated which after separation, washing and drying may be redigested in additional anhydrous carboxylic acid at elevated temperatures. On standing at room temperature the resulting product is a polymeric liquid.

(3) POLYMERIZATION

Once the required highly concentrated liquid has been obtained by either vacuum concentration as described above or by heating the dilute solution to carefully controlled temperatures or by any other suitable technique which avoids the formation of a second phase, polymerization of the highly concentrated viscous solution is effected, preferably by heat treatment in a closed vessel at a temperature not exceeding 90° C. and preferably between 60° C. and 90° C. As a result of heating in this manner, the viscosity of the liquid rises rapidly and in less than one minute after the liquid has attained the specified temperature throughout its volume, the viscosity of the liquid has usually reached a value equivalent to a high degree of polymerization, e.g. to the formation of polymers having from 10 molecules to more than 10,000 molecules in the chain and having molecular weights of one million or more. When the volume of liquid being processed exceeds the small volumes handled in laboratory experiments wherein uniformity of temperature of the liquid is obtained by readily available techniques and the rates of diffusion throughout the viscous solution are somewhat less than in smaller volumes, between 2 and 20 minutes are required, once the liquid has reached a uniform temperature, for the viscosity to rise to the extent indicated.

As described above, it is also possible to obtain a polymer by evaporating the initially prepared dilute solution at a constant elevated temperature until a heterogeneous mass of gelled material is obtained, and thereafter permit the gelled material to stand, but this procedure has been found to be less satisfactory than the perferred technique described above, since it is more difficult to control the degree of polymerization by this method than by heating to between 60° C. and 90° C. as described above.

The degree of polymerization is primarily a function of the temperature at which the concentrated solutions are heat treated and to a much lesser extent it is also a function of the time at which the solutions are held at temperature. At the higher temperatures in the range indicated (60–90° C.) the degree of polymerization is affected by the duration of the heat treatment to a greater extent than it is at the lower temperatures in the range, or even lower temperatures.

While it might appear that simply heating the dilute solutions to concentrate them would in effect constitute a simultaneous concentration and heat treatment, such a process is not at all equivalent to the preferred two step procedure. The advantage of preliminary vacuum concentration at low temperatures (15–25° C.) followed by heat treatment at higher temperatures (60–90° C.) is the fact that the equivalent concentration of oxide in the liquid can be pushed to much higher levels without deleterious side effects. In some instances this value may reach as high as 90%. In contrast, when simultaneous concentration and heat treatment are practiced, about the maximum concentration of oxide in the liquid which can be achieved without the formation of second phases of irreversible characteristics, such that they will not revert to purely liquid form on standing, is a value equivalent to about a 60% concentration of oxide in the liquid. Thus not only can closer control of molecular weight be obtained through the technique of vacuum concentration and subsequent heat treatment, but also a much higher concentration of the oxide may be obtained in the liquid without the development of extraneous phases, and as a consequence a much higher degree of polymerization and molecular weight can also be obtained by the preferred procedure.

In summary then three separate and distinct methods exist for the preparation of the polymeric liquids of this invention. The first, and most preferred technique, is vacuum concentration followed by heat treatment. The second is simultaneous heat treatment and concentration and the third is the preparation and thermal treatment of specific hydrous oxide products digested in glacial acetic acid, as described more fully below.

The following example further illustrates the preferred embodiment of this invention.

A solution of zirconium acetate in water, containing the equivalent of 11% zirconium oxide by weight and having a viscosity of between 2 and 4 centipoises was vacuum concentrated at 25° C. for 36 hours at which time it exhibited the equivalent of a zirconium oxide concentration on a weight basis of 82%, and a clear somewhat mobile liquid having a viscosity of 8500 centipoises was obtained. Measurements indicated that a polymer had been produced, exhibiting a molecular weight of approximately 1000, indicating that the polymer was composed of units containing 8 to 10 molecules in the chain, on the basis that the unit is comprised of recurring elements of the formula $ZrOOH^+$ with regularly inserted radicals of acetic acid to maintain the stability of the chain. Fibers of several inches in length and of exceptionally fine diameter were pulled from such a solution by inserting a stirring rod and, after a drop has formed, pulling the stirring rod slowly and continuously from the solution. On vacuum concentration to levels somewhat lower than about 80% of equivalent oxide, fiber pulling by the same technique is so difficult that from a practical standpoint it is useless. On the other hand, if a simultaneous concentration and heat treatment technique at about 80° C. is utilized, fiber pulling starts to become specifically evident at liquid concentrations of the order of 50% equivalent zirconium oxide by weight, and it is clear that a somewhat different product has developed as compared to similar solutions which have been only vacuum concentrated at the lower temperature.

Referring now to the vacuum concentrated solution which had reached a level of 82 weight percent equivalent oxide, when such solution was allowed to stand at 25° C. for one week the viscosity slowly rose and reached a value of the order of 20,000 centipoises and suitable measurements indicated that the number of molecules in the polymer chain is now of the order of 25. Fibers were spun much more readily from such a solution than the fresh concentrated solution originally prepared, indicating that the increase in chain length has facilitated spinning of the fibers. When a sample of the same 82% solution was heated in a closed container at 80° C. for 10 minutes, immediately after vacuum concentration, a permanent viscosity in clear mono-phase liquid form of the order of 350,000 centipoises was achieved from which fibers were spun or tension drawn with great ease. When a similar sample of the freshly concentrated 82% solution was heated at 80° C. for two hours, the viscosity reached a value of the order of 0.5×10^6 centipoises to 1.0×10^6 centipoises, while still a pure liquid. Hydraulic pressure accompanied by tension on the freshly formed strand was then required to produce a continuous mono-filament. Molecular weight determinations indicate that polymers having chain lengths of at least 10,000 molecules have been obtained in periods of two hours or less by heat treating the concentrated solutions at temperatures between 80 and 90° C. Heat treatment for periods up to two hours of such highly concentrated solutions at temperatures in the range of 70 to 80° C. yielded polymers having chain lengths of the order of 1,000 to 10,000 molecules in the chain, whereas heat treatment above 35° C. and below 70° C. for periods of a few hours of such highly concentrated solutions will yield molecules having chain lengths between 100 and 1,000 molecules per chain. The number of molecules or molecular units in a chain is a function of the temperature at which the heat treatment is carried out, and the time of heat treatment is primarily effective in establishing the total number of such chains of equivalent molecular size.

It has been pointed out earlier that the concentrate produced by a combined heat treatment and concentration followed by standing at room temperature in a closed container to stabilize the liquid normally cannot be brought past a concentration in the liquid of about 60% equivalent oxide because solids are produced which apparently represent irreversible phases which do not pass into solution above this level of concentration on standing. The viscosity of such a solution is about 450,000 centipoises and molecular weight determinations indicate that the molecule is again represented by a polymer having a chain length of at least 10,000 molecules. From the above, it will be seen that temperature in large measure determines the molecular weight of the polymer formed, and the concentration of the oxide simply establishes the amount of polymer which is produced, even though of the same chain length. There is some evidence that the constitution of the recurring monomer units will differ depending on the concentration at which the heat treatment takes place for the formation of the polymer; such indications will be given in later portions of this description.

To avoid the formation of extraneous second phases in liquids after concentration for specific times and temperatures, it has been found to be advisable to accomplish such heat treatment in sealed containers or at least in an atmosphere of an aliphatic carboxylic acid, preferably of the acid of which the salt is composed. Atmospheres of pure acetic acid or pure formic acid have been found to be most effective in overcoming any latent tendency to produce second insoluble phases which represent deleterious impurities.

Spinning concentrations for a modified zirconium acetate solution may be varied from about 65% by weight of equivalent zirconium oxide up to almost 90% by weight of equivalent zirconium oxide with the pure liquid characteristics still being maintained, but the concentration of equivalent oxide in the solution relative to the residual organic acid content determines the nature of the unit recurring in the formation of the polymer as a function of subsequent heat treatment. The constitution of the monomeric unit determined by determination of the relative concentrations of equivalent oxide versus acetate radical over this range of spinning concentrations indicates that the individual monomeric unit may vary from a relative proportion of equivalent oxide to acetate unit of 2:1 up to 4:1 in the case of zirconium. This same ratio has been found to obtain generally for quadrivalent metals. The longer the individual monomer length prior to spinning the more readily are threads and transparent sheets produced. It appears that the monomeric units are comprised of fixed whole number ratios such as 2:1, 3:1, and 4:1 and that concentrations between the amounts represented by these ratios may be comprised of mixtures of monomers exhibiting such ratios.

In the case of the trivalent metals such as aluminum, chromium, iron, and the like, similar conditions obtain. Again the first evidence of fiber spinning characteristic is obtained at a viscosity of approximately 10,000 centipoises or more. With the oxides of the trivalent metals, the unit forming the polymer chain may vary from a ratio of 2 moles of the oxide to 1 mole of the acid radical up to 8 moles of the oxide to 1 mole of the acid radical. In view of the fact that there are two metal atoms in each of such oxides, the ratio of metal atom to molecule of acid radical is twice those given. Again, the degree of formation of a chain is a function of the temperature of heat treatment and the nature of the chain with respect to the ratio of metal oxide to acid radical is a function of the concentration of the equivalent metal oxide in the solution prior to the onset of polymerization. Though it is difficult to define the individual components with certainty in the case of aluminum oxide, the successive ratios which may be produced as a function of the concentration of the solution will cover 2, 3, 4, 5, 6, 7, and 8 moles of equivalent aluminum oxide per mole of carboxylic acid radical.

Thus, for those oxides whose stable form takes the formula RO_2, the ratio of equivalent RO_2 oxide in the polymeric liquid to the amount of organic acid present with respect to the form of the monomer unit making up such polymer will cover the range from 2 moles of RO_2 oxide to 1 mole of organic acid radical up to 4 moles of RO_2 oxide to 1 mole of organic acid radical. In those cases where the oxides have the formula R_2O_3 in stable form such as aluminum oxide, the ratio of the polymeric liquid with respect to the form of monomer making up such polymeric chains will cover the range 2 moles of equivalent R_2O_3 oxide to 1 mole of organic acid up to 8 moles of equivalent R_2O_3 oxide to 1 mole of organic acid. These units then represent the building blocks for the polymer chain and it appears that the higher the ratio of equivalent oxide initially present the higher the viscosity and the higher the degree of polymerization.

While we do not wish to be bound to any specific theory, it appears that the building block for the monomeric unit is a positive hydroxylated ion of the metal oxide. In the case of zirconia, this ion will have the formula $ZrOOH^+$. These are believed to be strung in the form of chains and the terminal group at either end of the chain is an acetate radical. The number of zirconyl hydroxide units in each monomeric chain may vary as heretofore described with the number of acetate radicals for each monomeric unit remaining the same, so as to account for the variation in length. While these units have been designated as monomers, in all probability it is more proper to consider that the monomeric unit is represented by the positive ion whose formula has been given above, and that the individual units prepared as a function of concentration prior to heat polymerization are, in actual fact, small chain length polymers. Since an acetate radical exists at either end of the chain on a symmetrical basis, the actual number of zirconyl hydroxyl units in the lowest ratio would be four substituents of such zirconyl hydroxyl unit to two substituents of acetate, giving an overall ratio of 2 moles of zirconium oxide to 1 mole of acetic acid on an equivalent basis. There is considerable experimental evidence indicative that these small unit chains are more properly characterized as small polymers rather than individual monomer units. As described above, on straight vacuum concentration prior to heat treatment, the minimum concentration at which fibers could be spun was approximately 80%, equivalent to the ratio of 2 moles of zirconium oxide to 1 mole of acetic acid. However, when a simultaneous concentration and heat treatment was utilized, fibers were spun from fully polymerized masses containing as low as 50% zirconium oxide on an equivalent weight basis in the solution. The extraordinarily high viscosity of the liquid was evidence of the high degree of polymerization. The behavior of the heavily polymerized liquid of this 50% concentration on dilution with water on the one hand as against dilution with anhydrous acetic acid on the other gives a clue to the situation. When water is used as a diluent, the viscosity drops very precipitously and the change in viscosity which takes place even on the addition of a minor amount of water indicates that a pronounced depolymerization has taken place. When freshly distilled acetic acid in substantially water-free condition is used as the diluent in the same volume of addition, the drop in viscosity is very much less and relatively dilute solutions using acetic acid as the diluent exhibit much higher viscosity than a comparable concentration of polymerized oxide material than when diluted with water. Consequently this behavior on dilution with pure acetic acid, even though the salt is still water soluble, is believed to be indicative of high polymer formation, of the depolymerization effect of water itself, and of the nature of chain formation and of the polymerization process itself.

The formation of the high polymer as the result of heat treatment appears to be due to the splitting off of anhydrous acetic acid or other aliphatic carboxylic acid present at the terminals of the original molecule, resulting in a substantially indefinite lengthening of the chain with a consequent slight drop in viscosity as the result of dilution with the anhydrous acetic acid split off by heat. This may not only explain why the relatively low concentration equivalent to 50% equivalent zirconium oxide by weight is capable of forming polymers, but also indicates that at this concentration free water is presumably no longer present, and the diluent at this level and above is anhydrous acetic acid. In view of the presence of acetic acid as a diluent in the polymeric liquid itself, it is difficult to determine whether the fully polymerized material exhibits a comparable structure as the original building block, except extended in length with respect to the number of zirconyl hydroxyl units. Indicative that no more than a few acetate radicals are present in the chain even though heavily polymerized is the fact that, as the temperature is raised after formation of an essentially solid shape and before active carbonization takes place, the number of acetate substituents continues to drop and finally levels off asymptotically.

The particular carboxylic metal salt used for the purpose of preparation of these polymers will vary depending on the metal in question. In the case of zirconium, the preferred metal salt is the water soluble acetate which exhibits the ratio of 2 moles of acetate radical to 1 mole of zirconium oxide, sometimes designated as diacetozirconic acid. The zirconium acetate commonly designated as monoaceto-zirconic acid containing a ratio of 1 mole of zirconium oxide to 1 mole of acetate radical would exhibit in the free-water condition an equivalent oxide content of approximately 67% and is insoluble in water and only sparingly soluble in acetic acid. Yet by the techniques which have been described thus far, it is possible to produce a single phase liquid without any manifest precipitate present, such liquid being stable for an indefinite period and containing up to as high as approximately 90% equivalent zirconium oxide by weight, the balance being presumed to be some form of acetic acid.

In the case of the trivalent metals such as aluminum, iron, chromium, nickel, manganese, and the like, the formate is the preferred species and it is generally preferable to add up to 5% of the formic acid content of a polycarboxylic acid such as adipic. In the absence of adipic acid, it is difficult to prevent precipitation on simultaneous heating and concentration, though this defect does not develop in vacuum evaporation at room temperature. The salt used in every case as the starting material is the one which contains the lowest content of acid radical with respect to metal oxide needed to produce a water soluble solution at room temperature. Usually this is the salt which contains 1 mole of equivalent oxide to 2 moles of the acid radicals.

Titanium is something of a special case. The tetravalent, fully oxidized titanium material is difficult to produce in stable form at relatively low concentration, in view of the fact that precipitates containing titanium tend to form at relatively low temperatures and at low dilutions, such precipitates being of irreversible nature with respect to solubility, and as a consequence, constitute a deleterious second phase. However, two artifices may be utilized for the elimination of this defect. If trivalent titanium is used, it then may be treated as though titanium is acting as a trivalent element, and in this case, combinations of formic acid with a small amount of a polycarboxylic acid such as oxalic or adipic makes it possible to produce the high concentration polymer without formation of said insoluble phases, providing the evaporation is carried out without access of air so as to prevent oxidation. Tetravalent titanium salts may be used if a somewhat different technique is utilized. This involves mixing 1 mole or 190 grams of anhydrous titanium tetrachloride with 2 moles or 120 grams of glacial acetic acid and stirring until solution is complete. Two moles of water are added slowly and with care, this comprising 36 grams, and a clear solution is still maintained, equivalent to approximately 23% titanium dioxide by weight. Such a solution is then vacuum evaporated to at least half its volume at 15° C. and preferably to a factor of half to one-third its original volume, thus doubling to tripling the titanium oxide concentration and yielding concentrations of approximately 50% titanium dioxide or higher. The solution may now be heat treated to produce a mono-phase liquid polymer without precipitation of irreversible phases after being brought up to concentrations of titanium dioxide in a liquid phase by the continued vacuum evaporation prior to heat treatment to levels of the order of 80 to 85%. If these solutions are treated by simultaneous evaporation and heat treatment techniques, the alternative procedures described in the foregoing, irreversible hydrolysis tends to take place at levels below a concentration of titanium dioxide in the liquid of the order of 50%. As a consequence, the only technique which can be utilized for titanium involves vacuum concentration at a temperature of 15° C., followed by short time heat treatment for polymerization purposes. Addition of a small amount of a polycarboxylic acid such as oxalic or adipic represents a further stabilizing influence with respect to hydrolysis in the heat treatment.

As has been pointed out previously, generally the preferred treatment of these water soluble salts irrespective of starting composition is vacuum concentration at temperatures in the range of 15 to 25° C., followed by heat treatment in closed containers at a chosen temperature in the range of 70 to 90° C. Vacuum concentration is normally carried out until the equivalent oxide content reaches a level between 75 and 90% equivalent oxide by weight. The lower molecular weight oxide represents the concentrations which can be produced to the lower levels of this range, and the higher molecular weight oxides represent the concentrations which may be produced at the higher levels of this range. If simultaneous evaporation and application of heat is utilized, said heat being in a temperature range of 60 to 80° C. the maximum concentration normally which is achieved is approximately 60% equivalent oxide by weight before difficulty is experienced with insoluble phases which do not pass into solution on long standing. It is thus preferable to use the technique involving first evaporation to extremely high concentration followed by heat treatment. If dilution is required to produce polymeric materials more amenable to handling at later stages, such dilution is carried out with anhydrous acetic or anhydrous formic acid.

(4) FORMATION OF SOLID PRODUCTS

The liquid polymeric shape-forming materials from which solid shapes are to be formed are produced under conditions such that they are not exposed for any lengthy period of time to either water or water vapor. These polymeric liquids may be utilized to produce transparent to translucent sheets, slabs, shapes, fibers, and, most important, thin strong flexible monofilaments of indefinite length capable of withstanding very high temperatures and such monofilaments may be utilized to produce the type of threads which can be woven into fabric. In producing such slabs and fabrics, intermediate stages of heat treatment still yield relatively strong structures, at which stage of intermediate heat treatment a shape can be produced by lamination or weaving. Continuing the heat treatment to its ultimate stage will produce an organic-free, transparent to translucent object in strong, tough condition. When properly fired, these objects and particularly the fine diameter monofilaments exhibit no evidence of macroscopic crystallinity. X-ray determinations indicate that the fibers are crystalline in nature, and hence the individual crystal size is submicroscopic. In order to achieve this state of evident lack of macrocrystals, the formation of premature incipient nuclei from whatever source must be eliminated from the polymeric solutions from which the shapes are to be formed. Casual dirt, air bubbles, and water itself represent such deleterious materials in certain stages of preparation. Of these, water is by far the most critical. It has been indicated previously that water is a depolymerizing agent and its adverse and depolymerization effects are most pronounced at the highest levels of polymerization. High concentration polymerized materials are somewhat hygroscopic, and if freshly formed shapes are handled in such a way as to be deliberately exposed for relatively short intervals of time to normally humid atmospheres, the shape develops opacity on firing and the fired material is weak and brittle. For example, when the thread produced from a freshly polymerized batch of high polymer is immediately heat treated under the conditions to be specified hereinafter, a transparent, tough, flexible monofilament is obtained as the result of ultimate heat treatment. An examination under the microscope reveals no obvious evidence of crystallinity or nucleation. If the same filament is allowed to stand in air for 10 to 15 minutes before firing, the identical heat treatment produces a fiber which is almost opaque, even though the thread has a very small cross section. The opacity appears to be due to a combination of opalescence and the presence of discontinuous phases. This material is extremely brittle and must be handled with care to prevent breaking it up into fragments.

The desired condition of transparency, toughness, and flexibility in the continuous monofilaments may be obtained by heat treating the specimen in a somewhat drastic manner immediately after formation, with or without the use of specially controlled atmospheres. In forming shapes such as continuous monofilaments from suitably prepared polymeric materials, temperatures above the boiling point of the highest boiling constituent in the filament are applied immediately after formation of the filament, followed relatively quickly by final treatment at temperatures above red heat. In those cases where relatively massive structures are made, having a substantial thickness, it is not possible to apply the heat with the rapidity used for thin films and fibers, for example, in view of the possibility of forming gases which will disrupt the structure. As a consequence, the heat treatment of more massive articles is carried out more slowly but in an atmosphere of vapor of acetic or formic acid, the former acid being preferred, and such heat treatment is carried out just below the boiling point of the respective acid in question. Heat treatment is then continued slowly up to the point where manifest cracking of the organic acid radical starts to take place and still in the controlled atmosphere. After a temperature of organic acid cracking has been reached, final firing may then be completed without the need for controlled atmospheres. Cracking of the organic acid utilized for the purpose will generally start slowly at about 200° C. and become pronounced at temperatures of the order of 350 to 450° C.

Another technique which may be utilized both for the preparation of thin films and for the manufacture of thick cross sections is to heat the specimen gently while it is supported on a temperature resistant, water repellant surface such as a fluorinated plastic or a molded silicone surface, the heating being effected at a temperature slightly above the boiling point of the respective acid used in the metal salt preparation, such evaporation taking place in an atmosphere of anhydrous acid. This treatment is continued until the solid articles reach a constant weight. While thick sheets may be made directly by this procedure if the heat treatment is applied slowly and gently, it is preferable to make up such thick sheets by preparing a number of thin sheets under the described conditions and after weight stability has been achieved to allow the temperature to drop below the boiling point of the acid in question, while the specimen is still immersed in the atmosphere of its vapor, and then place one of the thin sheets on top of the other in the controlled atmosphere chamber. Under these conditions, cementing takes place without the intrusion of air and moisture, and as a result of the continuing heat treatment to the cracking temperature in the atmosphere of the anhydrous acid in question, cementation without the development of opacity is obtained.

Fibers or continuous monofilaments may be produced in a variety of ways. The two procedures found to be most desirable were: (1) pulling the fiber against its own weight from a fully polymerized liquid and thereafter immediately subjecting the freshly pulled fiber to heat treatment to yield the fiber in its final state and (2) extruding a polymerized liquid through a relatively large size orifice and rapidly attenuating the thread, using the material being extruded from the orifice as a constant feed. In the combined extrusion-tension technique of preparation, fibers of extraordinarily fine diameter of indefinite length have been produced. When pulling from a solution, the maximum length of fibers that have been made in this manner generally did not exceed a few feet before the attenuation is sufficient that the fiber pinches itself off. In the extrusion-tension technique, fiber or filament production rates of several feet per second are readily possible and diameters of fiber which are obtained in monofilament form may vary from approximately 0.5 microns up to several tens of microns, the diameter being most generally a function of the speed of attenuation.

In such extrusion-tension formation, pressure between about 1 and 50 pounds per square inch is applied to a hydraulic cylinder containing the fully polymerized water-free liquid, depending on the viscosity and degree of polymerization of the liquid polymer utilized. The orifices are of the order of 25 to 50 microns in diameter as a minimum value and may extend up to 10 times the values indicated by these ranges, depending on the thickness of the fiber which is desired. Immediately the fiber starts to extrude, it is grabbed with an appropriate tool and pulled directly into a graded hot zone maintained with an entry temperature of about 120° C. to 200° C. and an exit temperature of about 600° C. The length of this graded temperature zone will vary with the speed of attenuation. At speeds of the order of one foot per second, the zone need not be longer than about 12 inches in length, and at speeds of the order of 10 feet per second, the zone needs to be approximately 3 feet in length with the last half of such zone maintained at the top temperature of this preliminary heat treatment. Immediately after passing through such zone, the continuous monofilament may be wound on a mandrel, if desired, and stored in a completely dry atmosphere. At this stage, the fiber has a considerable degree of strength. Also at this stage, if heat treatment is continued with one fiber in contact with another, cementation and self-bonding will take place. However, rather than storing the intermediate heat treated monofilament, it is preferable to pull the fiber through a firing furnace at the same rate utilized in attenuation. The firing furnace is maintained at a temperature at which full consolidation of the fiber is achieved and all organic material is eliminated. After firing, the fiber is wound on a spool ready for spinning.

The temperature of firing depends on the oxide or mixture of oxides being processed. In the case of zirconium oxide, aluminum oxide and chromium oxide, minimum temperature for final consolidation and elimination of all organic material is approximately 2200° F. and such consolidation temperatures may extend to 3000° F. For the oxides of metals such as iron, manganese, nickel, cobalt, and titanium, the temperatures employed for ultimate consolidation are generally in the range of 1800 to 2000° F.

It is also possible to complex or stabilize the oxide products by the addition, before firing, of minor amounts of specific compounds useful for crystal stabilization purposes or modifications of properties. For example, small amounts of lime (CaO) may be incorporated in the zirconium oxide polymer for the production of a cubic structure in the fired article, produced from an initial monoclinic structure. Other additives may be used to achieve the formation of ferrites from a ferric oxide base. The addition of minor amounts of alkaline earths to titanium for the preparation of ferroelectrics represents still another modification of the process.

The monofilaments produced from the lower levels of vacuum concentration tend to be slightly more brittle and slightly more opalescent than those produced from higher levels of vacuum concentration. For example, the strength of the fiber produced from a polymer of an 89% Zr concentrate is substantially higher and the transparency is substantially more complete with little or no opalescence being exhibited than the strength and transparency of fiber produced from an 82% Zr concentrate from zirconium acetate.

Having described our invention, the following examples are intended to illustrate preferred modes of practicing the same and are not to be construed as limitative.

Example 1

Ten liters of zirconium acetate solution containing approximately 11% zirconium oxide by weight was clarified by filtration and was placed in a wide-mouth Pyrex beaker. A vacuum strength bell jar was placed over the beaker and the bell jar sealed to a stainless steel plate suitably fitted with outlets for evacuation purposes. A vacuum equivalent to about 15 millimeters of mercury was first applied and as the concentration and evaporation at a temperature of approximately 25° C. proceeded, the degree of vacuum was increased over a period of the first 4 hours to a value of approximately 1 millimeter of mercury and continued for approximately 20 hours. At this point, chemical analysis and gravity determination established that a concentration equivalent to 82% of zirconium oxide on a weight basis had been reached, and the viscosity of the solution immediately after preparation was approximately 8,500 centipoises.

The concentrated material in its beaker was removed from the vacuum chamber. A stirring rod was dipped into the viscous liquid and said viscous liquid was permitted to drop from the stirring rod. This produced an extremely fine filament which slowly solidified on exposure to air.

The beaker was covered and was immediately immersed in a constant temperature bath maintained at 80° C., so that the level of liquid in the beaker was substantially below the level of the constant temperature bath. After the temperature had again stabilized at 80° C., (after insertion of the beaker and its contents into the constant temperature bath) heat treatment was continued for 10 minutes. An exceptionally viscous, transparent material which appeared almost solid in its macroscopic characteristics but which showed minutely the flow characteristics of a liquid had been produced. This material was allowed to cool while still covered, and when cold was scooped into the barrel of a hydraulic extrusion chamber having an extrusion orifice of 10 mils in diameter. After the barrel had been filled, it was covered with the watch glass before the plunger was inserted. The material was allowed to stand for 30 minutes so as to permit all air bubbles to rise to the top. Pressure was then applied initially at a rate of a few ounces per square inch and eventually at a rate which stabilizes in the region of 5 to 7 pounds per square inch. The viscous material which first extruded from the barrel at the low pressure was grabbed in forceps and pulled slowly through a heating zone approximately 3 feet in length. The material first entered the top third of the heating zone, maintained at a temperature of 200° C., then it entered the middle third, maintained at a temperature of 400° C., and was then pulled through the bottom third, maintained at a temperature of 600° C. The furnace was capable of being opened on hinges throughout its entire length to permit the initial insertion of the fiber. After emerging from this first heating zone, the heat treated fiber had a brown-black color. The fiber was brought out into the air and passed around a six inch diameter pulley made of glass. One complete turn was taken around the pulley for anchoring purposes. The fiber was then brought into a furnace of tubular construction in which the tubular hot zone was 2 inches in diameter and 3 feet in length and again fitted with hinges so that the furnace could be opened to permit the insertion of the full length of the fiber. This furnace was maintained at a temperature of 1250° C. After emerging from the furnace, the fiber was wound under tension on a mandrel. Under the microscope the fiber appeared almost transparent with a very slight opalescence. The individual filament was approximately 6 microns in diameter. After achieving a steady state of extrusion and attenuation, the extrusion speed proceeded at a rate of 10 to 12 feet per minute and the rate of attenuation of the very thick column, relatively speaking, being attenuated from such an extrusion orifice finally reached levels of 8 to 10 times that of the extrusion rate so as to permit the diametral reduction available as the result of forming the fiber under tension.

Example 2

The same preparatory procedure is followed as in Example 1 except that the vacuum evaporation was continued until chemical analysis and specific gravity determinations indicated a concentration of zirconium oxide on a weight basis, equivalent to approximately 89% of such oxide. After heat treatment at 80° C. under the same conditions as described in Example 1 for a period of 30 minutes, the extremely stiff "liquid" product was spooned into the barrel of a hydraulic cylinder and allowed to stand for 4 hours so as to eliminate air bubbles. A 20 mil extrusion orifice was used. On reaching a steady state condition of extrusion, pressures required to maintain a feed rate of 200 feet per minute of extrusion were in the range of 20 to 25 pounds per square inch. The fiber formed at a rate of attenuation and tension of approximately 20 times that of the stabilized extrusion rate produce a monofilament after firing exhibiting a diameter of approximately 3½ microns. Using a polymeric material prepared as indicated in this example, the diameter of the finished fiber produced may be varied in accordance with the rate of tension attenuation. Practical limits of operation yielded diameters between 2 and 10 microns for the finished fiber. Fibers exhibiting diameters between 0.5 and 2 microns may be made with similar rate of attenuation by changing to an extrusion orifice approximately 5 mils in diameter.

Example 3

One hundred grams of the fully polymerized, stiff "liquid" as produced in Example 2 was diluted with 300 cc. of glacial acetic acid at 25° C. and stirred until solution was complete. A somewhat viscous liquid is obtained. This solution was then poured on a slab of polished fluorinated polymer designated in the trade as Teflon. The plastic plate supporting the film of liquid was placed in the bottom of a beaker. The plastic plates were separated from the bottom of said beaker on stilts of Teflon ½ inch high. Fifty cc. of glacial acetic acid were also placed in the bottom of the beaker. The contents of the beaker were then heated from the bottom in a constant temperature bath comprised of a heated wax so as to maintain the temperature at 105° C. until all of the acetic acid which had been added to the beaker had evaporated. Immediately thereafter the slab with its now apparently dry film of transparent material was placed in an oven which had been heated previously to 200° C. The oven temperature was maintained at this level while acetic acid was distilled into the heating zone. While on its Teflon slab in the oven, the film was held in the acetic acid atmosphere at 200° C. for 30 minutes. While still hot, the film which was now loose and exhibited a substantial degree of strength was removed from the plastic surface with a pair of forceps and transferred to a polished quartz surface placed in the oven. Fired alumina plates may be used instead of the quartz. The temperature of the oven was then increased to a range between 450 to 500° C. while still distilling acetic acid vapors into the hot zone. After maintaining the film at this temperature for about 30 minutes, the flow of acetic acid vapors was shut off and the heat treatment was continued for 20 minutes longer. The film was now brownish-black. The film was immediately inserted into a furnace, wherein it was heated in air at 1250° C. and maintained at this temperature for 30 minutes. On removal from the furnace and cooling, a transparent, almost water white, with a faint yellowish tinge, flat film was obtained having a thickness of 27 microns. The thickness of the original liquid film cast on the Teflon was about 3 times this thickness. The actual film which was processed in the manner described was approximately 4 inches square, being 2 inches on an edge.

Example 4

Four films produced as described in Example 3 were placed one on top of the other while at the 200° C. stage and while the atmosphere of acetic acid was maintained. Each period of heat treatment was doubled and a sheet of transparent zirconium oxide, free from bubbles, cracks, opacity and obvious crystallinity, approximately 4 mils in thickness was obtained at the end of the cycle. A very faint opalescence was evident in the product.

Example 5

Twenty grams of adipic acid were added to 10 liters of a solution of aluminum diformate containing approximately 10 grams of aluminum oxide per hundred grams of solution. This solution was then vacuum concentrated as described in Example 1 over a period of 24 hours. The thick liquid obtained was equivalent to 86% aluminum oxide by weight as determined by specific gravity and chemical analysis. The same procedure as described in Example 1 was then applied to this liquid except that the time of polymerization at 80° C. was 20 minutes. The temperature of the first heating zone after extrusion from the filament forming orifice was maintained at 120° C. rather than at 200° C. A water white transparent filament of round cross section and having a diameter of 2.7 microns was obtained as the result of the final firing at 1250° C.

Example 6

The same materials and procedures as defined in the previous example were utilized except that the raw materials were complexed by the addition of 200 cc. of a 10%

solution of chromium diformate to the solution of aluminum diformate. After firing at the final temperature, a transparent fiber of approximately 2.7 microns diameter was achieved in continuous monofilament form. The fiber had a pinkish red color. X-ray examination of the products made both in this example and the previous example indicated that the main constituent was alpha alumina, or corundum. The pinkish red fiber made in this example was comparable in its crystalline form and color to ruby.

Example 7

The same materials and procedures set forth in Example 5 were utilized except that 200 cc. of a 10% solution of cobalt acetate were added to the raw materials. Thereafter the solution was concentrated, polymerized, and formed into a continuous monofilament fiber as in Example 5. This fiber was blue in color and again X-ray examinations established that it was alpha corundum, thus being comparable in the main to the structure and color of natural sapphire.

Example 8

Ten liters of a 10% solution of chromium diformate were prepared and 20 grams of adipic acid added to such solution. After clarification by filtration, this solution was vacuum concentrated as indicated in Example 1 over a period of 40 hours to yield an extremely viscous, greenish-violet colored liquid containing approximately 90% chromium oxide by weight. The clear liquid was processed as in Example 1 for the preparation of continuous monofilaments using a 20 mil orifice and with speeds identical with those given in Example 1. The temperature for initial heat treatment immediately after extrusion and during attenuation was 120° C. prior to achieving the higher temperatures for final consolidation. A monofilament having a diameter of 6 microns and of circular cross section was obtained after firing at 1250° C. and the color was green, the filament being transparent.

Example 9

A significant increase in the toughness of the chromium oxide fiber and with the development of a yellowish green color was achieved as compared with the fiber of Example 8, through the elimination of the adipic acid addition, and the addition of 800 cc. of a calcium formate solution to the 10 liter batch to produce a solution containing 6% calcium oxide by weight.

Example 10

Freshly precipitated carbonated hydrous oxide of zirconia was prepared in the following manner: 1 mole of zirconyl oxychloride octahydrate is dissolved in 1500 ml. of distilled water. One mole of ammonium carbonate is dissolved in 1500 ml. of distilled water. The zirconium chloride solution is added to the carbonate solution with vigorous stirring. The pH of the resultant mixture is adjusted to 5.5 if it does not reach this value directly. The slurry is stirred vigorously for fiteen minutes at room temperature. The product, carbonated hydrous zirconium oxide, is filtered and washed with limited amounts of distilled water until the filter cake is free of chloride ion as determined qualitatively with a 1% silver nitrate solution. The filter cake is sucked "dry" on the filter and stored in sealed polyethylene bags. The zirconia content of the material is determined on each batch.

One mole of the freshly precipitated hydrous oxide was added to 1 mole of glacial acetic acid at room temperature and stirred vigorously for about 20 minutes. As a result a smooth, white, somewhat granular, precipitate was obtained which is completely insoluble in water and in the mother liquor. It appears to be zirconium monoacetate and is quantitatively formed by the technique described. The precipitate was separated from the motor liquor by filtration, then washed with a 1% solution of acetic acid and then with distilled water. The washed residue was dried at 100° C. The resulting dried product was digested in glacial acetic acid at 60° C. to 80° C. to form a gel. On standing for between 24 and 48 hours, a polymeric liquid is obtained. Between 0.1 mole and 0.5 mole of glacial acetic acid may be used for each mole of zirconium monoacetate.

The resulting polymeric liquid was converted to solid products by the techniques described in Examples 1 and 2.

Example 11

A solution of zirconium acetate in water, containing the equivalent of 11% zirconium oxide by weight was placed in a container wherein the surface exposed was approximately equal to the depth of the liquid. The solution was evaporated with some agitation at 80° C. until the liquid had reached a concentration equivalent to a zirconium oxide content of between 60% and 62%. The material was then a thick gel with a large amount of gas bubbles trapped in the gel. The container was removed from the evaporation and heat-treating zone, covered and then allowed to stand at room temperature for 48 hours. The resulting liquid was free from air bubbles and gel and exhibited a viscosity of 450,000 centipoises and a chain length of the order of 10,000 molecules. It was readily processed into fibers by drawing or extrusion and pulling.

In the above description wherever reference is made to concentration in the polymeric liquid this is not intended to imply that the oxide itself is present in the liquid. It appears that the metal is present as a hydrous derivative of the inorganic oxide. Hence the term "equivalent oxide" is deemed preferable and is intended to indicate that if a sample of the liquid is taken and subjected to analysis, the stated percentage would be reported as the oxide of the metal in question.

Having now described the invention in accordance with the patent statutes, we claim:

1. A process for producing a clear single phase liquid polymer containing at least 50% by weight of the oxide of a metal selected from the group consisting of metals whose hydrous oxides are precipitated at a pH more acid than 7 on treatment of aqueous solutions of salts of said metals with alkalies, which precipitates yield a pH of less than 7 after washing and dispersion in distilled water, which clear liquid polymer exhibits a viscosity at room temperature of at least about 8500 centipoises, and from which solid inorganic polymer products may be prepared which comprises: dissolving a water-soluble metal salt of a metal of said group and of an aliphatic carboxylic acid in water; clarifying the resultant solution to thereby remove extraneous undissolved solids and gases therefrom; thereafter subjecting the resultant clarified solution to vacuum evaporation while maintaining the temperature of the solution in the temperature range of 15° C. to 25° C.; and continuing the vacuum evaporation of said solution, for removal of volatile constituents until the resulting concentrate contains the equivalent of at least 50% by weight of the oxide of the metal whose salt is initially dissolved and exhibits a viscosity of at least about 8500 centipoises measured at room temperature.

2. A process for producing a positive hydroxylated ion base, water compatible clear liquid polymer containing at least 50% by weight of an inorganic oxide of a metal selected from the group consisting of metals whose hydrous oxides are precipitated at a pH more acid than 7 on treatment of aqueous solutions of salts of said metals with alkalies, which precipitates yield a pH of less than 7 after washing and dispersion in distilled water and exhibit a viscosity in such clear liquid in the range of 0.35 to 1.0×10^6 centipoises, from which solid inorganic polymer products may be prepared which comprises: dissolving a water soluble salt of said metal and

of an aliphatic carboxylic acid in water; clarifying the resultant solution to thereby remove extraneous undissolved solids and gases therefrom; thereafter subjecting the resultant clarified liquid to vacuum evaporation at a temperature range of 15 to 25° C. such that volatile constituents are removed; continuing the vacuum evaporation of said liquid until the liquid contains the equivalent of at least 50% by weight of the oxide of the metal whose salt is initially dissolved; thereafter replacing the vacuum with a controlled atmosphere consisting predominantly of vapor selected from the group consisting of vapor of carboxylic acid and mixtures of such vapor and noble gas and raising the temperature to a level between 60 and 90° C.; maintaining the liquid under the controlled atmosphere and at a temperature between 60° C. and 90° C. for a period of 2 to 20 minutes, and then cooling such liquid to room temperature while maintained under said controlled atmosphere.

3. The process of claim 1 wherein the salts of at least two of said metals are initially dissolved to yield a liquid polymer containing compounds of both of said metals.

4. The process of claim 1 wherein at least one of said metals is a metal which forms a weakly acidic hydrous oxide and at least one metal is a metal whose oxide is distinctly basic, the latter being present in no more than a minor amount sufficient to complex and stabilize the weakly acidic oxide.

5. The process of claim 1 wherein the carboxylic acid is one which exhibits a dissociation constant for the first hydrogen not less than 1.5×10^{-5}.

6. The process of claim 1 wherein in lieu of vacuum evaporation at a temperature in the range of 15° to 25° C. the clarified solution is concentrated first by gentle heating to temperatures between 60° C. and 90° C. under atmospheric pressure.

7. A process for producing a clear liquid polymer containing at least 50% by weight of an oxide of a metal selected from the group consisting of metals whose hydrous oxides are precipitated at a pH more acid than 7 on treatment of aqueous solutions of aliphatic carboxylic acid salts of said metals with alkalies, which precipitates yield a pH of less than 7 after washing and dispersion in distilled water and in which the aliphatic carboxylic acid in said salt is selected from the group consisting of aliphatic carboxylic acids exhibiting a dissociation constant for the first hydrogen not less than 1.5×10^{-5} which process comprises:

(1) dissolving said water soluble metal aliphatic carboxylate salt in water,

(2) clarifying the resultant solution to thereby remove extraneous undissolved solids and gases therefrom,

(3) evaporating the clarified solution at a temperature between about 60° C. and 90° C. until the liquid reaches a concentration equivalent to about 60% of metal oxide,

(4) permitting the resultant gel to stand undisturbed in a covered vessel at room temperature for between 24 and about 48 hours; and

(5) recovering the liquid polymer having a viscosity of about 450,000 centipoises, so produced.

8. The process of claim 7 wherein the metal salt is zirconium acetate and the original solution contains approximately 11% zirconium oxide by weight.

9. The process of claim 7 including in addition the step of drawing said liquid polymer into fibers.

10. A single phase liquid polymer suitable for the preparation of solid inorganic polymers which consists essentially of a liquid polymer having a metal oxide content equivalent to at least 50% by weight of said metal oxide, the metal being selected from the group of metals defined in claim 1.

11. Polymers based on positive hydroxylated metal ions derived from an oxide of a metal selected from the group consisting of metals whose hydrous oxides are acidic and consisting essentially of single phase liquid polymers having viscosities in the range of 0.35 to 1.0×10^6 centipoises at room temperature and consisting of units whose chain lengths exceed at least 1,000 molecules per chain.

12. Liquid polymers based on positive hydroxylated metal ions derived from an oxide of a metal selected from the group consisting of metals whose hydrous oxides are acidic and consisting essentially of single phase liquids exhibiting viscosities between about 8500 centipoises and 10,000 centipoises at room temperature and consisting of units whose chain lengths are from about 8 to 10 molecules in the chain.

13. Optically clear liquid polymers exhibiting viscosities in the range of 0.35 to 1×10^6 centipoises at room temperature and based on metal oxide selected from the group consisting of metal oxides represented by the general formulas MO_2 and M_2O_3 and an aliphatic carboxylic acid, the relative molar proportions of metal oxdie to carboxylic acid being as follows: between 4 to 1 and 2 to 1 with MO_2 and between 8 to 1 and 2 to 1 with M_2O_3 and wherein M represents a metal selected from the group consisting of the metals whose hydrous oxides are precipitated at a pH more acid than 7 on treatment of aqueous solutions of aliphatic carboxylic acid salts of said metals with alkalies, which precipitates yield a pH of less than 7 after washing and dispersion in distilled water.

14. Liquid polymers and liquids of claim 13 containing in addition a minor proportion of metal oxide represented by the general formula MO wherein M represents an alkaline earth metal.

15. The liquid polymers of claim 13 wherein the acid is selected from the group consisting of formic and acetic.

16. A diluted liquid polymer comprising the liquid polymer of claim 11, diluted with an added amount of alkyl carboxylic acid insufficient to depolymerize the resulting liquid product.

17. The method of forming solid articles from the liquid polymers of claim 12 which comprises forming a thin body of said liquid polymers and subjecting said body to temperatures between about 70° C. and about 120° C. in an atmosphere consisting essentially of at least one gas selected from the group consisting of noble gases and vapors of aliphatic carboxylic acids, and continuing such heat treatment until said solid non-liquid article is obtained.

18. The process of claim 17 wherein the last body which is heat treated is a filament formed by extrusion and attenuation.

19. The method of forming solid inorganic transparent articles from liquid polymers which includes subjecting the liquid polymers of claim 10 to temperatures sufficient to remove completely all organic portions of the polymer, yielding a solid transparent flexible article.

20. A solid transparent article comprised of a polymer chain of positive hydroxylated metal ions as defined in claim 2 stabilized by the presence of minor amounts of aliphatic carboxylic acid radical whose dissociation constant for the first hydrogen is not less than 1.5×10^{-5}.

21. Solid, transparent, continuous individual monofilaments characterized by a circular to ovoid cross-section, uniform diameters of at least 0.5 micron, and semi-infinite lengths relative to said diameter of uniform cross-section, comprised of a multiplicity of submicroscopic metal oxide crystals of at least one metal oxide of a metal whose hydrous oxide is acidic and in which the length, breadth, and thickness of said submicroscopic crystals are substantially equivalent to each other and in which the length of the filament is semi-infinite relative to the size of such submicroscopic particle.

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Dec. 24, 1968 B. C. RAYNES ET AL **3,418,179**

MATERIALS FOR PRODUCING SOFT SOLDER JOINTS

Filed Nov. 22, 1965 4 Sheets-Sheet 1

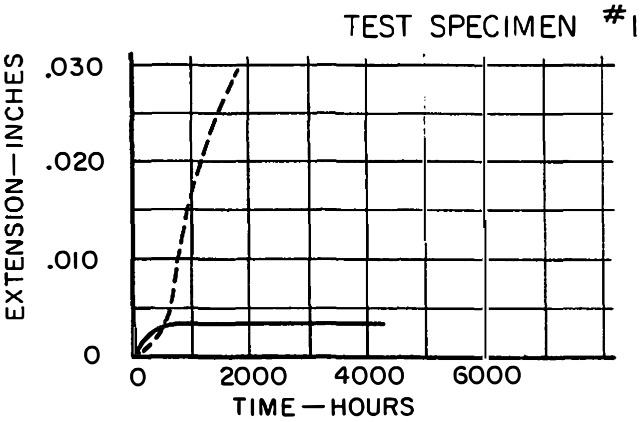

Fig. 1

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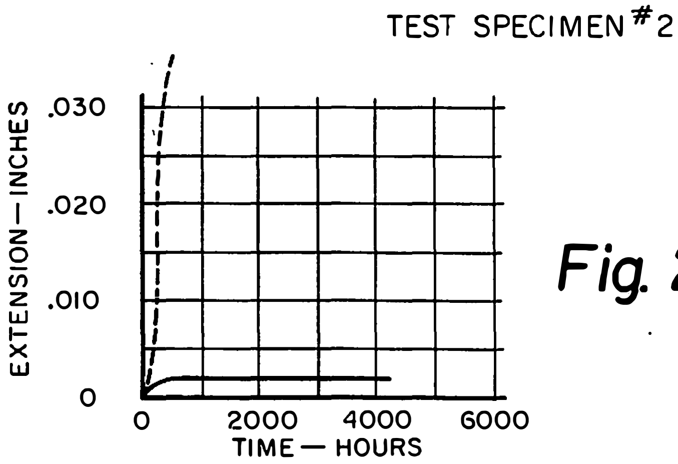

Fig. 2

DATA

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3 WROUGHT & 3 CAST COUPLINGS
66 % COPPER
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TEST SPECIMEN #3

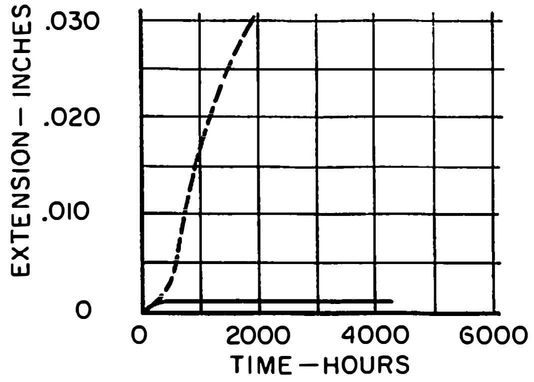

Fig. 3

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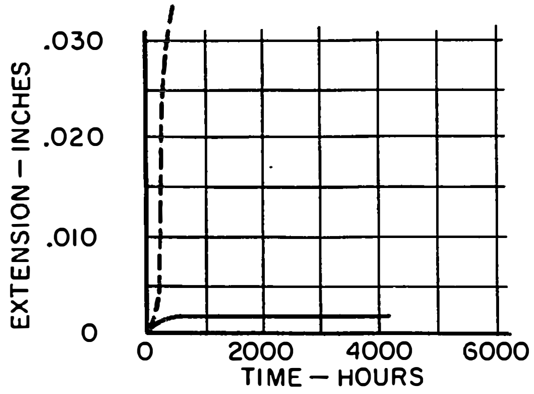

Fig. 4

DATA

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3 WROUGHT & 3 CAST COUPLINGS
50% COPPER
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LOAD: 16.0 LB.

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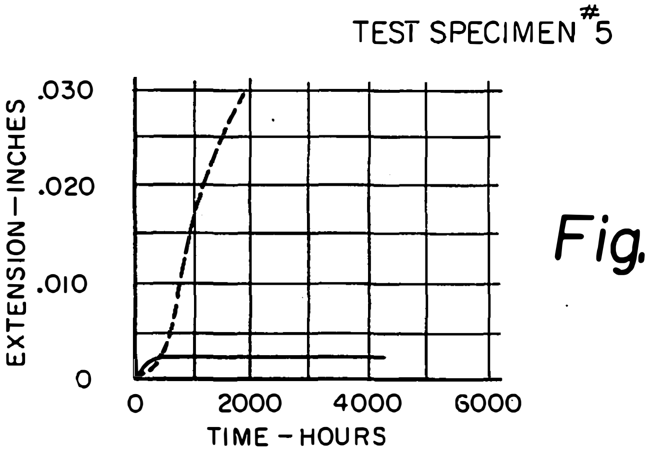

Fig. 5

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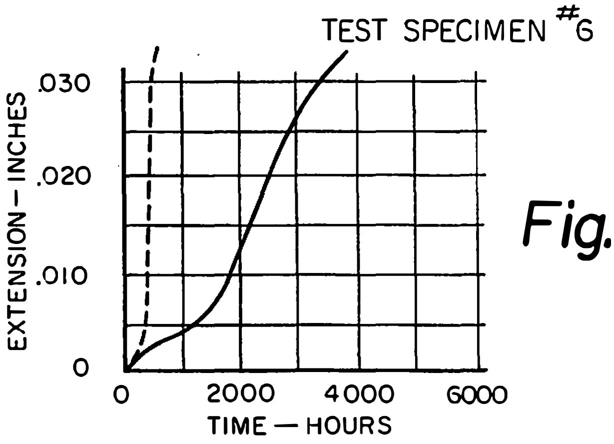

Fig. 6

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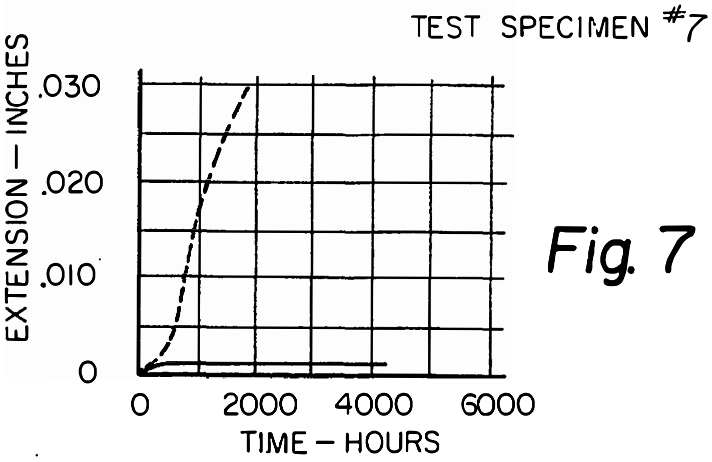

Fig. 7

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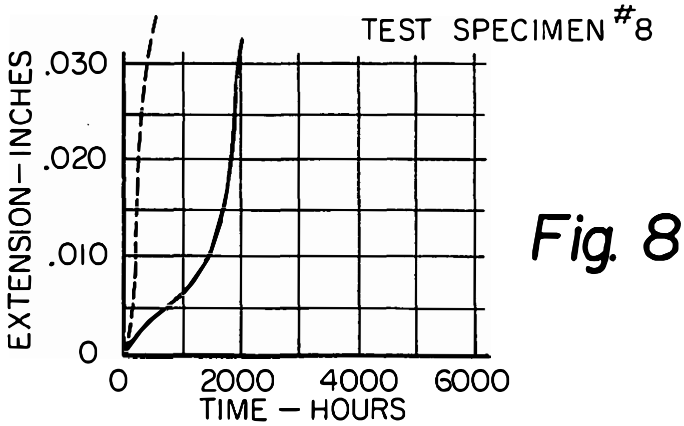

Fig. 8

DATA

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20% COPPER
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LOAD: 16.0 LB.

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3,418,179

MATERIALS FOR PRODUCING SOFT SOLDER JOINTS

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Filed Nov. 22, 1965, Ser. No. 509,053
8 Claims. (Cl. 148—24)

ABSTRACT OF THE DISCLOSURE

In the art of forming soft solder sweat joints between copper parts, a mixture of a flux and discrete particles of a solid, solder-reinforcing agent which is inert to electrochemical action in a soft solder-copper system.

This invention relates generally to the soldering art, and more specifically to the formation of soft solder joints. It is particularly concerned with sweat joints connecting copper fittings and tubing such as those found in plumbing systems, and with methods and materials for forming such sweat joints.

The resistance of a soft solder joint to substantially constant or static forces as distinguished from transient forces, is known as "creep strength." Because of its poor creep strength which may be less than one-eighteenth of the short term loading of the joint, the soft solder sweat joint is the weakest part of the present copper plumbing systems. This weakness in soft solder sweat joints results primarily from the low strength of current solder materials. It is believed this weakness is also due to defects in the form of voids which occur in the solder space.

Prior efforts have had little success in either increasing the strength of solder materials and joints or improving their solderability to decrease the occurrence of joint defects. Instead, copper plumbing systems, as they are now generally assembled and constituted, are over designed structurally, particularly in the length of the solder cup, in an effort to assure adequate all-over joint strength. Some idea of this over design may be had by noting that the 50/50 soft solder sweat joint creep load for one-half inch size plumbing is on the order of one hundred pounds in hot water service, while the screep load for the copper tube and fittings themselves is on the order of three thousand pounds or more, a factor of thirty or greater. The factor is greater still for larger size plumbing.

In spite of the overdesign of the solder cup to provide greater total strength in the joints, the unit creep strength afforded by the present solder materials is so low that the conventional soft solder joint operates at a calculated safety factor level of 2.8 which is one of the lowest in building construction. If the long term joint strength in conventional systems were to have a safety factor equivalent to that in the rest of the system, the length of the solder cup would have to be several times its present length.

The actual creep strength of sweat joints formed by conventional materials and techniques is often less than the calculated or rated strength because of voids occuring in the solder space. Such defects are found in systems installed by expert plumbers and are quite common in joints made by relatively unskilled persons. The mechanisms responsible for defect formations are numerous, but it has been discovered that poor surface wetting and rate of spreading of the solder and a capillary driving force which is insufficient completely to expel the flux from the joint and promote a complete fill are prominent factors.

It will be apparent from the foregoing that important advantages can be obtained by increasing the creep strength of a soft solder sweat joint. An improvement in the unit creep strength would improve the entire general strength of sweat plumbing systems. Concomitantly, it would be posible to eliminate much of the conventional over design by decreasing the solder cup length, as well as lightening other components including the tubing, and thereby provide for substantial cost reductions. An improvement in the joint strength would also afford increased reliability and safety factor and reduce the occurence of service failures.

Known prior art joints, such as brazed joints, exist which have substantially greater creep strength than soft solder joints. These joints require higher forming temperatures than do soft solder joints. This is a factor that may make brazed joints undesirable, especially in frame constructions where high temperatures may be dangerous. Thus, in spite of its poor creep strength, the soft solder joint is preferred and used because of ease of installation, its low temperature melting, and also because of its good capillary flow characteristics at low temperatures.

The copending application of Theodore D. Jaynes for Soft Solder Joints, Ser. No. 509,070, filed Nov. 22, 1965 and assigned to the same assignee as the present application, discloses basic discoveries which have made it possible to obtain copper sweat joints having unexpectedly high strength and to improve the overall strength of copper plumbing systems. In general, the inventions described in that application contemplate the introduction of a strengthening agent into the joint in order to improve the strength properties of the solder layer. The strengthening agent is preferably in the form of discrete particles which are unalloyed with the solder and are distributed throughout the joint. Several ways were disclosed for introducing the particles into the joint, including the electrodeposition of copper particles in the fitting, preplacing a quantity of particles in the fitting with a paste flux, and mixing or blending the particles in a suitable flux which is then applied in the usual manner to at least one of the parts to be joined.

The present invention is a novel advancement of the foregoing inventions disclosed in copending application Ser. No. 509,070. The invention resides in the discovery that, in addition to affecting a marked increase in the strength of soft solder materials, it is possible to improve the solderability of sweat joints and substantially reduce or eliminate the occurrence of voids in the solder layer by controlling the size and amount of the dispersion strengthening agent.

In carrying out the invention, the dispersion strengthening agent is preferably introduced into the solder joint by a flux vehicle. This may be accomplished by mixing or blending particles of the strengthening agent in a suitable flux, such as a commercially available corrosive paste flux, which is applied to the parts to be joined in the usual way. Alternate techniques for introducing the dispersion strengthening agent are set forth below. Copper powders have proved especially effective as the strengthening agent, although it is contemplated that materials such as glass or the like which will not cause electrochemical corrosion of a solder-copper system could be used.

The novel copper-flux material which comprises one aspect of the invention has several important advantages. As much as 80% by weight of copper can be introduced into a paste flux and the flux wiped onto a fitting in a manner similar to conventional flux. The major portions of the powder remains in the joint to strengthen the subsequently applied solder; however, as distinguished from prior attempts which have been made to add a strengthening agent directly to the solder, the application of the preferred copper powder in a flux vehicle does not adversely effect the flow characteristics of the solder and the times the temperatures of the soldering operation. The invention therefore provides a new flux material and soldering technique which result in greatly improved strength characteristics of the formed joint and yet do not require significant modification of standard soldering practices. Thus, the methods and materials of the invention can be used without special handling by both skilled and unskilled persons to form improved copper sweat joints.

It has been discovered that the optimum minimum amount of the dispersion strengthening agent should be on the order of about 20% by weight in the flux and that the minimum particle size distribution should be about 85% or less minus 325 mesh. Examination of sweat joints made by use of a flux compound containing from about 20% to about 80% by weight of copper powder having a particle size distribution of 85% or less minus 325 mesh indicate fewer microscopically visible voids and imperfections than in joints made according to other procedures. Large voids are almost eliminated. While the mechanism responsible for the substantial reduction of voids in the solder space is not clearly understood, it is believed that one prominent factor is an increase in the capillary force or dynamic action of the molten solder. This belief is based on observations that the solder meniscus advances evenly through the joints in such a manner as to almost completely expel flux sludges and avoid entrapment of flux and gas. Thus, the use of distributed copper particles promotes a complete fill of the joint by the molten solder and results in a larger solder area than in conventional sweat joints of the same size. The increased solder area is another reason for the greatly improved strength of joints made in accordance with this invention.

Among other advantages are that the new copper-flux can be used without changing the design of the usual plumbing fittings. The new flux material of this invention is relatively inexpensive and does not require special equipment, know-how or materials to produce. Further, it is characterized by a long shelf life and can be stored prior to use without deterioration.

Accordingly, the objects of the invention are to provide sweat joints of improved strength and methods and materials for making such joints. A more specific object of the invention is to provide for the use of a dispersion strengthening agent in an amount and size which has been found effective to increase the strength of the solder materials and to substantially reduce or eliminate the occurrence of voids in the solder layer.

Other features, objects, advantages and a fuller understanding of the invention will be apparent from the following detailed description and the accompanying drawings.

In the drawings, FIGURES 1 through 8 are graphs showing creep strength data of joints formed in accordance with the invention compared to creep strength data of conventional copper sweat joints.

As generally described above, the invention is concerned with the formation of soft solder joint by use of a strengthening agent which is in a form that is effective to increase the strength of the solder material and to reduce the occurrence of voids in the solder layer. The invention also pertains to methods and materials for introducing the strengthening agent into the joint. In the preferred embodiments to be descirbed, the strengthening agent is in the form of discrete particles which are added to the flux and the flux is applied to the metal parts in a manner similar to standard practice.

The primary matters of concern in carrying out the preferred concepts of the invention are the particular material selected as the strengthening agent, the particle size, and the amount of particles added to the flux. The specific composition of the flux itself is not of significant importance and various commercial fluxes can be selected depending upon the particular soldering application. Similarly, the soft solder which is used can be any conventional type.

In the specific examples set forth below, a conventional corrosive paste flux sold under the trade name Oatey No. 5 by the L. R. Oatey Co., Cleveland, Ohio was used as the vehicle for introducing the particles into the sweat joints. The soft solder used in forming the joints was a standard 50/50 tin-lead solder. These materials were selected simply because they are presently widely used in copper plumbing systems, and it is to be understood that the exemplary flux and solder are not limiting of the invention.

A primary requirement of any commercially acceptable technique and material for reinforcing copper sweat joints is to avoid altering the basic solder-copper system by introducing a new metal atom that might result in electrochemical corrosion. Because of this consideration, commerically pure copper particles, are a preferred strengthening agent, although it is contemplated that alloys containing copper could be used. Electrolytic copper powders which have a low percentage of alloying elements and may be considered commercially pure are particularly well suited for the purposes of the present invention. While copper is disclosed as a preferred strengthening material it is contemplated that inert materials, such as glass particles or the like, which will not induce corrosion or other detrimental actions in the joint could be used.

As noted above, another consideration in the formation of reinforced, void-free soft solder joints is the particle size of the strengthening agent. In forming sweat joints, the maximum particle size is determined by clearance of the fitting. The average total clearance of most fitting designs is approximately 0.006 inch, and in such designs it is preferred that the maximum particle size be 0.003 inch (100% minus 200 mesh). Particles having a maximum size of 0.003 inch can be distributed around the end of the tube or the inside of the solder cup and the two members maintained in concentricity in accordance with good soldering practice.

In accordance with this invention, it has been determined that the minimum particle size distribution should be on the order of 85% or less minus 325 mesh. The most preferred powders which have been used successfully in the flux combinations have a maximum particle size of approximately .003 inch (100% minus 200 mesh) and a minimum particle size distribution in the range of from about 50% to about 81% minus 325 mesh with the average minimum particle size being about 44 microns. Extremely finely divided powders, e.g. 100% minus 400 mesh, may have some strengthening effect. However, it has been observed that joints formed with such powders exhibit voids in the solder layer similar to conventional joints.

There are several commercially availabe copper powders which satisfy the foregoing parameter of particle size and can be used in accordance with the invention. The following are three typical electrolytic copper powders which have been used successfully:

(1) AMAX Type B electrolytic copper powder (American Metal Climax, Inc.) 99.5% min. Cu, apparent density 2.5–2.6 gm./cc.—

Screen analysis (mesh):	Percent
100, max.	0.2
150	1–11
200	13–23
250	3–10
325	17–27
Minus 325	45–53

(2) MD 201 granular copper power (Metals Disintegrating Corp.) 99.0% Cu, apparent density 2.4–2.8 gm./cc.

Screen analysis (mesh):	Percent
Minus 200	100
Minus 325	85

(3) Screened electrolytic copper powder.

Screen analysis (mesh):	Percent
100	0.0
150	1.1
200	12.7
250	9.5
325	19.8
Minus 325	55.5+

Another parameter of the preferred copper-flux is the amount of copper powder which is used. The preferred range of the copper powder or other strengthening agent in the flux is from about 20% by weight to about 80% by weight. While lesser amounts of copper powder may have some strengthening effect on the solder, it has been found that when the powder is below about 20% by weight in the flux the joints usually exhibit imperfections in the form of voids and are not visually different from unreinforced joints. Amounts of copper in excess of 80% also may provide improvements in the strength of the joints, but in such instances it is difficult to wipe the copper-flux onto a fitting and the stiff flux may be stripped off when the tube is assembled in the cup.

Copper powder in the amounts indicated can be readily mixed or blended into the flux without requiring any special handling techniques or equipment. As noted above, the resulting composition has a long shelf life and can be stored for a year or more before use.

In use the copper-flux can be applied in nearly the same manner as conventional fluxes, although it has been observed that paste fluxes containing large amounts of the powder apply somewhat more stiffly than the usual paste flux. The subsequently introduced soft solder is readily accepted into the joint and the finished joint will have an exterior appearance to that of an ordinary one. The soft solder may be placed in the joint in accordance with conventional practices, such as melting the solder by bringing it into contact with a surface heated to the soldering temperature, allowing the molten solder to flow into and fill the joint space, and then cooling the metal surfaces. The invention also can be practiced in conjunction with the constructions and methods disclosed in copending applications Ser. No. 429,562, now Patent No. 3,334,925, filed Feb. 1, 1965 and entitled Sweat Soldering Apparatus, and Ser. No. 462,673, filed June 9, 1965 and entitled Sweat Soldering Invention.

Accelerated screening creep tests of copper sweat joints formed by using the above-described copper-flux and method have shown a large improvement in the strength of the reinforced solder layer. As previously discussed, this improvement is due in part to an increase in the unit creep strength of the reinforced solder and also to the substantial elimination of voids in the solder space. In one such accelerated test, a test section of ½ inch wrought coupling joints placed under a load of 1000 pounds per square inch shear and containing three conventional joints in which the solder was reinforced by a copper-flux containing 66% by weight of the copper indicated a minimum improvement in strength of a factor of 7:1. The maximum strength improvement has not been determined, since this test is still in progress at the time of this writing. All three of the conventionally soldered joints failed at the end of 292 test hours, the first having failed after only 101 hours. One of the copper-flux coupling joints failed after 725 hours, but all of the remaining reinforced coupling joints have withstood over 3000 test hours.

Another accelerated test produced results similar to that set forth above. In this test, a ½ inch wrought fitting was made using 66% by weight copper-flux. A shear load of 600 pounds per square inch was applied to the fitting and the test is still in progress with no signs of failure after over 4000 hours. A similar load on a conventional 50/50 tin lead solder joint failed at the end of 1500 hours.

Extensive long term creep tests have also been conducted to show the improved creep strength of copper reinforced sweat joints under long term static shear loading. The test procedures which have been followed are similar to those described in the Building Materials and Structures (BMS) Report No. 58 by Swanger and Maupin, published Dec. 20, 1940 by the National Bureau of Standards. For the most part, higher loads were chosen than by Swanger and Maupin because of the increased strength of the copper-flux joints and the desired to reduce the total test time.

The following table summarizes the long term test results of several examples of copper-flux joints made in accordance with this invention. In each of these examples, the copper powders were mixed in an Oatey No. 5 corrosive paste flux referred to above. The copper powder was the previously described AMAX Type B electrolytic copper powder sold by American Metal Climax, Inc. in which all powder larger than minus 200 mesh (.003 inch) was screened out.

TABLE I

Example Number	Fitting Size, inch	Copper, Percent	Shear Load in Pounds per Square Inch	Number Failures	Cumulative Hours
1	½	66	370	0	3,655
2	½	66	570	0	3,656
3	½	50	370	0	3,655
4	½	50	605	0	3,672
5	½	34	370	0	3,672
6	½	34	595	11	3,672
7	½	20	370	0	3,672
8	½	20	605	12	1,922

Referring to the drawings, FIGURES 1–8 show plotted data for each individual example listed above in the table in comparison with plotted data for each individual example listed above in the table in comparison with plotted data calculated from the results of Swanger and Maupin. The solid lines in FIGURES 1–8 indicate the test results on the examples of the invention, while the dotted lines are based on the Swanger and Maupin data and indicate the average expected creep data for the test shear load or estimated data in the case of heavier loads.

The following Table II reports the results of modified short term tensile tests of conventional copper sweat joints and reinforced copper sweat joints made in accordance with this invention. By way of explaining the test procedures, it should be noted that ordinary tensile testing by standard rates of applied stresses does not reveal much about the strength of soldered joints. This is because the tube will fail under short term loads before the joint does unless there are extraordinary flaws in the joint. If a solid bar is substituted for the tubing, the fitting will frequently shear. Consequently, in conducting short term tensile tests, the procedure was to reduce the solder area of standard fittings by cutting down the cup length until the joints failed in the solder area. Joints of the same size were then made using the new copper flux and it was found that the average increase in reinforcement was from 10% to 15%.

AVERAGE TENSILE

Cut-Down Cup Length, inch	Flux Only, p.s.i.	Cu-Flux Reinforced (66% Cu, 34% Flux) p.s.i.	Percent Increase
⅜	3,140	3,500	+11
¼	2,480	2,780	+12
⅛	1,570	1,800	+15

It will be seen from the above that the strength inprovement in the ordinary copper sweat joints is substantial, and that this improvement can be obtained in a practical and easily accomplished manner by applying a flux containing the reinforcing agent to the parts to be joined and then introducing a molten soft solder in the usual way. The preferred flux which is used may be described broadly as flux vehicle containing from about 20% to about 80% by weight of the reinforcing particles, which are preferably in the form of a copper powder, having a minimum particle size distribution of about 85% or less minus 325 mesh and a maximum particle size which does not exceed one-half of the total clearance of the fitting design.

The finished joints may be broadly described as being characterized by a dispersion throughout the solder layer of free particles, preferably copper powder, having a minimum particle size distribution of about 85% or less minus 325 mesh. While the preferred technique of introducing the powder in the joints is by use of the novel flux, it is to be understood that copper particles of the specified size can be electrodeposited in the fitting. It is also contemplated that copper powder or other strengthening material can be preplaced in the cup or fitting with a paste flux.

As used herein, the term "free" in referring to the dispersion strengthening agent is intended to mean that the agent to substantially unalloyed in the solder layer. The term "copper" is used in the specification and claims in a broad sense and includes commercially pure copper as well as metals and alloys containing copper.

Many modifications and variations of the invention will be apparent to those skilled in the art in view of the foregoing detailed disclosure. Therefore, it is to be understood that, within the scope of the appended claims, the invention can be practiced otherwise than as specifically shown and described.

What is claimed is:

1. A composition of matter adapted for use in forming a soft solder sweat joint between copper parts, said composition of matter consisting essentially of a mixture of a paste flux and discrete particles of a solid, solder-reinforcing material which is inert to electrochemical action in a soft solder-copper system, said reinforcing material being present in an amount of from 20% to 80% by weight and having a minimum size of 85% or less minus 325 mesh.

2. The composition of matter as claimed in claim **1** in which the reinforcing material consists of copper powder.

3. A composition of matter adapted for use in forming a soft solder sweat joint between copper parts, said composition of matter consisting essentially of a mixture of a paste flux and discrete particles of a solid, solder-reinforcing material which is inert to electrochemical action in a soft solder-copper system, said reinforcing material being present in an amount of from 20% to 80% by weight and having a particle size of 100% minus 200 mesh and an average minimum particle size of approximately 44 microns.

4. A composition of matter as claimed in claim **3** in which the reinforcing material consists of copper powder.

5. A composition of matter adapted for use in forming a soft solder joint between copper parts, said composition of matter consisting essentially of a mixture of a paste flux and from about 20% to about 80% by weight copper particles.

6. The composition of matter as claimed in claim **5** wherein said copper particles are a commercially pure, electrolytic copper powder.

7. The composition of matter as claimed in claim **5** wherein the copper particles have a minimum size in the range of from about 50% to about 81% minus 325 mesh.

8. The composition of matter as claimed in claim **7** wherein the copper particles have a size of 100% minus 200 mesh.

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U.S. Cl. X.R.

29—496

Sept. 2, 1969 B. C. RAYNES ET AL **3,464,617**

SWEAT SOLDER FORM

Filed June 9, 1965 2 Sheets-Sheet 1

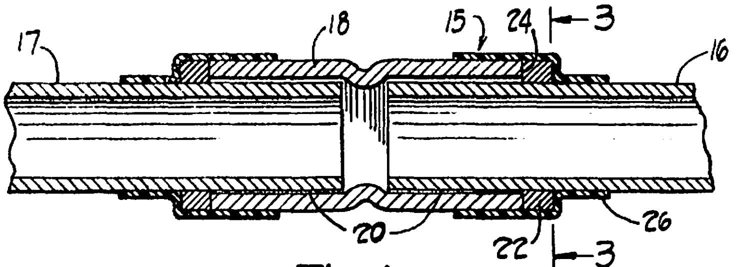

Fig. I

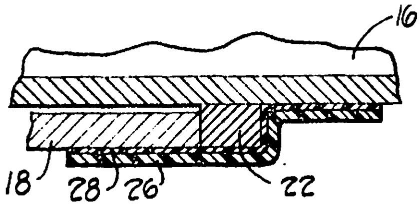

Fig. 2

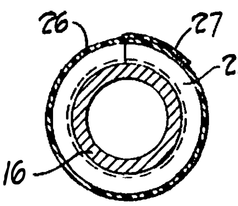

Fig. 3

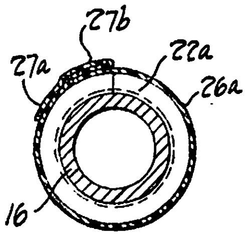

Fig. 5

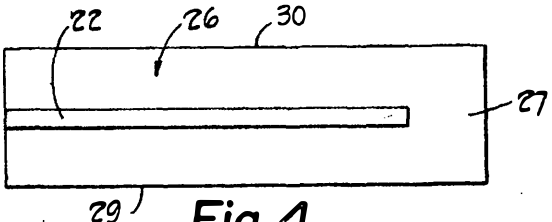

Fig. 4

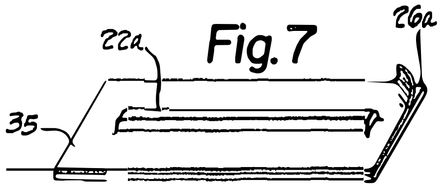

Fig. 7

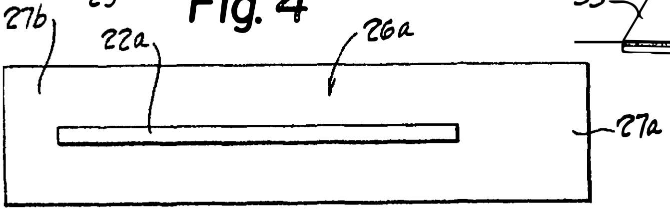

Fig. 6

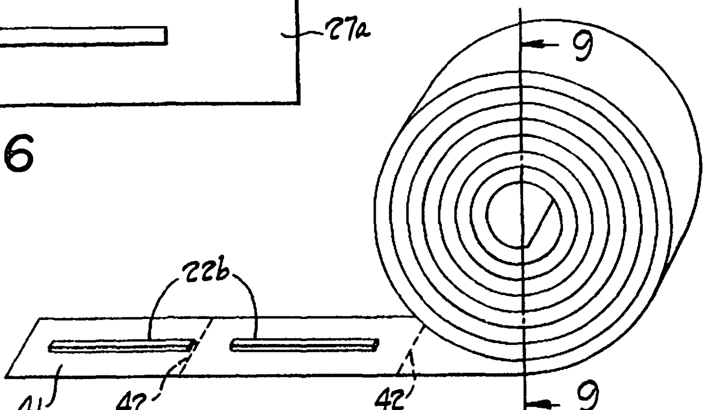

Fig. 8

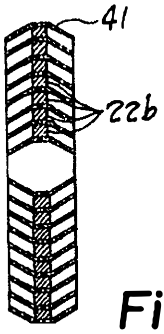

Fig. 9

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SWEAT SOLDER FORM

Filed June 9, 1965 2 Sheets-Sheet 2

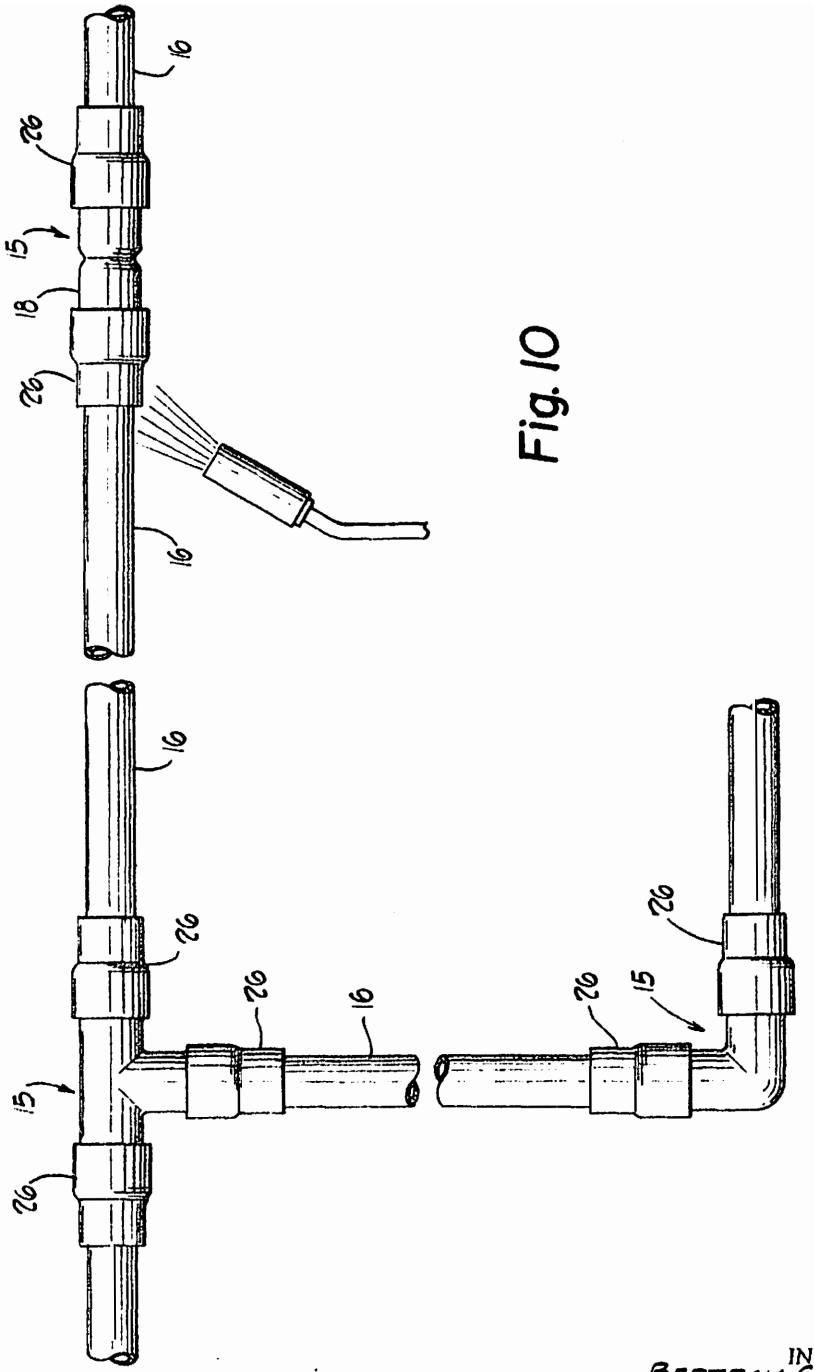

Fig. 10

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United States Patent Office

3,464,617
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3,464,617

SWEAT SOLDER FORM

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Filed June 9, 1965, Ser. No. 462,673
Int. Cl. B23k *3/06, 35/14*
U.S. Cl. 228—56 **12 Claims**

ABSTRACT OF THE DISCLOSURE

A length of adhesive coated tape and a length of solder, narower and shorter than the length of tape, secured to the tape by the adhesive. The tape and solder are used in sweat soldering a pipe and fitting together by wrapping the two about the pipe so as to form the solder into an encircling ring around the pipe, directly abutting the fitting. Portions of the tape extending beyond the solder are adhered by the adhesive to the pipe and fitting to hold the parts in assembled relationship.

The present invention relates generally to mechanical connections and hermetic seals between two telescoped members, and relates more specifically to methods and articles for joining tubular members by a process commonly referred to as "sweat soldering."

Improved methods and apparatus for sweat soldering pipes and fittings are disclosed in the copending application of Theodore D. Jayne, Ser. No. 429,562, filed Feb. 1, 1965, now Patent No. 3,334,925, and assigned to the assignee of this application. The present invention is an improvement over the copending application and is particularly useful to home handymen or others who prefer the "do it yourself" approach to home building, repair or maintenance. The invention will also appeal to skilled plumbers because of the efficiencies and savings that can be attained through the use of this invention.

The "sweat soldering" process is widely used to join copper pipes or tubes and copper fittings which are slipped over end portions of the tube or over a portion of a fitting which is equivalent to a tube. Each fitting has a sleeve, or "solder cup" as it is sometimes termed, which telescopes over an end portion of the tube. Diametrical clearances between the telescoped tubular members, i.e., the sleeve and the tube, range from less than .002 inch to .009 inch or larger. A "sweat joint" is made by causing capillary flow of molten soft solder into the clearance space.

An approved procedure for preparing such sweat joints may consist of the following steps: (1) cut the tube end, ream, deburr, and size as is required; (2) clean the tube end and the solder cup, i.e., the sleeve, with steel wool or the like to obtain a bright metal surface; (3) sparingly apply solder flux to the tube and cup surfaces to be joined; (4) assemble; (5) gauge the proper amount of solder by bending over a length of solder wire, e.g., 50–50 soft solder, corresponding to the nominal size of the fitting; (6) heat the tube and fitting evenly and place solder at the joint and melt with the heat of the tube and fitting; (7) heat the fitting until the solder is absorbed; and, (8) remove the excess solder with a brush while the solder is plastic, leaving a fillet around the fitting end.

As disclosed in more detail in the aforementioned copending application, there are several phases in the soldering process by which solder is introduced into the sweat joints. The solder is melted through contact at the joint space with the pipe and fitting that have been wetted by flux and heated to soldering temperature. The solder melts, wets the joint and first forms a puddle, which builds into

a bead as more solder is melted, and bridges the gap of the joint space to make "capillary contact." The liquid solder bridge enlarges as it is fed from the melting solder, moves into the joint space by capillary action and draws more molten solder with it. The free liquid surface of the solder is concave at the joint space and constitutes a driving meniscus. Thus, the liquid solder flows and fills the gap space to complete the sweat joint.

Most experts have for many years considered the formation of perfect sweat joints to be a simple matter. With relatively inexperienced persons this is by no means true. Relatively large size tubes and fittings of, for example four inches in diameter, have in recent years found increasing acceptance. With such large size couplings it is quite difficult for even skilled and experienced persons to make consistent and dependable joints in all situations.

Any number of imperfections in the listed phases of the soldering process may exist to produce defects in the complete sweat joint. For example, the solder movement into the joint may be limited by an inadequate supply of new liquid solder, inadequate solder entrance path into the joint gap, inadequate capillary forces, joint gap blockage, or inadequate flux.

Of particular interest here is the elimination, even with relatively unskilled persons, of those imperfections in the sweat joint which are the results of such factors as improper feeding of the holder to the joint, improper application of the heat to the pipe and fitting, and failure to maintain a desired gap by maintaining proper concentricity of the pipe and fitting. Most conventional methods of feeding the length of solder wire endwise into the gap, particularly hand feeding, are not able to assure a proper application of solder material completely around the joint at the proper moment during heating. Nor are they able to assure a continuous and unbroken feed to the joint gap. An uneven or discontinuous supply of the solder to the joint gap, as by the failure to melt the solder rapidly enough at the gap edge, does not suply the necessary reservoir of liquid solder.

Lack of concentricity, or more accurately, uneven spacing of the joint walls, provides a non-uniform capillary flow into the joint. If the gap becomes too big in areas, then the solder meniscus force is inadequate to provide an advance against gravity in combination with mild flow resistance from flux. This problem is especially acute in larger fittings, where the height to which solder must flow may be several inches. In these large fittings, the gap over large areas of the joint may allow solder to drain out of the joint rather than climb up into the upper portions of the joint.

Improper or uneven heating of the joint can also result in uneven or discontinuous solder flow. Untimely melting of the solder itself as by improper direct application of the heat source on the solder itself can produce uneven solder flow and even hinder formation of the driving meniscus.

An additional handicap of prior hand feeding methods is that they are unwieldy, particularly where the telescoped tubular members, the heat source, such as a torch, and the solder must all be hand held. This is especially a problem where the work is overhead since the continuous reaching up with both arms can become quite tiresome.

The present invention provides an improved method for applying the solder against a joint gap edge between two telescoping tubular members, such as a pipe and surrounding fitting. In addition, the improved method holds the pipe and fitting firmly in a pre-assembled position, so as to not only maintain a proper joint gap, but also to allow an entire length or run of pipe to be pre-assembled with fittings and placed in proper position, prior to sweat soldering the fittings.

Briefly, this method involves wrapping a length of pressure sensitive tape, with an adhered length of solder of proper volume for the joint, around the tube or pipe directly adjacent the joint, with the solder abutting the end of the fitting, and heating the assembly to melt the solder.

The sweat soldering of pipes and fittings in accordance with this invention is preferably accomplished by using a novel combination and arrangement of predetermined lengths of solder adhered to predetermined lengths of pressure sensitive adhesive tape. Each length of solder is predetermined to correspond to the outside circumferential length of a standard sized pipe. The length of solder is sufficiently large in cross section to provide a volume of solder sufficient to properly fill the joint gap between the pipe and surrounding fitting after the solder has been melted and has flowed between the two by capillary action. Preferably, the length of pressure sensitive adhesive tape is somewhat longer than the length of solder, although it is satisfactory if it merely corresponds in length. The solder is located in longitudinal alignment with the tape, intermediate the longitudinally extending edges of the length of tape. This preferred construction and arrangement provides an overlapping or extending portion of the tape that holds the solder and parts in place.

When a pre-assembled length of tape and solder is used to join a pipe and fitting, the length of tape is first positioned with the solder adjacent the fitting, and is wrapped about the pipe so as to form the solder into an encircling ring around the pipe and directly abutting the terminal end of the fitting at the joint gap. Portions of the tape that extend axially of the pipe and fitting at each side of the solder ring are pressed into tight surface contact with the pipe and fitting about the circumference of each. Heat is then applied to the fitting and tube preferably on either side of the tape, thereby causing the solder to melt and flow into the joint gap. The very presence of the tape itself tends to cause the worker to apply heat on each side of the joint, as he should, rather than directly to the gap and solder.

In a preferred embodiment, the pressure sensitive adhesive tape of the present invention is transparent so that the joint may be visually observed during soldering. It is also preferred that the tape undergo a visible change, such as a change in color, upon the application of heat sufficient to melt the solder, thereby indicating that the joint has been soldered. In this way, where a large number of joints are first taped and thereafter heated and soldered, it will be readily apparent to a workman or an inspector whether or not any taped joint has been left unsoldered.

Additionally, the tape should be non-combustible at the temperatures to which it is heated during the soldering operation, even when subjected to the direct flame of a soldering torch, for safety and so that the pipe and fitting are maintained in proper relationship throughout the soldering operation. The tape may be of a material that shrinks when heated, thereby firmly closing in behind the solder as the solder melts and runs into the gap.

It is contemplated that lengths of tape and adhered solder strips may be pre-cut to standard pipe sizes. Preferably strips of solder may be pre-cut and adhered in proper spaced relationship to a continuous tape or sheet of tape-like material that is perforated or marked to define separate tapes. For example, an elongated tape is scored across the width of the tape at spaced locations, each score defining the end of each length, and the tape may be formed into a roll. Where separate, pre-cut strips or a sheet of scored strips are provided, the adhesive side of the tape is preferably protected by a thin, smooth, protective strip.

The present invention results in considerable savings of solder by adhering the proper amount for each joint directly to the tape. Experience has shown that in hand feeding solder to a joint there is a tendency to utilize an excess of solder over that necessary. This feature therefore makes the present invention attractive to contractors who fabricate large installations where the waste becomes substantial, as well as to others of more limited skill to whom it assures a proper joint. Furthermore, substantially increased efficiencies can be obtained if a piping system can be first assembled and thereafter soldered. With the present invention, parts may be held by the tape in a pre-assembled arrangement and then subsequently soldered, permitting substantial savings in time.

Other attendant advantages of this invention and the various embodiments thereof will be readily appreciated as the invention becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawings in which:

FIGURE 1 is a longitudinal sectional view of a pipe and fitting wrapped and held in position ready to be soldered, in accordance with the present invention;

FIGURE 2 is an enlarged, fragmentary, view of the joint gap, solder and tape of FIGURE 1;

FIGURE 3 is a transverse sectional view of the assembly of FIGURE 1, taken along the line **3—3**, and looking in the direction of the arrows;

FIGURE 4 is a plan view of a length of tape and adhered solder as it appears in a pre-cut form prior to being applied to a pipe joint as in FIGURE 3;

FIGURE 5 is a transverse sectional view of a pipe and fitting wrapped with a length of tape and solder, similar to that shown in FIGURE 3, but depicting another embodiment wherein the tape extends beyond the length of solder at each end and is sealed by joining the two ends of the tape and then folding the ends in one direction around the pipe;

FIGURE 6 is a plan view of a pre-cut length of tape and solder, with the solder arranged on the tape in a manner to facilitate wrapping the tape as shown in FIGURE 5;

FIGURE 7 is a perspective view of a pre-cut length of tape and adhered length of solder material, whene an adhesive surface of the tape is covered by a protective covering;

FIGURE 8 is a side elevational view of a roll of prescored tape to which separate, spaced, lengths of solder are adhered;

FIGURE 9 is a transverse sectional view of the roll of tape shown in FIGURE 8, taken along the line **9—9** and looking in the direction of the arrows; and

FIGURE 10 is a diagrammatic showing of a pipe system pre-assembled and taped prior to soldering.

Referring now to FIGURE 1, a plumbing assembly having joints to be soldered in accordance with the present invention is indicated generally by the reference character **15**. The plumbing joint includes tubes or pipes **16**, **17** of copper or other suitable metal, and a sleeve or fitting **18** of copper or other metal. The copper pipes **16**, **17** and the copper fitting **18** in the form of a sleeve are all conventional in plumbing pieces.

The copper pipe **16** is shown telescoped into one end of the sleeve **18**, and the pipe **17** is shown telescoped into the opposite end of the sleeve **18**. A joint gap or space **20** is formed between each pipe **16**, **17** and the copper sleeve **18**. Because the relationship between each pipe **16** and **17** with the sleeve **18** is essentially the same, only the relationship between the pipe **16** and sleeve **18** and the associated solder assembly will be described in detail.

As shown in FIGURES 1, 2 and 3, a relatively narrow length of sloder material **22** is wrapped to form a split ring directly surrounding the pipe **16** and abutting the terminal end **24** of the fitting **18**. It will be understood, of course, that suitable flux (not shown) is applied to the pipe **16** within the joint gap **20**.

A length of flexible tape **26** having an adhesive surface or layer **28** (see FIGURE 2) enwraps the outside circumference of portions of both the pipe **16** and the sleeve **18**, as well as the solder **22**. The tape is shown in intimate, adhering, contact about the circumference of the pipe **16**, fitting **18**, and solder **22**.

As best shown in FIGURES 1 and 2, the width of the flexible tape **26** extends axially along the pipe **16** and fitting **18** a distance sufficient to contact adequate surface of both the fitting and the pipe to firmly hold the two together in their predisposed position prior to soldering. In the embodiment of FIGURE 4, one end of the length of solder is located adjacent one end of the tape and extends along the tape intermediate the two longitudinally extending edges **29**, **30**. The length of tape **26** exceeds the length of the solder **22** so as to provide an overlapping portion shown at **27** that provides further assurance of a firm, tight, connection between the pipe and fitting prior to soldering.

Because both the flexible tape **26** and the solder material **22** may be readily curved to the desired contour, a substantially flat, pre-cut length of tape and solder, as shown in FIGURE 4 of the drawings, may be quickly wrapped around the pipe **16** and fitting **18** and pressed into place to form the assembly shown in FIGURES 1, 2 and 3.

The body of solder material **22** may be of any conventional soldering material, for example, a 50–50 solder which is 50% lead and 50% tin, or 95–5 tin-antimony alloy. The solder material may also comprise a silver solder, as the present invention is also usable for silver soldering.

FIGURES 5 and 6 illustrate a second embodiment of a pre-cut length of tape with an adhered length of solder. A strip of solder **22*a*** is located with both ends spaced from adjacent ends of the tape. However, the strip is positioned closer to one end of the tape than the other. It is also spaced intermediate the two longitudinally extending edges of the length of tape, as in the embodiment of FIGURE 4. Thus, in this case, there are two extending flaps **27*a*** and **27*b***. The flap **27*a*** is somewhat longer than **27*b***. With this arrangement, as shown in FIGURE 5, the length of solder **22*a*** is wrapped about the outer circumference of the pipe **16** until the two ends of the solder abut each other. The flaps of **27*a*** and **27*b*** are pressed together and then folded about the pipe **17** and fitting **18**, with the extra length of flap **27*a*** being adhered about the outside of the already wrapped tape, thereby securing the tape tightly about the joint.

Pre-cut length of pressure sensitive tape having the proper length and quantity of solder already attached may be conveniently supplied in the form shown in FIGURE 7 of the drawings. As shown, the tape **26*a*** and length of solder **22*a*** of the embodiment of FIGURE 6 is covered with a flexible protective film **35**, which is in direct contact with the adhesive surface of the tape **26*a***. The flexible protective sheet **35** is suitably constructed so that it does not firmly adhere to the adhesive surface of the tape **26*a***, and it can therefore be readily removed when the tape and solder are to be applied to the joint. A waxed or plastic coated paper provides a suitable protective sheet.

As a preferred alternative to pre-cut lengths of tape, a roll of tape **40**, is shown in FIGURES 8 and 9 of the drawings. The roll **40** is made of a continuous strip of pressure sensitive, adhesive, flexible tape **41**. Desired lengths are delineated by spaced indicia **42**. These indicia **42** may be pre-scored lines, or simply printing, but are preferably perforations as shown. Lengths of solder **22*b*** are adhered to the adhesive surface of the strip of tape **41** in proper position with relationship to the pre-scored lines **42**, so as to form separate strips as shown in FIGURE 4 or FIGURE 6 of the drawings, when the tape is torn along the perforated or pre-scored lines **42**. With this arrangement, a protective film over the adhesive surface is not required, inasmuch as the rolled configuration protects the adhesive surface, as illustrated in FIGURE 9.

In a preferred form of the present invention, the tape **26** is essentially transparent, non-combustible at the temperatures at which the sweat soldering is accomplished, and undergoes a visible change, i.e., becomes visibly scorched or changes color, when the pipe **16** and fitting **18** are heated to a temperature sufficient to melt the solder **22**. The color change may occur because of the composition and properties of the tape itself or may be achieved or enhanced by incorporating into the tape or applying to the tape any of the known waxes, compounds or paints that change color when a certain temperature range is reached. Ideally, the tape will also shrink upon heating to close in the space previously occupied by the ring of solder prior to heating, thereby maintaining the original tightness. Suitable tapes include those made from fluorocarbon resins, or vinylidene chlorides. Advantageously, the tapes may be reinforced by fiberglass for strength and to resist stretching, thereby being better suited to maintain the wrapped parts in proper position with uniform spacing between the pipe and fitting. The tape is coated with a suitable pressure sensitive adhesive, for example, a silicone adhesive.

It will be apparent from the above description, that in accordance with this invention, the tape holds the tubes **16** and **17** in the fitting or sleeve **18**, and, additionally, holds the solder material **22** in direct contact with the pipes **16**, **17** at the opening of the joint gap **20**. As shown in FIGURE 10, a number of fittings or an entire system or portion of a system have been pre-assembled and held in proper relationship and position with the tape prior to heating and soldering. To solder a taped joint, a source of heat, such as a torch, is provided and applied to the pipe and sleeve on either side of the tape so that the joint area is properly heated and the solder is melted by the heat of the two members being soldered. With the pipes **16**, **17** properly centered initially within the fitting or sleeve **18**, the tape **26** surrounding the fitting and pipe at each joint gap **20** and extending beyond the gap so as to encircle both the pipe and the fitting in tight, adhering relationship, will hold the sleeve and the telescoped tubes in assembled, uniformly spaced, relationship. Thus, the tube and sleeve need not be held by hand while being soldered. Furthermore, the tape shields the solder material from the direct application of heat and also from entry of gases and other materials during the sweat soldering process.

When the joint area is heated to the soldering temperature, each body of solder material in contact with the tubes **16**, **17** adjacent each end of the sleeve **18** immediately melts and wets the joint edges to form a solder bridge and a driving meniscus. The melting solder flows into each joint space **20** by capillary action and fills the joint space. The tape is sufficiently transparent for the operator to see the solder flow and stop the application of heat. Once the joint is completed the appearance of the tape readily indicates the fact that it has been heated and therefore that the joint has been soldered. The length of tape may be either left in place or removed after the joint is soldered.

The significance of maintaining the pipe and fitting in proper, pre-aligned and essentially concentric relationship during the soldering operation will be readily appreciated from the fact that a uniform gap about the entire circumference of the joint will draw melted solder uniformly into the joint, whereas if the gap is too large in places, so as to exceed the maximum permissible capillary dimension between the pipe and fitting, the solder will not flow sufficiently into the gap. On the other hand, if the pipes are in contact, there will be little or no solder to form a seal at the line of contact.

The spacing is, of course, more critical in large diameter pipes, inasmuch as the solder must flow a substantially greater distance to provide a complete and adequate seal. By way of example, in a four inch copper pipe to be sweat soldered to a copper fitting, the maximum permissible capillary dimension between the pipe and the fitting which will draw the melted solder a distance of four inches from the opening from which the solder is applied, is approximately 0.004 inch. Thus, if the gap dimension is greater than 0.004 inch it is probable that the solder will not be drawn entirely up and around the entire circumference of the telescoped portions of the copper pipe.

In summary, the present invention uniformly provides a proper supply of solder material circumferentially of the joint gap and touching the edge of the fitting at the joint gap entrance. That is, for a given length of solder material adhered to a predetermined length of tape, the width and thickness of the solder material is correlated to provide a volume of solder that will adequately fill the gap joint when the solder is melted and drawn by capillary action into the joint gap. With the arrangement of the present invention, the solder melts annularly due to the heat from the pipe and fitting and uniformly provides a continuous circumferential supply of liquid solder to the joint gap entrance. The pressure sensitive adhesive tape holds the fitting and each tube, in a predisposed relationship so that, if positioned initially, the pipes will be properly positioned during the soldering process. Thus, an even flow and uniform advancement of the liquid solder into the joint space is obtained.

Although the invention has been described in preferred forms with a certain degree of particularity, it should be understood that the present disclosure of the preferred forms has been made only by way of example and that numerous changes and the details of construction and the combination and arrangement of parts may be resorted without departing from the spirit and scope of the invention as hereinafter claimed.

What is claimed is:

1. An article of manufacture for use in assembling pipes and fittings or the like comprising a length of tape having an adhesive coating on one surface, said tape being of a predetermined width, and a length of solder material shorter than the length of tape and narrower than the width of the tape, adhered to the adhesive coating; said length of solder extending along the tape in general longitudinal alignment therewith and said adhesive coating extending beyond the width and length of the solder material whereby the tape will adhere to a pipe and fitting, hold the solder in place and maintain the pipe and fitting in assembled relationship.

2. The articles of claim **1** wherein the length of solder material extends along the tape intermediate longitudinally extending edges of the tape.

3. The article of claim **2** wherein the length of solder material is adhered to the adhesive coating of the length of tape with one end of the length of solder material located at one end of the length of tape.

4. The article of claim **2** wherein the length of solder material is adhered to the adhesive coating of the length of tape with both ends of the length of solder material spaced inwardly from both ends of the tape.

5. The article of claim **1** wherein the length of the solder essentially corresponds with the outside circumferential length of said pipe to be sweat soldered.

6. The article of claim **5** wherein the solder material constitutes a predetermined volume sufficient to essentially fill an annular joint between the tube and surrounding fitting when the solder material is melted.

7. The article of claim **1** wherein the tape is comprised of a material that shrinks when heated to a temperature at which the solder material melts.

8. The article of claim **1** wherein the tape includes a material that undergoes a visually observable change when heated to a temperature at which the solder material melts.

9. The article of claim **1** wherein the tape is transparent.

10. The article of claim **1** wherein the tape is noncombustible at temperatures sufficient to melt the solder material.

11. A combination of tape and solder which comprises a strip of tape of predetermined width, one surface of which is coated with a pressure sensitive adhesive; said tape including length delineating means at locations spaced along the length of the strip of tape; a plurality of strips of solder narrower in width than the width of the tape and shorter in length than the distance between successively spaced delineating means, said strips being adhered to the tape by the pressure sensitive adhesive and extending along the tape between successive delineating means and intermediate longitudinally extending edges of the tape, and said adhesive coating extending beyond the width and length of the solder strips.

12. An article for use in sweat soldering fittings and pipes, which comprises: a strip of tape that is noncombustible at soldering temperatures, essentially transparent and heat shrinkable, and that undergoes a visible change when heated to soldering temperatures; an adhesive coating covering one surface of the tape, suitable for adhering the tape to a pipe and fitting or the like; and a strip of solder material adhered to the tape by the adhesive at a location spaced from edges of the tape so that said adhesive coating extends beyond the width and length of the solder material; whereby the tape will adhere to a pipe and fitting, hold the solder in place and maintain the pipe and fitting in assembled relationship.

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JOHN F. CAMPBELL, Primary Examiner

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U.S. Cl. X.R.

29—500

March 9, 1971 B. C. RAYNES ET AL **3,568,304**

METHODS OF FORMING SOFT SOLDER JOINTS

Original Filed Nov. 22, 1965 4 Sheets-Sheet 1

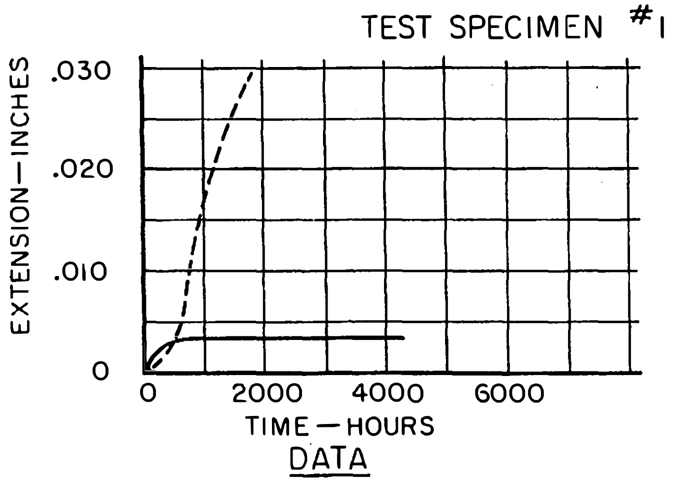

Fig. 1

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3 WROUGHT & 3 CAST COUPLINGS
66 % COPPER
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LOAD: 8.7 LB.

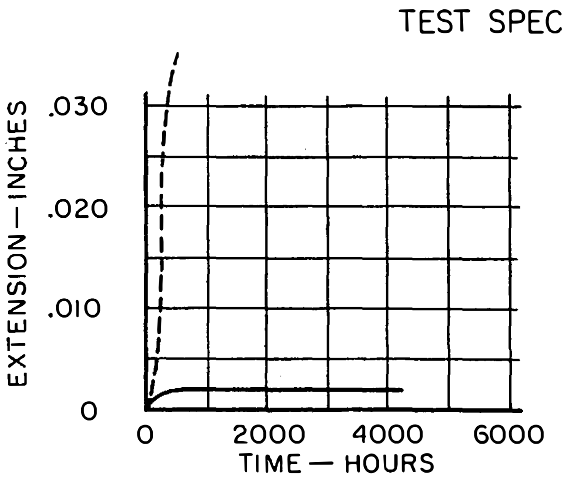

Fig. 2

DATA

1/2 M COPPER TUBING
3 WROUGHT & 3 CAST COUPLINGS
66 % COPPER
SHEAR: 570 LB/IN^2
LOAD: 14.6 LB.

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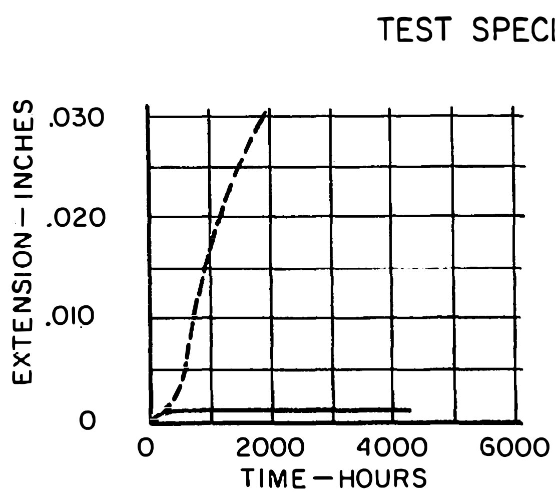

Fig. 3

DATA

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3 WROUGHT & 3 CAST COUPLINGS
50 % COPPER
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LOAD: 8.8 LB.

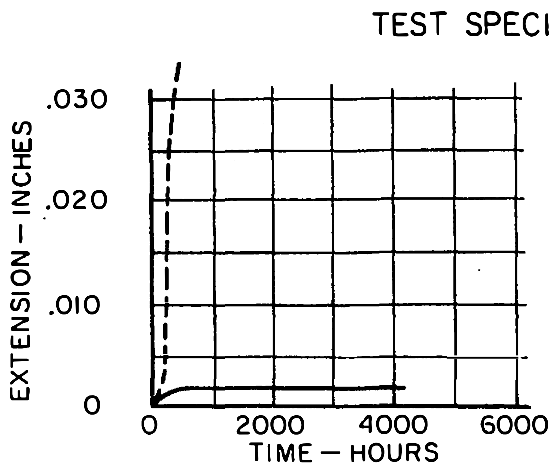

Fig. 4

DATA

1/2 M COPPER TUBING
3 WROUGHT & 3 CAST COUPLINGS
50% COPPER
SHEAR: 605 LB/IN.^{2}
LOAD: 16.0 LB.

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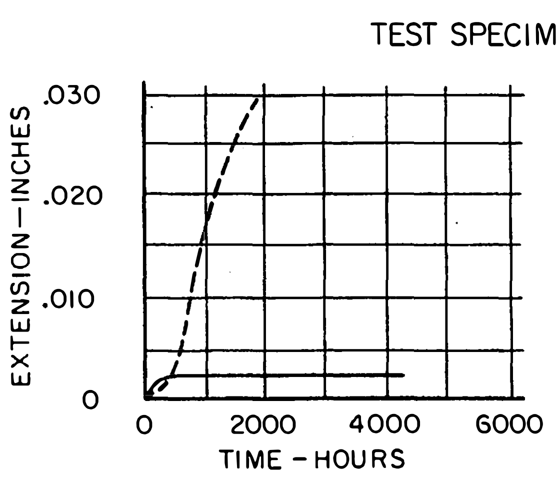

Fig. 5

DATA

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3 WROUGHT & 3 CAST COUPLINGS
34 % COPPER
SHEAR: 370 LB./IN.^{2}
LOAD: 8.8

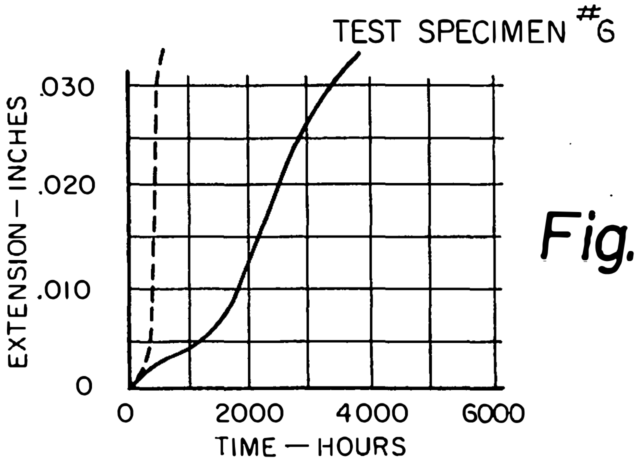

Fig. 6

DATA

1/2 M COPPER TUBING
3 WROUGHT & 3 CAST COUPLINGS
34 % COPPER
SHEAR: 595 LB/IN.^{2}
LOAD: 15.6 LB

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METHODS OF FORMING SOFT SOLDER JOINTS

Original Filed Nov. 22, 1965 4 Sheets-Sheet 4

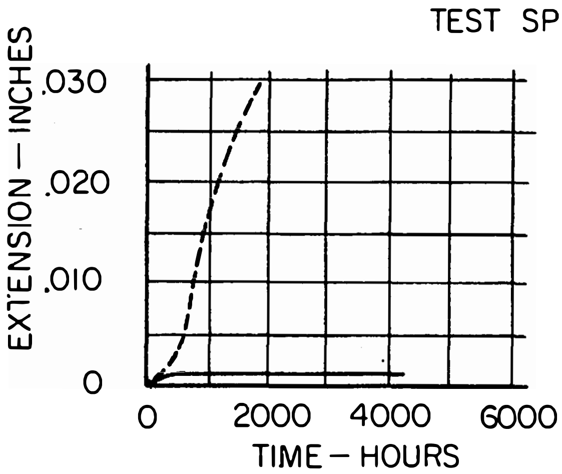

Fig. 7

DATA

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3 WROUGHT & 3 CAST COUPLINGS
20% COPPER
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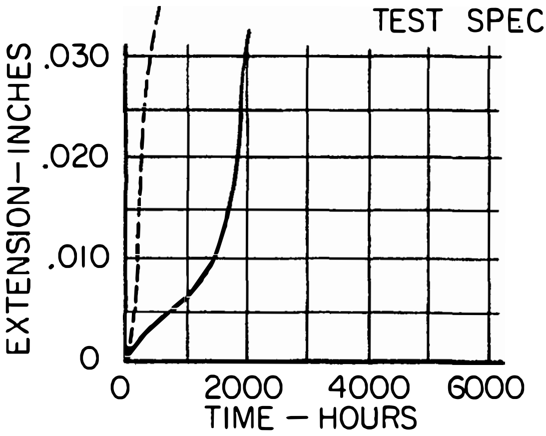

Fig. 8

DATA

1/2 M COPPER TUBING
3 WROUGHT & 3 CAST COUPLINGS
20% COPPER
SHEAR: 605 LB/IN^2
LOAD: 16.0 LB.

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Patented Mar. 9, 1971

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METHODS OF FORMING SOFT SOLDER JOINTS

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Original application Nov. 22, 1965, Ser. No. 509,053, now Patent No. 3,418,179, dated Dec. 24, 1968. Divided and this application May 17, 1968, Ser. No. 729,981

Int. Cl. B23k *31/02*

U.S. Cl. 29—489 14 Claims

ABSTRACT OF THE DISCLOSURE

In the art of forming soft solder sweat joints connecting tubular copper members, the method of introducing into the joint area around one of the members a solder-reinforcing agent consisting of copper, and thereafter introducing a molten soft solder.

CROSS-REFERENCE TO RELATED APPLICATION

This application is a division of application Ser. No. 509,053 of Bertram C. Raynes et al., filed Nov. 22, 1965 and entitled "Soft Solder Joints and Methods and Materials for Producing the Same," now Pat. No. 3,418,179.

BACKGROUND OF THE INVENTION

This invention relates generally to the soldering art, and more specifically to the formation of soft solder joints. It is particularly concerned with methods for forming sweat joints connecting copper fittings and tubing such as those found in plumbing systems.

The resistance of a soft solder joint to substantially constant or static forces as distinguished from transient forces, is known as "creep strength." Because of its poor creep strength which may be less than one-eighteenth of the short term loading of the joint, the soft solder sweat joint is the weakest part of the present copper plumbing systems. This weakness in soft solder sweat joints results primarily from the low strength of current solder materials. It is believed this weakness is also due to defects in the form of voids which occur in the solder space.

Prior efforts have had little success in either increasing the strength of solder materials and joints or improving their solderability to decrease the occurrence of joint defects. Instead, copper plumbing systems, as they are now generally assembled and constituted, are over designed structurally, particularly in the length of the solder cup, in an effort to assure adequate all-over joint strength. Some idea of this over design may be had by noting that the 50–50 soft solder sweat joint creep load for one-half inch size plumbing is on the order of one hundred pounds in hot water service, while the creep load for the copper tube and fittings themselves is on the order of three thousand pounds or more, a factor of thirty or greater. The factor is greater still for larger size plumbing.

In spite of the over design of the solder cup to provide greater total strength in the joints, the unit creep strength afforded by the present solder materials is so low that the conventional soft solder joint operates at a calculated safety factor level of 2.8 which is one of the lowest in building construction. If the long term joint strength in conventional systems were to have a safety factor equivalent to that in the rest of the system, the length of the solder cup would have to be several times its present length.

The actual creep strength of sweat joints formed by conventional materials and techniques is often less than the calculated or rated strength because of voids occurring in the solder space. Such defects are found in systems installed by expert plumbers and are quite common in joints made by relatively unskilled persons. The mechanisms responsible for defect formations are numerous, but it has been discovered that poor surface wetting and rate of spreading of the solder and a capillary driving force which is insufficient completely to expel the flux from the joint and promote a complete fill are prominent factors.

It will be apparent from the foregoing that important advantages can be obtained by increasing the creep strength of a soft solder sweat joint. An improvement in the unit creep strength would improve the entire general strength of sweat plumbing systems. Concomitantly, it would be possible to eliminate much of the conventional over design by decreasing the solder cup length, as well as lightening other components including the tubing, and thereby provide for substantial cost reductions. An improvement in the joint strength would also afford increased reliability and safety factor and reduce the occurrence of service failures.

Known prior art joints, such as brazed joints, exist which have substantially greater creep strength than soft solder joints. These joints require higher forming temperatures than do soft solder joints. This is a factor that may make brazed joints undesirable, especially in frame constructions where high temperatures may be dangerous. Thus, in spite of its poor creep strength, the soft solder joint is preferred and used because of ease of installation, its low temperature melting, and also because of its good capillary flow characteristics at low temperatures.

SUMMARY OF THE INVENTION

The copending application of Theodore D. Jaynes for Soft Solder Joints, Ser. No. 509,070, filed Nov. 22, 1965 and assigned to the same assignee as the present application, discloses basic discoveries which have made it possible to obtain copper sweat joints having unexpectedly high strength and to improve the overall strength of copper plumbing systems. In general, the inventions described in that application contemplate the introductions of a strengthening agent into the joint in order to improve the strength properties of the solder layer. The strengthening agent is preferably in the form of discrete particles which are unalloyed with the solder and are distributed throughout the joint. Several ways were disclosed for introducing the particles into the joint, including the electrodeposition of copper particles in the fitting, preplacing a quantity of particles in the fitting with a paste flux, and mixing or blending the particles in a suitable flux which is then applied in the usual manner to at least one of the parts to be joined.

The present invention is a novel advancement of the foregoing inventions disclosed in copending application Ser. No. 509,070. The invention resides in the discovery that, in addition to affecting a marked increase in the strength of soft solder materials, it is possible to improve the solderability of sweat joints and substantially reduce or eliminate the occurrence of voids in the solder layer by controlling the size and amount of the dispersion strengthening agent.

In carrying out the invention, the dispersion strengthening agent is preferably introduced into the solder joint by a flux vehicle. This may be accomplished by mixing or blending particles of the strengthening agent in a suitable flux, such as a commercially available corrosive paste flux, which is applied to the parts to be joined in the usual way. Alternate techniques for introducing the dispersion strengthening agent are set forth below. Copper powders have proved especially effective as the strengthening agent, although it is contemplated that materials such as glass or the like which will not cause electrochemical corrosion of a solder-copper system could be used.

As much as 80% by weight of copper powders can be introduced into a paste flux and the flux wiped onto a fitting in a manner similar to conventional flux. The major portion of the powder remains in the joint to strengthen the subsequently applied solder; however, as distinguished from prior attempts which have been made to add a strengthening agent directly to the solder, the application of the preferred copper powder in a flux vehicle does not adversely affect the flow characteristics of the solder and the times and temperatures of soldering operation. The methods of this invention utilizing the copper flux material therefore result in greatly improved strength characteristics of the formed joint and yet do not require significant modification of standard soldering practices. The methods of the invention can be used without special handling by both skilled and unskilled persons to form improved copper sweat joints.

It has been discovered that the optimum minimum amount of the dispersion strengthening agent should be on the order of about 20% by weight in the flux and that the minimum particle size distribution should be about 85% or less minus 325 mesh. Examination of sweat joints made by use of a flux compound containing from about 20% to about 80% by weight of copper powder having a particle size distribution of 85% or less minus 325 mesh indicate fewer microscopically visible voids and imperfections than in joints made according to other procedures. Large voids are almost eliminated. While the mechanism responsible for the substantial reduction of voids in the solder space is not clearly understood, it is believed that one prominent factor is an increase in the capillary force or dynamic action of the molten solder. This belief is based on observations that the solder meniscus advances evenly through the joints in such a manner as to almost completely expel flux sludges and avoid entrapment of flux and gas. Thus, the use of distributed copper particles promotes a complete fill of the joint by the molten solder and results in a larger solder area than in conventional sweat joints of the same size. The increased solder area is another reason for the greatly improved strength of joints made in accordance with this invention.

Accordingly, an object of the invention is to provide methods of making sweat joints of improved strength. A more specific object of the invention is to provide for the use of a dispersion strengthening agent in an amount and size which has been found effective to increase the strength of the solder materials and to substantially reduce or eliminate the occurrence of voids in the solder layer.

Other features, objects, advantages and a fuller understanding of the invention will be apparent from the following detailed description and the accompanying drawings.

DESCRIPTION OF THE DRAWINGS

In the drawings, FIGS. 1 through 8 are graphs showing creep strength data of joints formed in accordance with the invention compared to creep strength data of conventional copper sweat joints.

DESCRIPTION OF THE PREFERRED EMBODIMENT

As generally described above, the invention is concerned with the formation of soft solder joints by use of a strengthening agent which is in a form that is effective to increase the strength of the solder material and to reduce the occurrence of voids in the solder layer. In the preferred embodiments to be described, the strengthening agent is in the form of discrete particles which are added to the flux and the flux is applied to the metal parts in a manner similar to standard practice.

The primary matters of concern in carrying out the preferred concepts of the invention are the particular material selected as the strengthening agent, the particle size, and the amount of particles added to the flux. The specific composition of the flux itself is not of significant importance and various commercial fluxes can be selected depending upon the particular soldering application. Similarly, the soft solder which is used can be any conventional type.

In the specific examples set forth below, a conventional corrosive paste flux sold under the trade name Oatey No. 5 by the L. R. Oatey Co., Cleveland, Ohio was used as the vehicle for introducing the particles into the sweat joints. The soft solder used in forming the joints was a standard 50–50 tin-lead solder. These materials were selected simply because they are presently widely used in copper plumbing systems, and it is to be understood that the exemplary flux and solder are not limiting of the invention.

A primary requirement of any commercially acceptable technique and material for reinforcing copper sweat joints is to avoid altering the basic solder-copper system by introducing a new metal atom that might result in electrochemical corrosion. Because of this consideration, commercially pure copper particles are a preferred strengthening agent, although it is contemplated that alloys containing copper could be used. Electrolytic copper powders which have a low percentage of alloying elements and may be considered commercially pure are particularly well suited for the purposes of the present invention. While copper is disclosed as a preferred strengthening material it is contemplated that inert materials, such as glass particles or the like, which will not induce corrosion or other detrimental actions in the joint could be used.

As noted above, another consideration in the formation of reinforced, void-free soft solder joints is the particle size of the strengthening agent. In forming sweat joints, the maximum particle size is determined by clearance of the fitting. The average total clearance of most fitting designs is approximately 0.006 inch, and in such designs it is preferred that the maximum particle size be 0.003 inch (100% minus 200 mesh). Particles having a maximum size of 0.003 inch can be distributed around the end of the tube or the inside of the solder cup and the two members maintained in concentricity in accordance with good soldering practice.

In accordance with this invention, it has been determined that the minimum particle size distribution should be on the order of 85% or less minus 325 mesh. The most preferred powders which have been used successfully in the flux combinations have a maximum particle size of approximately .003 inch (100% minus 200 mesh) and a minimum particle size distribution in the range of from about 50% to about 81% minus 325 mesh with the average minimum particle size being about 44 microns. Extremely finely divided powders, e.g. 100% minus 400 mesh, may have some strengthening effect. However, it has been observed that joints formed with such powders exhibit voids in the solder layer similar to conventional joints.

There are several commercially available copper powders which satisfy the foregoing parameter of particle size and can be used in accordance with the invention. The following are three typical electrolytic copper powders which have been used successfully:

(1) AMAX Type B electrolytic copper powder (American Metal Climax, Inc.) 99.5 min. Cu, apparent density 2.5–2.6 gm./cc.

Screen analysis:

	Percent
On 100 mesh, max.	0.2
On 150 mesh	1–11
On 200 mesh	13–23
On 250 mesh	3–10
On 325 mesh	17–27
Minus 325 mesh	45–53

(2) MD 201 granular copper powder (Metals Disintegrating Corp.) 99.0% Cu, apparent density 2.4–2.8 gm./cc.

Screen analysis, percent:

100% minus 200 mesh
85% minus 325 mesh

(3) Screened electrolytic copper powder.

Screen analysis:	Percent
On 100 mesh	0.0
On 150 mesh	1.1
On 200 mesh	12.7
On 250 mesh	9.5
On 325 mesh	19.8
Minus 325 mesh	55.5+

Another parameter of the preferred copper-flux is the amount of copper powder which is used. The preferred range of the copper powder or other strengthening agent in the flux is from about 20% by weight to about 80% by weight. While lesser amounts of copper powder may have some strengthening effect on the solder, it has been found that when the powder is below about 20% by weight in the flux the joints usually exhibit imperfections in the form of voids and are not visually different from unreinforced joints. Amounts of copper in excess of 80% also may provide improvements in the strength of the joints, but in such instances it is difficult to wipe the copper-flux onto a fitting and the stiff flux may be stripped off when the tube is assembled in the cup.

Copper powder in the amounts indicated can be readily mixed or blended into the flux without requiring any special handling techniques or equipment. As noted above, the resulting composition has a long shelf life and can be stored for a year or more before use.

In use the copper-flux can be applied in nearly the same manner as conventional fluxes, although it has been observed that paste fluxes containing large amounts of the powder apply somewhat more stiffly than the usual paste flux. The subsequently introduced soft solder is readily accepted into the joint and the finished joint will have an exterior appearance similar to that of an ordinary one. The soft solder may be placed in the joint in accordance with conventional practices, such as melting the solder by bringing it into contact with a surface heated to the soldering temperature, allowing the molten solder to flow into and fill the joint space, and then cooling the metal surfaces. The invention also can be practiced in conjunction with the constructions and methods disclosed in copending applications Ser. No. 429,562, filed Feb. 1, 1965 and entitled Sweat Soldering Apparatus, and Ser. No. 462,673, filed June 9, 1965 and entitled Sweat Soldering Invention.

Accelerated screening creep tests of copper sweat joints formed by using the above-described copper-flux and method have shown a large improvement in the strength of the reinforced solder layer. As previously discussed, this improvement is due in part to an increase in the unit creep strength of the reinforced solder and also to the substantial elimination of voids in the solder space. In one such accelerated test, a test section of ½ inch wrought coupling joints placed under a load of 1000 pounds per square inch shear and containing three conventional joints in which the solder was reinforced by a copper-flux containing 66% by weight of the copper indicated a minimum improvement in strength of a factor of 7:1. The maximum strength improvement has not been determined, since this test is still in progress at the time of this writing. All three of the conventionally soldered joints failed at the end of 292 test hours, the first having failed after only 101 hours. One of the copper-flux coupling joints failed after 725 hours, but all of the remaining reinforced coupling joints have withstood over 3000 test hours.

Another accelerated test produced results similar to that set forth above. In this test, a ½ inch wrought fitting was made using 66% by weight copper-flux. A shear load of 600 pounds per square inch was applied to the fitting and the test is still in progress with no sign of failure after over 4000 hours. A similar load on a conventional 50–50 tin lead solder joint failed at the end of 1500 hours.

Extensive long term creep tests have also been conducted to show the improved creep strength of copper reinforced sweat joints under long term static shear loading. The test procedures which have been followed are similar to those described in the Building Materials and Structures (BMS) Report No. 58 by Swanger and Maupin, published Dec. 20, 1940 by the National Bureau of Standards. For the most part, higher loads were chosen than by Swanger and Maupin because of the increased strength of the copper-flux joints and the desire to reduce the total test time.

The following table summarizes the long term test results of several examples of copper-flux joints made in accordance with this invention. In each of these examples, the copper powders were mixed in an Oatey No. 5 corrosive paste flux referred to above. The copper powder was the previously described AMAX Type B electrolytic copper powder sold by American Metal Climax, Inc. in which all powder larger than minus 200 mesh (.003 inch) was screened out.

TABLE I

Example Number	Fitting size, inch	Copper, percent	Shear load in pounds per square inch	Number failures	Cumulative, hours
1	½	66	370	0	3,655
2	½	66	570	0	3,655
3	½	50	370	0	3,655
4	½	50	605	0	3,672
5	½	34	370	0	3,672
6	½	34	595	11	3,672
7	½	20	370	0	3,672
8	½	20	605	12	1,922

Referring to the drawings, FIGS. 1–8 show plotted data for each individual example listed above in the table in comparison with plotted data for each individual example listed above in the table in comparison with plotted data calculated from the results of Swanger and Maupin. The solid lines in FIGS. 1–8 indicate the test results on the examples of the invention, while the dotted lines are based on the Swanger and Maupin data and indicate the average expected creep data for the test shear load or estimated data in the case of heavier loads.

The following Table II reports the results of modified short term tensile tests of conventional copper sweat joints and reinforced copper sweat joints made in accordance with this invention. By way of explaining the test procedures, it should be noted that ordinary tensile testing by standard rates of applied stresses does not reveal much about the strength of soldered joints. This is because the tube will fail under short term loads before the joint does unless there are extraordinary flaws in the joint. If a solid bar is substituted for the tubing, the fitting will frequently shear. Consequently, in conducting short term tensile tests, the procedure was to reduce the solder area of standard fittings by cutting down the cup length until the joints failed in the solder area. Joints of the same size were then made using the new copper flux and it was found that the average increase in reinforcement was from 10% to 15%.

AVERAGE TENSILE

Cut-down cup	Flux only, p.s.i.	Cu-flux reinforced, p.s.i.[1]	Percent increase
Length, inch:			
⅜	3,140	3,500	+11
¼	2,480	2,780	+12
⅛	1,570	1,800	+15

[1] 66% Cu and 34% flux.

It will be seen from the above that the strength improvement in the ordinary copper sweat joints is substantial, and that this improvement can be obtained in a practical and easily accomplished manner by applying a flux containing the reinforcing agent to the parts to be joined and then introducing a molten soft solder in the usual way. The preferred flux which is used may be described broadly as flux vehicle containing from about 20% to about 80% by weight of the reinforcing particles, which are preferably in the form of a copper powder, having a minimum particle size distribution of about 85% or less minus 325 mesh and a maximum particle size which does not exceed one-half of the total clearance of the fitting design.

The finished joints may be broadly described as being characterized by a dispersion throughout the solder layer of free particles, preferably copper powder, having a minimum particle size distribution of about 85% or less minus 325 mesh. While the preferred technique of introducing the powder in the joints is by use of the novel flux, it is to be understood that copper particles of the specified size can be electrodeposited in the fitting. It is also contemplated that copper powder or other strengthening material can be preplaced in the cup or fitting with a paste flux.

As used herein, the term "free" in referring to the dispersion strengthening agent is intended to mean that the agent is substantially unalloyed in the solder layer. The term "copper" is used in the specification and claims in a broad sense and includes commercially pure copper as well as metals and alloys containing copper.

Many modifications and variations of the invention will be apparent to those skilled in the art in view of the foregoing detailed disclosure. Therefore, it is to be understood that, within the scope of the appended claims, the invention can be practiced otherwise than as specifically shown and described.

What is claimed is:

1. A method of forming a soft solder sweat joint connecting copper members comprising the steps of applying to at least one of the members a composition of matter consisting essentially of a mixture of a paste flux and from about 20% to about 80% by weight copper particles having a mesh size of 85% or less minus 325 mesh, subsequently introducing a molten soft solder, and thereafter allowing the solder to cool and form a joint between the members which is reinforced by free copper.

2. The method as claimed in claim 1 wherein said copper particles are a commercially pure, electrolytic copper powder.

3. The method as claimed in claim 1 wherein the copper particles have a minimum size in the range of from about 50% to about 81% minus 325 mesh.

4. The method as claimed in claim 3 wherein the copper particles have a size of 100% minus 200 mesh.

5. A method of forming a soft solder sweat joint connecting copper members comprising the steps of introducing into the joint area between said members a soft solder reinforcing material consisting of copper particles, the copper particles having a minimum size of 85% or less minus 325 mesh, subsequently introducing a molten soft solder, and thereafter allowing the solder to cool and form a joint between the members which is reinforced by free copper.

6. The method as claimed in claim 5 wherein the copper particles are introduced into the joint area by applying to at least one of the members a paste flux containing the copper particles.

7. The method as claimed in claim 5 in which the copper particles consist of commercially pure, electrolytic copper powder.

8. The method as claimed in claim 5 wherein the copper particles have a minimum size in the range of from 50% to 81% minus 325 mesh.

9. The method as claimed in claim 5 in which the copper particles are 100% minus 200 mesh.

10. The method as claimed in claim 5 wherein the average minimum size of the copper particles is approximately 44 microns.

11. A method of forming a soft solder sweat joint connecting copper members comprising the steps of applying to at least one of the members a composition of matter consisting essentially of a paste flux and discrete particles of a solid, solder-reinforcing material which is inert to electrochemical action in a soft solder-copper system, the reinforcing material being present in the flux in an amount of from 20% to 80% by weight and having a minimum size of 85% or less minus 325 mesh.

12. The method as claimed in claim 11 in which the solder-reinforcing agent consists of copper particles.

13. A method of forming a soft solder sweat joint connecting copper members comprising the steps of applying to at least one of the members a composition of matter consisting essentially of a paste flux and discrete particles of a solid, solder-reinforcing material which is inert to electrochemical action in a soft solder-copper system, the reinforcing material being present in the flux in an amount of from 20% to 80% by weight and having a particle size of 100% minus 200 mesh and an average minimum particle size of approximately 44 microns.

14. The method as claimed in claim 13 in which the solder-reinforcing material consists of copper particles.

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U.S. Cl. X.R.

29—492, 495, 503

Sept. 10, 1968 S. S. CARLTON ET AL **3,401,114**

PROCESS USING COAL IN SEWAGE TREATMENT

Filed Oct. 15, 1965

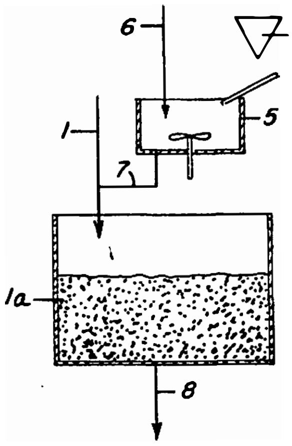


FIG. 1

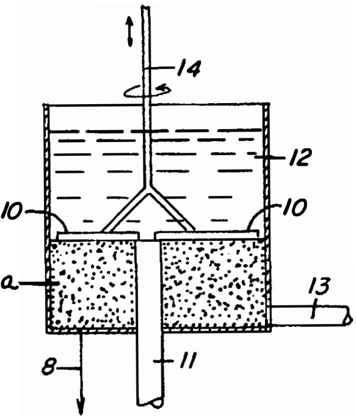
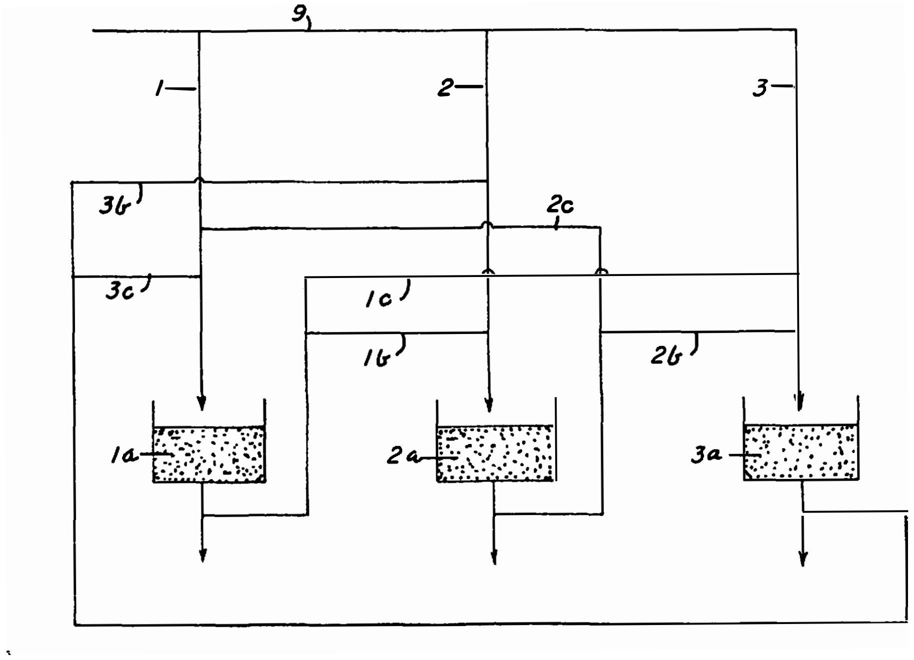


FIG. 3

FIG. 2



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PROCESS USING COAL IN SEWAGE TREATMENT

Stuart S. Carlton, Parma, and Bertram C. Raynes, Pepper Pike Village, Ohio, assignors, by direct and mesne assignments, of one-half to Rand Development Corporation, Cleveland Ohio, and one-half to the United States of America as represented by the Secretary of the Interior, jointly

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14 Claims. (Cl. 210—30)

ABSTRACT OF THE DISCLOSURE

Raw sewage is passed through a bed of coal to filter out solids and adsorb soluble contaminants. As filtered-out solids collect at the surface of the bed to coat the coal and thereby inhibit flow of additional sewage through the bed, the top layer of the bed is removed.

The invention relates to the purification of raw sewage. The phrase "raw sewage," as used in the specification and claims, includes municipal waste waters originating from domestic or industrial sources, or both, or a combination of either or both with storm waters which are also collected by the sewers serving the municipality; wastes originating from specific industries including, but not restricted to, abattoirs, oil refineries, breweries and chemical and manufacturing plants; and other sources of waters which contain impurities of types desired to be removed and capable of removal by the process of this invention.

Pollution of the nation's water supplies by contaminants present in sewage is becoming an increasingly acute problem. At present, conventional sewage treatment plants are incapable of removing a large percentage of all the pollutants present in sewage. As a result these pollutants have been returned to the nation's water supplies thereby lowering their quality as evidenced by foaming, taste and odor problems. Aside from aesthetic considerations, increasing concern is rising over the possible long term effects of these pollutants on health.

Soluble compounds within raw sewage comprise the potentially hazardous materials. They include:

(a) phosphates;
(b) COD- and BOD-producing materials (chemical and biochemical oxygen demand materials that help consume oxygen from water);
(c) alkyl benzene sulfonate (ABS) synthetic detergent which is poisonous to plants and animals, causes foaming, and is a COD- and BOD-producing material;
(d) linear alkyl sulfonate (LAS) biodegradable detergents;
(e) dyes;
(f) complex metals ions such as multivalent tungsten and chromium (products of metallurgical-type industry);
(g) organic cyanides (products of metallurgical-type industry);
(h) nitrogen-containing organic matter from human and industrial wastes.

Present raw sewage treatment systems are capable of removing substantial portions of the suspended matter and other solids, but cannot remove a large percentage of the soluble contaminants, removal of ABS and phosphates being especially poor. In fact, present soluble contaminant removal processes result in the formation of soluble nitrates which, together with phosphates, stimulate destructive algae growths in bodies of water which receive the treated effluents.

The object of this invention is to provide a new, efficient, economical raw sewage treating process for removing from the sewage a large percentage of the suspended matter and soluble compounds present therein, without the formation of deleterious nitrates.

A further object of the invention is to provide a sewage filtering process wherein a consistently high rate of flow of sewage through the filter bed is maintained without the need for backwashing of the filter medium to remove filtered solids therefrom.

It has now been discovered that suspended matter and other solids and soluble organic compounds may be removed from raw sewage by contacting the raw sewage with coal. The coal acts as a filter for the suspended matter and other undissolved solids and it acts as an adsorbent for the soluble pollutants.

Further objects and advantages will be had from the following description of the process.

Raw sewage can be brought into direct contact with coal by any of the known solid-liquid contacting expedients suitable for filtration and adsorption.

One particular advantageous contacting step as shown in FIG. 1 involves the percolation of a stream of raw sewage **1** through a bed of particulate coal **1**–*a* in which suspended matter and other undissolved solids are filtered out of the liquid, and dissolved pollutants are adsorbed by the coal. Alternatively, some particulate coal can be admixed into raw sewage in mixer **4**, the coal and sewage supplied to the mixer by hopper **5**, and conduit **6**, respectively. The mixture can then be passed to the coal bed **1**–*a* via conduit **7**. In any case, clear effluent passes from the bed by way of conduit **8**.

A plural stage contacting system as shown in FIG. 2 is also advantageous for the purposes of this invention. Raw sewage from a sewage supply line **9** passes through conduit **1** first to a bed of coal **1**–*a* which has previously exhausted its adsorptive capacity, the bed thereby functioning only as a filter medium. The thus treated sewage is then passed through conduit **1**–*b* or **1**–*c* to a fresh bed of coal **2**–*a* or **3**–*a*, respectively, which acts as an adsorbent for dissolved compounds. When the latter bed **2**–*a* or **3**–*a* has exhausted its adsorptive capacity it can be converted to the preliminary treatment filter bed by suitable piping **2** or **3**, respectively, and valving (not shown), in which case another bed of fresh coal can be established as new adsorbent in that bed which was inoperative during the immediately preceding operation. Conduits **3**–*c* and **3**–*b* enable bed **3**–*a* to be connected to beds **1**–*a* and **2**–*a*, respectively. Conduits **2**–*b* and **2**–*c* enabled bed **2**–*a* to be connected to beds **3**–*a* and **1**–*a*, respectively. Under this arrangement a continuous process is assured wherein two of the three beds function together during treatment and the third bed is loaded with fresh coal to function as the adsorbent in the next cycle.

A consistently high rate of flow can be maintained through a filter bed or filter-adsorption bed without a need for backwashing the filter medium to remove filtered-out sewage solids that obstruct flow. This is accomplished by the continuous withdrawal, as by scraping, pumping or otherwise, of the surface layer of the bed containing the filtered-out sewage solids and coals coated with the same, thereby continually reforming a surface layer of uncoated coal particles. As shown in FIG. 3, motor driven blades **10** may be used to scrape the surface layer of bed **1**–*a*, the resulting scraped portions being removed through conduit **11** from the area between the bed **1**–*a* and raw sewage **12**. Fresh coal particles can then be added to the bed through conduit **13** to compensate for undesirable reductions in coal bed height, or the drive shaft **14** for blades **10** may be longitudinally movable to compensate for such bed thickness variations. The filter bed surface need not be circular shaped since other geometrical shapes are appropriate. Furthermore, the scraper blade need not be restricted to the rotary type, since a reciprocating blade that moves back and forth across the bed surface would function adequately for the purposes of the invention.

Regular commercial coals such as sub-bituminous, low volatile bituminous, medium volatile bituminous and high volatile bituminous are effective for the purposes of this invention. Anthracite and lignite are inefficient for raw sewage treatment.

Particulate coals with particle sizes of −20 to +250 mesh are effective for the purposes of this invention. Coal particles outside this range may also be used, but at a reduced operational efficiency.

Process variables depend upon such matters as (1) the particular coal utilized, (2) coal particle size, (3) the particular raw sewage being treated, (4) the required product quality and (5) the particular contact expedient being employed. Room temperature and atmospheric pressure are adequate for the purposes of the invention. Further, there is no need for temperature control in the process except to prevent freezing. A bed thickness from 2 inches to 25 feet or more may be used in the process. For example, a 6-inch bed will provide effective filtration but minimal adsorption. A 12-inch or more bed is generally required for effective adsorption. As to flow rates, filtration and adsorption may be accomplished with flow rates up to 400 gallons per square foot of bed per hour. A simple pressure developed by a head of 1 to 10 feet of liquid above the coal bed will achieve desirable flow rates.

Consumption of new coal in the process is a function of the quantity of sewage being treated and the degree of product purification desired, rather than of apparatus configuration or of using the option of admixing a portion of the coal into the raw sewage stream as described above. In the case of waters which are only slightly contaminated, or where the flow rate may be low, consumption of new coal may be as low as one ton or less per million gallons of raw sewage. Where high levels of contamination are encountered or where high flow rates must be accommodated, quantities of as high as ten tons or more per million gallons of sewage may be required.

The process is capable of removing 90–100% of the suspended matter and other undissolved solids from raw sewage, and producing a clear effluent in which BOD has been diminished 60–90%, COD has been diminished 60–90%, phosphates have been diminished 60–100% and ABS has been diminished 80–95%. The following examples indicate the effectiveness of the process:

Example 1

A filter bed was prepared of high volatile-A bituminous coal, crushed and sized to −60 to +100 mesh, and loaded into a 48-inch diameter filter bed to an effective height of 18 inches. Raw municipal sewage, having had no pretreatment except comminution to reduce the size of large solids, was passed through this filter at a flow rate of 21.6 gallons per square foot per hour. Additional coal of the same size and rank was admixed into the filter feed at a rate of one pound per 4700 gallons. The filter surface including admixed coal, a portion of the filter bed, and accumulated sewage solids was continuously removed at the rate of ⅙ inch per hour, for a total coal consumption of 2 tons per million gallons. The effluent was clear, with the following measured reductions in impurity content between the raw sewage and final effluent:

	Percent
COD	72
BOD	68
Suspended matter and other undissolved solids	93.2

Example 2

A filter bed was prepared and operated as in Example 1, except that no coal was admixed into the raw sewage.

The clear filtrate was then passed through a bed of high volatile bituminous-C coal eleven feet deep, at a rate of 30 gallons per square foot per hour. The following reductions in impurity content were observed between the raw sewage and the final effluent:

	Percent
COD	80
BOD	88
ABS	84
Suspended matter and other undissolved solids	95
Phosphorus	73

Example 3

A quantity of odorous and highly colored meat-packing plant waste was passed at a rate of approximately 15 gallons per square foot per hour through an 18-inch bed of high volatile bituminous-A coal in a size range of −10 to +20 mesh. The filtrate was clear, odorless and contained a reduction of 89% COD from an original value of 2280 p.p.m.

Spent removed coal, after being dried, may be immediately burned to generate useful power and dispose of the contaminants. Thus the many tedious time-consuming and expensive steps of digestion, elutriation, chemical conditioning, and vacuum filtration associated with existing sewage treatment processes may be eliminated.

Except for the purpose of protecting the system from damage by exceptionally large or uncommon types of solid matter such as rocks, logs, large pieces of cloth, or other materials of this type which it may be desired either to remove by the use of screens or gratings, or to reduce in size by grinding or shredding, no pretreatment of the sewage is required prior to its introduction into the filtration-adsorption bed. The conventional steps of removing grit (sand, cinders, silt) and primary sedimentation to remove a portion of suspended organic matter are thus avoided. Undesirable nitrate formation, which results from conventional treatment, is also avoided.

Thus, the process of the present invention creates a new coal market, provides a new, efficient, economical treatment for raw sewage, thereby affording cleaner water supplies, and provides for economical and more effective disposal of the pollutants.

While the particular process herein described is well adapted to carry out the objects of the pesent invention, it is to be understood that various modifications and changes may be made all coming within the scope of the following claims.

What is claimed is:

1. A method for treating raw sewage containing insoluble phosphates, suspended matter, other undissolved solids, and soluble compounds comprising
   (a) filtering said sewage through a compact mass of particulate coal, said coal selected from the group consisting of sub-bituminous, low volatile bituminous, medium volatile bituminous and high volatile bituminous to filter out said insoluble phosphates, suspended matter and other undissolved solids, whereby solid sewage materials and soluble compounds coat the coal at the surface layer of the mass through which the sewage initially enters said mass;
   (b) removing said surface layer of the mass which contains filtered-out sewage solids, and leaving in place the portion of the mass beneath the surface layer as said filtered-out sewage solids accumulate and inhibit flow of liquid into and through the mass, thereby continuously maintaining a surface layer of coal substantially uncoated with sewage solids; and
   (c) removing clear effluent from the coal mass.

2. The method of claim 1 wherein said soluble compounds include COD-producing material.

3. The method of claim 1 wherein the particle size of the coal is −20 to +250 mesh.

4. The method of claim **1** wherein said soluble compounds include BOD-producing material.

5. The method of claim **1** further comprising burning said removed coal to dispose of adsorbed contaminants and filtered-out solids.

6. The method of claim **1** wherein said soluble compounds are selected from the group consisting of ABS, LAS, soluble phosphates, dyes, complex metal ions, organic cyanides, and nitrogen-containing organic wastes.

7. The method of claim **1** wherein particulate coal selected from the group consisting of sub-bituminous, low volatile bituminous, medium volatile bituminous and high volatile bituminous is added to said raw sewage prior to contacting said sewage with said contact mass.

8. The method of claim **1** wherein said surface layer is removed by backwashing.

9. The method of claim **8** wherein said soluble compounds are selected from the group consisting of ABS, LAS, soluble phosphates, dyes, complex metal ions, organic cyanides, and nitrogen-containing organic wastes.

10. A method for treating raw sewage containing insoluble phosphates, suspended matter, other undissolved solids, and soluble compounds comprising passing said raw sewage rapidly through a first bed of particulate coal to filter out said insoluble phosphates, suspended matter and other undissolved solids on the surface layer of said bed, whereby coal particles in said layer become coated with sewage solids, removing a first filter effluent, passing the first filter effluent through a second bed of particulate coal to adsorb said soluble compounds on the coal and removing a clear first adsorbent effluent, continuing the passage of first filter effluent through said second bed until the adsorption capacity of said second bed is depleted, then passing raw sewage rapidly through the second bed whereby said second bed acts only as a filter bed, and removing second filter effluent, passing said second filter effluent through a fresh bed of particulate coal to adsorb said soluble compounds and removing second adsorbent effluent from said fresh bed; said coal in said first and second beds being selected from the group consisting of sub-bituminous, low volatile bituminous, medium volatile bituminous and high volatile bituminous.

11. The method of claim **10** wherein said soluble compounds include COD-producing material.

12. The method of claim **10** wherein said soluble compounds include BOD-producing material.

13. The method of claim **10** wherein raw sewage is continuously treated by utilizing each depleted adsorbent bed as a new filter bed, and establishing another fresh coal bed as a new adsorbent bed for effluent from each new filter bed.

14. The method of claim **13** wherein three beds of coal are incorporated in the continuous operation, and while two of the three beds are functioning as a filter bed and an adsorption bed respectively, a fresh bed of coal is substituted for a former filter bed in the remaining bed to await utilization as an adsorption bed in the next cycle of operation.

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