

through the angular distance necessary to effect a complete stop and cut-off operation. As soon as the cut-off stroke is completed the latch 54 will be withdrawn from the notch 49 and the disc 36 and shaft 28 will be immediately picked up by the clutch and the stock feeding movement resumed.

It will be understood that by varying the sizes of the feed rolls 21 and 27, rings of different diameter may be formed. The circumference of the rolls 21 and 27 should be substantially the same as the length of the ribbon making up a single ring. The position of the cut-off mechanism can be adjusted by moving the frame 72 and the cam 78 along the shaft 76. Likewise the position of the bending pins 61 and 65 can be adjusted by the micrometer screws in order to accommodate rings of a considerable range of sizes.

As is seen in Figures 3 and 5 the guide member 57^a is mounted in cylindrical bushings 85 which are carried in brackets 86 on the supporting frame 87. The guide 57^a may be given a rotary movement by adjusting the set screws 88 and 89 and its vertical position may be adjusted by the set screws 90 and 91. These adjustments are provided so that the guide 57^a can be positioned to receive the ribbon from different sizes of feed rolls and also so that it can be adjusted to properly deliver the ribbon to the guide roll 58 and the bending pins 61 and 63.

As is seen in Figure 7 the guide roll 58 is mounted on a vertical shaft 92 which fits within a sleeve 93. The vertical position of the sleeve 93 and the shaft 92 can be regulated by the screws 94 and 95, screw 94 having threaded engagement with the frame and screw 95 being adapted to abut against the frame.

In the operation of my improved ring forming machine it is merely necessary to place a reel of ribbon on the arm 3 and feed the ribbon up over the guide rolls 9 and 14 and between the feed rolls 21 and 27. Preferably the ribbon is formed slightly thinner on one edge than on the other and the reel is so arranged that the thin edge of the ribbon is toward the front as is seen in Figure 1. The surface of the feed rolls 21 and 27 may be contoured to fit this tapered section ribbon and the top roll 27 is provided with a flange 27' (Fig. 2) to prevent the ribbon from running off the rolls. The desired frictional engagement is obtained between the ribbon and the rolls by the action of the adjustable weight 20 on the lever arm 15. As both the top and bottom feed rolls 21 and 27 are driven the maximum driving effort can be produced with a minimum pressure on the ribbon and in this way the ribbon can be fed without distorting its cross-sectional dimensions. After it leaves the feed rolls the ribbon passes through the guide 57^a. In starting the machine in operation the end of the ribbon is bent by hand around the guide roll 58, past the primary bending pin 61 and between the secondary bending pin 65 and the inner end of the groove 63' in the bar 63. After this initial manual bending the motor 46 may be started and the ribbon will be fed by the feed rolls and bent by the pins 61 and 65 into a ring of accurate diameter. As soon as a complete ring has been formed the feed rolls will stop and the cut-off knives will act to sever the ring. The feed rolls will then again start and feed through the machine a length of ribbon sufficient to form one complete ring. When this has been done the machine will again stop and

the cut-off operation will be repeated. This cycle will be continued until the roll of ribbon is exhausted or the driving motor is stopped.

By forming the ribbon slightly thinner on the inside edge than on the outside edge the resulting ring will be of uniform thickness across its entire width. This is due to the thickening of the metal on the inside of the neutral axis of the ring due to the compression which takes place during the forming operation and the reduction in thickness at the outside due to the tensile force exerted thereon. By supplying a properly shaped ribbon the finished rings will be of substantially uniform thickness and, due to my improved forming method, each ring will be of uniform diameter within very close limits regardless of variations in the characteristics of the ribbon, etc.

Although I have described in considerable detail the illustrated embodiment of a machine for carrying out my improved method it will be understood by those skilled in the art that many variations and modifications may be made in the specific apparatus illustrated and described. Other types of devices might be provided for bending and cutting off the ribbon in accordance with my improved method. I do not therefore wish to be limited to the specific form herein described and illustrated but claim as my invention all embodiments thereof coming within the scope of the appended claims.

I claim:

1. The method of forming a ring from a metal wire or the like which includes the steps of moving the ribbon in the direction of its length, imposing a primary bending force on the moving ribbon whereby the moving ribbon will be bent to form a ring, imposing a second bending force on said moving ribbon opposite to said primary force whereby the ribbon will assume a ring form of diameter different from that of the primary bend.

2. The method of forming a ring of wire or the like which includes the steps of moving the wire in the direction of its length, bending the moving wire to form a ring, and then while continuing said bending of the moving wire, re-bending the moving wire to form a ring of different diameter, said re-bending taking place before a complete ring is formed.

3. The method of forming a ring of wire or the like which includes the steps of moving the wire in the direction of its length, bending the moving wire to form a ring, and then, while continuing said bending of the moving wire, re-bending the moving wire to form a ring of different diameter, said re-bending being in a direction opposite to the first bending.

4. The method of forming a metal ribbon or the like into ring form which includes the steps of first bending the ribbon to form a ring of one diameter and then re-bending the ribbon to form a ring of another diameter, said re-bending being effected on one part of the ribbon while the first bending is being effected on another part of the ribbon and before a complete ring has been formed by said first bending.

5. The method of forming rings of metal ribbon, wire or the like which includes the steps of moving the ribbon in the direction of its length, bending the moving ribbon to form a ring of a predetermined diameter, and re-bending the moving ribbon, at a point adjacent said first bending while continuing said first bending, to

UNITED STATES PATENT OFFICE

2,111,575

REFINING OF NONFERROUS METALS

James R. Stack, New Dorp, Staten Island, N. Y.,
assignor to Nassau Smelting & Refining Com-
pany, Incorporated, New York, N. Y., a corpo-
ration of New York

Application July 18, 1936, Serial No. 91,298

14 Claims. (Cl. 204—57)

This invention relates to the refining of non-ferrous metals and more particularly to the refining of copper bearing materials.

Considerable quantities of scrap materials containing substantial amounts of copper and lesser amounts of tin, lead, zinc, iron and other metals are obtained from discarded materials, such as used telephone and other electrical equipment, machine shop turnings, refinery and foundry scraps and materials from various other sources. Efforts have been made heretofore to refine these low grade materials to obtain the constituent metals therefrom in usable forms.

In one process which has been used heretofore, the impure material is charged into a blast furnace and smelted to remove the major portion of the iron. The metal obtained from the blast furnace is transferred to a converter and substantially all of the lead, zinc and tin are removed by blowing with air. In some instances copper matte or leady copper matte is added to the converter charge to assist in the removal of lead and tin. The resulting fumes are collected in a bag house in the form of a dust or fume and the latter material is treated to separate the metals or compounds contained therein. The remaining metal is transferred to a reverberatory furnace and is further refined by blowing and poling, after which it is cast into anodes which are electrolytically refined in a standard sulphuric acid electrolyte. The principal objections to this process are that the metal must be carried through a number of refining steps in order to obtain pure copper and the bag house dust or fume containing the lead, tin and zinc is difficult to treat to recover the constituent metals.

In another process which has been practiced previously, the scrap material is treated in a blast furnace to eliminate the iron and the resultant molten metal is charged into a converter where substantially all of the zinc only is removed by blowing with air. The metal from the converter is cast into anodes and is electrolyzed for the production of copper in a sulphuric acid electrolyte of relatively low concentration. During the electrolysis most of the metals other than copper, such as lead and tin, are converted into insoluble compounds, and some of these compounds adhere to the anodes, some remain suspended in the electrolyte and the balance fall to the bottom of the electrolytic cell in the form of anode slimes. Any dissolved antimony is rendered insoluble as any oxychloride by the presence of chlorine ions, previously added to the solution, or by other known means. The

anode slimes produced are treated to recover the metallic values therein. Among the objections to this process are the high cost of the electrolytic refining due to the abnormally high cell voltage necessitated by the low conductivity of the electrolyte and the large amount of slimes produced. Furthermore, it is very difficult to treat these slimes to separate and recover the various metals contained therein. These slimes also interfere with the operation of the cell and in addition carry considerable quantities of copper down with them.

Among the objects of the present invention are the provision of an effective and economical method of refining low grade copper bearing materials to obtain the principal constituents thereof in usable forms and the provision of electrolytic processes for separation of metals such as copper, lead and tin without the production of large amounts of slimes.

A further object of the invention is to provide new and improved electrolytes for use in the aforesaid electrolytic refining processes.

In accordance with one embodiment of the invention, the material to be refined is smelted in a blast furnace in the usual manner to remove the iron therefrom and the metal obtained from the blast furnace is transferred to a converter where substantially all of the zinc, but as little lead and tin as possible, is removed by blowing with air. The zinc fumes from the blast furnace and the converter are conveyed to a bag house and collected in the form of dust. The blown converter metal is cast into anodes which are electrolyzed for the production of pure copper cathodes in an electrolyte in which lead, tin and copper are all soluble. Since both lead and tin are more electropositive than copper, they will not be deposited upon the cathode but will be dissolved and remain in the electrolyte. When the quantity of lead and tin in the electrolyte has built up to the point where the copper will not be deposited in a sufficiently pure state, a portion of the electrolyte is removed, the copper content thereof is partially depleted by electrolysis with an insoluble anode, the remainder of the copper is thrown out of solution by replacement, and the lead and tin are subsequently recovered, preferably by electrolysis.

The above described and other objects and features of the invention will be more apparent from the following detailed description thereof taken in conjunction with the accompanying drawing in which is outlined a flow sheet of a process embodying the invention.

shaft from rotation, and means operated by said drive shaft for moving said latch pin out of locking position to permit rotation of said roll shaft and roll.

- 5 30. In apparatus for forming rings from metallic ribbon or the like, means for feeding the ribbon in the direction of its length, primary bending means interposed in the path of the ribbon and adapted to deflect the ribbon sufficiently to

cause it to take a permanent set and be bent into ring form, and secondary ribbon bending means interposed in the path of the ribbon as it leaves said primary bending means, said secondary bending means being adapted to re-bend said ribbon into a ring of different diameter than that 5 formed by said primary bending means.

DEAN M. SOLENBERGER.

the copper from the anodes during the electrolysis but, since they are both electropositive to copper and are not near copper in the electromotive series of metals, they will not deposit at the cathodes at the initial concentration of the electrolyte. Consequently, the lead and tin will remain in solution in the electrolyte while the copper is deposited in a pure state on the cathodes. It will be evident that in this process, more copper will deposit at the cathodes than will be dissolved from the anodes and in order to maintain the concentration of the bath at the desired value, this deficiency is made up by dissolving copper in the electrolyte externally of the electrolytic cell. This is preferably accomplished by circulating a portion of the electrolyte through oxidizer tanks containing particles of copper and by blowing air through the electrolyte in these tanks to render the copper more soluble, although the copper may be added in other ways.

During the electrolysis just described, a small amount of slimes will be produced which contain antimony and precious metals originally present in the anode, together with some copper and small amounts of lead, tin and other elements. These slimes are collected and treated for the removal of copper and the recovery of the precious metals contained therein.

In view of the fact that neither the lead nor the tin is deposited at the cathode, these metals will gradually increase in concentration in the electrolyte and will eventually render the electrolyte ineffective for the deposition of pure copper. Consequently, a portion of the solution is removed from time to time and the lead and tin present therein are removed. This portion of the electrolyte will, of course, contain copper in solution and the copper is removed therefrom in order to obtain the lead and tin unmixed with copper. This is preferably accomplished by first electrolyzing the solution, using an insoluble anode of a type well-known in the art, until a substantial portion of the copper is deposited out. The solution is then removed to a separate container where the remainder of the copper is removed by cementation, by means of lead, tin, or a mixture thereof preferably in slab form. Upon the addition of the replacement metal, the copper precipitates out, and the electrolyte is separated from the free copper by decantation or in any other convenient manner.

The copper free electrolyte, which consists essentially of a solution of lead and tin, may then be electrolyzed and, since lead and tin are close together in the electromotive series, these metals will deposit simultaneously as a lead-tin alloy at the cathode. If the tin content of the resulting alloy is sufficiently high, the alloy may be used directly as a solder and in this case the cathodes are melted and cast into solder bars. If it is desired to produce an alloy containing a higher quantity of tin or to obtain pure tin, some or all of the lead may be removed before electrolysis by precipitating it out by means of a suitable reagent, such as sulphuric acid, added in a quantity just sufficient to react with the quantity of lead which it is desired to remove.

In the electrolysis involving the deposition of a lead-tin alloy, or of the tin alone, an anode consisting of a lead electrode surrounded by a porous diaphragm cell is preferably employed. An anode of this type is used to prevent dissolving of the anode, which would alter the composition of the deposit, and to prevent oxidation of the tin to the stannic form which will not deposit readily. A

current density of from 10 to 25 amperes per square foot may be employed in this step of the process and the bath is preferably heated to a temperature of 100 to 150° F. by any suitable means.

It is not essential that the lead and tin be removed from the copper-free electrolyte by electrodeposition, and they may, if desired, be separated by purely chemical methods. For example, the lead may be precipitated as a sulphate and after removal of the resulting precipitate the tin may be removed as an insoluble stannate. The products obtained may be used or disposed of in their precipitated forms, or may be further treated to obtain other useful compounds or the metals lead and tin therefrom.

After the lead and tin have been removed from the solution, either by electrolysis or by chemical means, the latter is transferred to an evaporator and concentrated to a point where any salts of such metals as zinc, iron and nickel contained therein will crystalize out. These crystals are removed from the concentrated solution by any suitable filtering apparatus and the concentrated solution is employed to make up fresh electrolyte. If desired, some or all of the solution may be re-used after the removal of the lead and tin without having the compounds of zinc, iron, nickel and similar metals removed.

The various steps of the preferred process may be readily followed by means of the flow sheet outlined in the accompanying drawing. The principal steps of the process have been described hereinabove and a few auxiliary, and more or less conventional, steps are indicated on the flow sheet. These latter are of such a nature as are well understood in the art, and a detailed description thereof is unnecessary for a complete understanding of the invention.

The aromatic sulphonic acids are preferably used in the electrolyte in carrying out the electrolytic steps in the refining process embodying the invention for several reasons. In the first place, they dissolve not only the copper but also the lead and tin. In addition, they have a high conductivity, they are relatively non-volatile, and are not appreciably decomposed electrolytically. They, therefore, permit the electrolytic deposition of pure copper without the precipitation of substantial quantities of the lead and tin as slimes. Their high conductivity lowers the power consumption and their stability makes them economical to use because they may be recovered and reused.

Among the aromatic sulphonic acids which may be employed are the mono and poly sulphonic acids of phenol, benzol (benzene), toluol (toluene), the cresols, the xylenes, the xylenols, naphthalene, the naphthols, anthracene, phenanthrene, and related compounds. The related chloro and nitro sulphonic acids of aromatic hydrocarbons may, likewise, be used. In addition, satisfactory results may be obtained by using other acids which dissolve copper, lead and tin, such, for example, as hydrofluosilicic and fluoroboric acids and the sulphonic acids of aliphatic compounds like methane, ethane, propane, etc. Mixtures of these acids may, of course, be used if desired, and it is within the purview of the invention to employ any acid which forms soluble salts of copper, lead and tin and which has sufficient conductivity to render it an effective electrolyte.

Since the acids mentioned above dissolve copper, lead and tin, it is obvious that the invention

may be practised to refine copper bearing metals that include either one or both of lead and tin. For example, scrap brasses may contain no tin, while bronzes may be free from lead. These materials may be carried through the refining steps described in the same manner that is employed for materials containing both lead and tin, the only difference being that the products obtained would not include lead or tin, as the case may be.

From the foregoing description, it is apparent that the invention provides simple, effective and economical processes for refining non-ferrous metals. It also provides new and improved electrolytes and electrolytic processes for the separation of metals, including copper, lead and tin. Various modifications and changes may, of course, be made to adapt the invention to varying conditions. Hence, the invention is not limited to the specific embodiments described herein, but embraces all modifications and equivalents falling within the scope of the annexed claims.

What is claimed is:

1. The method of refining metallic materials containing principally copper and small amounts of lead and tin which comprises making such material into an anode and electrolyzing the same in an electrolyte consisting of the mono and poly sulphonic acids of benzene, phenol and cresol and the related chloro and nitro sulphonic acids to dissolve the copper, lead and tin anodically while maintaining the copper concentration of the electrolyte substantially constant and sufficiently high so that only copper deposits at the cathode while the lead and tin build up in the electrolyte and subsequently recovering the lead and tin from the electrolyte.

2. The method of refining metallic materials containing principally copper and small amounts of lead and tin which comprises making such material into an anode and electrolyzing the same in an electrolyte consisting of copper and an acid of the group consisting of the mono and poly sulphonic acids of benzene, phenol and cresol and the related chloro and nitro sulphonic acids to dissolve the copper, lead and tin anodically while maintaining the copper concentration of the electrolyte substantially constant and sufficiently high so that only copper deposits at the cathode while the lead and tin build up in the electrolyte, removing a portion of the electrolyte when a substantial amount of lead and tin has accumulated therein and recovering the lead and tin from said portion.

3. The method of refining metallic materials containing principally copper and small amounts of lead and tin which comprises making such material into an anode and electrolyzing the same in an electrolyte consisting of copper and an acid of the group consisting of the mono and poly sulphonic acids of benzene, phenol and cresol and the related chloro and nitro sulphonic acids to dissolve the copper, lead and tin anodically while maintaining the copper concentration of the electrolyte substantially constant and sufficiently high so that only copper deposits at the cathode while the lead and tin build up in the electrolyte, removing a portion of the electrolyte when a substantial amount of lead and tin has accumulated therein, removing the copper from said portion and electrolyzing said portion to deposit the lead and tin therefrom as an alloy.

4. The method of refining metallic materials containing principally copper and small amounts

of lead and tin which comprises making such material into an anode and electrolyzing the same in an electrolyte consisting of copper and an acid of the group consisting of the mono and poly sulphonic acids of benzene, phenol and cresol and the related chloro and nitro sulphonic acids to dissolve the copper, lead and tin anodically while maintaining the copper concentration of the electrolyte substantially constant and sufficiently high so that only copper deposits at the cathode while the lead and tin build up in the electrolyte, withdrawing a portion of the electrolyte when a substantial amount of lead and tin has accumulated therein, removing the copper from said portion, chemically precipitating the lead from said portion and electrolyzing the remaining solution to deposit the tin therefrom electrolytically.

5. The method of refining metallic materials containing principally copper and small amounts of lead and tin which comprises making such material into an anode and electrolyzing the same in an electrolyte consisting of copper and an acid of the group consisting of the mono and poly sulphonic acids of benzene, phenol and cresol and the related chloro and nitro sulphonic acids to dissolve the copper, lead and tin anodically while maintaining the copper concentration of the electrolyte substantially constant and sufficiently high so that only copper deposits at the cathode while the lead and tin build up in the electrolyte, withdrawing a portion of the electrolyte when a substantial amount of lead and tin has accumulated therein, removing the copper from said portion, chemically precipitating the tin from said portion and electrolyzing the remaining solution to deposit the lead therefrom electrolytically.

6. The method of refining metallic materials containing principally copper and small amounts of lead and tin which comprises making such material into an anode and electrolyzing the same in an electrolyte consisting of copper and an acid of the group consisting of the mono and poly sulphonic acids of benzene, phenol and cresol and the related chloro and nitro sulphonic acids to dissolve the copper, lead and tin anodically while maintaining the copper concentration of the electrolyte substantially constant and sufficiently high so that only copper deposits at the cathode while the lead and tin build up in the electrolyte, withdrawing a portion of the electrolyte when a substantial amount of lead and tin has accumulated therein, removing the copper from said portion by successive electrolysis and cementation steps and recovering the lead and tin from the resulting solution.

7. The method of refining metallic materials consisting essentially of copper with small amounts of iron, zinc, lead and tin which comprises smelting the materials and blowing the smelted material with air to separate the iron and zinc and to leave a metal consisting essentially of copper with small amounts of lead and tin, making the latter metal into an anode and electrolyzing the same in an electrolyte consisting of copper and an acid of the group consisting of benzene sulphonic acid, phenol sulphonic acid, cresol sulphonic acid and the corresponding chloro and nitro sulphonic acids to dissolve the copper, lead and tin anodically while maintaining the copper concentration of the electrolyte substantially constant and sufficiently high so that only copper deposits at the cathode while the lead and tin build up in the electrolyte and subsequently recovering the lead and tin from the electrolyte.

8. The method of refining metallic materials containing principally copper and small amounts of lead and tin which comprises making such material into an anode and electrolyzing the same in an electrolyte consisting of about 20%, an acid of the group consisting of the mono and poly sulphonic acids of benzene, phenol and cresol and the related chloro and nitro sulphonic acids and about 3% of copper as a salt of said acid to dissolve the copper, lead and tin anodically while maintaining the copper concentration of the electrolyte substantially constant and sufficiently high so that only copper deposits at the cathode while the lead and tin build up in the electrolyte and subsequently recovering the lead and tin from the electrolyte.

9. The method of refining metallic materials containing principally copper and small amounts of lead and tin which comprises making such material into an anode and electrolyzing the same in an electrolyte consisting of copper and a sulphonic acid of benzene to dissolve the copper, lead and tin anodically while maintaining the copper concentration of the electrolyte substantially constant and sufficiently high so that only copper deposits at the cathode while the lead and tin build up in the electrolyte and subsequently recovering the lead and tin from the electrolyte.

10. The method of refining metallic materials containing principally copper and small amounts of lead and tin which comprises making such material into an anode and electrolyzing the same in an electrolyte consisting of copper and a sulphonic acid of phenol to dissolve the copper, lead and tin anodically while maintaining the copper concentration of the electrolyte substantially constant and sufficiently high so that only copper deposits at the cathode while the lead and tin build up in the electrolyte and subsequently recovering the lead and tin from the electrolyte.

11. The method of refining metallic materials containing principally copper and small amounts of lead and tin which comprises making such material into an anode and electrolyzing the same in an electrolyte consisting of copper and a sulphonic acid of cresol to dissolve the copper, lead and tin anodically while maintaining the copper

concentration of the electrolyte substantially constant and sufficiently high so that only copper deposits at the cathode while the lead and tin build up in the electrolyte and subsequently recovering the lead and tin from the electrolyte.

12. The method of refining metallic materials containing principally copper and small amounts of lead and tin which comprises making such material into an anode and electrolyzing the same in an electrolyte consisting of about 20% of a sulphonic acid of benzene and about 3% of copper as a salt of said acid to dissolve the copper, lead and tin anodically while maintaining the copper concentration of the electrolyte substantially constant and sufficiently high so that only copper deposits at the cathode while the lead and tin build up in the electrolyte and subsequently recovering the lead and tin from the electrolyte.

13. The method of refining metallic materials containing principally copper and small amounts of lead and tin which comprises making such material into an anode and electrolyzing the same in an electrolyte consisting of about 20% of a sulphonic acid of phenol and about 3% of copper as a salt of said acid to dissolve the copper, lead and tin anodically while maintaining the copper concentration of the electrolyte substantially constant and sufficiently high so that only copper deposits at the cathode while the lead and tin build up in the electrolyte and subsequently recovering the lead and tin from the electrolyte.

14. The method of refining metallic materials containing principally copper and small amounts of lead and tin which comprises making such material into an anode and electrolyzing the same in an electrolyte consisting of about 20% of a sulphonic acid of cresol and about 3% of copper as a salt of said acid to dissolve the copper, lead and tin anodically while maintaining the copper concentration of the electrolyte substantially constant and sufficiently high so that only copper deposits at the cathode while the lead and tin build up in the electrolyte and subsequently recovering the lead and tin from the electrolyte.

JAMES R. STACK.