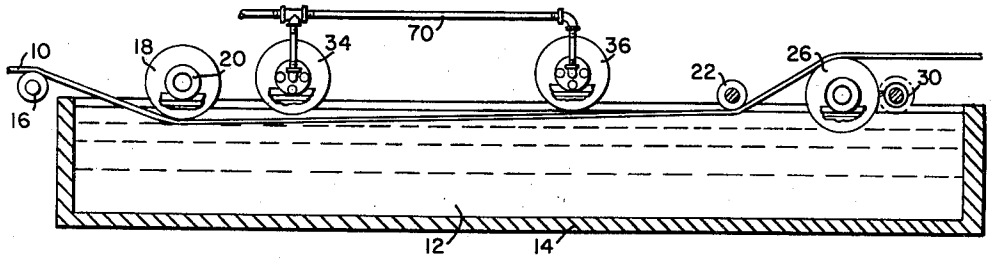
Dec. 2, 1958 E. C. McHENRY 2,862,839

APPARATUS FOR AND METHOD OF REMOVING OXIDES FROM STRIP

Filed Dec. 5, 1956

Fig.1



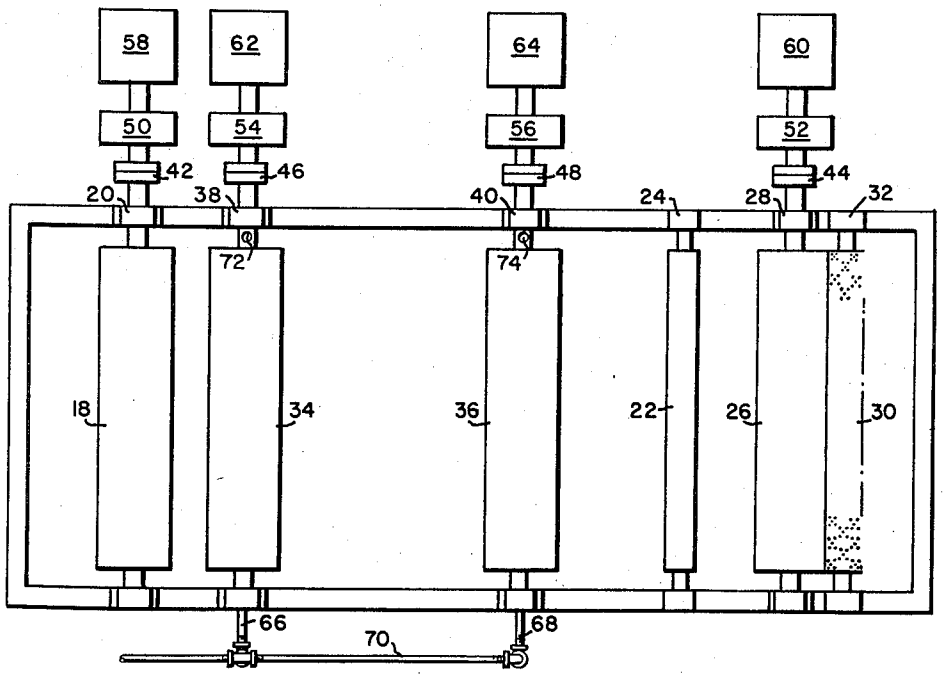


Fig.2

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APPARATUS FOR AND METHOD OF REMOVING OXIDES FROM STRIP

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7 Claims. (Cl. 134—15)

This invention relates to apparatus for, and the method of, removing oxides from the surface of strip material formed from refractory metals.

In producing strip material of refractory metal of the class of titanium, titanium base alloys, zirconium and zirconium base alloys, it is necessary in processing the metal into strip of commercial quality to remove oxides, scale and the like therefrom. Attempts have been made in the past to effectively remove the oxides from such metal strip by continuously passing the strip through a heated alkali metal caustic bath formed of molten salts such as the commercially available Virgo or Kolene salts and thereafter pickling the treated strip. While such procedure has been effective in the production of stainless steel strip, it has not proven to be successful in the cleaning of metal strip formed of refractory metal of the class of titanium, titanium base alloys, zirconium and zirconium base alloys. Where such process is utilized in attempting to clean the strip of refractory metal, it is found that the metal immersion rolls which are utilized to maintain the strip immersed in the molten alkali metal caustic bath accumulate metal oxides which have been removed from the strip by the bath with the result that such metal oxides are picked up on the strip from such rolls and are carried thereby into a pickling tank which is usually positioned adjacent the caustic bath tank. It has been impossible heretofore to remove such oxides from the strip in the sulfuric and nitric hydrofluoric acids normally employed as pickling solutions with the result that imperfect strip material is obtained and a high rate of rejection is encountered.

An object of this invention is to provide apparatus for facilitating the removal of oxides from the surface of strip formed from refractory metal of the class of titanium, titanium base alloys, zirconium and zirconium base alloys.

Another object of this invention is to provide apparatus in conjunction with a molten alkali caustic metal bath for maintaining a strip of refractory metal immersed therein and effect a reaction between the caustic of the bath and the oxides and to effect the removal of the metal of such oxides from the caustic bath without detrimentally affecting the strip.

A further object of this invention is to provide for passing a strip of refractory metal through a molten alkali metal caustic bath to effect a reaction between the caustic of the bath and the oxides on the surface of the strip to remove oxides therefrom and to rotate and continuously cool an idler roll in the bath out of contact with the strip to attract the oxides so removed from the strip and thereby free the bath of such oxides without detrimentally affecting the strip.

Other objects of this invention will become apparent from the following description when taken in conjunction with the accompanying drawing in which:

Figure 1 is a view in side elevation and partly in section of apparatus embodying features of this invention, and

Fig. 2 is a top plan view of a portion of the apparatus illustrated in Fig. 1.

Referring to the drawing, and in particular to Fig. 1 thereof, this invention is illustrated by reference to the immersion of a strip **10** of refractory metal of the class of titanium, titanium base alloys, zirconium and zirconium base alloys in a heated alkali metal caustic bath **12** usually having a sodium base and which is in a molten state, the caustic bath being contained in an iron-base tank **14**. Associated with the tank **14** at the entrance end thereof is a roll **16** of asbestos or the like over which the strip **10** passes to enter the metal caustic bath **12**, the roll **16** being supported in any suitable manner. As illustrated, a roll **18** formed of an iron-base metal and commonly termed an immersion roll is disposed adjacent the entrance end of the tank **14** with at least a portion of the roll **18** immersed in the caustic bath for holding the strip **10** immersed in the bath. The roll **18** may be of any suitable type and is preferably mounted with the ends of its shaft in suitable bearings (not shown) assembled in bearing housings **20** which are carried on the upper edges of the opposite sides of the tank **14**.

In this embodiment a small hold-down roll **22** is disposed in spaced relation with respect to the immersion roll **18** being suitably mounted with the ends of its shaft in suitable bearings (not shown) mounted in bearing housings **24** on the tank **14** so as to effectively engage the strip **10** and maintain it immersed in the caustic bath for the distance between the roll **18** and a point closely adjacent the hold-down roll **22**. Adjacent the exit end of the tank **14** there is disposed a wiper roll **26** formed of an iron-base metal which is also suitably mounted with the ends of its shaft in suitable bearings (not shown) mounted in bearing housings **28** carried on the upper edges of the opposite sides of the tank **14** for effecting a wiping of the strip **10** as it emerges from the caustic bath **12**. In order to insure that the wiping roll **26** is clean, a cleaning brush **30** is disposed adjacent the wiping roll **26** and in contact therewith for effectively removing any accumulation of dirt or the like from the wiping roll **26**; the cleaning roll **30** is of the same length as the wiper roll **26** and is suitably mounted with the ends of its shaft disposed in suitable housings **32** carried on the upper edges of the tank **14**.

In accordance with this invention a pair of idler rolls **34** and **36** formed of an iron-base metal are disposed in spaced relation to one another between the immersion roll **18** and the hold-down roll **22**, with at least the lower edges of the rolls **34** and **36** immersed in the caustic bath **12** contained in the tank **14** but out of contact with the strip **10** which passes therebelow. The rolls **34** and **36** are suitably supported in operative relation by having the ends of their shafts mounted in suitable bearings (not shown) supported in bearing housings **38** and **40**, respectively, carried on the upper edges of the opposite sides of the tank **14**. As illustrated in Fig. 2, each of the rolls **18**, **26**, **34** and **36** is connected as through suitable couplings **42**, **44**, **46** and **48**, respectively, and gear reducers **50**, **52**, **54** and **56**, respectively, to be driven by independent motors **58**, **60**, **62** and **64**, respectively, the rolls **34** and **36** being usually driven at a slower rate of speed than the rolls **18** and **26** as will be explained more fully hereinafter. For purposes of clarity in showing the relative positioning of the different rolls, the strip **10** has been omitted from the showing made in Fig. 2.

In accordance with this invention one end of the shaft of each of the rolls **34** and **36** is suitably drilled and connected as by conduit **66** and **68**, respectively, to a pipeline **70** for permitting the continuous admission of a suitable coolant to the interior of the rolls **34** and **36** throughout the operation of the apparatus. The op-

posite end of the shaft of each of the rolls **34** and **36** is also suitably drilled so as to provide an opening **72** and **74**, respectively, which is connected to the interior of the associated roll for effecting the circulation of the air through each of the rolls **34** and **36**.

In practice the alkali metal caustic bath may be any of the well known commercial salt baths which usually have a sodium base and are preferably heated and maintained at a temperature in the neighborhood of 875° F. to 975° F. so that the salt bath is in a molten state and will readily react with the oxides normally contained on the surface of the strip **10** as the strip is admitted to the tank **14** beneath the roll **18**. While many variations in the composition of the alkali metal caustic bath are possible, a typical example of a suitable caustic bath is that of the commercially known Virgo salt having about 88.55% sodium hydroxide, about 7.66% sodium nitrate, 1.72% sodium chloride and 0.53% sodium carbonate with traces of manganese dioxide present. The Kolene salts formed of alkali metal hydroxides, nitrates and chlorides as described in Patent 2,458,661 are also effective for reacting with the oxides normally contained on the surface of the strip **10**.

In utilizing the apparatus and practicing the process of this invention the strip **10** is admitted to the metal caustic bath **12** and passed beneath the immersion roll **18** and the hold-down roll **22** and emerges from the bath thereafter to pass over the wiper roll **26** and from thence to a pickling tank (not shown) containing a suitable pickling solution. As will be appreciated, with the temperature of the caustic bath **12** at from 875° F. to 975° F., the rolls **18** and **26** which are rotated with a portion thereof immersed in the bath **12** soon attain substantially the temperature of the bath **12**. These rolls are driven at a rate dependent upon the speed at which the strip **10** is passed through the bath **12** in the tank **14**. Usually such rolls are driven at a speed in the neighborhood of 10 revolutions per minute.

In accordance with this invention a coolant such as air is supplied through the pipe **70** from a source (not shown) to provide a continuous supply of cool air to the interior of the idler rolls **34** and **36** to effect a substantial lowering of the temperture of such rolls below the temperature of the immersion roll **18** and the wiper roll **26** and the temperature of the bath **12** in which the lower edges of the rolls **34** and **36** are immersed. The rolls **34** and **36** are preferably driven at a speed somewhat lower than the speed of the rolls **18** and **26** so as to permit adequate cooling of the surface of the rolls **34** and **36** as they are exposed to the atmosphere to thereby continuously present cooled surfaces for immersion in the bath **12**. In practice the rolls **34** and **36** are rotated at a speed in the neighborhood of 2 to 3 revolutions per minute and the temperature of such rolls is preferably maintained at below 650° F. In actual practice it is found that the roll **36** will be maintained at a substantially cooler temperature than the roll **34**, as a smaller portion thereof, as illustrated in Fig. 1, is maintained immersed in the caustic bath **12**. Usually the roll **36** will be found to have a temperature from 50 to 75° cooler than the temperature of the roll **34** which in practice is preferably maintained at a temperature of not over 625° F.

As the strip **10** enters the bath **12**, the molten alkali metal caustic bath reacts with the oxides contained on the strip **10** and certain of the oxides go into solution in the bath. Prior to this invention since the rolls **18** and **26**, while being at substantially the temperature of the bath **12**, are in effect cooler than the bath **12**, they preferentially attracted the oxides in the bath with the result that a buildup of such metal and oxides accumulated on the surface of such rolls and was picked up by the strip **10** during its contact with such rolls. Such deposits on the rolls **18** and **26** when picked up therefrom by the strip **10**, caused the damage to the strip, it being found substantially impossible to remove such picked up metals

and oxides from the strip in the pickling tank (not shown). It is to be noted that when analyzed the material accumulated or picked up by the cooled rolls where the strip being treated is a titanium base alloy comprised of from 55 to 75% titanium dioxide and the balance caustic compounds.

With the rolls **34** and **36** being disposed as described hereinbefore and cooled to a temperature substantially lower than the temperature of the rolls **18** and **26**, the oxides dissolved in the bath **12** from the strip **10** are no longer attracted to the warmer rolls **18** and **26**, but instead are preferentially attracted by the cooler surfaces of the slowly rotating idler rolls **34** and **36** with the result that the pickup of such oxides from the bath **12** is substantially isolated to the idler rolls **34** and **36** which, while partially immersed in the bath, are out of contact with the strip **10**. Thus since the oxides are removed from the bath **12** and deposited on the idler rolls **34** and **36**, the rolls **18** and **26** are substantially free therefrom with the result that such oxides are no longer deposited on the rolls **18** and **26** and rolled into the strip **10** as the strip is contacted thereby and rejections by reason of such pickups on the strip **10** are minimized.

By providing for the preferential accumulation of the oxides on the rolls **34** and **36** it is no longer necessary to shut down the line to clean the submersion roll **18** or the wiper roll **26**, as the idler rolls **34** and **36** can be readily removed from the assembly and replaced before any detrimental amounts of the oxides are deposited on the rolls **18** and **26** as the strip **10** passes through the bath. Prior to the development of the apparatus and method of this invention, in utilizing the standard equipment without the idler rolls **34** and **36**, it was the general practice to have to change the immersion roll **18**, hold-down roll **22** and wiper roll **26** one to three times in a 24-hour period of operation. The apparatus and method of this invention, however, has so improved operating conditions that only the idler rolls **34** and **36** must now be changed and this only at approximately every 3 to 5 days as opposed to the shorter intervals of the previous practice. With the idler rolls **34** and **36** present there is no necessity to change or clean the submersion, hold-down and wiper rolls, and as a matter of practice such rolls are only changed at very infrequent intervals of from two to three months. In addition to effecting economies through eliminating the frequent shutdowns of the apparatus, the apparatus and method of this invention have made it possible to overcome the disadvantages of the previous practice and to produce good clean strip material.

I claim:

1. In apparatus for removing oxides from strip material formed from refractory metal selected from the class of titanium, titanium base alloys, zirconium and zirconium base alloys, the combination of, a tank adapted to contain a molten alkali metal caustic bath for reacting with the oxides on the strip, an immersion roll at least partially below the top of the tank and adapted to be at least partially immersed in said bath and in contact with the strip for holding the strip immersed therein, an idler roll partially below the top of the tank and adapted to be at least partially immersed in said bath out of contact with the strip, means for effecting rotation of the idler roll, and means for cooling the rotating idler roll to a temperature substantially less than the temperature of the immersion roll, the cooled idler roll cooperating in said bath to preferentially attract and receive metal oxides removed from the strip in said bath to thereby maintain the immersion roll substantially free from said metal oxides.

2. In apparatus for removing oxides from strip material formed from refractory metal selected from the class of titanium, titanium base alloys, zirconium and zirconium base alloys, the combination of, a tank adapted to contain a molten alkali metal caustic bath for reacting with the oxides on the strip, an immersion roll

at least partially below the top of the tank and adapted to be at least partially immersed in said bath and in contact with the strip for holding the strip immersed therein, a pair of idler rolls disposed in spaced relation to each other and partially below the top of the tank and adapted to be at least partially immersed in said bath out of contact with the strip, means for effecting rotation of the idler rolls, and means for cooling each of the rotating idler rolls to a temperature substantially less than the temperature of the immersion roll, the cooled rotating idler rolls cooperating in said bath to preferentially attract and receive metal oxides removed from the strip in said bath to thereby maintain the immersion roll substantially free from said metal oxides.

3. In apparatus for removing oxides from strip material formed from refractory metal selected from the class of titanium, titanium base alloys, zirconium and zirconium base alloys, the combination of, a tank adapted to contain a molten alkali metal caustic bath for reacting with the oxides on the strip, a rotatable immersion roll at least partially below the top of the tank and adapted to be at least partially immersed in said bath and in contact with the strip for holding the strip immersed therein, means for effecting the rotation of the immersion roll, a rotatable idler roll partially below the top of the tank and adapted to be at least partially immersed in said bath out of contact with the strip, means for cooling the idler roll to a temperature substantially less than the temperature of the immersion roll, means for effecting the rotation of the idler roll at a speed substantially slower than the speed of the immersion roll but fast enough to present a cooled surface to the caustic bath, the cooled surface of the idler roll cooperating in said bath to preferentially attract and receive metal oxides removed from the strip in said bath to thereby maintain the immersion roll substantially free from said metal oxides.

4. In apparatus for removing oxides from strip material formed from refractory metal selected from the class of titanium, titanium base alloys, zirconium and zirconium base alloys, the combination of, a tank adapted to contain a molten alkali metal caustic bath for reacting with the oxides on the strip, a rotatable immersion roll at least partially below the top of the tank and adapted to be at least partially immersed in said bath for contacting and holding the strip immersed therein, means for effecting the rotation of the immersion roll, a pair of rotatable idler rolls disposed in spaced relation to each other and partially below the top of the tank and adapted to be at least partially immersed in said bath out of contact with the strip, means for cooling the idler rolls to a temperature substantially less than the temperature of the immersion roll, means for effecting the rotation of the idler rolls at a speed substantially slower than the speed of the immersion roll but fast enough to present cooled surfaces thereof for immersion in the caustic bath, the cooled surfaces of the idler rolls cooperating in said bath to preferentially attract and receive metal oxides removed from the strip in said bath to thereby maintain the immersion roll substantially free from said metal oxides.

5. In the method of removing oxides from strip material formed from refractory metal selected from the class of titanium, titanium base alloys, zirconium and zirconium base alloys, the steps comprising, passing the strip having oxides thereon into a molten alkali metal caustic bath, passing the strip beneath and in contact with at least one rotatable immersion roll partially immersed in the bath to maintain the strip in the bath and effect a reaction between the caustic and oxide on the strip and remove oxides therefrom, maintaining a rotatable idler roll partially immersed in the caustic bath but out of contact with the strip, rotating the idler roll, and cooling the rotating idler roll to maintain the rotating idler roll at a temperature substantially less than the temperature of the immersion roll whereby oxides removed from the strip in the caustic will preferentially be deposited on the cooled rotating idler roll to maintain the immersion roll substantially free from such oxides.

6. In the method of removing oxides from strip material formed from refractory metal selected from the class of titanium, titanium base alloys, zirconium and zirconium base alloys, the steps comprising, passing the strip having oxides thereon into a molten alkali metal caustic bath beneath at least one rotatable immersion roll at least partially immersed in the bath and in contact with the strip, the molten caustic bath reacting with oxides on the strip to remove oxides therefrom, rotating an idler roll at least partially immersed in the caustic bath but out of contact with the strip, and cooling the rotating idler roll to a temperature substantially less than the temperature of the immersion roll whereby the rotating idler roll continuously presents a cooled surface to the caustic bath, the continuously presented cooled surface functioning to preferentially attract the oxides removed from the strip in the caustic bath and maintain the immersion roll substantially free therefrom.

7. In the method of removing oxides from strip material formed from refractory metal selected from the class of titanium, titanium base alloys, zirconium and zirconium base alloys, the steps comprising, passing the strip having oxides thereon into a molten alkali metal caustic bath having a temperature of from 875° F. to 975° F., maintaining the strip immersed in the caustic bath by means of a rotating immersion roll in contact therewith, the immersion roll having a temperature developed therein closely approximating the temperature of the bath, the molten caustic bath reacting with oxides on the strip to remove metal in the form of oxides therefrom and form a compound insoluble in the bath, rotating an idler roll at least partially immersed in the caustic bath but out of contact with the strip, and cooling the rotating idler roll to a temperature of less than 650° F. to continuously present a cooled surface to the caustic bath, the cooled surface of the idler roll functioning to preferentially attract the insoluble compounds to maintain the immersion roll substantially free therefrom.

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