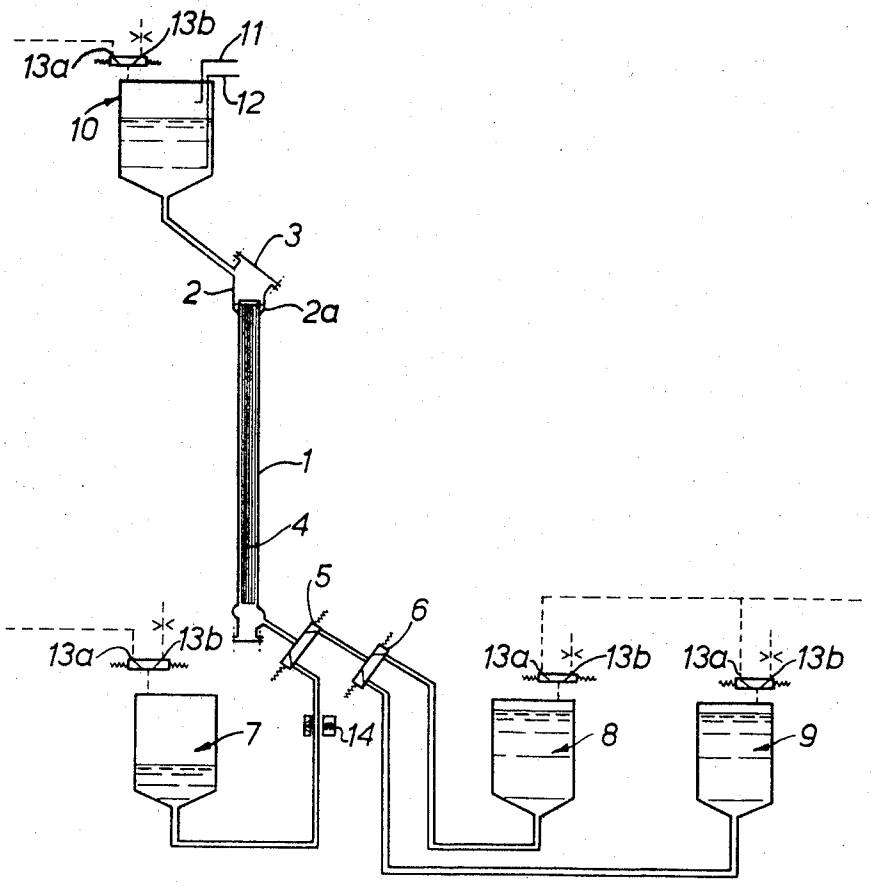
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PICKLING APPARATUS

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PICKLING APPARATUS

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ABSTRACT OF THE DISCLOSURE

Apparatus for the pickling of metallic objects comprising an elongate pickling vessel and means for causing oscillatory turbulent flow of treatment liquid to and fro along the pickling vessel and over the metallic objects contained therein while maintaining the pickling vessel full of treatment liquid.

This invention relates to apparatus for performing pickling processes in which metallic objects are treated with an etchant liquid usually an acid, so that the outer surface layer is removed by chemical action, to leave a clean cocntamination free surface.

The efficiency of any pickling process can be related to several factors, the most important of which are the etching of material from the surface being pickled at a uniform rate over the whole surface, involving good heat transfer and gas dispersion at the surface being treated, together with efficient mixing of the etchant liquid. In addition the speed with which the etching process can be stopped, once the desired amount of material has been removed from the object being pickled, is also important. Together these factors under ideal conditions give very precise control over the whole pickling operation such that the desired amount of material is removed and at the same time pitting and contamination of the cleaned surface is avoided.

In conventional types of pickling apparatus a series of horizontally disposed baths are normally employed. The metallic objects to be pickled are totally immersed in one of these baths containing etchant liquid, the latter being agitated, by propellers or pump circulators for example, to ensure adequate mixing while rotation or oscillation of the objects being pickled may also be provided. When sufficient material has been removed from the objects undergoing pickling, the etching action is stopped by the rapid transfer, using mechanical means, of the objects to another bath containing liquid capable of rapidly stopping the etching action. Further washing of the pickled objects can be provided by transfer to other baths. Other types of pickling apparatus include the Di-phase pickling tank in which etchant and stop solutions occupy the same tank as two separate phases, separated by an interphase. Provision is made for mixing within each phase and for the passage of the objects being pickled directly from the etchant phase to the stop phase. Further washing of the pickled objects can be provided by transfer to other tanks. Collectively however known pickling plants possess disadvantages which allow only inadequate control over the pickling operation because of the slow transfer between the etchant and stop sections, and inadequate mixing of the etchant liquid. In addition they often require elaborate safety schemes to protect operating personnel from toxic and splash hazards and also employ complex mechanical linkages which are liable to corrosion by the etchant liquid.

It is an object of this invention to provide apparatus suitable for the efficient pickling of metallic objects which will obviate the disadvantages of known pickling plants.

According to the present invention apparatus for the pickling of metallic objects comprises an elongate pickling vessel, a number of storage tanks for containing treatment liquids, means for filling the pickling vessel with liquid from any one of said storage tanks and means for causing oscillatory turbulent flow of liquid to and fro along the length of the pickling vessel, while maintaining the pickling vessel full of liquid.

In a preferred arrangement the pickling vessel is in the form of a vertically arranged tube, means being provided for connecting any one of the storage tanks with the lower end of the pickling vessel, a surge tank being connected with the upper end of the pickling vessel and means being provided to force liquid from a storage tank to fill the pickling vessel and to cause turbulent oscillatory flow of liquid upwards and downwards in the pickling vessel by cycling of liquid from the storage tank through the pickling vessel into the surge tank and then back from the surge tank through the pickling vessel into the storage tank.

Fuel for water cooled nuclear reactors may comprise clusters of nuclear fuel elements; each element consisting of a stack of uranium dioxide fuel pellets enclosed in a sheath of zirconium or zirconium alloy. It has been established that under operative conditions in a water-cooled nuclear reactor, the work hardened and contaminated surface layer formed on fuel element cans of zirconium or zirconium alloy during fuel element manufacture, is considerably less resistant to corrosion by high temperature water and steam than the base metal. It is therefore necessary for this layer to be removed before the fuel element clusters are loaded into the nuclear reactor.

A pickling apparatus embodying the invention and capable of processing clusters of nuclear fuel elements canned in zirconium or zirconium alloy will now be described with reference to the accompanying drawing showing a schematic arrangement of the apparatus in side elevation.

The apparatus consists of a vertical 8 inch bore cylindrical pickling vessel **1** constructed of polypropylene reinforced with fibre-glass, apart from an upper load bearing section **2** of stainless steel lined with polypropylene and equipped with a polypropylene support ring **2***a* and a removable lid **3** also lined with polypropylene for loading and unloading the pickling vessel **1** with a nuclear fuel element cluster **4**. Each fuel element cluster typically consists of 36 fuel elements each 13 feet in length, attached at their upper ends to a circular perforated stainless steel plate, equipped with a lifting eye, and spaced apart at their lower ends by a perforated polypropylene grid. Support for the nuclear fuel element cluster being provided by the location of the stainless steel perforated plate on the prolypropylene support ring **2***a* in the upper load bearing section **2** of the pickling vessel **1**, the support ring **2***a* being provided with channels permitting liquid flow to and from the pickling vessel **1**. The lower end of the pickling vessel **1** is connected by linked piston operated valves **5** and **6** and polypropylene piping to three mild steel polypropylene lined storage tanks **7**, **8** and **9** containing respectively etchant acid, demineralised water for washing the fuel element cluster **4** after etching to stop the etchant action, and a detergent composition in demineralised water used to degrease the fuel element cluster **4** before the pickling process commences. The upper load bearing section **2** of the pickling vessel **1** connects to a mild steel polypropylene lined surge tank **10** equipped with "high" **11** and "low" **12** liquid level detectors. The linking of the valves **5** and **6** ensures that only one storage tank **7**, **8** or **9** can be on line with the pickling vessel **1** and the surge tank **10** at any one time. Solenoid operated gas valves **13***a* and **13***b* respectively control the supply and exhaust of compressed air or

other suitable gas such as nitrogen to and from the storage tanks **7**, **8** and **9** and the surge tank **10**. A gas/liquid interface detector **14** is positioned on the line leading from the valve **5** to the etchant liquid storage tank **7**. The plant is arranged so that all the storage tanks are at a lower level than the pickling vessel ensuring that the latter is self draining, and that treatment liquids are not in contact with valves **5** and **6** unless the plant is operational. Only one valve **5** is exposed to attack by the etchant acid and that only for the duration of the etching cycle.

In operation the admission of compressed air or other suitable gas such as nitrogen through the appropriate gas supply value **13***a* to the upper part of any one of the storage tanks **7**, **8** or **9** above the liquid/gas interface in the tank causes liquid to be forced out of the tank to fill the pickling vessel **1**. The liquid overflows from the pickling vessel **1** into the surge tank **10** has its gas valve **13***b* open to exhaust. When the liquid overflowing into the surge tank **10** reaches the level of the high liquid level detector **11** it causes the storage tank gas supply valve **13***a* to shut and its gas exhaust valve **13***b* to open while the surge tank **10** gas exhaust valve **13***b* closes and the gas supply valve **13***a* opens to admit compressed air or other suitable gas such as nitrogen into the upper part of the surge tank **10** above the liquid/gas interface in the surge tank **10**. This causes the liquid in the surge tank **10** to be forced back down the pickling vessel **1**. When the liquid in the surge tank **10** reaches the level of the "low" liquid level detector **12** it actuates the reversal of the gas valves **13***a* and **13***b* of both the storage tank and the surge tank such that the valve **13***a* in the storage tank again admits compressed air or other suitable gas such as nitrogen into the storage tank and the valve **13***b* in the surge tank **10** is again connected to exhaust. Thus liquid is again forced upwards through the pickling vessel **1**. Repetition of this cycle causes an oscillatory turbulent flow of liquid upwards and downwards in the pickling vessel **1** over a fuel element cluster **4** which is contained therein. The duration of oscillation of the liquid in the pickling vessel **1** can be pre-set by automatic equipment or can be manually controlled.

A typical sequence of treatment cycles employed in the pickling of zirconium or zirconium alloy canned fuel element clusters will now be given:

	Duration, mins.
(1) Detergent wash (alkaline decreasing in demineralised water at 50° C.)	5–10
(2) Demineralised water wash—cold	at least 5
(3) Demineralised water wash—cold	at least 5
(4) Etchant liquid wash (2% of azeotrope hydrofluoric acid and 20% concentrated nitric acid in demineralised water at 30° C.)	2–10
(5) Stop—demineralised water wash—cold	2–5
(6) Demineralised water—cold	at least 5
(7) Demineralised water—cold	at least 5

The operation of all these cycles is controlled remotely by press buttons except in the case of the etching and stop-demineralised water wash cycles, when the pressing of a single button cycles etchant liquid for a pre-set time, at the end of which the liquid is discharged from the pickling vessel **1** into the storage tank **7** past the liquid/gas interface detector **14** which senses the completion of the discharge of etchant liquid from the pickling vessel and then rapidly actuates valves to cycle the stop-demineralised water wash for a pre-set time.

The pickling apparatus described minimises handling damage to the objects being pickled and lends itself to the employment of a variety of combinations of etching, stop and wash cycles, of variable duration and in addition during the etching cycle the oscillatory turbulent flow provides good mixing, heat transfer and gas dispersion resulting in an almost uniform surface removal rate. These factors coupled with a very rapid transfer from etching to stop cycles, and the absence of any toxic and splash hazards for the operating personnel combine to provide an efficient pickling apparatus.

I claim:

1. Apparatus for the pickling of metallic objects comprising an elongate pickling vessel for receiving said objects, a number of storage tanks for containing treatment liquids, means for filling the pickling vessel with liquid from any one of said storage tanks and means for causing oscillatory turbulent flow of liquid to and fro along the length of the pickling vessel, while maintaining said pickling vessel full of liquid.

2. Apparatus for the pickling of metallic objects as claimed in claim **1** wherein the pickling vessel is in the form of a vertically orientated tube, provided with means for connecting any one of the storage tanks while the lower end of the pickling vessel, and a surge tank connected to the upper end of the pickling vessel, means being provided to force liquid from any one storage tank to fill the pickling vessel and to cause oscillatory turbulent flow of liquid upwards and downwards in the pickling vessel.

3. Apparatus for the pickling of metallic objects as claimed in claim **2** wherein means are provided for the admission of gas under pressure to said storage tanks and to said surge tank above the level of liquid therein, oscillatory turbulent flow of liquid from any one of the storage tanks to and fro along the length of the pickling vessel being established by the admission of gas under pressure into the storage tank above the level of liquid therein, to drive liquid from the storage tank along the length of the pickling vessel into the surge tank, the liquid then being driven from the surge tank back along the length of the pickling vessel by the admission of gas under pressure into the surge tank above the level of liquid therein.

4. Apparatus for the pickling of metallic objects as claimed in claim **2**, wherein the storage tanks are set at a lower level than the pickling vessel wherein the pickling vessel is self-draining into the storage tanks.

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