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METHOD AND DEVICE FOR THE PREVENTION OF SELECTIVE CORROSION OF TUBES AND MACHINERY PARTS OF COPPER OR COPPER CONTAINING ALLOYS.

APPLICATION FILED JUNE 11, 1919.

1,335,210. **Patented Mar. 30, 1920.**

Fig.1

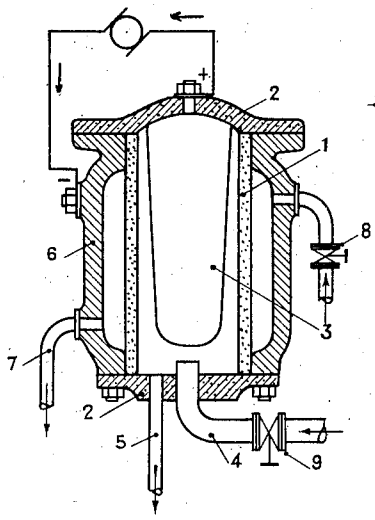


Fig.3

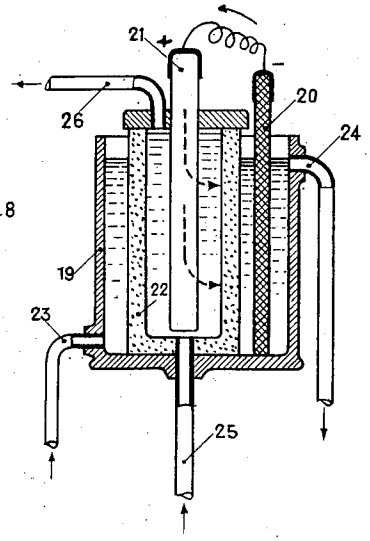
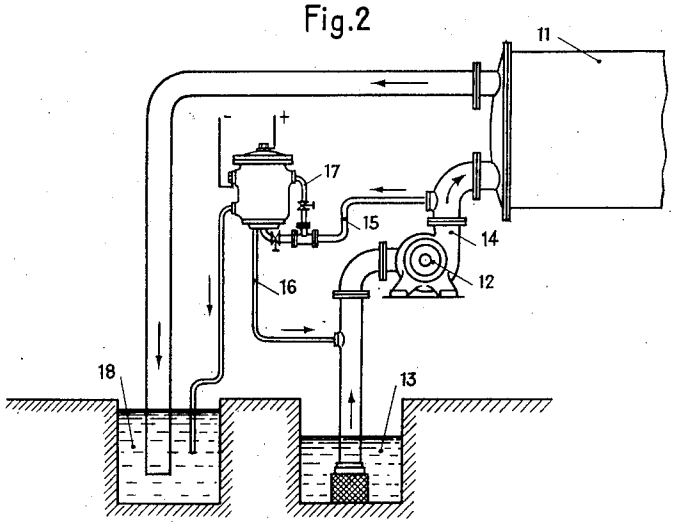


Fig.2



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UNITED STATES PATENT OFFICE.

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METHOD AND DEVICE FOR THE PREVENTION OF SELECTIVE CORROSION OF TUBES AND MACHINERY PARTS OF COPPER OR COPPER CONTAINING ALLOYS.

1,335,210. Specification of Letters Patent. Patented Mar. 30, 1920.

Application filed June 11, 1919. Serial No. 303,406.

To all whom it may concern:

Be it known that I, FRANZ VON WURSTEMBERGER, a citizen of the Republic of Switzerland, residing at Hardturmstrasse 19, Zurich, Switzerland, have invented certain new and useful Improvements in Methods and Devices for the Prevention of Selective Corrosion of Tubes and Machinery Parts of Copper or Copper Containing Alloys; and I do hereby declare the following to be a clear, full, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same, reference being had to the accompanying drawing, and to letters or figures of reference marked thereon, which form a part of this specification.

For the prevention of selective corrosion of tubes and machinery parts of copper and copper containing alloys which are in contact with water containing ions, electrolysis may be employed to produce an easily soluble hydrolytically decomposable acid reacting salt to neutralize the corrosion qualities of the water.

The invention consists of a process to produce this preventive means outside of the main water stream in a separate vessel and further contrivances for the execution of this process.

Selective corrosion or pitting is understood to be the phenomenon whereby fluids which according to their chemical composition are not considered as decomposers of metal heavily attack single areas of metallic parts which are immersed in the fluid or are in contact with it whereas other parts remain unaffected.

This phenomenon occurs on anodes of copper immersed in sodium salt solutions under the influence of electrolysis, or on aluminium anodes in chlorid solutions. In practice it is known as the cause of destruction of pump impellers and tube sets of copper and copper containing alloys, which are in contact with sea water or with water which conducts electricity, owing to the presence of any kind of salt which it contains in solution.

Careful investigations have shown that the cause of selective corrosion is entirely due to the alteration of the surface of the metallic parts in question and not to the metal not being homogeneous, and that the phenomenon is due to electrolytically different qualities which the different areas acquire under the influence of certain deposits. As such, slightly soluble salts of the metal in question come into consideration and accordingly selective corrosion does not occur in liquids which attack the metal but transform it into an easily soluble salt. The production of selective corrosion is due to the presence of different factors of a chemical and physical nature which are dependent on the nature of the metal in question as also on the salts contained in the water.

One quality which water producing selective corrosion must possess at any rate is a certain electric conductivity. It does not follow however that all water conducting electricity produces selective corrosion.

The behavior of copper and copper containing alloys in contact with water which possesses a certain electric conductivity owing to the presence of certain chemicals is briefly explained as follows:

Two different areas of a piece of metal immersed in the water are to be considered as two electrodes in short circuit through the metal itself. At first as soon as the piece of metal is immersed a difference of potential usually arises between the two areas, which difference is dependent on the nature of the layer with which the surface of the two areas are covered under the action of oxidation in the air before immersion. The layer may only accidentally be absolutely the same on both areas. Under the influences of this difference of potential one area becomes an anode the other a cathode. However this difference of potential disappears quickly as the resulting electric current, produces salts on the anode, through which the concentration of metallic ions there is increased.

The galvanic element formed by the two areas is polarized in this way. By such

local electrolysis the whole metal surface is brought in a short time to an equal potential which is higher than the potential of a bright, newly immersed piece of the same metal.

A continuous attack on any spot is only possible where constant anodic depolarization takes place. Such depolarization may occur through mechanical erosion of deposited anode products or through chemical transformation of those products into slightly soluble compounds, under chemical influence, which is equivalent to a reduction of the concentration of metal ions on this spot. The polarizing layer which is found on copper in water containing chlorid consists of protochlorid of copper CuCl and basic chlorids of various structure $Cu_x(OH)_yCl_z$.

As depolarizers have been found: hot water, which transforms CuCl by hydrolysis into protoxid of copper, further compounds of all sorts with alkaline reaction, which transform the CuCl into Cu(OH), hydrate of protoxid.

The character of the attack due to such a depolarization depends on the nature of the deposit with alkaline reaction, for instance hydroxid of magnesium deposited in solid form will produce a distinctly limited area of attack according to its slight solubility. On the contrary the easily soluble caustic soda solution NaOH will act as depolarizer as far as it can spread by diffusion.

As polarizers, *i. e.* chemicals favoring equalizing of potentials or preventing local attack we have found an addition of acid to be essential. Direct addition of acid however is not practicable because of its secondary action of destroying metals.

On the contrary, an addition of easily soluble hydrolytically decomposable salts of acid reaction as chlorid of aluminium $AlCl_3$ and protochlorid of iron $FeCl_2$ as well as chlorid of iron $FeCl_3$ were found to be good. In practice the best way to produce such a salt is by employing electrolysis.

According to the invention the electrolytic production of an easily soluble hydrolytically decomposable acid reacting salt as preventive means takes place outside of the main stream of water in a separate vessel through which a branch of the water stream flows and carries with it the preventive means to the main water stream before it comes into contact with the metal to be protected.

Contrivances according to the invention consist of electrodes through which electric direct current flows and which are arranged in a vessel in such a manner as to keep the anode and cathode products separate from each other, the former of which serving as preventive means, the latter being carried away.

For this purpose the electrodes are placed in two chambers of a vessel, the chambers being separated from each other by a semi-permeable wall and through which separate water streams are made to flow. The inlet of the chamber containing the electrode which is subjected to dissolution, is connected to the main water stream so that part of the corrosive water flows through this chamber, takes up the preventive means produced there and leads it into the main water stream.

In the chamber in which the cathode is placed, the cathode products are formed, such as hydrogen, caustic soda (NaOH) and other hydroxids. They are carried away by means of a special washing out device.

It is advantageous to use the vessel itself as cathode electrode.

If only a limited production of the preventive salt is desired the electric current may be produced by the difference of potential of two electrodes of different material, without employing an outer source of electricity. For instance a combination of an aluminium electrode with a carbon electrode immersed in sea water both connected together electrically will produce a current which attacks the aluminium electrode and produces chlorid of aluminium $AlCl_3$.

Figure 1 shows an exemplification of the invention,

Fig. 2 its application to a condensing plant.

Fig. 3 is a modification.

In the exemplification shown in Fig. 1 the anode chamber is formed by a semi-permeable clay well or diaphragm closed at the top and at the bottom by covers 2 of insulating nonporous material. A solid iron anode 3 is fastened to the upper cover. Through the pipe branch 4 which is connected to the delivery branch of the pump, salt water is admitted to the chamber; the water washes away the protochlorid of iron $FeCl_2$, which is formed at the anode and carries it through the pipe 5, which is connected with the suction branch of the pump, to the main stream of water, where on one hand it prevents the formation of basic chlorid of copper by forming basic chlorid of iron with the air contained in the water and on the other by its own hydrolytic decomposition and of that of the $FeCl_3$ it prevents the decomposition of any chlorids of light metals present in the water. The clay cell is surrounded by a cast iron casing 6 which acts as cathode.

In the space between cell and cast iron casing salt water supplied by a pipe connected to the pump delivery pipe, is made to circulate. The cathode products are discharged through the branch 7 into the discharge channel. 8 and 9 are regulation devices on the circulating water piping.

Fig. 2 shows schematically a condensing plant with water inlet and discharge pipes. Water is led to the condenser 11 from the supply inlet pipe or main duct 13 with the aid of the pump 12. By means of pipe 15 water is tapped from the delivery branch 14 of the pump 12 and through the pipe 16, which is connected to the suction pipe of the pump, it is led back to the main stream of water so that the electrolytic apparatus is in series with the main pump 12. A portion of the water is led through pipe 17, instead of pipe 15, to the cathode chamber in order to discharge the cathode products into the discharge channel 18.

Fig. 3 shows the contrivance containing electrodes of different materials. 19 is the vessel, 20 a carbon cathode, 21 an aluminium anode, 22 is the semipermeable wall, 23—24 is the pipe line for the washing out water of the cathode chamber, 25—26 are in and outlet branches for the water flowing through the chamber of the anode.

The direction of the electric current is indicated with arrows in dotted lines.

An apparatus built in accordance with the invention can be installed anywhere near the plant for which it is required, where the electric connections, the water supply and discharge pipes or ducts can be easily and satisfactorily arranged. As shown in the example the circulating water for the anode and cathode chambers can be taken from the main pump or be supplied by an auxiliary pump.

No disadvantage is connected with the action of the anode products, and furthermore the working of the device can be easily checked by examining the anode and its products.

In my copending application Serial No. 302,627, filed June 7, 1919, I have shown another form of my invention.

What I claim now as my invention is:

1. The art of preventing selective corrosion of water-contacting machinery parts of copper or copper containing alloys, comprising supplying from a chamber separated from but connected to the water inlet of such machinery a salt having, when hydrolyzed, an acid reaction.

2. The art of preventing selective corrosion of water-contacting machinery parts of copper or copper containing alloys, comprising forming in a vessel separate from but connected to the water supply of such machinery a salt having an acid reaction when hydrolyzed.

3. The art of preventing selective corrosion of water-contacting machinery parts of copper or copper containing alloys, comprising forming by electrolysis in a vessel separate from but connected to the water supply of such machinery a salt having, upon hydrolysis, an acid reaction.

4. The art of preventing selective corrosion of water-contacting machinery parts of copper or copper containing alloys, comprising forming by electrolysis between suitable electrodes in a vessel a salt capable of preventing such corrosion, said vessel being divided by an electrolytic diaphragm into anode and cathode chambers, the anode chamber of said vessel being connected to the water supply for said machinery to supply anode products thereto, and the cathode chamber discharging out of said supply.

5. The art of preventing selective corrosion of water-contacting machinery parts of copper or copper containing alloys, comprising forming by electrolysis between suitable electrodes in a vessel a salt capable of preventing such corrosion, said vessel being divided by an electrolytic diaphragm into anode and cathode chambers, the anode chamber of said vessel being connected for reception from and discharge into the water supply to said machinery, and the cathode chamber receiving water from such supply and discharging to waste.

6. The art of preventing selective corrosion of water-contacting machinery parts of copper or copper containing alloys, comprising forming by electrolysis between suitable electrodes in a vessel a salt capable of preventing such corrosion, said vessel being divided by an electrolytic diaphragm into anode and cathode chambers one contained within the other, supplying water to and discharging anode solution from the interior anode chamber to the water supply for said machinery, and supplying water to the cathode chamber and discharging cathode solution to waste.

7. The art of preventing selective corrosion of water-contacting machinery parts of copper or copper containing alloys, comprising forming by electrolysis between suitable electrodes in a vessel a salt having, upon hydrolysis, an acid reaction, said vessel being divided by an electrolytic diaphragm into anode and cathode chambers, the central anode chamber being connected by a pipe to the discharge side of a machinery water supply pump and also connected by a pipe to the suction side of such pump, and the outer cathode chamber connected by a pipe to the discharge side of such pump and the chamber arranged to discharge water.

8. The art of preventing selective corrosion of water-contacting machinery parts of copper or copper containing alloys, comprising forming between dissimilar electrodes in water a salt having upon hydrolysis an acid reaction and capable of preventing such corrosion, supplying the anode solution to the machinery water and allowing the cathode solution to waste.

9. The art of preventing selective corro-

sion of water-contacting machinery parts of copper or copper containing alloys, comprising forming in water between an insoluble cathode and a soluble metal anode, an anode solution containing a salt having an acid reaction after hydrolysis, said electrodes being metallically connected, supplying the anode solution to the machinery water and discharging the cathode solution, said electrodes being contained in diaphragm separated chambers.

In testimony that I claim the foregoing as my invention, I have signed my name.

FRANZ VON WURSTEMBERGER.