

Prevention of Corrosion in Paper Making Machines

CATHODIC POLARISATION WITH PLATINUM-TITANIUM ANODES

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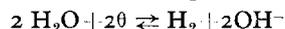
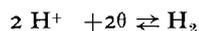
Corrosion problems can become severe in paper-making machines in which the pulp is dried over steam-heated cast-iron cylinders. Paper with a smooth bright surface will be produced provided that the cylinder remains smooth and bright, but corrosive media in the pulp attack the surface. This article describes the successful application of cathodic polarisation, using platinum-titanium anodes, to a large paper-drying cylinder to give it complete protection from corrosion

In paper-making machines the paper pulp is dried over cast iron cylinders heated with steam. One machine of this type, known as a Yankee machine, consists of only one big dryer. The cylinder may be 5 metres in diameter and 5 metres in length, and have a time of revolution of 2 to 15 seconds. Such machines are normally in continuous operation day and night. A Yankee machine produces a paper with a smooth and bright surface, provided the cylinder is smooth and bright. However, this is a great problem for a great number of paper mills, because the surface is broken down by corrosive agents in the pulp. It seems clear that Cl ions are responsible for the main part of this corrosion, and paper mills situated near the sea therefore have the most trouble. The present paper describes an equipment for cathodic polarisation now in use at some paper mills, by which the cast-iron cylinder can be completely pro-

tected against corrosion and by which other advantages can also be obtained.

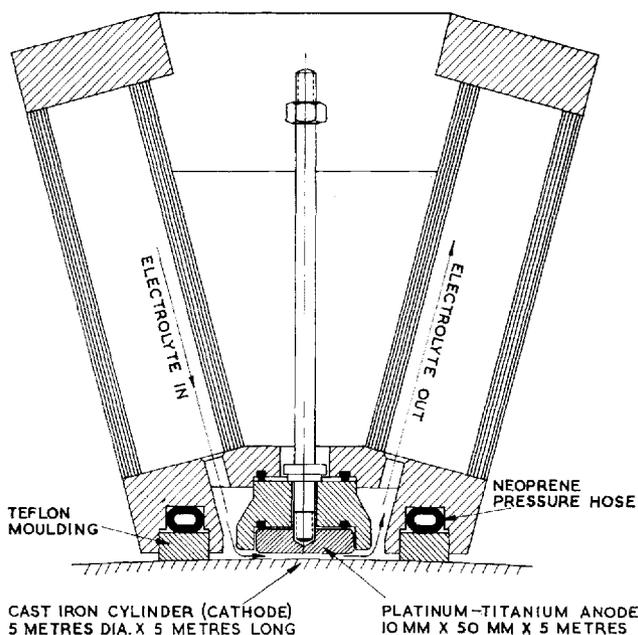
After laboratory studies had been carried out the polarisation unit shown in Fig. 1 was designed. It consists of an anode plate 2 to 5 cm wide and as long as the cylinder to be protected. It is embedded in a body of glass fibre epoxy, this being fastened by screws to a rigid beam of steel. The anode plate is made of 10 mm thick titanium to which a foil of 50 μm platinum has been spot-welded. The distance between the cylinder and the anode plate is a few tenths of a centimetre, and electrolyte is pressed through the gap. Fabric water may be used as electrolyte if the electrical conductivity is sufficient. The cylinder and the anode plate are connected to a suitable current source, giving a total current of 2 to 4 amp per square metre of cylinder surface.

When a surface element of the cylinder passes the anode plate it is cathodically polarised. The electrolytic double layer is charged and hydrogen develops according to the reactions:



After the element has passed the polarisation unit, the charge of the double layer keeps it cathodically protected for a few tenths of a second. But when the double layer has lost its charge the element is still protected against corrosion for a considerable period of time because a strong basic layer was formed on the surface during polarisation according to the chemical reactions referred to.

Fig. 1 The design of platinum-clad titanium anode adopted for the cathodic polarisation of the cast-iron cylinder of a paper-making machine



Just after polarisation this layer has a thickness of approximately one-hundredth of a centimetre and a pH of 10 to 11. It adheres to the cylinder on its rotation and, in the basic layer, a protective film of Fe_2O_3 or Fe_3O_4 is formed. The pH of the basic layer decreases because OH ions diffuse out in the paper pulp, and subsequently the protective film dissolves. The polarisation current is adjusted so that the protective layer is intact a little longer than is the time of revolution of the cylinder.

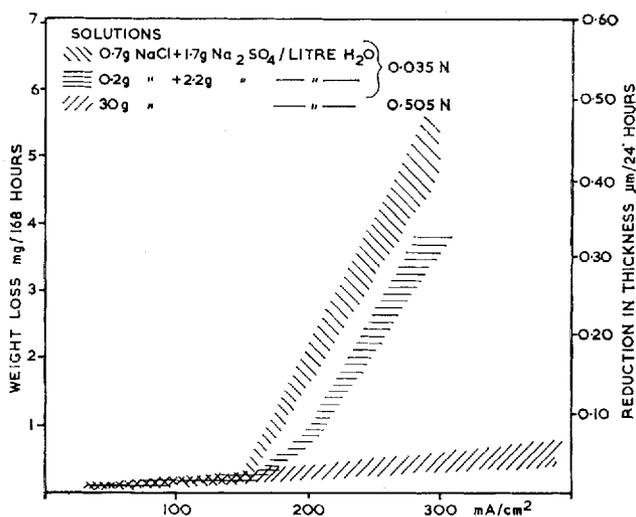
Anode Design

Generally that part of the cylinder not covered by paper is small and therefore the space which can be allowed for the anode unit is rather limited. It can be seen in Fig. 1 that the breadth of the unit is partly governed by the width of the anode plate, which consequently must be made as small as possible. This results in a high current density on the anode, generally of the order of 0.2 amp/cm^2 .

At this current density the consumption of platinum is considerable when the electrolyte contains Cl ions. The amount is also dependent on the temperature and on the concentration of the electrolyte.

From the point of view of practical anode-cylinder distance and maximum cell voltage, the electrolyte to be circulated through the polarisation unit should have an electrical conductivity of $6 \text{ to } 8.10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$. This corresponds to a solution of 2 g NaCl/l

Fig. 2 Effect of current density on platinum losses in chloride solutions. The anode consisted of rolled and recrystallised platinum with an exposed surface of 0.785 cm^2



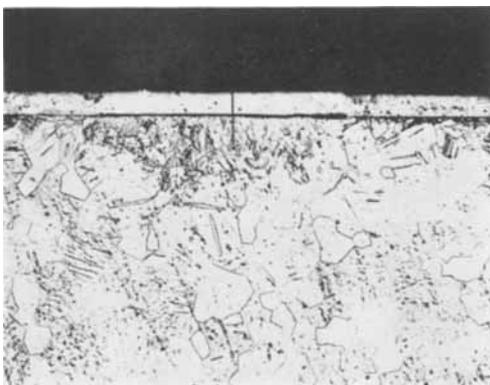


Fig. 3 A satisfactory spot welded joint between platinum and titanium ($\times 100$)

at 70°C , or generally for Ca , Na , SO_4 , Cl , NO_3 ions to a 0.035 N solution. If the paper mill is situated near the sea the fabric water contains NaCl , but generally not in the required quantity, and therefore NaCl or another inexpensive salt such as Na_2SO_4 must be added.

The platinum loss has been measured in different solutions at 70°C at different current densities and the results are shown in Fig. 2. In dilute solutions of 0.035 N containing NaCl and Na_2SO_4 , it is seen to vary between 0.05 and $0.20\ \mu\text{m}/24$ hours at $0.2\ \text{amp}/\text{cm}^2$. In stronger solutions the loss is smaller, but for many practical reasons such solutions are not desirable. No measurable platinum loss occurs when the solution is free of Cl ions, but unfortunately this is a rare situation in practice.

A platinum loss of $0.1\ \mu\text{m}/24$ hours means that the platinum thickness must be at least $30\ \mu\text{m}$ in order that the anode shall have a life of one year. Thus platinised titanium cannot be used, as the thickness of the platinum layer is generally limited to 1 to $2\ \mu\text{m}$. Instead the anodes were made by spot welding $50\ \mu\text{m}$ platinum foil to the titanium base. The distance between the spots was approximately $0.4\ \text{cm}$, and each spot had a diameter of 0.05 to $0.1\ \text{cm}$.

Titanium is known to form intermetallic compounds with most other metals, including

platinum, as can be appreciated from the platinum-titanium equilibrium diagram. Such metals are generally difficult to weld together because of cracking in the hard and brittle weld zone. However, when the welding time is kept as short as 3 to 6 msec the diffusion zone is narrow and very satisfactory spot welds can be obtained between platinum and titanium. Small cracks can be seen in the weld zones, but they cause no practical inconvenience. The anodic properties of platinum are made inferior by alloying it with titanium, and a very thin weld zone such as is shown in Fig. 3 is most desirable, since only a small amount of titanium has diffused into the platinum layer. Further study of the spot welding mechanism has been carried out, and the results will be published elsewhere.

As is well known, the "break through" voltage of titanium oxide formed in sea-water is 12 to 15 volts, and it is not much different in dilute NaCl solutions. In sulphate solutions the oxide is stable up to 90 to 100

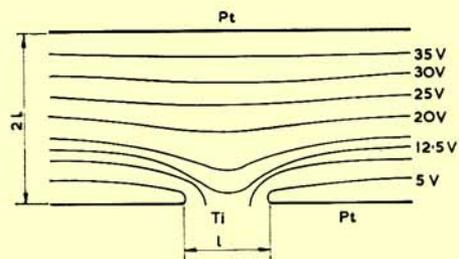


Fig. 4 Equipotentials in the anode-cathode space near a scratch in the platinum layer

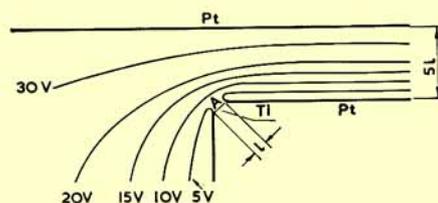


Fig. 5 Equipotentials in the anode-cathode space near a local dissolution of the platinum layer at the edge of the anode

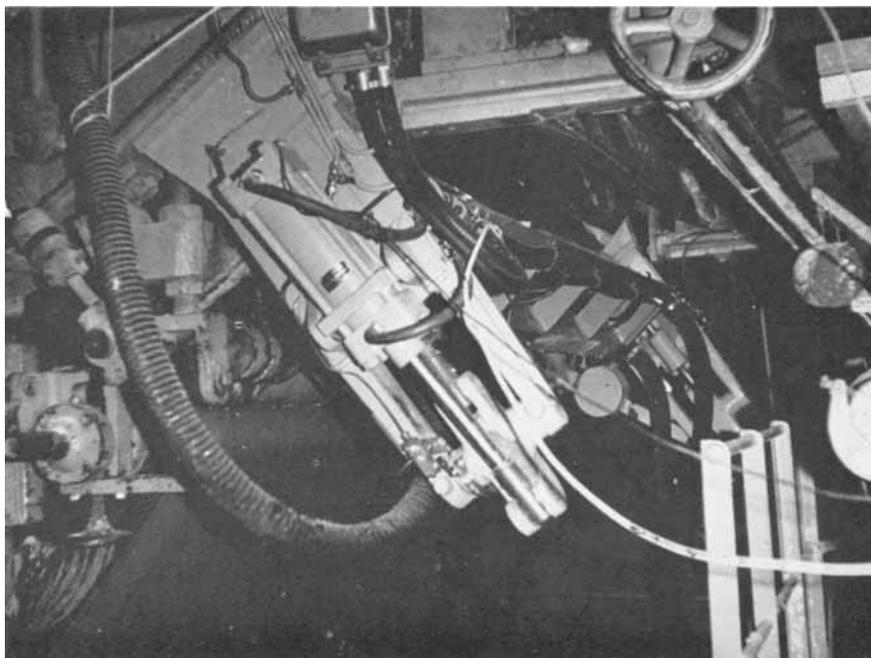


Fig. 6 The platinum-clad titanium anode structure in position on a relatively small machine making tissue paper

volts and in mixtures of sulphates and chlorides the stability can be noticeably increased compared with pure NaCl solutions. Suppose that the oxide is stable up to 15 volts. What is the effect of a scratch in the platinum foil or of an area of uncovered titanium formed, for instance, by excessive platinum dissolution? If the cell voltage does not exceed 15 volts there is no harmful effect apart from the corresponding reduction of the anode surface, as only a small current can pass through the titanium oxide. This is generally the situation when platinised titanium anodes are used for cathodic protection.

In the polarisation unit described above, a cell voltage of 40 to 50 was necessary in order to avoid excessive salt content in the electrolyte. In such circumstances the voltage across the titanium oxide layer might exceed 15 volts. A closer investigation was performed in a plane model of the anode-cathode space made of electrically conducting paper, in which the equipotentials were drawn in the

usual way. It can be seen in Fig. 4 that the titanium oxide will keep stable at a cell voltage of 40, if the flaw in the platinum layer is not wider than one-half of the anode-cathode distance. In Fig. 5, A represents a local dissolution of the platinum at one of the anode edges. It is seen to be without any harmful consequence.

The polarisation unit was originally designed for a Norwegian paper mill which for many years had had corrosion trouble. It was set into operation early in 1963 and since then it has worked successfully in that the drying cylinder is still metallically clean without any trace of rust. It has also proved to be a very effective cylinder cleaner, probably because the hydrogen development strips fibre and paper remnants off the surface. This has a favourable influence on the paper quality and on the speed of production. In Fig. 6 the anode unit is shown mounted on a machine for making tissue paper and wadding. The surface of the cylinder has remained clean and mirror-like.