On the Development of a Mercury-free Ternary Aluminium Anode for Cathodic Protection

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The development of a new mercury-free ternary aluminium anode (CIFTAL) for cathodic protection of marine structures is described. The new anode demonstrated a current efficiency of 83.5% to 85.4% in a current density range of 5.6 to 166.7 mA dm^{-2}. The current efficiency remained practically stable at 1.4 $mAcm^{-2}$ over a test period of 300 days. The service trials of the anode on steel trawlers and aluminium (Indal M 57 S) sheathed wooden boats have shown satisfactory performance in terms of uniform dissolution, current efficiency and driving voltage. In the wake of legislations restricting the use of anodes containing mercury in an endeavour to control the mercury pollution of the near shore aquatic environment, the new anode (CIFTAL) with its stable current output and high current efficiency merits significance in marine cathodic protection.

The development of galvanic anodes and the design of cathodic protection system have progressed since early 19th century when Sir Humphrey Davy made use of zinc blocks for cathodic protection of copper sheathed ship bottom of the Royal Navy. Recent emphasis on offshore petroleum production and increased activities in ocean engineering have spurred the development of less costly anodes of high electrical output for cathodic protection. In the early days, zinc and magnesium anodes have been used with varying advantages, but aluminium having high ampere-hour capacity (theoretically) is to be carefully alloyed as the free element on formation of a passive film over it, hinders the free dissolution of the metal and lowers the effective potential.

Reding & Newport (1966) have made a comprehensive study on the effect of alloying 37elements and their combination on different grades of aluminium which lead to the most promising ternary alloy containing mercury and zinc. Based on the studies of several investigators, (Hine & Weig, 1964; Lennox *et al.*,1968) on binary alloys of Al-Sn it appeared feasible that a ternary alloy of aluminium, zinc and tin might provide high current capacity and high driving voltage. The effects of operating variables on galvanic anode performance and the correlation of test parameters for laboratory and field tests using data obtained on the CB 75–74 alloy and fabrication procedure for this high purity Al-Zn-Sn alloy were discussed by Ponchel & Horst (1968). During the course of development of galvanic anodes, the suitability of Al-Zn-Hg, Al-Zn, Al-Zn-Sn and Al-Sn has been examined and it was found that Al-Zn-Hg anode holds promise for marine applications (Shenoi et al., 1972). Many attempts in ternary anodes development faced difficulties in attaining high current efficiency as a result of difficulties experienced in heat treatment, stringent requirements on purity of raw materials and precise control of minor alloy additions. In India, there were two significant achievements in ternary aluminium anodes and both these are of the Al-Zn-Hg type (Shenoi et al., 1972;Mukherjee et al., 1973). The present study reports on the development and field test data of a ternary galvanic anode free from mercury for cathodic protection of marine structures. This mercury-free anode, called CIFTAL, appears to be a new invention in India.

Materials and Methods

High purity electrical conductor grade aluminium conforming to IS: 398 (Part I)–1976, electrolytic zinc (Cominco Binani Zinc) and tin (Analar, BDH) were the metals used.

The alloying was done in a muffle type furnance which was flushed continuously with nitrogen. The experimental approach consisted in preparing several batches of binary and ternary composition and studying their electrochemical performance with reference to electrode potential and anode current efficiency in natural seawater in the laboratory for a preliminary screening. The current capacity was determined in the laboratory by determining the weight loss after removing the deposits and corrosion products by chemical cleaning. The test consisted of placing centrally a cylindrical anode to protect a sandblasted steel drum having a wetted area of 1645 cm². The current output was determined by recording the voltage drop across a resistor connected between the anode and the container. These tests were generally of short term (30–60 days) duration and the more promising ones which consisted of Al with small additions of zinc and tin were tested for longer periods in the laboratory prior to field tests. Laboratory tests were carried out with cylindrical (20 x 60 mm) and cuboid specimens (72 x 26 x 6 mm). The anode geometrics used in field studies are shown in Figs. 1 to 3.

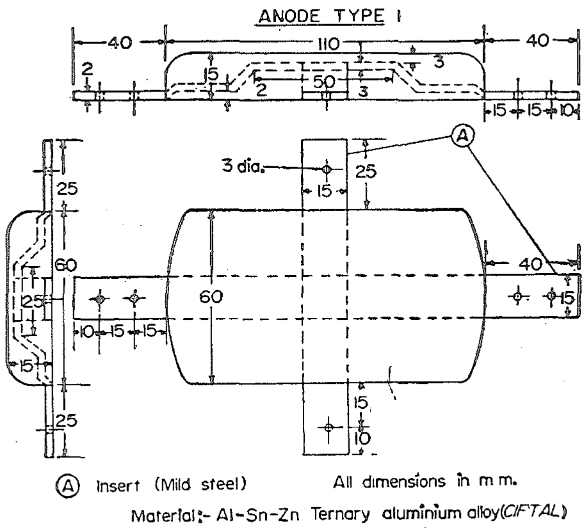

Fig. 1. Anode (Type I) used on aluminium sheathed wooden boats

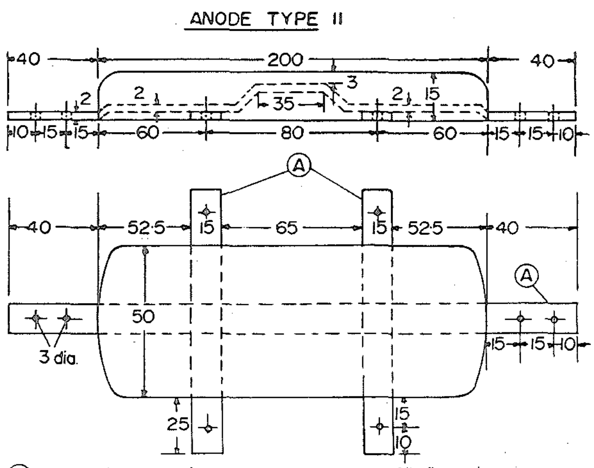

Fig. 2. Anode (Type II) used on steel trawlers

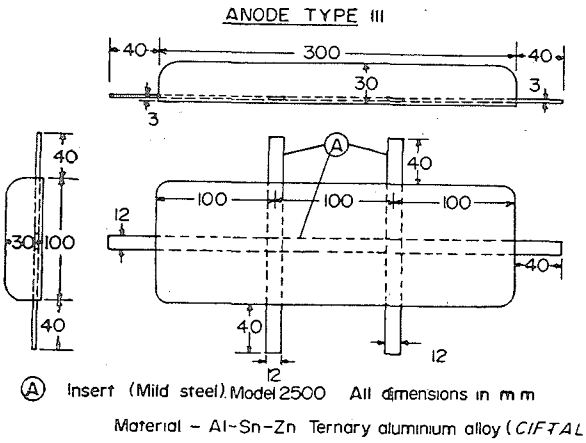

Fig. 3. Large anode (Type III) used on steel trawlers and marine structures

Results and Discussion

The open-circuit potential-time behaviour of the Al-Sn-Zn anode is shown in Fig. 4. Immediately on introduction into seawater, the anode registered a potential of -1055mV with reference to saturated calomel electrode which with the elapse of time showed very

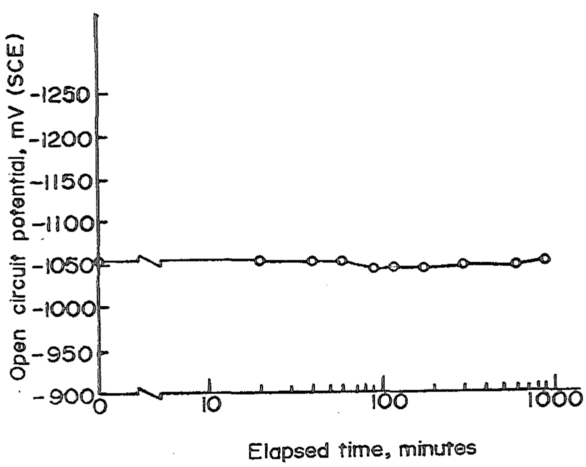

Fig. 4. The open circuit potential time behaviour of Al-Sn-Zn anode in sea water

slight fluctuation. A stable potential was maintained for a longer duration.

Fig. 5 shows a plot of current density in the range of 5.6 mA dm^{-2} to 166.7 mA dm^{-2} versus current efficiency for the Al-Sn-Zn anode tested in seawater. The cylindrical anodes were used but the experiments were repeated with anodes produced in three batches so that the influence of production variables could also be known. The scatter of test results were practically insignificant.

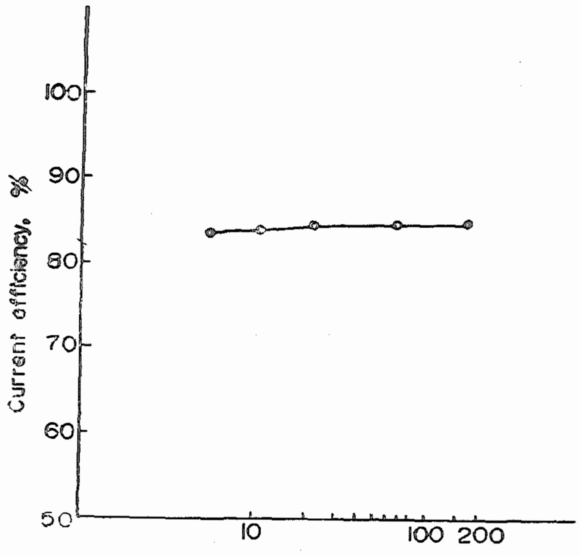

Fig. 5. Plot of anode current efficiency versus current density in the range of 5.6 mA dm^{-2} to 166.7 mA dm^{-2}

The applied current density varied from 5.6 to 166.7 mA dm^{-2}, the latter value represents a severe electrical current demand for any cathodic protection system. The ability of the anode to function at a high current efficiency and a highly stable performance are evident (Fig. 5).

The stringent test for the new alloy is its ability to function at its high current efficiency for longer periods. Results of cuboid specimens in quiescent seawater for nearly 10 months are shown in Fig. 6. The current density employed was 140 mA dm^{-2}. The data show the stability of the anode performance. The specimen had undergone uniform dimensional change evidencing negligible dissolution due to non-uniform attack. Galvanic anode current capacity is largely contributed by stringent control of composition and production variables especially the heat treatment procedures.

The field trials

The field testing of anodes was carried out on steel trawlers and aluminium sheathed wooden boats. All the anodes were weld-on types but those installed on aluminium sheathed wooden trawlers were fastened to the hull by screwing. The anode placements were such as to insure adequate protection by uniform distribution of current over the hull and hull appendages. Because of widely varying conditions of water velocity, salinity and painting schedules, the aluminium hull potential was kept at –0.9 V with respect to Ag/AgCl (Ravindran & Balasubramanian, 1973) while the steel hull was kept at the generally accepted value of –0.8 V referred to Ag/AgCl Electrode (Mallon & Kolbe, 1979). Some of the experiments were also conducted with the new Al-Zn-Sn anodes placed on the port side and another set of Al-Sn-Hg commercial anodes on the starboard side. Fig. 7 shows an array of CIFTAL anodes and Fig. 8 shows the appearance of the Al-Zn-Sn (CIFTAL) anodes and the commercial anodes (Al-Zn-Hg) after service trials. Several such tests were conducted, the duration of which varied from 12 to 18 months. In every case a high degree of protection was afforded to the hull and a near depletion of the anode materials was noticed. There were no signs of polarisation of the anode as a result of hard corrosion products.

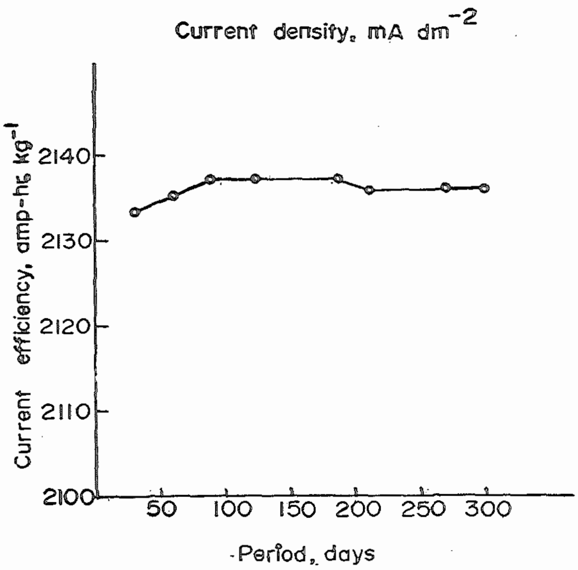

Fig. 6. Plot of anode current efficiency as a function of time at 1.4 mA cm^{-2}

A great majority of fishing vessels operate in the near-shore waters and are generally anchored in the harbour. This necessitates the use of sacrificial anodes that will cause least pollution to the aquatic environment. Several maritime regulatory agencies have laid down regulations barring the use of anodes which contain mercury as a constituent for cathodic protection of vessels calling on inshore water or of coastal marine structures. As these regulations are being made mandatory, the development of CIFTAL, the mercury-free Al-Zn-Sn anode of high electrical output may be considered as a welcome addition to marine cathodic protection system.

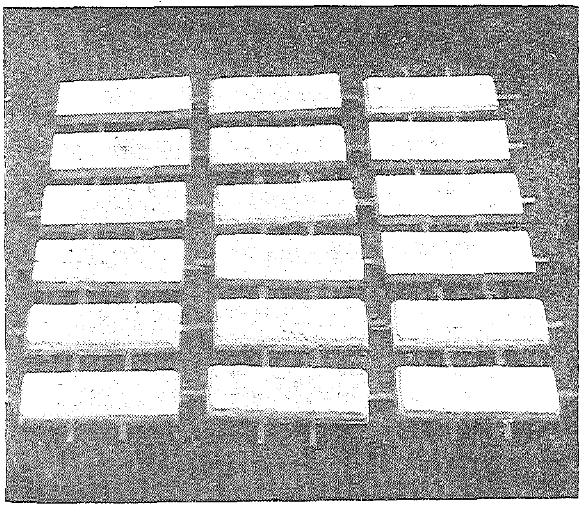

Fig. 7. An array of model 2500 Type III CIFTAL (Al-Sn-Zn) anodes

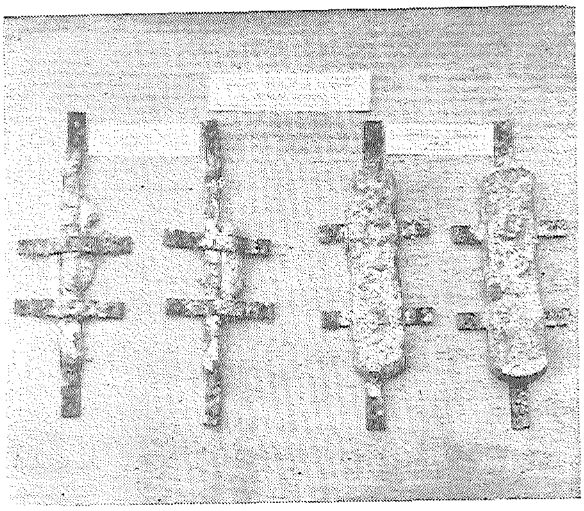

Fig. 8. Photographs of CIFTAL (Al-Sn-Zn) and commercial Al-Zn-Hg anode after service trials on fishing boats

On the basis of electrochemical characteristics and present cost level the CIFTAL, the mercury free, Al-Zn-Sn anode is an attractive material for both short and long term marine cathodic protection. The absence of mercury in its composition coupled with its high current efficiency, current output and large driving voltage will be of distinct advantage over mercury based alloys for seawater applications.

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