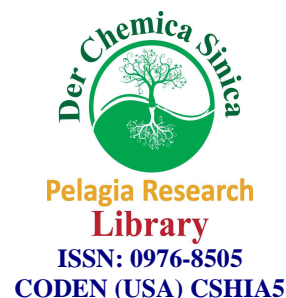




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Corrosion of copper plated NST60Mn and NST50 steels in NaCl, H₂SO₄ and NaOH solutions

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ABSTRACT

The corrosion characteristics of copper-electroplate on two Nigeria standard steels (NST60Mn and NST50) in three corrosive media (0.1M NaOH, 3.5M NaCl, 0.1M H₂SO₄ solutions) were studied. NST60Mn and NST50 steels substrates were plated in acid sulphate bath. The results of copper corrosion study in three corrosive media after 30 days revealed that copper plated steels have lower corrosion rates than the naked as-received steels whereas the copper-coated steels have 3.06×10^{-3} , 6.46×10^{-4} , and 1.2×10^{-3} corrosion rates ($\text{mgmm}^{-2}\text{day}^{-1}$) in 3.5M NaCl, 0.1M H₂SO₄, and 0.1M NaOH respectively. These will produce a good combination with some other more protective metal plating over coats when used in these environments.

Keywords: Nigeria standard steels, copper-plating, copper corrosion, corrosive media

INTRODUCTION

There are different ASTM standards [1] applicable in the selection and design of copper and its alloys for engineering uses. These include: B224-04, B226-04, B227-04, B228-04, B229-04, B246-05, B248-07 and B248M-07; the B281-88(2008) Standard practice for preparation of copper and copper-base alloys for electroplating and conversion coatings; B432-09 Standard specification for copper and copper alloy clad steel plate, and the B452-02 Standard specification for copper-clad steel wire for electronic application.

An array of low carbon steels (ST30LC, NST44); mild steel (NST50-2) and medium carbon steels (NST60Mn) and other high carbon steel are of repute standards of structural steels that are made in Nigeria. These are used in numerous areas such as wire drawing, steel rolling and machine components and machine tools fabrication to mention a few.

Pure copper has accepted application as earthen rod in electrical wiring. Copper priming is often useful on steel for its good adhesion and enhanced appearance [2]. In the recent years, earthen rods are produced from copper coated steel rods which in no long time wear away due to the very hostile characteristics of their surroundings of application. The numerical strength of cottage industries involved in soap making and production of detergent is growing at very alarming rate. With these industries, large amount of chemicals such as NaOH, NaCl and H₂SO₄ used have serious corrosive impact on various appliances used in the processes. Hence the need to undercoat the base steel materials prior to the deposition of more resistant overcoat such as Ni, Cr, Cd and so on. The local manufacturing/engineering industries use assortment of steels in the making of machine parts for both industrial and domestic uses. These devices are used under diverse working situations such as very harsh or moderately aggressive

(corrosive) environments in which application of heat treatment does not completely eliminate the steel surface vulnerability to corrosion.

Hot dipping [2], anodising [3], electroplating [4], electroless plating [5], autocatalytic plating, [6], and galvanising [7,8] are few of the vast known techniques of metal plating processes.

Copper plating on steel possesses good corrosion resistance, but once the foundation metal is exposed by a pin hole or scratch, a strong voltaic effect is set up at the breaks under the coating and it results in flaking of the film coat. For a decorative reason, copper coating is always disallowed from oxidation by over-coating with lacquer. High throwing power baths are often used such as acid sulphate and fluoborate baths; cyanide and pyrophosphate (alkaline) baths.

The effects of surface finishing and Saccharin additive on copper plating of steels were studied and reported by Ajibola and Oloruntoba, 2014 [9]. The film properties improve as the substrate surface improves, with the highest copper plate stability and adhesion obtained on 600 μm finishing from the acid bath with and without saccharin-550 additive [9]. Using electroplating, very thin film of metal of moderately high chemical resistance to corrosive surroundings could be developed with improved aesthetic value and wear resistance of the steel surface. Non-ferrous metals such as Ag, Au, Si, Co, Al, Cr, Te, Mg, Pb, Ti, Cu, Zn, Sn, Ni, Mo and alloys of brass and bronze [10] possess low strengths but have superior corrosion resistance when compared with the ferrous metals. Some are more costly and are used for very special and exceptional purposes [11, 12].

Corrosion can be defined as the slow deterioration and surface wastage of a metal due to its reaction with its surroundings [3, 13]. Corrosion is a key material predicament usually facing both small and big engineering industries and household which requires greater attention. Many identified factors are responsible for corrosion of which the material properties, nature and aggressiveness of the environment are the major causes.

Except for few ones, metals and alloys are susceptible to corrosion. For these reasons, so much significance is attached to its prevention and control due to intolerable losses that may happen whenever the problem strikes. Thus, corrosion is monitored, measured quantitatively, stopped and inhibited by different techniques such as metal coating, painting, anodic protection and inhibition. Different reports by Jope *et al*, 1995 [14]; Wu *et al*, 1993 [15]; Talati and Gandhi, 1983 [16] have been published on the successful use of inhibitors on copper corrosion management. Corrosion management is a complex science that needs extensive understanding of corrosion chemistry and of the process or system being assessed. The corrosion process combines the oxidation and reduction reactions to return refined metals to their more stable ore (mineral) states [17, 18].

Copper platings are used in various areas requiring resistance to atmospheric exposure (such as hand rails, lock bodies, roofing, hardware, grille work, kick plates and doorknobs). It is applied in the freshwater delivery lines and plumbing fixtures, where superior resistance to corrosion by different types of soils and waters is significant. Some other areas where copper plating is most frequently found useful include: seawater and freshwater supply lines, shafting, valve stems, heat exchangers (liquid-to-gas or gas-to-gas), condensers, steam power plants, and chemical process (containing corrosive contaminants), and marine hardware where biofouling from marine organisms, high resistance to seawater and hydrated salt deposits is of serious importance [19,20]. Some other chemical and industrial plant and process equipments engage exposure to a variety of both organic and inorganic chemical reagents [21,22,23]. Hence the trend and extent of corrosion damages done on some steel equipment, Vat and vessels are investigated with the view to protecting these facilities with copper prime undercoat prior to the deposition of superior corrosion resistant overcoat.

MATERIALS AND METHODS

The materials used in the experiment include: mild steel (NST50-2) and medium carbon steel (NST60Mn), emery paper grit (60 μm , 120 μm , 320 μm , 400 μm and 600 μm), copper plated steel samples, electrolytic cell, hand files and polishing machine. HCl and NaOH. Standard analytical grade of NaCl, HCl, H₂SO₄ and NaOH were procured from the chemical store.

Standard lengths of NST50-2 and NST60Mn steel specimens were produced and obtained from ASTC-Rolling mill section Kogi state, Nigeria. Steel samples were hot rolled and cut to length (40 mm) x width (15 mm) x thickness

(5.5 mm). The chemical compositions (Table 1) were determined using Atomic Absorption Spectrometer (AAS) Thermo series 2000 Model. The samples surface were grinded and polished to 600 μm smoothness on the ELE polishing machine (EL 78/260) and the initial weight of the specimen was determined on electronic digital weight meter (model DT-502A).

Based on the B115-00(2004) standard specification for electrolytic copper cathode, steel samples were electroplated with pure copper in the acid sulphate bath comprising of 200g/l $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 50g/l H_2SO_4 , 1.0g/l phenol (inhibitor) and 0.5g/l saccharin-550 (organic brightener) operated at 50 $^\circ\text{C}$ bath temperature, current density (c.d) = 1 A/dm^2 , 95 % current efficiency and 2 V applied voltage.

The corrosion study was performed based on the G 31 practice for laboratory immersion corrosion testing of metals using four substrates consisting of as-received NST50 and NST60Mn and copper plated NST50 and NST60Mn steels. 500 ml of each of the corrosive media were prepared from 3.5M NaCl, 0.1M H_2SO_4 , and 0.1M NaOH.

Each of the four samples was fully immersed into the 3 media for 30 days. The sample was removed from at every 2 days interval and properly cleaned and the final weight of the sample was measured. The initial total surface area of the specimen (making corrections for the areas associated with plating-mounting holes) and the mass loss during the test are determined. The average corrosion rate may then be obtained according to Oloruntoba [24] as follows:

$$\text{Corrosion rate} = (K \times W)/(A \times T \times D) \quad (1)$$

where:

T = time of exposure in hours,

A = area in cm^2 ,

W = mass loss in grams,

D = density in g/cm^3

and constant (K) in the corrosion rate equation is taken as milligrams per square decimetre per day (mdd) $2.40 \times 10^6 \times D$

In the present case, the size of specimen is assumed to be the same. Hence $(K)/(A \times T \times D)$ is a constant factor. The weight loss per unit surface area (mg/mm^2) as measure of corrosion is determined as the ratio of the difference in weight between the original weight (W_i), and the final weight (W_f) and the total surface area (A_t) of the sample after immersion at every 2 days interval. This is mathematically expressed as

$$\text{Weight loss per unit surface area (mg/mm}^2\text{)} = (W_i - W_f)/A_t \quad (2)$$

Table 1: Chemical composition (%) of as-received Nigeria standard steel samples

Samples	Fe	%C	%Si	%Mn	Ni	N ₂	%P	%S	%Cu
NST50	98.199	0.176	0.217	1.26	-	0.01	0.007	0.013	0.118
NST60Mn	98.429	0.324	0.164	0.756	0.10	-	0.009	0.015	0.203

RESULTS AND DISCUSSION

The photomicrographs of copper electroplated steels and thin section of copper plate on 600 μm polished as-received steel substrates are shown in Plate 1(a and b).

The graphical representations of results of immersion test of as-received steels (NST60Mn and NST50) and Cu-plated steels (Cu-plated NST60Mn and Cu-plated NST50) for 30 days in NaCl, H_2SO_4 , NaOH are presented in Figures 1 -3 respectively.

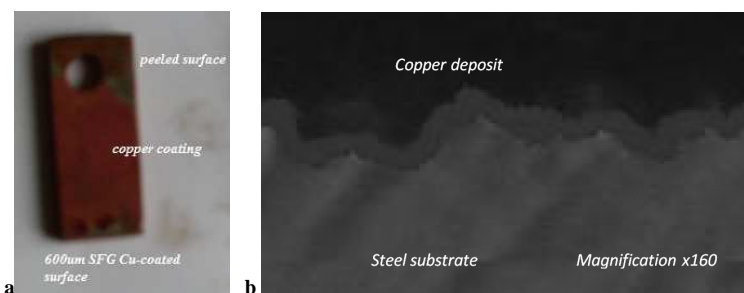


Plate 1: Photomicrograph of (a) Copper electroplated steels and (b) thin section of copper plate [9]

Copper corrosion in aqueous solutions of NaCl

Plate 2(A-D) shows the photomicrographs of the surfaces of impact of corrosive media on the copper plated steel immersed in 3.5M NaCl solution after 30 days. The plot of the corrosion rate (mg/mm²)-time curves for the four specimens: as-received NST60Mn (sample A), as-received NST50 (sample B), Cu-plated NST50 (sample C) and Cu-plated NST60Mn (sample D) in 3.5M NaCl are shown in Figure 1.

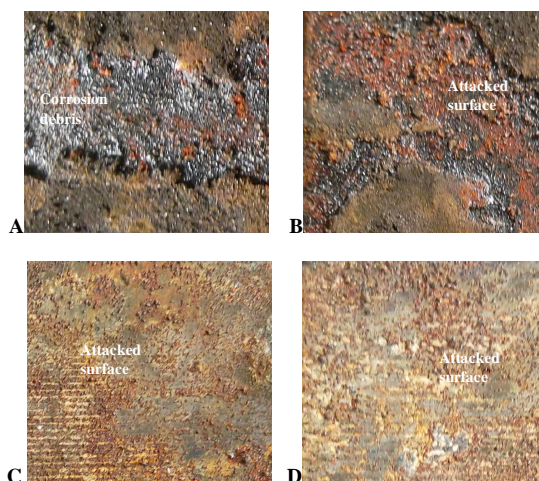


Plate 2: Micrographs showing corrosion of samples A, B, C and D in 3.5M NaCl solution

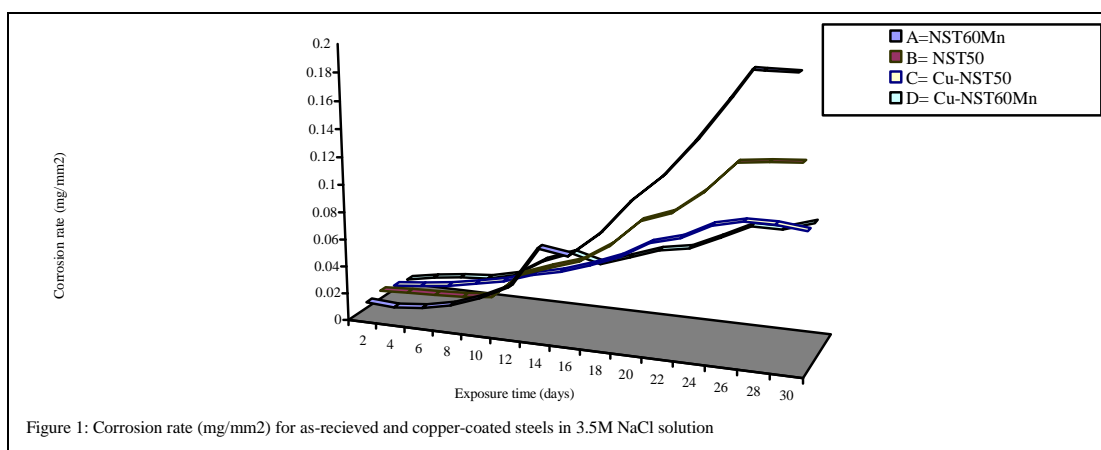


Figure 1: Corrosion rate (mg/mm²) for as-received and copper-coated steels in 3.5M NaCl solution

Copper corrosion in aqueous solutions of H₂SO₄

For all the four samples in the early 12 days, the corrosion rate (mg/mm²) increases as the time increases at almost same rate. There are very little corrosion rate with gentle slopes. Sample A has a sharp rise in corrosion rate between

the 12th and 28th day after which the rate was constant until 30th day while sample A shows increasing corrosion rate for 15 days (between 12th and 26th day) after which the corrosion rate was constant until the last day of immersion. The sample A has the highest level of weight loss in 3.5M NaCl for the period of the 30 days. The corrosion rate (mg/mm^2) of as-received steels increased tremendously after 12 days. The coated steels have lower corrosion rate in the NaCl solution than steel samples (A and B) in Figure 1. The sample C showed higher corrosion rate between the 16th and 26th day after which the corrosion rate becomes constant until the last day. The corrosion rate of sample D increased with gentle slope until the 28th day. The rate is constant between the last 3 days of immersion for the coated samples (C and D). Comparatively, the corrosion rates (mg/mm^2) of 0.217, 0.1368, 0.0867 and 0.0839 were measured for samples A, B, C and D respectively within the 30 days of immersion in 3.5M NaCl solution.

Plate 3(A-D) shows the photomicrographs of the surfaces of impact of corrosive media on the copper plated steel immersed in 0.1M H_2SO_4 solution after 30 days.

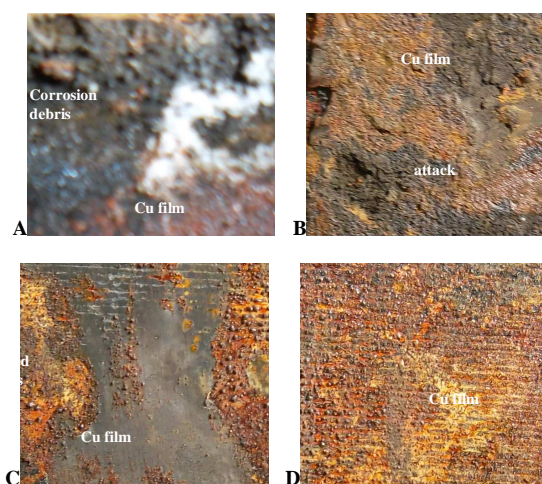
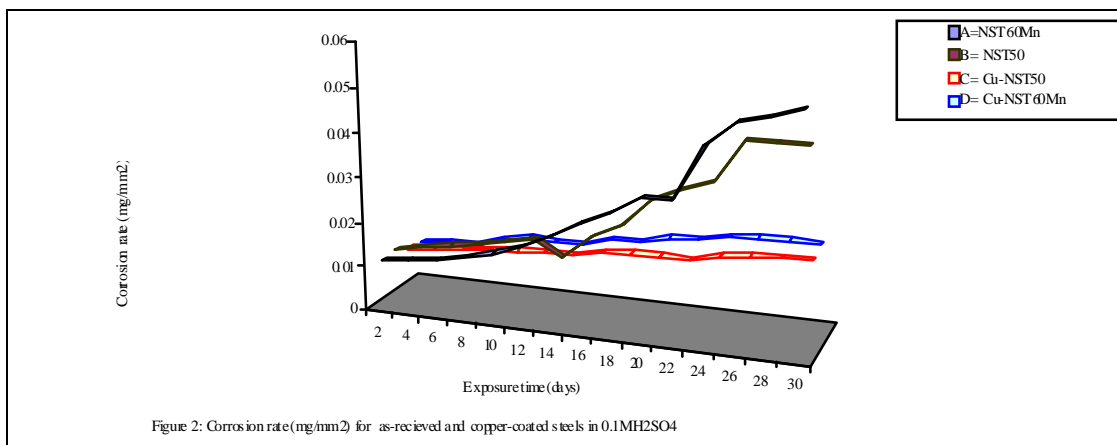


Plate 3: Micrograph of corrosion of samples A, B, C and D in 0.1M H_2SO_4

Figure 2 shows the plot of the corrosion rate curves of four specimens: as-received NST60Mn (sample A), as-received NST50 (sample B), Cu-plated NST50 (sample C) and Cu-plated NST60Mn (sample D) in 0.1M H_2SO_4 . The corrosion rate increased with exposure time at almost same rate for all the four samples within the early 6 days and consequently at very close rate between 6th and 12th day. For sample A, the corrosion rate increases with exposure time for the 30 days of immersion except for the period of 2 days (between 20th and 22nd day). The figure shows a drop in corrosion rate in sample B between the 12th and 14th day after which there was a rise in the corrosion rate value until the 26th day. The corrosion rate was also constant between 26th and 28th after which there was a fall corrosion rate until the last day. Figure 2 shows that the coated steels have lower corrosion rate in the H_2SO_4 solution than the uncoated (as-received) steel samples. The corrosion rate increased with exposure time at almost same rate for the two coated-steel samples within the 30 days of immersion. Comparatively, the highest corrosion rate (mg/mm^2) values of 0.0521, 0.0434, 0.0171 and 0.0188 were measured for as-received steels (A and B) and cu-coated steels (C and D) respectively within the 30 days of immersion in 0.1M H_2SO_4 .

The plated steel samples have lower corrosion rate in brine as compared with the as-received steel samples in the same medium. This is due to the fact that copper ions (copper I and copper II) form more stable complexes in chloride solution. Consequently copper plated steel is more protected in brine than the uncoated steel. For further enhanced performance (reduced corrosion rate) in brine, a variety of inhibitors can also be used such as the diphenylamine has been reported by the Institute of Technology, Banaras Hindus University India [22,23].



Copper corrosion in aqueous solutions of NaOH

The photomicrographs of the surfaces of impact of corrosive media on the copper plated steel immersed in 0.1M NaOH solution after 30 days are illustrated in Plate 4(A-D).

Figure 3 shows the plot of the corrosion rate curves of four specimens: as-received NST60Mn (sample A), as-received NST50 (sample B), Cu-plated NST50 (sample C) and Cu-plated NST60Mn (sample D) in 0.1M NaOH. In Figure 3, the corrosion rate increased with exposure time at almost same rate and at very close values for all the four samples in the first 8 days and for three samples A, B and C extends to the 12th day. There was a drop in the corrosion rate in sample A between the 12th and 14th day after which there was an increase in the corrosion rate of the sample as the exposure time increased.

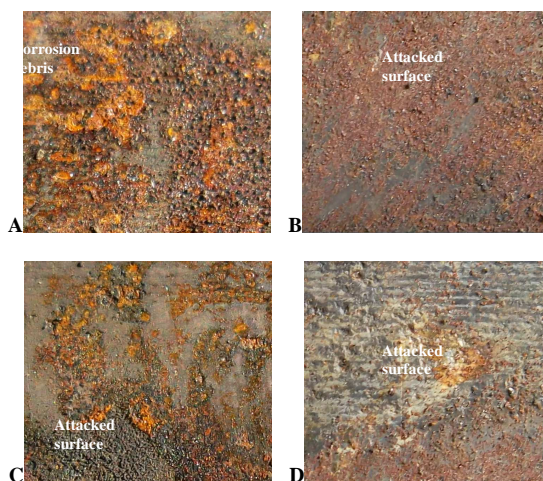
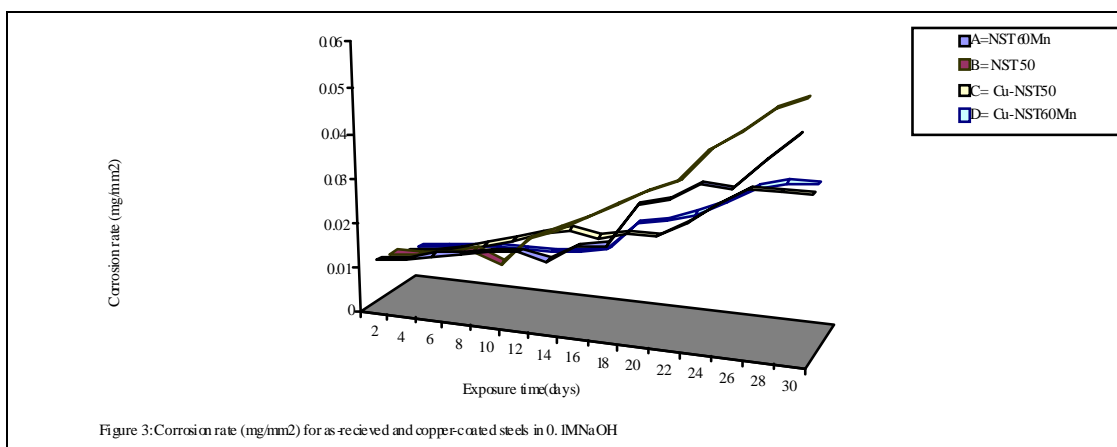


Plate 4: Micrograph of corrosion of samples A, B, C and D in 0.1M NaOH

Sample C shows a drop in the corrosion rate between the 14th - 16th and 18th - 20th day after which there was rise in the corrosion rate of the sample as the exposure time increased until the 26th day when the corrosion rate become constant until the 30th day. Comparatively, the highest corrosion rate (mg/mm²) values of 0.0471, 0.0532, 0.0316 and 0.032 were measured for as-received steels (A and B) and cu-coated steels (C and D) respectively within the 30 days of immersion in 0.1M NaOH.

The corrosion rates (mgmm⁻²day⁻¹) of the samples (as-received steel and copper coated steels) for 365 days in the 3 media are presented in Table 2.



For sample B, the corrosion rate increases with exposure time for the 30 days of immersion except for the period of 2 days (between 20th and 22nd day). Sample B shows the highest corrosion rate of the four samples in NaOH solution

Table 2: Corrosion rates (mgmm⁻²day⁻¹) of as-received steels and Copper-coated steels in 3 media

Media	Total Exposure time (days)	Corrosion rate of as-received steel (mgmm ⁻² day ⁻¹)	Corrosion rate of Cu-coated steel (mgmm ⁻² day ⁻¹)
3.5M NaCl	30	7.23x10 ⁻³	3.06x10 ⁻³
0.1 M H ₂ SO ₄	30	2.01x10 ⁻³	6.46x10 ⁻⁴
0.1M NaOH	30	1.93x10 ⁻³	1.2x10 ⁻³

Conclusions and Recommendations

The following conclusions could be drawn based on the results of the experiments;

The corrosion resistant characteristics of plated steels in 0.1M NaOH, 3.5M NaCl and 0.1M H₂SO₄ was determined. The Cu-coated samples show very close similar trend of corrosion rate per exposure time in all the 3 media. Cu-coated steels have corrosion rates (mgmm⁻²day⁻¹) in the order of 3.06x10⁻³, 6.46x10⁻⁴, and 1.2x10⁻³ in 3.5M NaCl, 0.1M H₂SO₄, and 0.1M NaOH respectively. The copper on steel as undercoat will produce a good combination with some other more protective metal plating over coats when used in these three environments, and hence copper coated steels can be effectively used as the earthen rod in regions where such environment are dominated by these media.

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