

Performance of Ni-P-TiO₂-ZrO₂ Electroless Nano-composite Coatings in A Paper Mill Digester

Manoj Kumar¹, Sulaxna Sharma^{2*}, Awanish Sharma^{1*}

¹Department of Allied Sciences , Graphic Era Deemed to be University, Dehradun, UK, (India)

²Department of Chemistry, IHET, THDC Tehri, UK (India)

ABSTRACT

In Pulp and Paper mills, Digester house is main section and corrosion is a huge trouble in this part. The existence of sulfides, thiosulphates and sodium chloride in cooking liquor and silicone (Si) in steel create the stern corrosion trouble in digesters. A digester is constructed mainly into three sections top, mid and bottom. In our earlier study bottom and mid part in-plant tests were completed. Therefore, an in-plant test of six month time was performed in the top part of a batch digester. This digester is made of mild steel of volume 20 m³. The newly developed electroless Ni-P-TiO₂-ZrO₂ nano-composite coatings (alternate material) along with mild steel (conventional material) were selected as the test materials. It is accomplished that top part of digester is exaggerated due to stress as well as pitting corrosion. The top part can be constructed of these newly developed coatings without strict risk of deterioration.

Keywords : *electroless, coating, Ni-P-TiO₂-ZrO₂, SEM ,in-plant and corrosion*

I. INTRODUCTION

A wide-ranging corrosion is experienced by process equipment and machinery items in diverse sections of paper mill. Digester house is one such section which is severely affected by corrosion [1-5] found that corrosion in kraft digester was due to , high C and Si , movement of gases and liquor intrude on walls of digester and change in chemical concentration. A like conclusion was drawn in test reports [6-8], with regard to the dependence of the corrosivity of liquor on its composition. It has been squabbled that a higher concentration of polysulfides may show passivating effect. By the way, the current corrosion test emerges to be very important in-plant test performed with alternate and conventional materials in the digester of a mill. The alternate materials are selected newly developed electroless Ni-P-TiO₂-ZrO₂ nano-composite coatings and conventional material is mild steel (MS).

II.EXPERIMENTAL

2.1. Materials and Methods (MM)

First base coupons of mild steel (MS) grade (AISI-1040) are prepared properly by methods of shaping, milling and surface grinding. The dimensions of all samples is as 1 cm × 1 cm × 0.4 cm. An acidic electroless procedure is taken for nano-composite coatings [9-14].



(a)



(b)

Figure 1: (a) Ni-P-TiO₂-ZrO₂ EL nano-composite (as-plated) and (b) MS coupons

2.2 Composition of electroless bath (CEB)

The experimental set up planned for coatings is shown below in Figure 2. The bath composition and working environment for nano-composite coatings are chosen as; nickel sulphate 35.18 gpl, trisodium citrate 48.53 gpl sodium acetate 22.21gpl, sodium hypophosphite 23.07 gpl, synthesized TiO₂ and ZrO₂ nano-particles 2gpl each, pH fluctuated in between 5.6 to 5.8 and temperature range 82 to 87 °C.



Figure 2: Experimental set up for electroless Ni-P-TiO₂-ZrO₂ nano-composite coatings

2.3 Characterization of coatings (COC)

The micrographs of as-plated and heated nano-composite coated coupons were evaluated by Fourier scanning electron microscopy (FESEM).

2.4 Details of in-plant test

For in-plant test in batch digester, the paper mill uses 80% poplar and 20% baggasse and eucalyptus as raw material for making printing paper. The digester used in in-plant study has a capacity of 20 m³ and it is constructed of mild steel. The pulping cooking liquor consist NaOH (90 gpl as NaOH) and Na₂S (20 gpl as NaOH) having pH ~13.7. The temperature accomplished during process is 160⁰C and it operates at a pressure of roughly 6 Kg/Cm².

III. RESULTS AND DISCUSSION

3.1 Characterization of coatings

The SEM micrographs of Ni-P-TiO₂-ZrO₂ EL nano-composite coated (as-plated and annealed, 400 °C Argon atmosphere) coupons are discussed [15-16]. From SEM micrograph figures it is clear that EL nano-composite plated surface in all cases have glow surface with steady sharing of titania and zirconia nano-particles. It may increase in corrosion resistance of developed electroless nano-composite coatings [14, 17].

3.2 Corrosion rate

The cooking liquor of mill has a sulfidity of about 20%. This is the sulfidity usually pragmatic in Indian mills. However, it is much lesser than that observed in mills of USA, Canada and Scandinavia etc. (~40% or so). From the in-plant corrosion test it is seen that the corroded coupons show only uniform corrosion rate. The crevice corrosion is observed only on mild steel coupon. The corrosion rate of materials is given in Table-1. The degree of pitting attack in case of coated coupons is within the limit of acceptability [15], for a material of construction. The maximum corrosion rate is experienced by mild steel followed by Ni-P-TiO₂-ZrO₂ (as-plated) and Ni-P-TiO₂-ZrO₂ (heated). Thus mild steel show least resistance from the standpoint of uniform corrosion. As indicated in [15], for alkaline pH as in digester, Cr (chromium) and N (nitrogen) in stainless steels appear to be more important than Mo (molybdenum) in providing corrosion resistance. Probably this may result into development of new duplex stainless steels, without Mo, having equivalent mechanical properties and resistance against localized corrosion. Such types of steels are also possible to be cost valuable.

Table-1: Corrosion rates (mils per year) of samples in alkaline sulfide solution

Materials	Corrosion rate (mpy)
Mild Steel (MS)	5.807
Ni-P-TiO ₂ -ZrO ₂ (as-plated)	01.260
Ni-P-TiO ₂ -ZrO ₂ (heated, 400 ⁰ C)	1.781

IV. CONCLUSIONS

The present real circumstance corrosion test point up that Ni-P-TiO₂-ZrO₂ EL nano coatings have been effectively plated on mild steel. The colours of coatings is grayish white and as-plated EL nano-composite coatings have amorphous character and heated coated coupon reveals development into crystallization character. This type of behavior of coatings may increase in wear, hardness and corrosion resistance.

REFERENCES

- [1] A. H. Tuthill (Ed.), "Stainless Steels and Specialty Alloys for Modern Pulp & Paper Mills", NiDi, Reference Book Series no. 11025:138.

- [2] A. Wensley, "Corrosion and protection of Kraft batch digesters", *Technical Association of Pulp and Paper Industry Journal*, 79 (10), 1996,153.
- [3] D. C. Bennet, "Cracking of continuous digester-review of history", Proc. of 4th International Symposium on Corrosion in Pulp & Paper Industry, 4, 1983.
- [4] C. G. V. Essen, "Corrosion Problems in Sulfate Pulp Mills", *Technical Association of Pulp and Paper Industry Journal*, 33 (7), 1950, 14A.
- [5] R. S. Peoples, G. L. Cricson, "Corrosion of Alkaline Pulping Digesters", *Technical Association of Pulp and Paper Industry Journal*, 35, 1952, 403-411.
- [6] F. W. Flynn , F. H. Riehter, F. B. Snyder, "Uneven Corrosion in Alkaline Pulping Digesters", *Technical Association of Pulp and Paper Industry Journal*, 36 (10), 1953, 433-438.
- [7] R. A. Huseby and M. A. Schil, "Corrosion of MS and MS Welds in Sulfate Digesters", *Technical Association of Pulp and Paper Industry Journal*, 34(5), 1951, 202.
- [8] S. J. Clarke, "Canadian Batch Digester Corrosion Survey", 86th Annual Meet 1 of 3 Montreal Que, Feb. P , 2000, 239.
- [9] A. Sharma and A. K. Singh, "Electroless N-P-PTFE- Al_2O_3 Dispersion Nanocomposite Coating for Corrosion and Wear Resistance", *Journal of Materials and Engineering Performance*, 23 (1), 2014,142-151.
- [10] Y. de-Hazan, D. Werner, M. Z'graggen, M. Groteklaes, T. Graule , "Homogeneous Ni-P/ Al_2O_3 Nanocomposite Coatings from Stable Dispersions in Electroless Nickel Baths", *Journal of Colloid and Interface Science*, 328 (1), 2008,103-109.
- [11] I. Apachitei , F. D. Tichelaar , J. Duszczuk , L. Katgerman , "The Effect of Heat Treatment on the Structure and Abrasive Wear Resistance of Autocatalytic Ni-P and Ni-P-SiC Coatings", *Surface and Coatings Technology*, 149 (2-3), 2002,263-278.
- [12] F. A. Esfahani , M. Sarafbidabad, "Evaluation of Corrosion Rate and Surface Oxides Formed of Zr-2.5%Nb as an Implant Material in Ringer's Solution", *Indian Journal of Science and Technology*, 9(6), Doi no:10.17485/ijst/2016/v9i6/74612, 2016.
- [13] J. K. Dennis and K. S. Sagoo, "Wear Behaviour of Engineering Coatings and Surface Treatments", *Metal Finish*, 89, 1991, 111–121,.
- [14] K. Zielinska, A. Stankiewicz and I. Szczygiel, "Electroless deposition of Ni-P-nano- ZrO_2 composite coatings in the presence of various types of surfactants", *Journal of Colloid and Interface Science*, vol. 377, 2012, pp. 362–367.
- [15] A. Sharma, "Corrosion Investigations in Pulping and Bleaching media", Ph.D. Thesis, Indian Institute of Technology Roorkee, 2006.
- [16] M. Momenzadeh, S. Sanjabi, "The effect of TiO_2 nanoparticle co-deposition on microstructure and corrosion resistance of electroless Ni P coating", *Mater. Corros*, Vol. 10, pp. 1002, 2011.
- [17] S. H. Wang, H. Y. Yang, "Characterization of Ni-P/ TiO_2 MMC Coatings Prepared by Electroless Plating Process on Mg-Nd-Zn-Zr Magnesium Alloys", *Material Science Forum*, 690, 2011, 422.