Effect Of Linear Alkyl Benzene Sulfonate Containing Detergents On Electroless Nickel/TiO$_2$ Composite Coatings

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Abstract— Corrosion is a major challenge that has continued to plague engineering materials and components. One way to mitigate this menace is via electroless composite deposition. In this study, electroless nickel/TiO$_2$ nanoparticles composite coatings on mild steel substrate were investigated. However, due to the high surface area of nanoparticles, they tend to agglomerate and settle out of suspension leading to poor codeposition. The effect of two common household detergents containing Linear akylbenzene sulfonates (LABS) as surfactants was studied. Parameters investigated include; effects of temperature, bath agitation, concentration of the particles and effect of surfactant concentration in the bath. The results showed that significant deposition occurred from 80°C and above. Also, deposit thickness increased with increasing bath agitation and temperature, as well as with increase in labs2 detergent. Although, both surfactants had similar composition, labs2 had in addition sodium silicate and exhibited enhanced incorporation of the TiO$_2$ nanoparticles.

Keywords—Electroless; Codeposition; Composite coatings; Nanoparticles; Detergents; Surfactants.

I. INTRODUCTION

Majority of failures such as corrosion and wear of engineering components begin from the surface. [1] This decreases the life span and utilization of the components. Since these problems are prevalent on the surface, there is the need to apply suitable coatings to mitigate them. Amongst others, such as electrolytic deposition, chemical vapour deposition (CVD), physical vapour deposition (PVD), thermal spraying, electroplating, electroless composite coating is preferred due to its numerous benefits such as good mechanical properties, superior corrosion and wear resistance, uniform coating thickness, excellent surface finish and adhesion characteristics [2]. Also, It has a broad range of applications viz; petroleum, chemical, plastics, optics, aerospace, nuclear, electronic devices, computer, and printing industries dues to its wear resistance and excellent corrosion properties [3]. It is also good for soldering and brazing purposes. The chemical reduction of aqueous metal ions coated to a base substrate without the passage of external current is referred to as electroless plating [4]. Electroless coating is an autocatalytic process where the substrate develops a potential when it is immersed in an electroless bath containing a stabilizer, reducing agent and others. The coating process is achieved through charge transfer procedure. Each parameter has its specific role on the operation and influences the process response variables. Temperature is key in activating the reaction mechanism which controls the ionization process in the solution and charge transfer from source to the substrate [5].

However, a major disadvantage of electroless composite deposition is the agglomeration of nano particles leading to non-uniform distribution of these particles in the coatings. One way to alleviate this problem is the used of surfactants such as Sodium Dodecylsulphate (SDS), Dodecyltrimethyl Ammonium Bromide (DTAB) and Cetyltrimethylammonium Bromide (CTAB) [6]. However, these surfactants are not readily available and expensive. Although, readily available, there is paucity in the literature on the use of household detergents as surfactants in electroless composite deposition. Hence in this study, two common household detergents containing Linear Alkyl Benzene Sulfonates (LABS) derivatives were identified and utilized. Key parameters investigated were effects

of temperature, bath agitation, concentration of the nanoparticle in the bath and effect of surfactant [7].

II. MATERIALS AND METHOD

Mild steel samples ($450 \times 200 \times 0.02$ mm^3) were utilized as the substrate material for the coating process. The substrates were finished by surface grinding and disc polishing to obtain smoothly finished surfaces. The samples were cleaned with acetone for 15min to remove any surface contaminant and rinsed with distilled water for 2min to remove residual chemical adhesion. The surfaces were activated by pickling with 50vol. % of hydrochloric acid for 30sec, rinsed with running tap water and distilled water and dried with hot hand dryer before transferring into the plating bath whose composition is as shown in table 1. These detergents will hereafter be named as labs 1 and labs 2 respectively. Both detergents contain the same chemical compounds. However, Labs 2 contains additional Sodium silicate as shown in table 2.

Table 1. Bath composition and operating conditions used coating

Constituents	Bath composition (g/l)
Nickel Sulphate	30
Sodium Hypophosphite	40
Nano TiO$_2$	1.5, 3, 4.5, 6
pH	4, 5, 6
Temperature	80, 84, 88 $\pm$ 2 °C

The investigations were carried out using a magnetic stirrer with a hot plate. The apparatus was switched on for the magnet to agitate the bath. The speed and heat knobs were adjusted until the temperature and speed stabilized at the required temperature and rpm respectively. While waiting for the optimization of the temperature, each specimen was dipped into hydrochloric acid to pickle the surface and rinsed in a solution containing NaOH and Na$_2$CO$_3$ to clean the outside of the sample of the unwanted particles and contaminants. When the temperature and speed had been optimized, each mild steel plate was submerged into the electroless bath.

Table 2. Composition of surfactants utilized

Type of surfactant	Concentration (g/l)	Constituents
Labs 1	0.5, 1.0, 1.5, 2.0	Sodium triphosphate, Sodium carbonate, Sodium sulphate
Labs 2	0.5, 1.0, 1.5, 2.0	Sodium triphosphate, Sodium carbonate, Sodium sulphate, Sodium silicate

The deposition procedure was carried out for 2 hours after which the specimen was withdrawn from the bath and rinsed in distilled water. It was then dried with drier (air blower). Finally, the weight gain was determined using electronic weighing balance with an accuracy of 0.01mg. The coated samples were then analyzed for deposit thickness and chemical composition [5].

Different concentrations of linear Alkyl Benzene Sulfonate derivative containing household detergents were utilized as the surfactants in this study.

The coatings were characterized using; Dry Film Thickness (DFT MCT 200 Coating) test, Micro hardness test, Roughness test and Positive Material Identification (PMI X – M ET 7500) test to determine the chemical composition of the coatings [8].

III. RESULTS AND DISCUSSION

The effect of each parameter on particle incorporation and coating characteristics are discussed as follows;

A. Effect of Surfactants on Deposit Thickness

It is evident from Fig. 1 that the thickness of the coatings remained constant for labs 2 concentration between the range of 0.5g/l-1.5g/l. However, at the concentratration of 1.5g/l, there occured a sudden increase in deposit thickness. It is appears that at a concentration of surfactant lower than 1.5g/l, the surface tension was not sufficient to move the nickel and TiO$_2$ particles to actively take part in the deposition process. However, at concentrations beyond 1.5g of LABS1, the surfactant may have enhanced the adsorption of particles onto the substrate and becomes co-deposited as the nickel gets reduced onto the surface of the substrate leading to improved deposit thickness.
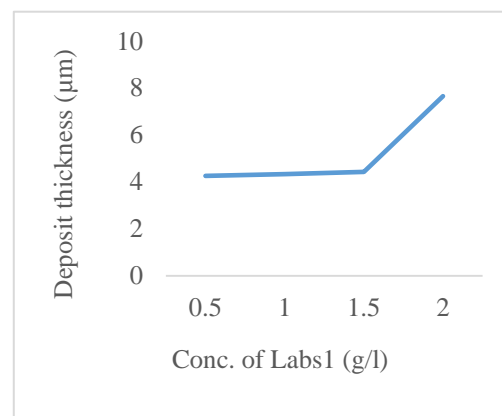

Fig. 1. Effect of Surfactant on deposit Thickness, in 1hr at bath agitation of 400rpm and 88°C, BN particle concentration in the bath 6g/l.

In Fig. 2, it was observed that the concentration of 2g/l of LABS2 surfactant greatly enhanced the deposit thickness of the substrate. This is probably because LABS2 contains an additional chemical compound called Sodium Silicate which may have improved the coating thickness of the substrate. Silicate containing compounds are known to enhance the corrosion

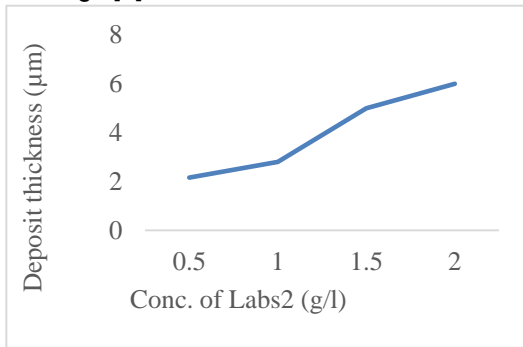resistance of coatings when incorporated into the coatings [9].

Fig. 2. Effect of labs2 on deposit thickness produced at $88^{\circ}C$, 400rpm in 1hr and 6g/l of TiO_2 particle.

B. Effect of Concentration of Labs1 and Labs2 on TiO_2 Content in the Deposit

Fig. 3. Shows the effect of concentration of Labs1 and Labs2 on amount of TiO_2 in the deposit produce at 88ºC.
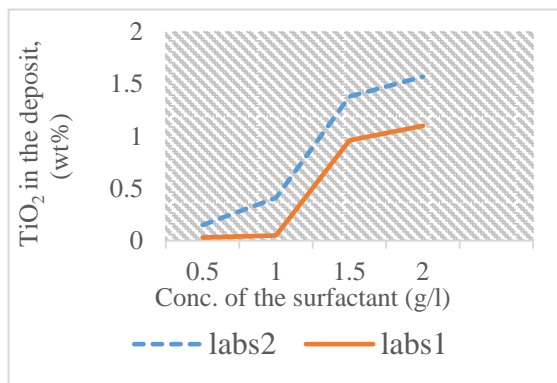

Fig. 3. Effect of concentration of labs1 and labs2 on TiO_2 in the deposit produce from a bath of 88ºC.

As can be seen, both labs increase the amount of TiO_2 in the deposit respectively, but the amount of TiO_2 in the deposit was higher with labs2 surfactant. This is an indication that labs2 was more effective in enhancing the incorporation of TiO_2 in the deposit more than labs1. This is probably because labs2 contain sodium silicate that may have enhanced the codeposition of the particle. Silicate containing compounds are reported to enhance the corrosion resistance of coatings. According to [10], sodium silicate is responsible for enhancing the stability of suspension and have a strong influence on wetting, adsorption and adhesion behaviour. Consequently, sodium silicate may have facilitated he uniform distribution of particles in the coatings with improved deposit properties. It is also reported [11] to be effective on calcium ions creating an irreversible reaction that pulls dirt away from the material.

C. Effect of TiO_2 Content on the Hardness of the Deposit

Fig. 4. Shows the effect of TiO_2 nanoparticles on the hardness of the coatings. Surface hardness of the coatings evidently increases with increase in the TiO_2 particles content of the coating. This is understandable as TiO_2 particles are relatively harder compared to the metal matrix. It has been reported [12] that incorporation of nanoparticles onto coatings, increases the micro-crystalinity of such coatings leading to improve hardness.
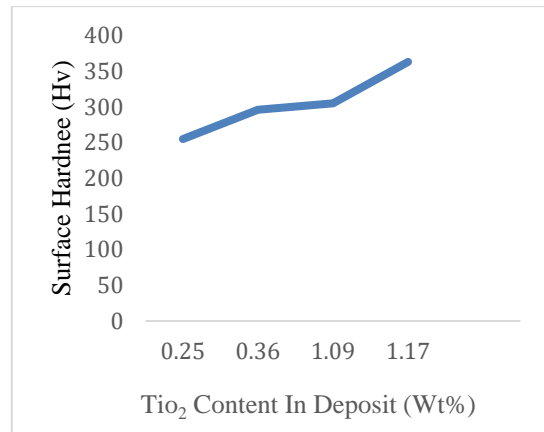

Fig. 4. Effect of TiO_2 content on the surface hardness of the deposit produced from a bath at 88ºC.

D. Effect on Ni Content on Surface Roughness of the Deposit.

Fig. 5. Shows the effect of Ni content in the deposit on its surface roughness. Evidently, surface roughness is seen to increase with increase in Ni content of the deposit. Similarly, it has been reported [13] that increase in the Ni content of the deposit, in turn increases the surface roughness of coatings
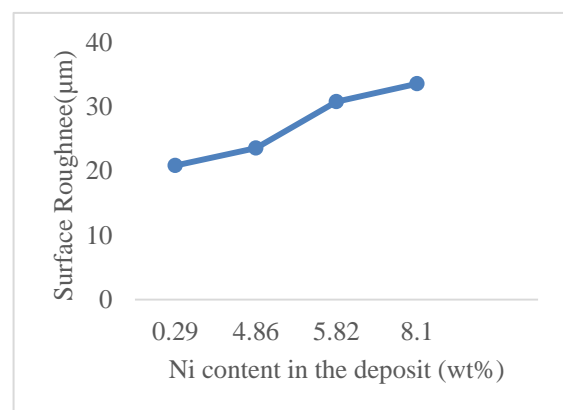

Fig. 5. Effect on Ni content on Surface roughness of the deposit produced from a bath at 88ºC and 0.2g/l of Labs2.

E. Effect of Concentration of Labs and without Labs on TiO_2 Content in the Deposit

Fig. 6. Shows the effect of concentration of Labs and without Labs on amount of TiO_2 in the deposit produce at 80-88°C. As can be seen, concentration of labs increases the amount of TiO_2 content in the deposit more than the concentration without labs. Labs play an important role in enhancing the corrosion resistance of the coatings [14].
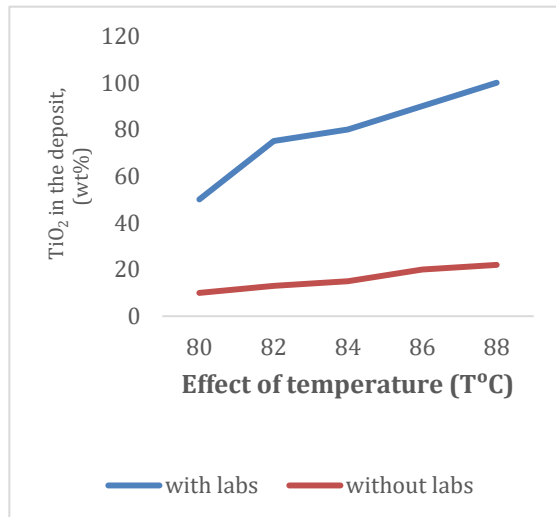

Fig. 6. Effect of concentration of labs and wihout labs on TiO_2 in the deposit produce from a bath of 80-88°C.

IV. Conclusion

The effect of surfactants on the characteristics of electroless nickel composite coatings were studied. Both detergents were found to improve the nanoparticle codeposition. However, Labs2 was evidently more effective. Furthermore, it was observed that hardness of the coatings increased with increase in particle content of the coatings. Also, deposit thickness increased with increasing Ni content of the coatings. TiO_2 content in the deposit increased with increase in labs2. Concentration of TiO_2 with labs enhanced the corrosion resistance of the coatings more than concentration without labs. It was also observed that the concentration of 2g/l of LABS2 surfactant greatly enhanced the deposit thickness of the substrate.

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