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Nanocrystalline Nickel Electrodeposition on Carbon Steel Using Eco-Friendly Aqueous *Ananas comosus* Juice

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The present study aims to investigate the effect of *Ananas comosus* juice on nickel electrodeposition on mild steel. The effect of this additive on electrodeposition behaviour, bath composition, surface morphology and corrosion performance of the nickel electrodeposited mild steel were investigated. The bath constitutents are optimized through Hull cell experiments. To investigate the nature of the deposits, FT-IR, scanning electron microscopy, EDAX, XRD and electrochemical methods are applied. Current efficiency and polarization studies were carried out. The results confirmed the influence of *Ananas comosus* juice on nickel electrodeposition.

Keywords: ***Ananas comosus*** **juice, Hull cell, Nickel electrodeposition.**

INTRODUCTION

Electrodeposition is an economic method for the application of metallic coating on engineering components. This technique is employed in the industry to enhance the appearance of metal surfaces, to safeguard substrates from corrosion and to provide good electrical and thermal contact [1]. Nickel electrodeposition plays a vital role in the surface finishing process. Its commercial importance has been identified from the usage of nickel in the form of metal and salts for the electrodeposition process. Nickel electrodeposition from Watt's bath has various wide ranges of decorative application, corrosion and wear resistance properties [2]. Electrodeposited nickel has a long life span and has greater resistance to friction and abrasive wear and tear [3]. The electrodeposition on metals depends to a large extent on the type of additional agents used in the plating electrolytes. Organic additives are added in traces to electroplating baths to modify the structure, morphology and properties of the metal deposits [4]. Organic additives have been used as stress reducers, levellers, brighteners, *etc*. Mohanthy *et al*. [5] studied the effect of thiourea on nickel electrodeposition. Saccharin, *p*-toluene sulfonamide, sodium *m*-benzene disulfonate, sodium 1,3,5-napthalene trisulfonate and O-sulfobenzaldehyde [6] have been used as stress reducers in Watt's-type nickel baths. Various organic additives such as cetyl tetraalkylammonium bromide, aromatic carbonyl compounds and amine-aldehyde reaction products, methane sulphonic acid and its derivatives, *etc*. were used in nickel electrodeposition as additives. Nowadays, green addition agents are popularly used as additional agents in the electrodeposition process. Felicita *et al*. [7-14] used several novel green extracts normally containing carbonyl compounds as major component as additives. The present work aims to study the effect of *Ananas comosus* juice on nickel electrodeposition.

EXPERIMENTAL

Carbon steel specimens of approximate composition: sulphur (0.026 %), phosphorus (0.06 %), manganese (0.40 %), carbon (0.10 %), iron (99.414 %). Carbon steel plates (AISI-1079) were mechanically polished to obtain a smooth surface. The scales and rust on the steel plates were removed by dipping in 10 % HCl and then subjected to electrocleaning process. These steel plates were washed with water and used for experiment as such. The pH of bath solution was measured using a digital pH meter (Equipetronix, model: 7020) and adjusted with 10 % H_2SO_4 or Na_2CO_3 solution. Nickel plate of 99.99 % purity was used as anode and activated each time by immersing in 10 % HCl followed by water-wash. *Ananus comosus* juice was prepared by using fresh *Ananus comosus* fruit. Nickel electrodeposition was done by using Watt's bath and its optimized conditions are given in Table-1. Hull cell was used to optimize the bath composition in the presence of *Ananus comosus* juice. The plated steel was examined using scanning electron micro-scopy (SEM) and energy dispersive spectroscopy (EDS) for the elemental analysis. The crystal structure was studied by X-ray diffraction study. The inclusion of addition agent in the deposit was confirmed by FT-IR, GC-MS and hardness study.

RESULTS AND DISCUSSION

Hull cell studies

Effect of *Ananas comosus*: Watt's bath compositions are given in Table-1. Watt's bath solution gave a coarse dull deposit between the current density range of 1 and 4A dm^{-2} at 1A cell current. To improve the nature of deposit, *Ananas comosus* juice was added to the solution. With the increase in the concentration, the nature of deposition was improved and became bright at a concentration of 64 mL of *Ananas comosus* juice. The hull cell panels were bright in the current density range of 1-3.5 A/dm^2. With further increase in the concentration of *Ananas comosus* juice became burnt at higher current density region. Thus, the concentration of *Ananas comosus* juice is kept at 64 mL as optimum.

Effect of nickel sulphate: The nickel sulphate concentration varied from 10-300 g L^{-1} keeping the amount of *Ananas comosus* juice fixed at 64 mL. At low current density region, dull and streaky deposits and at high current density range, burnt deposits were obtained. With increase in the concentration of nickel sulphate, the brightness range was extended to higher and lower current density regions. At a concentration of 112 g L^{-1}, a satisfactory bright deposit was obtained over a current density range of 0.5-3.0 A dm^{-2} was obtained. Above this concentration of nickel sulphate, no improvement in the nature of deposit was obtained. Hence, the concentration of nickel sulphate was fixed at 112 g L^{-1} as optimum.

Effect of nickel chloride: Nickel chloride was added to increase an anode dissolution and the conductance of bath solution. The concentration of nickel chloride varied from 2-70 g L^{-1}. At lower concentrations, the hull cell panels showed semi bright deposit at low current density region and burnt at high density region. The semi-bright and burnt regions were found to be reduced with the increase in the concentration of $NiCl_2$ at 20 g L^{-1} and the deposit was bright over a current density range of 1-3.5 A dm^{-2}. Further increase in the concentration did not introduce any effect on the nature of deposit and conductance. So, the concentration of nickel chloride was fixed at 20 g L^{-1} in the bath solution.

Effect of boric acid: Boric acid was added to produce smoother, more ductile deposits and increase the current density range of the bath solution. The concentration of boric acid varied from 1-40 g L^{-1}. At lower concentrations, the hull cell panels had shown dull deposit at low current density region and burnt at high current density region. The dull and burnt regions were found to be reduced with increase in the concentration of boric acid and at 32 g L^{-1}, the deposit was bright over a current density range of 1-3 A dm^{-2}. Further increase in the concentration did not introduce any effect on the nature of deposit and conductance. So the concentration of boric acid was fixed at 32 g L^{-1} in the bath solution.

Effect of pH: The pH of bath solution varied from 2-6. At pH 6, the Hull cell panels has shown burnt deposit at high current density region. Satisfactory deposit was obtained at pH 5, while at lower pH, the specimens had dull deposit at low current density region. Thus, the pH of bath solution was kept at 5 as optimum.

Effect of temperature: The plating experiments were carried out in the thermostat. The temperature of the thermostat varied from 293-323 K at room temperature, the deposition was bright in the current density range 1-3 A dm^{-2} at 1 A cell current. Above 303 K, the deposit was dull in low current density range. Therefore, the optimum temperature range was 303 K.

Optimized bath: By varying the components in basic bath in the above conditions made an optimized bath. This optimized bath contained 64 mL of *Ananas comosus* juice. The bath composition and operating conditions are shown in Table-1.

Effect of current density on current efficiency: Current efficiency of nickel electrodeposited carbon steel obtained from Watt's bath and optimized bath with *Ananas comosus* juice were measured at various current densities. At lower current density (1 A dm^{-2}), the current efficiency of nickel electrodeposited carbon steel obtained from Watt's bath and optimized bath with *Ananas comosus* juice were found to be 65 and 92 %, respectively. The current density ranges from 1-4 A dm^{-2}, the efficiency was found to be increased and reached the maximum at 4 A dm^{-2}. The efficiency obtained were 75 and 99 %, respectively. Further increase in the current density, decreased the current efficiency (Table-2) as a result of hydrogen evolution. The increase in current efficiency in the current density range of 1-4 A dm^{-2} confirmed the influence of additive *Ananas comosus* juice. There was no hydrogen evolution in the current density range from 1-4 A dm^{-2} in the presence of additive. There was a major difference in the efficiency of Watt's bath and the optimized bath, but in both the current efficiency was increased and then decreased.

TABLE-1
ORIGINAL AND OPTIMIZED WATTS BATH COMPOSITION AND OPERATING CONDITIONS FOR NICKEL ELECTRODEPOSITION

Bath composition	Concentration (g L^{-1})		Operating conditions	
	Original	Optimized	Original	Optimized
Nickel sulphate	300	112	Temperature: 30 °C	Anode: Nickel metal (99.99 % pure)
Nickel chloride	60	20	Anode: nickel metal (99.99 % pure)	Cathode: carbon steel
Boric acid	40	32	Cathode: carbon steel	Time: 10 min
pH	4-5	5	Time: 10 min	Plating time: 20 min
Ananas comosus juice	–	64 m L^{-1}		Bright current density range: 0-3 Adm^{-2}

TABLE-2
EFFECT OF CURRENT DENSITY ON CURRENT EFFICIENCY DURING NICKEL ELECTRODEPOSITION ON CARBON STEEL

Current density (A/dm^2)	Current efficiency (%)	
	Watts bath	Optimized bath + ananas
1	65	92
2	69	95
3	73	96
4	75	99
5	68	94

Polarization studies: The potential of carbon steel cathode was measured galvanostatically with respect to saturated calomel electrode. The variation of potential in Watt's bath and optimized bath with *Ananas comosus* juice is shown in Fig. 1. The shift in the cathode potential towards negative direction was observed for nickel electrodeposited carbon steel obtained from Watt's bath and optimized bath with *Ananas comosus* juice. This showed the effect of *Ananas comosus* juice on nickel electrodeposition.

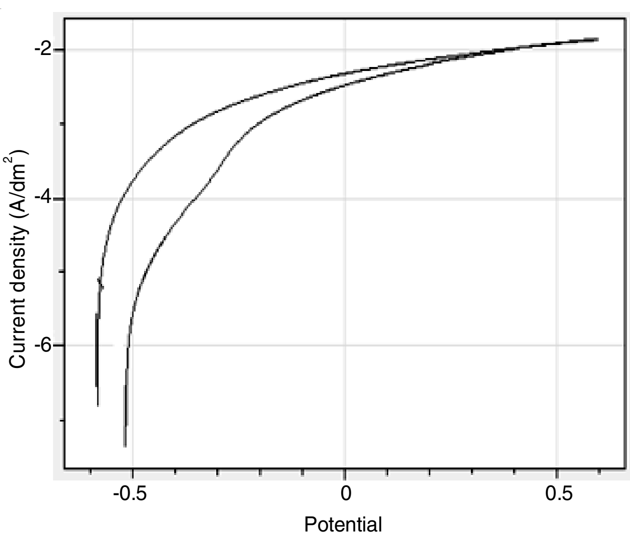

Fig. 1. Effect of additive on cathodic polarization during nickel eletrodeposition

SEM analysis: The surface morphology of metal specimen of Watt's bath and optimized bath in the presence of aqueous *Ananas comosus* juice were obtained by scanning electron microscopy. The SEM images of Watt's bath and optimized bath are shown in Fig. 2. The micro-cracks and tearing debris are clearly visible on the SEM image obtained from the Watt's bath. The surface of plated metal appeared to be smoother without any cracks. This was due to the effect of *Ananas comosus* juice on nickel electrodeposition. The incorporation of juice enhanced the appearance of metal and also prevented from the micro-cracks.

EDAX analysis: EDAX spectrum of nickel electrodeposited carbon steel from Watt's bath showed the presence of nickel, iron and carbon on the metal surface. The weight percentages of nickel, iron and carbon in nickel electrodeposited carbon steel from Watt's bath were found to be 80, 14.78 and 5.22 %, respectively. But in nickel electrodeposited carbon steel from optimized bath had 91.13 % of nickel and 2.51 % of oxygen. There was no iron on the metal surface, which showed the presence of additive and no open pores was present. This led to the conclusion that the deposition was uniform in the presence of additive. The inclusion of additive was also confirmed by the presence of oxygen with 2.51 % and the amount of carbon which was increased to 6.36 % (Fig. 3).

FT-IR analysis: The FT-IR spectrum of nickel electrodeposition is obtained in the range of 4500-500 cm^{-1}. The FT-IR spectrum of pure *Ananas comosus* juice is given in Fig. 4a. The peaks at 3321, 1635 and 1454 cm^{-1} correspond to the O-H *str.*, C=O *str.* and CH *bend.* frequencies. This confirmed the presence of major compound 2-hydroxymethyl furfural. The relative abundance of 2-hydroxymethyl furfural was 100 %. The FT-IR spectrum of scrapped deposit obtained from the optimized bath is shown Fig. 4b. It was observed that C=O stretching frequency in the free state had shifted from 1643-1635 cm^{-1}. The C-C stretching was found in the range of 2358 and 2121 cm^{-1}. The O-H stretching was also shifted from 3736-3321 cm^{-1}. The peak at 1454 cm^{-1} related to aliphatic C-H

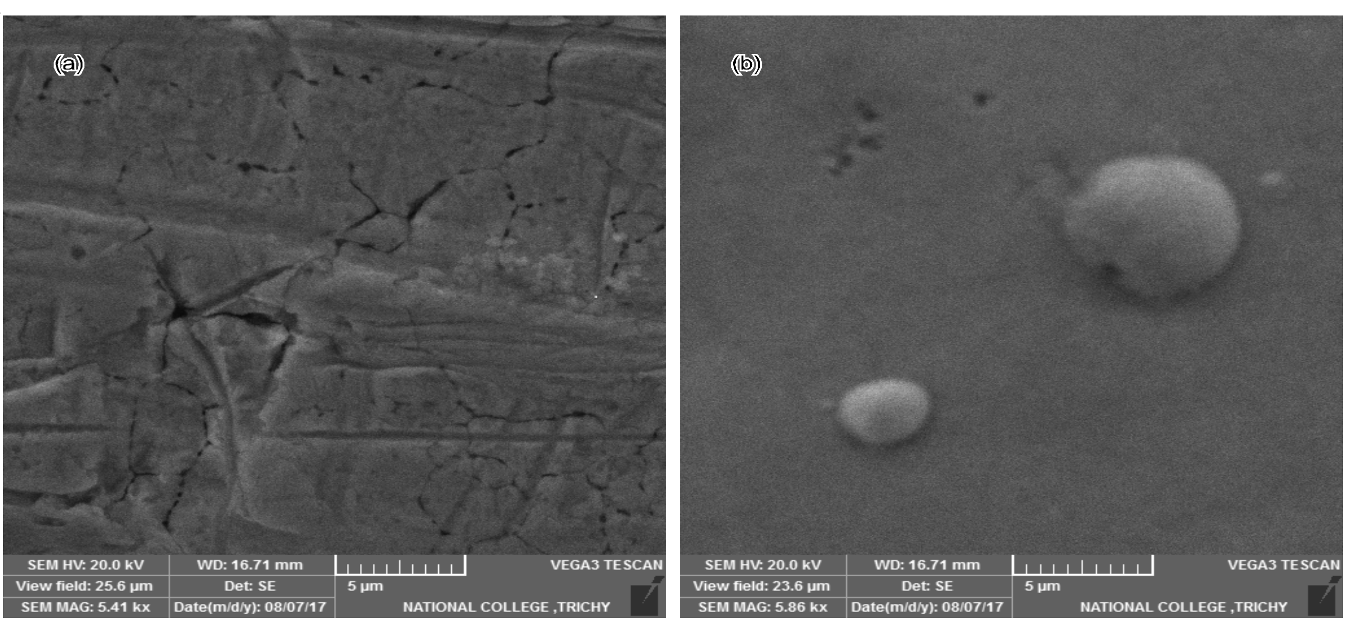

Fig. 2. SEM images obtained for nickel electrodeposition from watts bath (a) and nickel electrodeposition from (b)

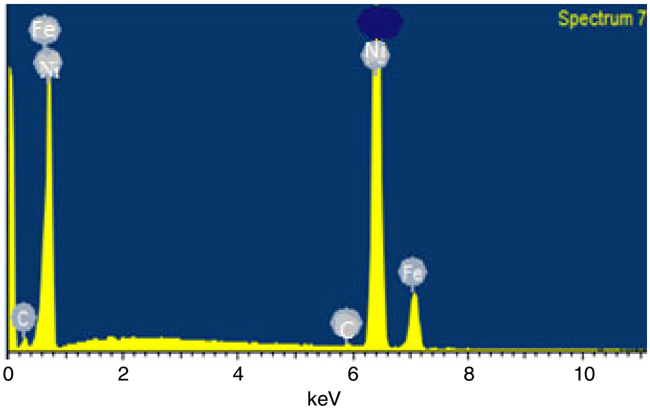

Fig. 3. EDAX image obtained for nickel electrodeposition from optimized bath

bending was shifted to the range of 1510 cm^{-1}. These observations showed that the major component was coordinated with Ni^{2+} during electrodeposition.

X-Ray diffraction studies: X-ray diffraction studies carried out on thin film of nickel electroplated carbon steel obtained from Watt's bath and optimized bath are shown in Fig. 5. Intensity of peaks of nickel electrodeposited carbon steel from optimized bath was lower and the peak width was broader than that of nickel electrodeposited carbon steel obtained from Watt's bath. The average crystal size was found to be 7.95 nm against 36 nm of nickel electrodeposited carbon steel obtained from Watt's bath. The size was calculated by using Scherrer equation.

$$d = \frac{B\lambda}{\beta \cos\theta}$$

where d is the average crystallite size of phase under investigation, B is the Scherrer constant (0.89), λ is the wavelength of X-ray beam used, β is the full-width half maximum (FWHM) of diffraction and θ is the Bragg's angle. The incorporation of *Ananas comosus* juice influences the growth of nickel crystal such that it brought about a reduction in the crystal size. The juice which was incorporated in the deposit acted as protrusion in a metal electrolyte interface resulting in a higher current density which increased the rate of nucleation and inhibited the growth of nickel crystal and finally gave fine grained deposits.

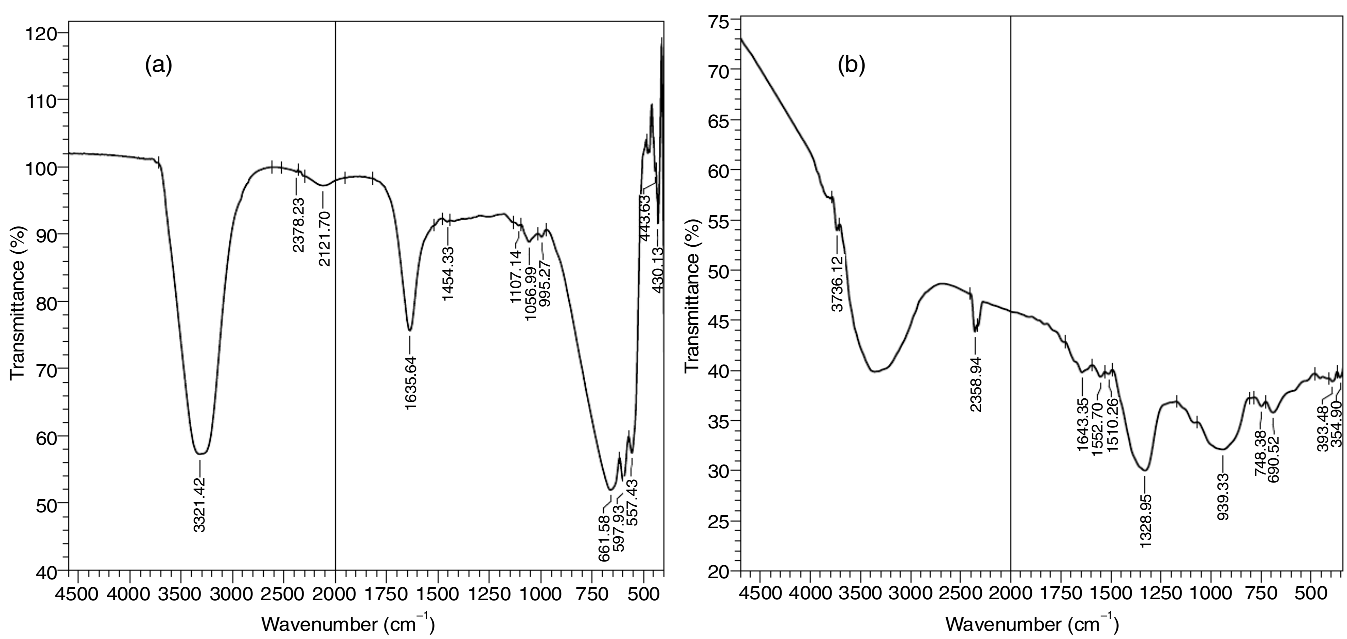

Fig. 4. FTIR spectrum of *Ananas comosus* juice (a) and scrapped deposit obtained from optimized bath (b)

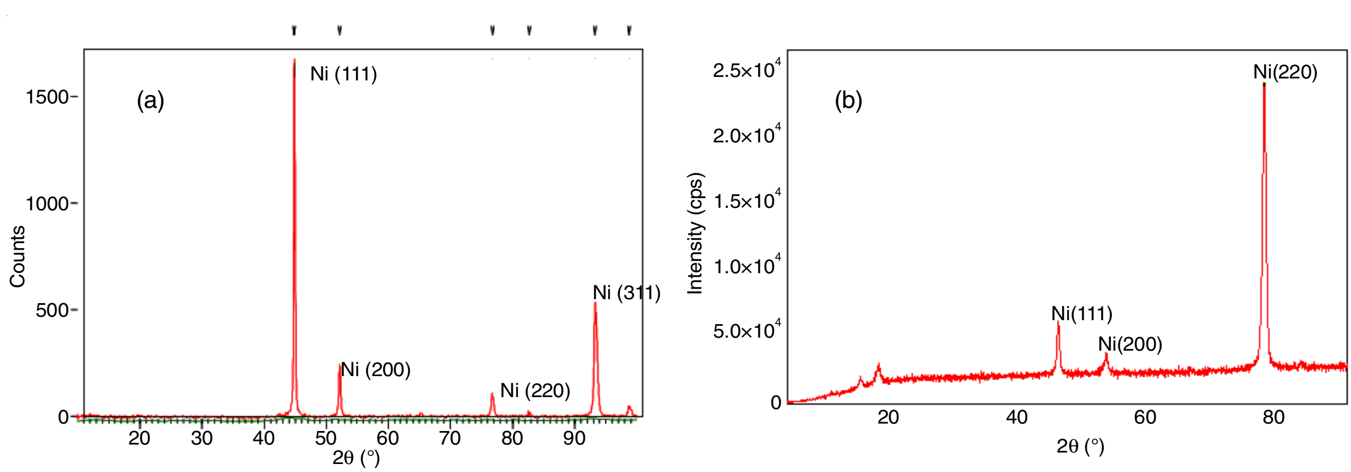

Fig. 5. XRD patterns obtained for nickel electrodeposition from watts bath (a) and optimized bath (b)

Some of the compounds present in *Ananas comosus* juice are tentatively identified by using the GC-MS spectrum (Fig. 6). The compounds identified in *Ananas comosus* juice with their peak are given in Table-3. The relative abundance peak found at 12.69 was a base peak, which corresponds to furfural.

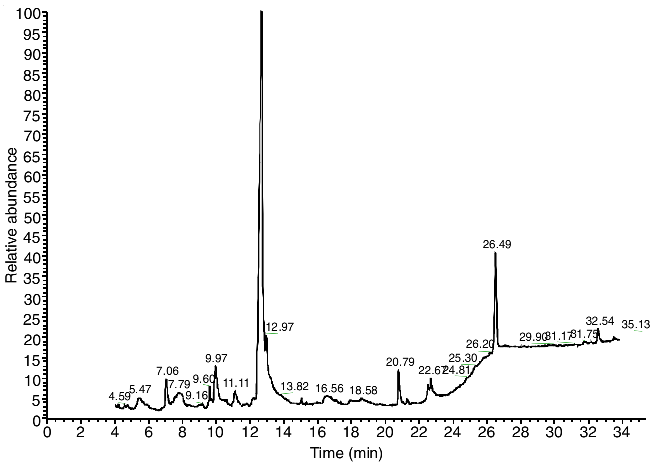

Fig. 6. GC-MS spectrum of *Ananas comosus* juice

TABLE-3
COMPOUNDS PRESENT IN THE ANANAS JUICE WITH THEIR PEAK

Peak	Compounds
9.97	2,5-Furandicarboxaldehyde (m.f. $C_6H_4O_3$, m.w. 124)
12.69	5-Hydroxymethyl furfural (m.f. $C_6H_6O_3$, m.w. 126)
20.79	N-isobutoxycarbonyl-c-aminobutyric acid pentyl ester (m.f. $C_{14}H_{27}NO_4$, m.w. 273)
26.49	4',5'-Dihydro-4'-(1-pyrrolidinyl)-cholestano[2,3-d]cinnoline-3',6'-dicarboxylic acid dimethyl ester (m.f. $C_{37}H_{59}N_3O_4$, m.w. 609)
7.06	4-Amino-2-chlorobenzonitrile (m.f. $C_7H_5N_2Cl$, m.w. 152)

Hardness of nickel electrodeposited carbon steel: Hardness is a measure of resistance power of solid matter, when a compressive force is applied. Hardness of the deposit obtained from Watt's bath and optimized bath at various current density is given in Table-4. The hardness of optimized bath was increased when compared with the Watt's bath. The increase in the hardness of optimized bath showed the influence of *Ananas comosus* juice on the deposit.

TABLE-4
HARDNESS OF THE NICKEL ELECTRODEPOSITED FROM WATTS BATH AND OPTIMIZED BATH AT VARIOUS CURRENT DENSITIES

Current density (A/dm^2)	Watts bath (Hv)	Optimized bath (Hv)
1	70.5	181
2	102	239
3	113	251
4	144	305
5	163	312

Conclusion

The nickel deposits on carbon steel obtained from this optimized bath showed better characteristic properties than the nickel deposits obtained from Watt's bath. This confirms the influence of *Ananas comosus* juice on electrodeposition of nickel. The current efficiency of nickel electrodeposited carbon steel obtained from optimized bath is found to be increased than in the case of nickel deposits on carbon steel obtained from Watt's bath. XRD spectra revealed that the reduction in the parti-cle size of nickel electrodeposit on carbon steel obtained from optimized bath than the Watt's bath. EDAX and FTIR analyses revealed that the inclusion of *Ananas comosus* juice on nickel electroplated carbon steel was obtained from optimized bath. Polarization studies reveals that nickel deposits obtained from the optimized bath on carbon steel function as mixed inhibitor controlling both anodic and cathodic processes.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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