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ABSTRACT

Electroplating of Zinc-Nickel alloy on mild steel substrate was obtained in the presence of a new brightener on steel surface by electrodeposition technique. Effect of bath constituents, pH, current density, and temperature on the nature of deposit was studied by Hull cell experiments. The bath composition and operating parameters were optimized by Hull cell experiments. Further investigations on the surface characteristics of deposit were carried out by using SEM and Reflectance studies. SEM analysis in the presence of this brightener confirmed the change in surface morphology and reflectance studies showed the formation of the bright coating. Corrosion studies were done using Tafel polarization and Electrochemical Impedance technique. Inclusion of brightener in the zinc-nickel alloy coating was confirmed by FTIR technique. The properties like brightness and corrosion resistance of Zinc-Nickel alloy deposit improved in the presence of new brightener.

Keywords: Brightener, Electrodeposition, Zinc-Nickel, Impedance, Tafel polarization.

1. INTRODUCTION :

Electroplated thick zinc coatings were used for many years to give protection for metallic parts economically, whereas nowadays the traditional zinc coatings are replaced by its alloys due to its ineffectiveness in aggressive or high temperature environments towards corrosion [1]. The alloys of zinc with nobler Fe group metals (Ni, Co, Fe, etc.) can give better protection efficacy than pure zinc coatings [2-7]. Zn-Ni coatings are widely accepted as an eco-friendly alternative to toxic coatings such as cadmium [1, 8-9]. From the literature available it is evident that zinc-nickel alloy is the most commonly exploited alloy in the commercial applications [10]. Zn-Ni alloys obtained by electrodeposition process, with the amount of nickel varying in between 8% and 14% by weight, give corrosion protection five to six times superior to that obtained with pure zinc deposits [11]. Although nickel is more noble metal than zinc, the co-deposition of Zn-Ni is anomalous and a higher percentage of zinc is present in the final deposit [10-12].

The most desirable property such as corrosion resistance can be enhanced in the presence of organic additives called brighteners which are required in a minimal amount in the plating bath solution. These brighteners affect the electro-crystallisation process by getting adsorbed on the cathode surface [13]. This modifies the surface characteristics of coatings [14-16]. Organic additives called brighteners are gaining attention as they not only give an excellent decorative look but also enhance the corrosion resistance capability of the coating. They have functional groups which are electroactive. From the available literature, it is found that the condensation product of various aldehydes and amines was found to act as good brighteners due to the presence of electroactive groups [17-20].

2. METHODOLOGY :

Plating bath solutions were freshly prepared using analytical grade chemicals in distilled water. Standard Hull cell of 267 ml capacity was used to optimize the bath constituents and bath variables. Hull cell experiments were carried out without agitation [21]. The pH value of the plating bath solution was measured using a digital pH-meter and adjusted with 10% v/v H_2SO_4 or sodium bicarbonate solution.

Zinc plate of 99.99 % purity was used as anode and activated each time by immersing in 10% v/v HCl for 4-5 seconds, followed by washing with running water. Mild steel plates of standard Hull cell size were mechanically polished to obtain smooth surfaces. Scales and dust on steel plates were removed by dipping in 10% v/v HCl solution. After that the steel plates were washed with distilled water, dried and then used for the experiments. After the experiment was completed, the plate was removed from the solution and subjected to bright dip in 1% v/v HNO_3 solution for 3-5 seconds, followed by washing with water and then drying.

A new condensation product (VG) was produced from a minimum concentration of Vanillin and Glycine in the acetic acid medium under reflux condition for 3 hrs at 343K [21-23]. Thin layer chromatography technique was used to confirm the formation of the condensation products. Product obtained was diluted in a 100 ml standard flask with double distilled water and an exact volume of this solution was added in zinc-nickel plating bath. Bath containing VG was thoroughly mixed for one hour before conducting the electroplating process.

Corrosion behavior of Zn-Ni alloy coatings obtained from the plating bath in presence and the absence of (VG) were studied in 3.5 wt.% NaCl solution by galvanostatic polarization method and electrochemical impedance spectroscopic technique, using the electrochemical workstation (Instrument model CHI660D). A three-electrode assembly was used. The working electrode (WE), *i.e*. Zn-Ni coated mild steel plate was masked with a lacquer to expose 1 cm^2 area. A platinum foil was used as a counter electrode (CE) with saturated calomel as a reference electrode (RE). Polarization experiments were performed in the potential range between -0.9 V and -1.4 V at the scan rate of $0.01 Vs^{-1}$. Impedance spectra were measured with the perturbation signal amplitude of 0.005 V at frequencies between 100 kHz and 1 Hz.

Composition and surface morphology of the deposits were analyzed using SEM images. X-ray diffraction studies were used to find the preferred orientation of Zn-Ni alloy crystallites and phases present in the alloy deposit, both in the presence and absence of VG. X-ray Diffractometer with CuKα radiation was used to obtain XRD spectra. JCPDS powder diffraction file cards were used for phase identification.

Preferred orientation of the deposits was determined by Markesan's method, using the following equation for calculating the texture coefficient (T_c)

$$T_c = \frac{I(\mathrm{hkl})\sum I_o(\mathrm{hkl})}{\sum I(\mathrm{hkl})/I_o(\mathrm{hkl})} X\ 100 \quad (1)$$

Where I(hkl) is the peak intensity of Zn-Ni electrodeposit and $\sum I$ is the sum of the intensities of independent peaks. The index 'o' refers to the intensities for the standard Zn-Ni sample (JCPDS 10-0209). The orientation with the maximum texture coefficient value is the preferred orientation of the Zn-Ni alloy crystallites in the deposit [24]. Percentage reflection of the deposit was determined using ocean optics USB 4000 Spectrophotometer, referenced against a silver mirror. The reflectivity of silver mirror was set at 100 % and measurements were carried out at different surface points of the deposited sample.

3. RESULTS & DISCUSSION :

Electrodeposition process:

The bath constituents and operating conditions were optimized by Hull cell experiments to get a bright deposit over a wide current density range [25]. The plating bath composed of zinc sulphate, nickel sulphate, sodium sulphate, Cetyltrimethylammonium bromide (CTAB) and boric acid. Zinc sulphate and nickel sulphate were used as the main electrolytes, while sodium sulphate was used as an additional electrolyte, which increased conductivity of the plating bath solution. CTAB was used as a wetting agent, while boric acid was added to improve the morphology, brightness and adhesion of the deposited nickel. From the available literature, it has also been found that boric acid can act as a good catalyst by lowering the over-voltage, which prefers deposition of nickel instead of hydrogen evolution. Also, the literature revealed that boric acid plays an important role because it forms a complex, from which nickel can be discharged more easily [26].

3.1 Hull cell studies :

During the Hull cell experiments, a particular concentration of a constituent or parameter, at which a good bright deposit is obtained was fixed as the optimum concentration. Optimized concentration of brightener VG was found to be $60 mlL^{-1}$(Fig. 1b). Keeping the concentration of brightener constant (60ml), concentration of zinc sulphate was differed from 0.2 to 0.6 M (Fig.1c) and the optimized concentration was found to be 0.5M. Concentration of nickel sulphate was varied in range 0.01 to 0.3M and the optimized value was decided as 0.1M (Fig.1d). Similarly, Na_2SO_4 concentration was varied from 0.14 to 0.34M and optimized value was 0.26M (Fig.1e). The optimum concentration of boric acid was 0.26M (Fig. 1f) and CTAB was 0.01M (Fig.1g). Hull cell studies (Fig.1h) depicted the optimized pH value as 3.0 to get bright deposit. The optimized temperature was found to be 298K (Fig.1i).

Zinc-nickel electrodeposition was carried out for a fixed time of 10 minutes, at varying currents ranging from 1-3A, using optimized zinc-nickel plating bath. At 2A current, bright zinc-nickel coating was obtained in current density range of 1.0 - 8.0Adm^{-2}. At 3A current bright zinc-nickel coating was noticed in current density range of 1.5 - 6.5Adm^{-2} (Fig.1j). Patterns obtained in Hull cell experiments are depicted in Fig.1. Table 1 gives detailed information on an optimized zinc-nickel plating bath.

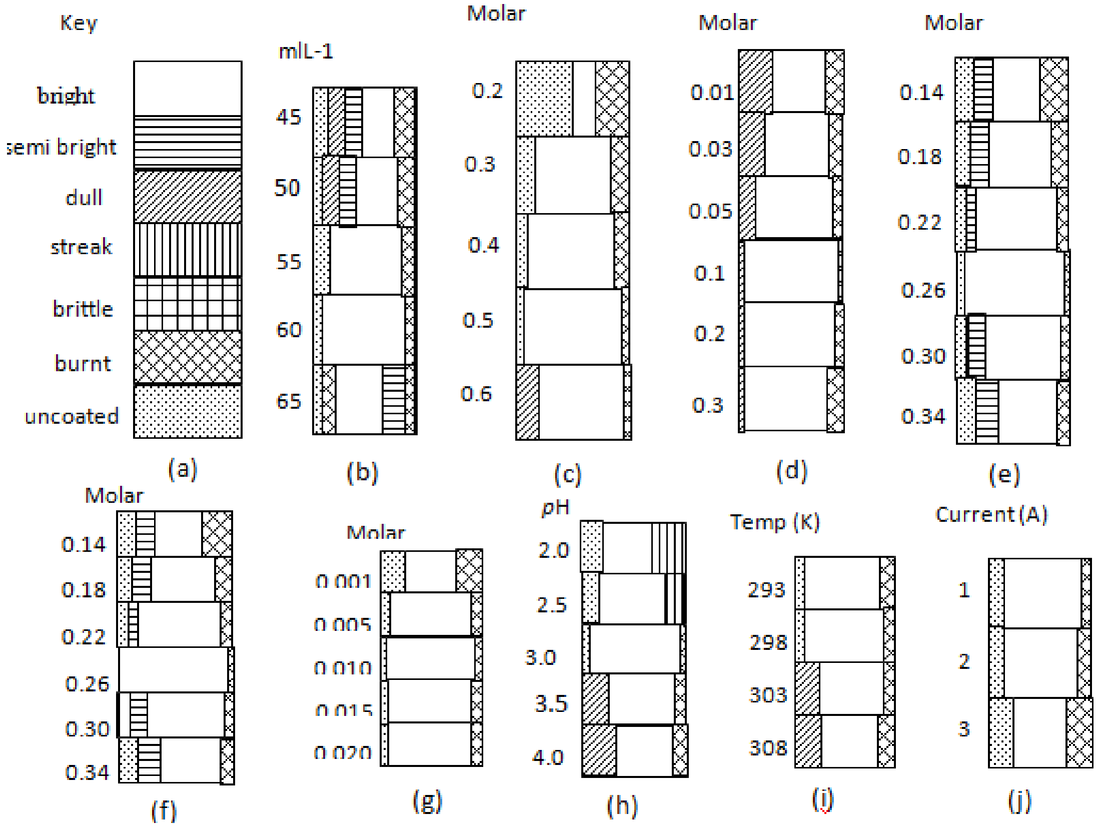

Fig. 1 : Hull cell result codes: (a) consolidated result codes; Influence of (b) Brightener (VG) (c) Zinc Sulphate (d) Nickel Sulphate (e) Sodium sulphate (f) Boric acid (g) Cetyl trimethyl ammonium bromide (CTAB) (h) *p*H (i) Temperature (j) Current.

Table 1: Optimized zinc-nickel plating bath composition and parameters

Bath components	**Molar Concentration**	**Operating parameters**
Zinc sulphate ($ZnSO_4.7H_2O$)	0.5M	Anode: Zinc plate (99.99%)
Nickel sulphate ($NiSO_4.6H_2O$)	0.1M	Cathode: Mild steel plate
Sodium sulphate (Na_2SO_4)	0.26M	Temperature : 298K
Boric acid (H_3BO_3)	0.26M	pH : 3.0
CTAB	0.01M	Bright Current Density : 1-8 Adm^{-2}
Brightener (VG)	60 mlL^{-1}	

3.2. Impedance and Polarization studies :

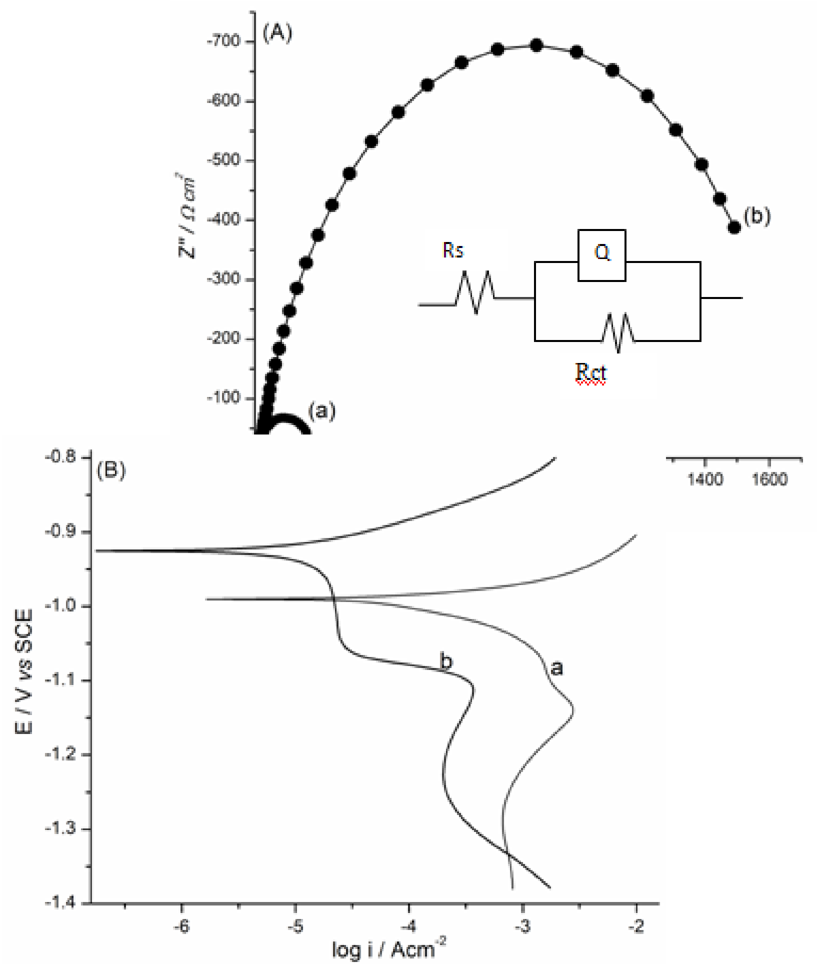

Fig. 2 : (A) Nyquist plot (B) polarization curves of zinc-nickel alloy coating in 3.5 weight % sodium chloride solutions. Zinc-nickel alloy coatings seen in (***a***) absence of VG and (***b***) presence of VG.

Impedance Spectroscopy and polarisation technique were used for corrosion resistance study. Fig. 2(A) shows the comparison of Nyquist impedance plot of dull and bright zinc-nickel alloy deposits. The value of charge transfer resistance for the dull and bright deposit was found to be 181 Ωcm^2 and 1664 Ωcm^2 respectively. This result reveals that bright zinc-nickel coating increases the corrosion resistance thereby reducing the corrosion rate of steel.

Fig. 2(B) shows Tafel curves where the I_{corr} value is found to be 0.9136mA/cm^2 for a dull deposit and 0.0265mA/cm^2 for bright deposit. The decrease in I_{corr} value, deposition potential (E_{corr}) value shifts in more noble direction and rate of corrosion is reduced. Results obtained infer that bright zinc-nickel coating is successful in acting as a good shielding layer for the base metal (steel) and also to enhance the corrosion resistance of the bright coating, making it more durable.

3.3 Current Efficiency and throwing power

Current efficiency and throwing power were measured at different current densities, by using an optimized zinc bath. Current efficiency was found to be 72% at 2.0 Adm^{-2}. It became 88% at 5.0 Adm^{-2} and above that, it was found to decrease.

Table 2: Current efficiency and throwing power at varying current densities.

Current density (Adm^{-2})	Current efficiency (%)	Throwing power (%)
2	72	21
3	78	23
4	85	28
5	88	30
6	80	20

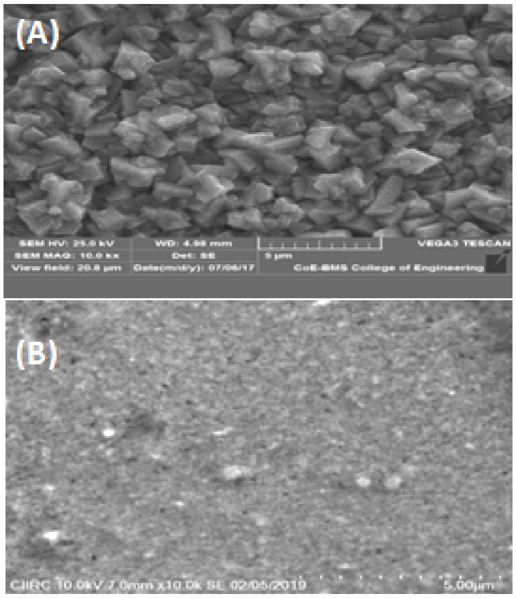

Fig. 3: SEM photomicrographs of zinc-nickel alloy electrodeposits at current density 4 Adm^{-2} noticed in(A) absence of VG and (B) presence of VG.

Throwing power is an important characteristic feature of a plating bath which determines its quality and efficiency. It was determined using Haring and Blum cells at different current densities. At 2 Adm^{-2}, the throwing power was 21%. At 5 Adm^{-2} it was found to be to 30 % (Table 2).

3.4 Adhesion and porosity measurements:

Coated mild steel plates obtained in the absence and presence of VG were bent from 90^0 to 180^0. No crack or removal of peel was noticed in a zinc-nickel deposit. This indicated good adherence and ductility of zinc-nickel deposits on mild steel.

3.5 SEM analysis and Reflectance studies:

SEM images depict irregular and coarse-grained zinc-nickel alloy deposit obtained in absence of VG (Fig. 3A). Addition of VG increases the formation of new nuclei by decreasing growth of nuclei and ensuring the formation of refined deposit of zinc-nickel crystallite grains (Fig. 3B). This results in the creation of smooth and bright deposit. Fig. 4 depicts the reflectance and degree of entire reflection in case of dull and bright zinc-nickel deposit. It is clearly visible from the reflectance spectra that inclusion of VG into plating bath results in enhancement of reflection. Only 4 -7 % of difference in reflectance was noticed at different points on the surface of zinc-nickel alloy coating [22]. These results confirmed that VG can be used as a brightening agent for zinc-nickel alloy coatings.

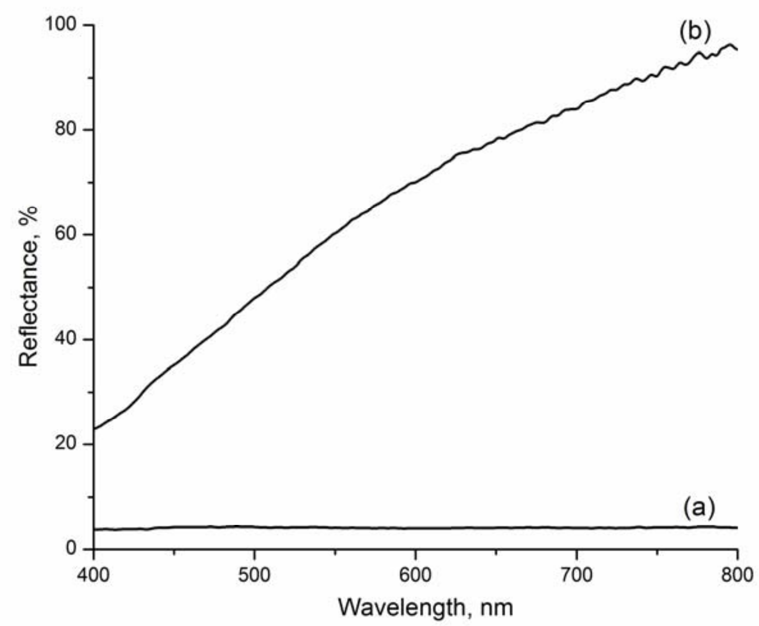

Fig. 4: Reflectance spectrum of zinc-nickel alloy electrodeposition at 4 A/dm^2 in (a) dull and (b) bright zinc-nickel alloy coating

3.6 X-ray diffraction Analysis :

This technique was utilized to know the presence of various phases of zinc and zinc-nickel alloy metal in zinc-nickel alloy coating. Also, texture coefficient was calculated to know the orientation of crystallites in absence and presence of VG in plating bath, its consequent influence on the structure of zinc-nickel alloy deposits.

XRD spectra observed in Fig. 5 shows the formation of lines corresponding to η-phase of zinc and γ-Ni_5Zn_{21} phase of zinc-nickel alloy. All the peaks obtained in the spectra correspond to zinc metal and also to zinc-nickel alloy indicating no impurity in the coatings. In bright zinc-nickel deposits, increase in intensity of γ-Ni_5Zn_{21} phase line was observed due to the increase in percentage of nickel.

Diffraction pattern also shows the broadening of X-ray diffraction peaks in bright zinc-nickel alloy deposit. Broadening of XRD peaks usually correspond to reduction in size of zinc-nickel crystallites in the deposit which is also supported by SEM result. The average size of zinc-nickel alloy crystallites in dull and bright zinc coating was calculated by using Scherer's equation. From the X-Ray Diffraction peaks obtained, average size of zinc –nickel crystallites was 107 nm in dull deposit whereas in bright deposit, it was found to be 47 nm. These results confirmed the formation of fine- grained deposit.

Texture coefficient calculations of bright deposits indicated (611) and (630) as the predominant preferred orientations (Fig. 6). Experimental results and calculations infer that some of the zinc-nickel alloy crystallites were oriented parallel to (611) plane and some of them were oriented parallel to (630) plane. Orientation in preferred direction arises because different faces of the crystal show different growth rates, because of adsorption of VG on cathode surface [14, 27]. Surface modifications like refinement in grain structure, smoothening and preferred orientation along (611) and (630) planes of zinc-nickel alloy deposit were accountable for bright appearance of the coating.

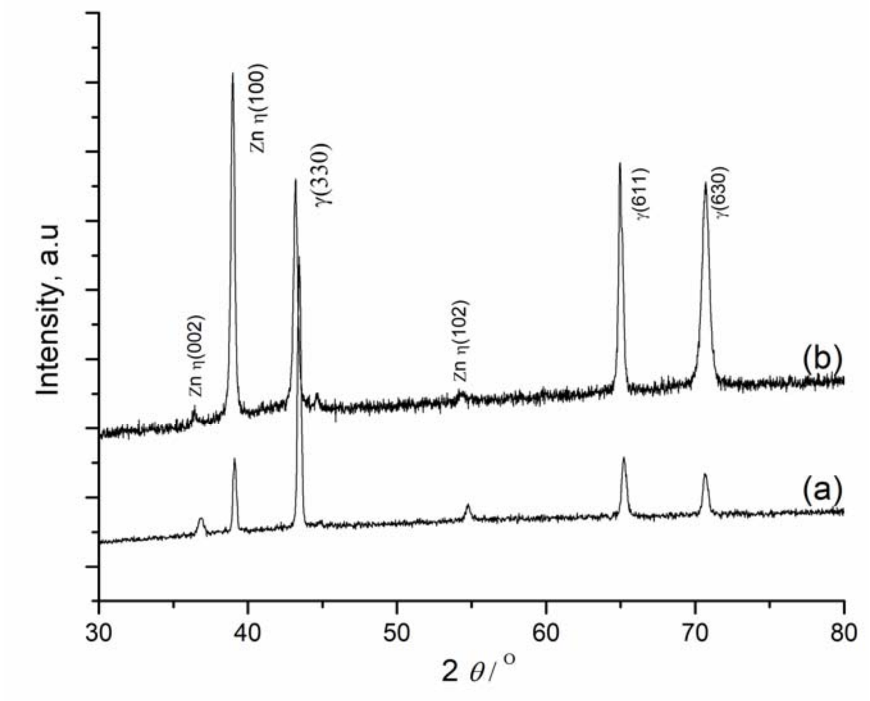

Fig. 5: X-Ray diffraction pattern of zinc-nickel electrodeposition observed in (a) dull and (b) bright deposits.

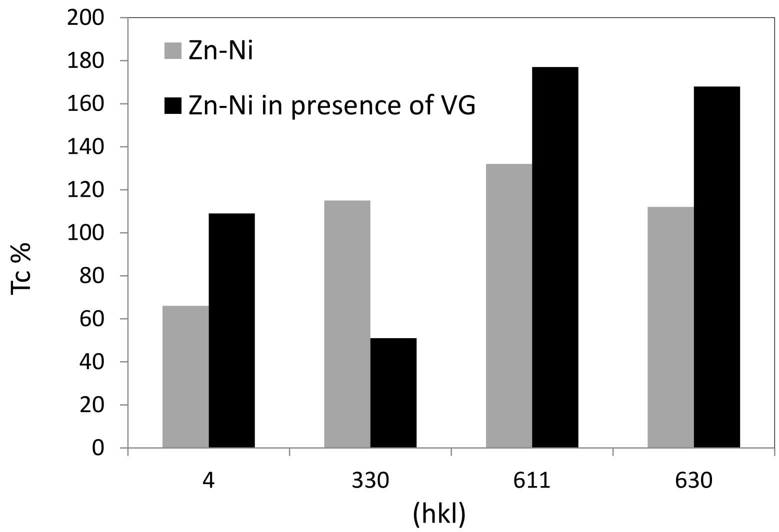

Fig. 6: Preferred orientations for zinc-nickel alloy deposits in absence and presence of VG

3.7 FTIR Analysis:

To test the presence of (VG) in bright zinc-nickel deposit, its IR spectrum obtained from optimized zinc-nickel bath was used (Fig. 6). Absorption peaks observed at 1522 cm^{-1} correspond to –C=N stretching of imines and 1709 cm^{-1} correspond to stretching of *C=C* and *N-H* bonds. Peaks observed at 3130 cm^{-1}, 3307 cm^{-1} and 3487 cm^{-1} corresponds to *N-H* bond with primary and secondary amines stretching. Absorption peaks revealed bonds present in brightener and its inclusion in bright zinc-nickel coatings on mild steel substrate.

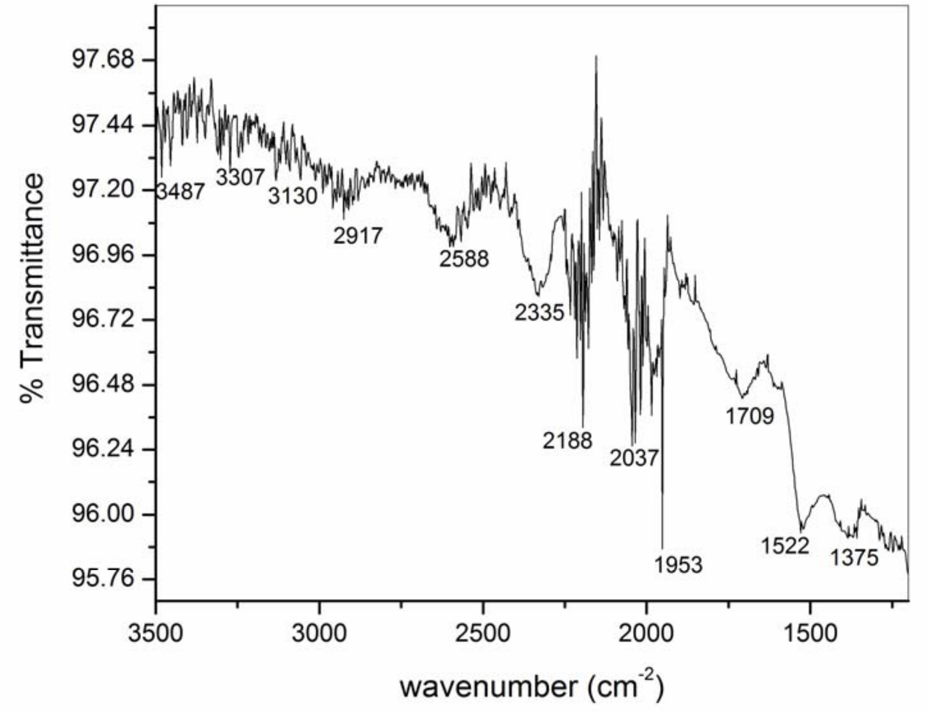

Fig. 7: IR spectrum of scraped bright zinc-nickel deposit

4. CONCLUSION :

Newly synthesized brightener (VG) was successful in giving even, refined and shining zinc-nickel alloy coatings. Corrosion studies done by Electrochemical Impedance spectroscopy and Tafel polarisation technique confirmed enhancement in corrosion resistance and shielding capacity of bright zinc-nickel coating, observed in the presence of newly synthesized brightener (VG). SEM, XRD and Reflectance analysis revealed enhancement of fine-grained nature of zinc-nickel alloy crystallites and brightness in zinc-nickel alloy deposit. XRD studies also depict the presence of η and γ-phases of pure zinc and zinc-nickel alloy in the deposits. The proposed studies indicate that the brightener (VG) may act as a good additive for bright zinc-nickel alloy deposition.

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