Studies On The Influence Of Accelerators In Electroless Plating Process

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Abstract: It is found on many occasions that the rate of electroless nickel plating (EN)   with hypophosphite as the reducing agent is below 20 µ/hr and so for a viable industrial process high speed electroless nickel plating is a subject of practical interest. Sulphur containing organic compounds are widely used as accelerators. Among them thiourea and its derivatives play a significant role and many of the compounds of this class still remain unexplored. Hence in the present investigation, focus is made on the role of accelerators, mainly thiourea and its derivatives in EN process. Also an attempt has been made to make use of concepts of mixed potential theory in electroless plating process. The results are presented and discussed.
Keywords: Electroless plating, Thiourea, Polarization.

Introduction

It is known that the additives have an important role in the plating process for they can act as accelerator – inhibitors, partial accelerators and accelerators only besides their complexing ability for the metal ion. Sulphur bearing organic compounds are some of the potential additives often tried in plating, battery electrolyte and pickling baths(1-8). From the detailed literature survey it is obvious that very few publications are available for derivatives of thiourea such as methyl, diphenyl, N,N'-Ethylene , p-tolyl and acetyl have been tried as a accelerators for EN plating (9-13). Hence there is good scope to study the structural aspects of these additives related to their performance as the accelerators. Also the mode of action of thiourea derivatives such as anodic and cathodic tafel polarization, Cyclic volatametric studies ,impedance measurements and hydrogen permeation studies have already been been reported as described earlier (14-16).

However it is interesting to note that whether the acceleration of additives of EN plating process follows chemical mechanism or electrochemical route.

Experimental Procedure

The following compounds of A.R grade were used as additives in the present study
1.Thiourea   – Merck (Germany).
2.Methyl thiourea - Fluka.A.G (Switzerland)
3.N,N' – Ethylenethiourea- Fluka.A.G (Switzerland)

The bath used in the present study had the following composition [14-16].

Nickel sulphate hexahydrate	0.1M
Sodium hypophosphite	0.2M
Glycolic acid	0.6M

Experiments were performed with various additives in the concentration ranges from 0.1 x 10-3mM – 10 x 10-3mM. Each experiment was repeated minimum

three times to get reproducible results. The rate of deposition was a calculated using the following formula.

Rate of deposition (μ hr^{-1}) = **W x 60 x 10^4 / DAt,** Where W = weight of the deposit (g) D = density of the deposit (g cm^{-3}); t = plating duration (min); A = surface area of the specimen (cm^2).Mild steel specimens of compositions, C = 0.08%, P = 0.07%, Si = O%, S = O%, Mn = 0.41% and Fe remainder, and of size 4 x 1 x 0.020 cm were used for weight gain measurements.

The polarisation studies were carried out using 1cm^2 area of electrolessly nickel coated specimens as the working electrodes. The measurement was made with BAS –100A, Electrochemical analyser. The auxiliary electrode and the reference electrode used were of platinum plate of 4cm^2 area and saturated calomel electrode respectively. A constant quantity of 200ml of bath solution was taken in a 250ml beaker. The bath temperature and pH were maintained at 88 ±1°C and 5.5±0.1°C. No agitation was provided. In order to understand the effectiveness of the mixed potential theory in clearing up the EN process .Tafel polarisation measurements were carried out both in the presence and absence of accelerators in the potential range of ±300mV from the OCP with all the bath ingredients under the plating condition.

Results and discussion

Weight gain studies
The results of electroless nickel deposition rates obtained in the present study by weight gain method are presented in tables 1-6. These tables also include the deposition rate of nickel obtained in the absence of the additives. It can be seen from these tables that thiourea and its derivatives are noted to alter the nickel deposition rate up to certain concentrations beyond which they inhibit the plating process. The effectiveness of these compounds in enhancing the rate of electroless nickel deposition is discussed compound wise below:

Thiourea (TU)
Thiourea (TU) has three possible coordination sites in which 'S' is the dominant coordination centre (1,2) in its reaction as inhibitor or accelerator. It can be seen from table 4.6 that the additions of thiourea in various concentrations ranging from 1.31 x 10^{-3} mM to 13.14 x10^{-3} mM influences the rate of deposition. The plating rate is increased up to a concentration of 5.26 x 10^{-3} mM and beyond that the deposition rate is decreased almost to zero value at 13.14 x10^{-3} mM. At an optimum concentration of 5.26 x 10^{-3} mM of TU, the highest rate of 23.63 μ/hr was observed.

Methyl thiourea (MeTU)
Table 2 gives the values of electroless nickel deposition rate in the presence of various concentrations of MeTU. It is seen from the table that the acceleration effect starts even at 0.55 x 10^{-3} mM of MeTU. Above this concentration, MeTU inhibits the deposition rate. The maximum plating rate of 32.8 μ/hr is achieved with even trace amounts of (1.11 x 10^{-3} mM) the compound. This is a most welcome feature of a good accelerator. Among different compounds used in the present work, MeTU is seen to give the highest deposition rate. The compound is classified as accelerator-inhibitor (3).

N,N' – Ethylenethiourea (N,N'–EtTU)
Table 3 indicates the influence of N,N'–EtTU on the rate of electroless nickel deposition. From the table it is clear that a maximum plating rate of 29.02 μ/hr is achievable with an optimum concentration of 2.94 x 10-3 mM. As in the earlier cases here also the plating rate is found to decrease with increase in concentration of the accelerator beyond the optimum concentration and the rate of decrease is found to be much pronounced. With 9.79 x 10-3 mM of the compound the rate is found to be almost nil. Hence this compound could also be grouped under accelerator – inhibitor(3).

Table 1 Effect of thiourea (TU) on rate of deposition pH 5.5 Ë0.1Temp. 88°C

Concentration of TU x10^{-3} mM	Rate of deposition (~/hr)
0	15.00
1.314	21.12
2.628	21.87
3.942	22.54
5.255	23.63
6.570	19.50
7.884	16.11
9.198	12.62
10.512	8.86
11.826	3.21
13.140	0.04

Table 2 Effect of methyl thiourea (MeTU) on rate of deposition pH 5.5 Ë0.1 Temp. 88°C

Concentration of MeTU x10⁻³ mM	Rate of deposition (~/hr)
0	15.00
0.55	24.38
1.11	32.80
2.22	28.72
3.33	24.31
4.44	19.12
5.55	18.20
6.66	13.77
7.77	9.75
8.87	9.46
9.98	6.63
11.09	3.12

Table 3 Effect of N,N'-ethylene thiourea (N,N'-EtTU) on rate of deposition pH 5.5 Ë0.1 emp. 88°C

Concentration of N,N'-EtTU x 10⁻³ mM	Rate of deposition (~/hr)
0	15.00
0.98	19.19
1.96	20.64
2.94	29.02
3.91	24.33
4.89	21.86
5.87	19.17
6.85	17.64
7.83	8.21
8.81	3.89
9.79	0.70

Tafel polarisation studies

Like the corrosion of a metal in an electrolyte, the electroless plating process could also be approached through the concept of mixed potential theory provided the reduction process is dominated by a charge transfer process. In EN the two partial reactions viz., the reduction of Ni^{2+} ion and the oxidation of $H_2PO_2^-$ take place simultaneously at the same rate on the metal surface at the mixed potential (E_{mp}). Such polarisation curves have been traced by following one of the methods (9,10).

(i)   by applying the steady state galvanostatic or potentiostatic pulse stimuli to the partial reactions separately,

(ii)   by applying potential scanning techniques using a rotating disc electrode.

The plating rate and E_{mp} are obtained from E Vs log i plot through the Tafel extrapolation method (11,12). This method suffers from the usual limitations associated with the theory of mixed potentials. For example, extrapolation of the polarisation curves for the decomposition of the reducing agent to the plating potential is not valid if the catalytic properties of the surface change with potential over the range of interest. It is also not valid if the rate determining step and hence the Tafel slope for any process changes in the potential range through which the polarisation curve is extrapolated. At the mixed potential-

$$i_{dep} = i_m = i_{red} \qquad (1)$$

Where i_{dep} = deposition current

i_m = Current for metal ion reduction

i_{red} = Current for the oxidation of the reducing agent

Using Faradays law, the nickel deposition current can be converted into equivalent plating rate [13] that is obtainable from the weight gain method.

Rate (mg/cm²/hr) or (~/hr) = 1.09 i_{dep} (mA/cm²)

The above mentioned bath with or without the presence of different concentrations of the accelerators was used for the polarisation measurements under the same conditions mentioned earlier. The results are presented in table 6.

From the results of the deposition current (i_{dep}) it is clear that the role of accelerators are not at all reflected. Further shift of the mixed potential (E_{mp}) is also not in a regular way. Hence this technique seems not to serve any useful purpose in the evaluation of the accelerators. Similar is the findings put forth by Mittal et al (13) in their studies with

electroless nickel plating in presence of sodium hypophosphite as the reducing agent. However with dimethylamineborane or a mixture of sodium hypophosphite and sodium borohydride as the reducing agent, they report the usefulness of the above technique and find good correlation between the rate of deposition obtained through this method with weight gain method. The reason cited is that in the case of sodium hypophosphite, the chemical mechanism dominating over the electrochemical mechanism. With Ni-P-B system, the very powerful reducing action of DMAB over hypophosphite has been quoted as the reason. It is also practically noted that the action of 1 gm of DMAB is equivalent to 11 gm of sodium hypophosphite. Thus it becomes confirmed that the Tafel polarisation technique in electroless nickel plating with sodium hypophosphite as a reducing agent may not be helpful in getting at the plating rate as the chemical mechanism predominates.

Table 4. Comparative account of all the accelerators obtained from weight gain studies

Name of the accelerators	Optimum concentration of accelerators x10^{-3} mM	Rate of deposition (~/hr)
No accelerator	---	15.00
MeTU	1.11	32.80
N,N'-EtTU	2.94	29.02
TU	5.26	23.63

Table 5. Tafel polarisation and weight gain results for the rate of electroless nickel plating in the presence and absence of accelerators

Accelerators and its concentration x 10^{-3} mM	E_{mp} (mV)	I_{dep} (mA)	Potentiostatic rate (~/hr)	Weight gain method (~/hr)
No accelerator	-495	1.25	1.36	15.00
MeTU				
0	-495	1.25	1.36	15.00
0.55	-520	0.79	0.86	24.38
1.11	-605	0.15	0.16	32.80
2.22	-415	0.32	0.35	28.72
N,N'-EtTU				
0	-495	1.25	1.365	15.00
0.98	-520	0.63	0.687	19.19
2.94	-710	2.82	3.074	29.02
4.894	-440	0.2	0.217	21.86
TU				
0	-495	1.25	1.35	15.00
2.63	-525	0.79	0.86	21.87
5.26	-615	0.32	0.34	23.63
6.57	-405	0.16	0.17	19.50

Table 6. Energy of activation calculated for the electroless nickel plating in the presence and absence of accelerators

S.No	Accelerator	Activation Energy (E_a) K.J.mol^{-1}
1	No accelerator	-59.16
2	MeTU	-79.56
3	N,N'-EtTU	-78.66
4	TU	-67.39

Application of adsorption isotherms

In the present study the values of fractional surface coverage (θ) were obtained using values of rates of deposition in the presence and absence of additives (r_o) from weight gain method.

The fractional surface coverage is written as

$$\theta = 1 - (r_o / r_t) \qquad (2)$$

Suppose that the adsorption of all the additives on the metal surface follows the Langumuir isotherm; then the fractional surface coverage is given by

$$\theta = KC_0 / 1 + KC_0 \qquad (3)$$

Where C_0 denotes the bulk concentrations of the additives and K is the adsorption constant. Equations 4.15 and 4.16 can be combined and rearranged to give.

$$(1 / r_t) = (1 / r_o) + (K / r_o) C_o \qquad (4)$$

The Langumuir isotherm was tested by plotting $1/r_t$ Vs C_0 for all the compounds. A straight-line relationship was obtained in all the cases thereby confirming that the adsorption process obeys Langumuir adsorption isotherm. The results are presented in figure 1 - 3.

Fig.1 Langumuir isotherm plot for EN process in the presence of different concentrations of TU
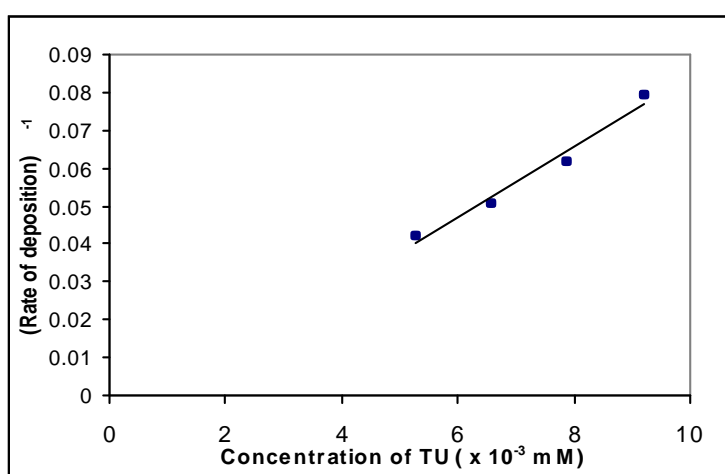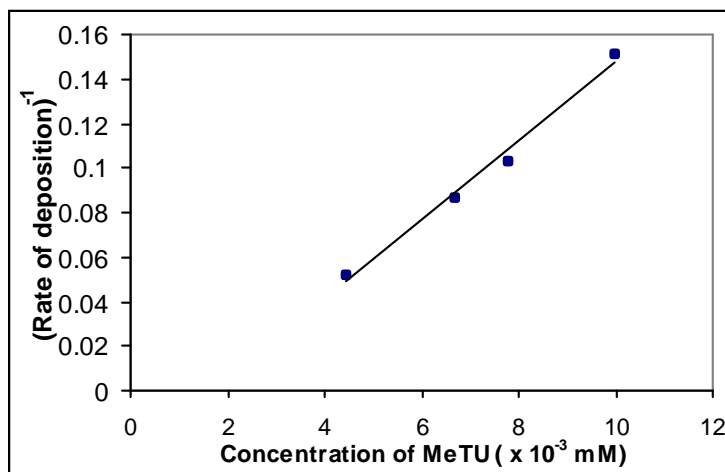

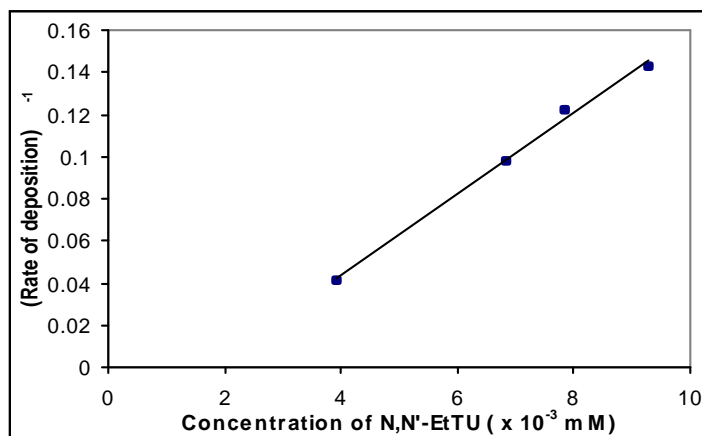**Fig.2 (a) Langumuir isotherm plot for EN process in the presence of different concentrations of MeTU**

Fig.3 Langumuir isotherm plot for EN process in the presence of different concentrations of N,N'-EtTU

Activation Energy

The relationship between the rate of reaction and temperature on electroless nickel plating can be expressed through the Arrhenius equation.

$$v = A e^{-Ea/RT} \qquad (5)$$

$$\log v = \log A - E_a / RT \qquad (6)$$

From the slope of the log v Vs 1 / T straight line plot, one can calculate the activation energy (E_a)

$$E_a = \text{Slope} \times 2.303 \times R \qquad (7)$$

Where R is the gas constant. Figures 4- 7, represent the Arrhenius plots for the EN process in the presence and absence of the accelerators at their optimum concentration. The values of E_a calculated from figures are presented in table 6. From the results it is evident that all the accelerators in trace quantities are able to bring down the activation energy of EN process compared to that in their absence. The order of performance with all the compounds is well reflected in their activation energy values.
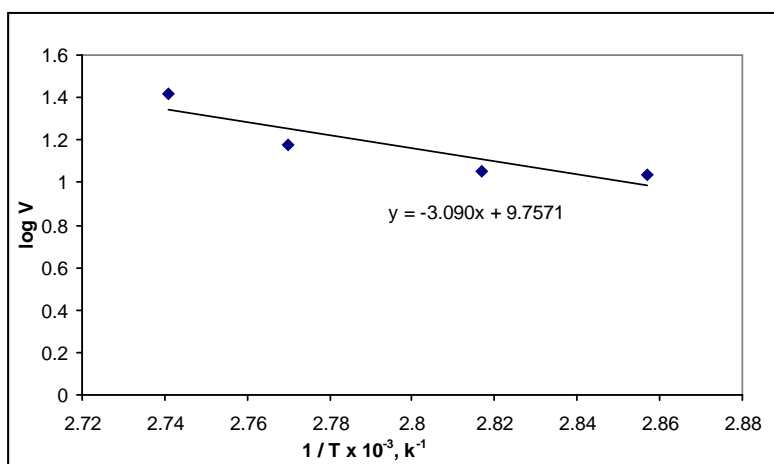

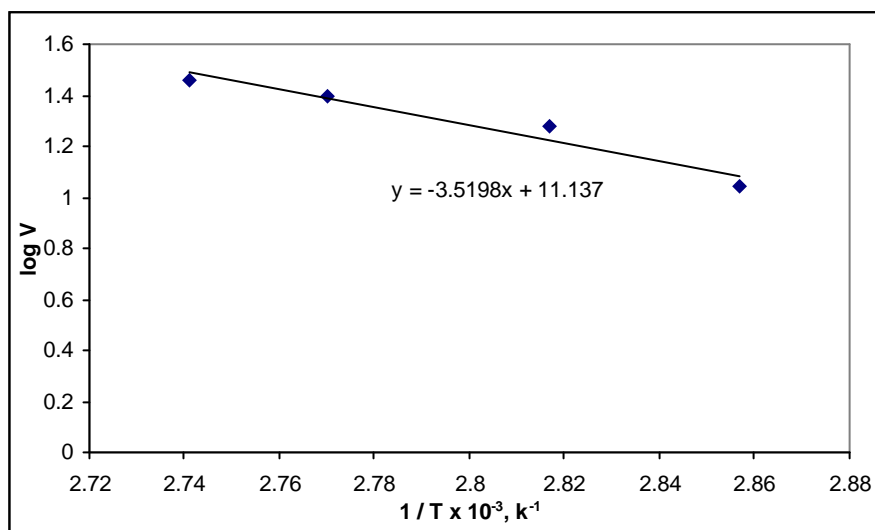**Fig. 4 log v Vs 1/T curves of EN in the absence of accelerators**

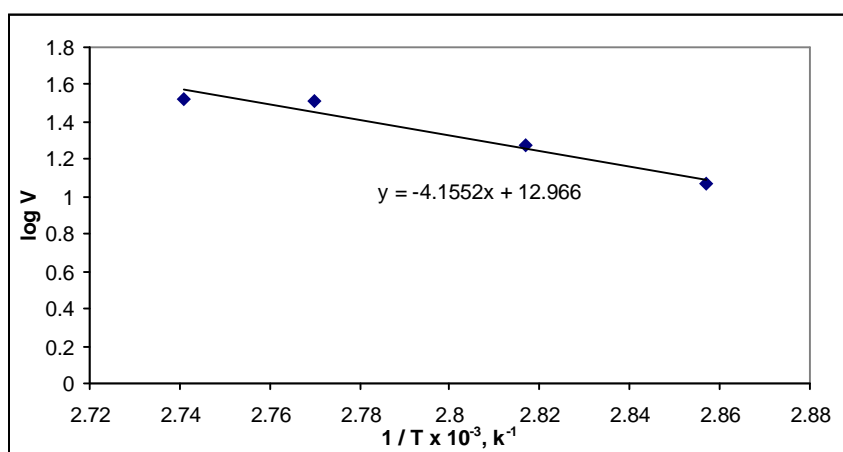**Fig. 5 log v Vs 1/T curves of EN with 5.26 x 10^{-3} mM of TU**

Fig. 6 log v Vs 1/T curves of EN with 1.11 x 10^{-3} mM of MeTU
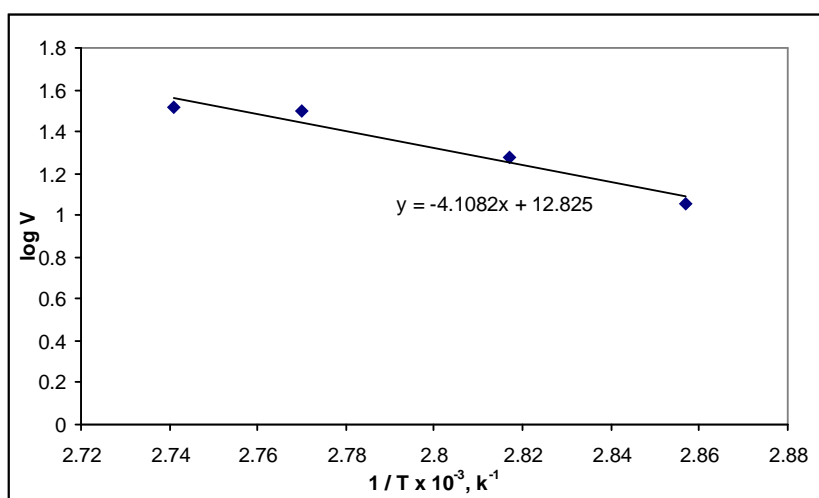

Fig. 7 log v Vs 1/T curves of EN with 2.94 x 10^{-3} mM of N,N'-EtTU

Mechanism and Model proposed for the acceleration effects

The electroless deposition of metals is based either on the electrochemical reduction process or on the chemical reduction or on the both to different extents. It is dependent on the nature of the reducing agent used in the EN bath. In the electrochemical reduction process, it is the combination of corrosion and two conjugate reactions (16) i.e. oxidation of the reducing agent and reduction of metal ions. This approach explains the vitality of the catalytic surface and the solution chemistry, which accounts for the difference in rates of deposition. However this approach does not explain the incorporation of the non-metals. In another approach the electroless deposition is considered as a chemical reduction process. Though this mechanism may not explain the electrochemical features such as the mixed potential theory, still it is very useful as it provides an understanding in the development of electroless nickel and its composites particularly.

The use of accelerators in electroless nickel bath of interest is mainly involved in the oxidation of $H_2PO_2^-$ ions directly and which in turn results in the enhanced indirect nickel ion reduction.

The performance of the compounds as accelerators is mainly controlled through their adsorption on the metal surface and hence results in the application of suitable adsorption isotherm. In the present case the adsorption of the compounds on the metal surface is found to obey the Langumuir adsorption and this leads to a decrease in activation energy values of the plating process.

Donelly et al (18) in their studies with the thio compounds predict, the adsorption to occur through the sulphur atom mainly even if nitrogen atom is also present in the molecule. Adsorption through sulphur atom can be predicted from the "Principle of Hard and Soft acids and bases"(19), the metal being the "soft acid" and the sulphur compounds are "soft bases". Soft pairs have the strong tendency to interact, which is evident from the general rule of acid-base interaction (20). The sulphur atom of the molecule being the most polarisable and lowest electronegative one can easily establish adsorption on the catalytic surface of the metal. In the tetrahedral hypophosphite ion, the higher electronegativity of oxygen atom causes the phosphorus to be positively charged. A reactive intermediate formation is envisaged through a chemical interaction between the $P^{\delta+}$ of the $H_2PO_2^-$ ion and $S^{\delta-}$ of the accelerator, which probably accounts for the weakening of the P-H bond in $H_2PO_2^-$.This results in the easy oxidation of the hypophosphite. The free radical formed through cleavage of P-H bond of $H_2PO_2^-$ combines with OH^- of the EN solution and produces the $H_2PO_3^-$ ions. The reduction in pH during EN is quite understandable with evolution of hydrogen. Further following the cleavage of P-H bond the electron on the P atom can be easily transmitted to the metal surface through the polar sulphur atom of the accelerator molecules and this accounts for the negative shift of the steady state potential (E_{mp}) of the metal in presence of the accelerator. This results in the catalytic activity of the metal surface to be enhanced for the accelerated metal ion reduction. Also $H_2PO_2^-$ ion can be further reduced elemental phosphorus which can be codeposited with nickel resulting in the formation of Ni-P alloy.

The XPS analysis carried out with electroless nickel deposition in the presence of thioglycolic acid and cysteine (8,16-17) as accelerators suggest the presence of trace amount of accelerator on the surface and S^{2-} in the inner layer of the deposit.

The performance grading of the different accelerators evaluated through different techniques such as weight gain and potentiodynamic polarisation are rated as follows:

METU > N,N'-EtTU > TU
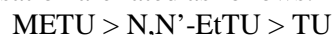
In the case of thiourea and its derivatives the best performance of METU is attributed to the +I effect of –CH3 group in the molecule in enhancing the reactivity of sulphur atom .However ,the closed ring structure of N,N'-EtTU has partly reduced the +I effect of the ethylene groups and hence its performance is next only to the METU and this accounts for its improved position compared to TU .

Conclusions

1. A new bath formulation that has stability over the wide range of pH based on nickel sulphate, sodium hypophosphite and glycolic acid has been formulated.
2. No correlation is found between the rates of deposition obtained from E_{mp} and weight gain studies suggesting that with hypophosphite as the reducer only chemical mechanism predominate.
3. The following is the order of performance among the accelerators used.
   MeTU > N,N'-EtTU > TU> .
4. The order of performance of accelerators is ascertained from the activation energy measurements.
5. Langmuir adsorption isotherm has been proposed to account for their adsorption behaviour.

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