



## Calculation of the Amount of Hydrogen Absorbed by Steel During the Mechanical Plating Operation

### Experimental

The polarisation resistance values obtained by Electrochemical Impedance Spectroscopy (EIS) in the initial report (mentioned above) were used to calculate the equivalent current density for hydrogen discharge. The average value of  $1677 \Omega/\text{cm}^2$  was used for Macuguard SA containing inhibitor and  $230 \Omega/\text{cm}^2$  was used for the uninhibited acid. In order to convert these values to current densities, a form of the Stern-Geary equation was used. The cathodic and anodic Tafel constants were determined by carrying out potentiodynamic scans on a 5% solution of the Macuguard with and without inhibitor using an EG&G potentiostat in conjunction with a silver/silver chloride reference electrode. The results of these scans are shown in figures 1 and 2. A Tafel fit was performed using CorrWare to calculate the values of  $\beta_a$  and  $\beta_c$ .

### Results and Discussion

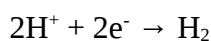
#### 1. Calculation

The potentiodynamic scans are shown in figure 1 (anodic branch) and 2 (cathodic branch). The effect of the inhibitors in the formulation can clearly be seen. Because the scale of the potentiodynamic scans is logarithmic, the difference between the uninhibited and inhibited values is almost an order of magnitude. The anodic and cathodic Tafel constants obtained from the data fitting and the resultant equivalent corrosion current densities are shown in table 1.

The anodic reaction is as follows:



The cathodic reaction is as follows:



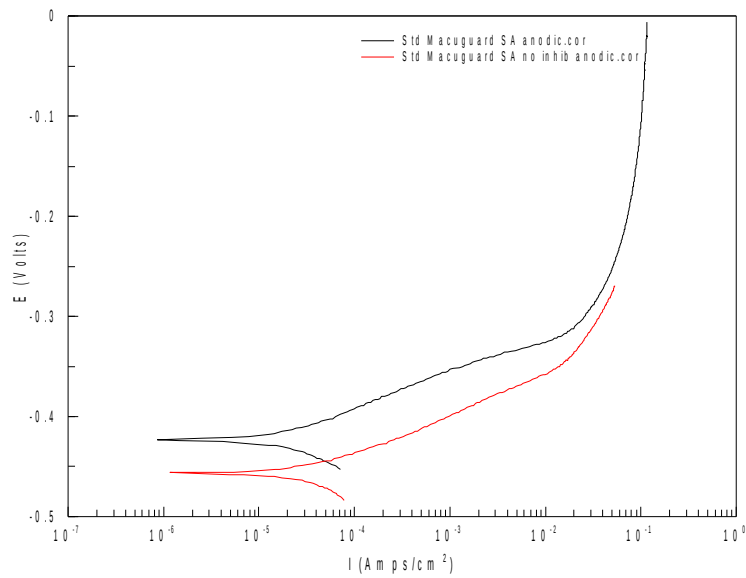
The cathodic reaction is written in the form of hydrogen liberation but it must be appreciated that absorbed atomic hydrogen could also be a product. However, this does not change the overall mass balance. The rate of dissolution of iron and production of hydrogen can be calculated by applying

Faraday's law to the corrosion current density.

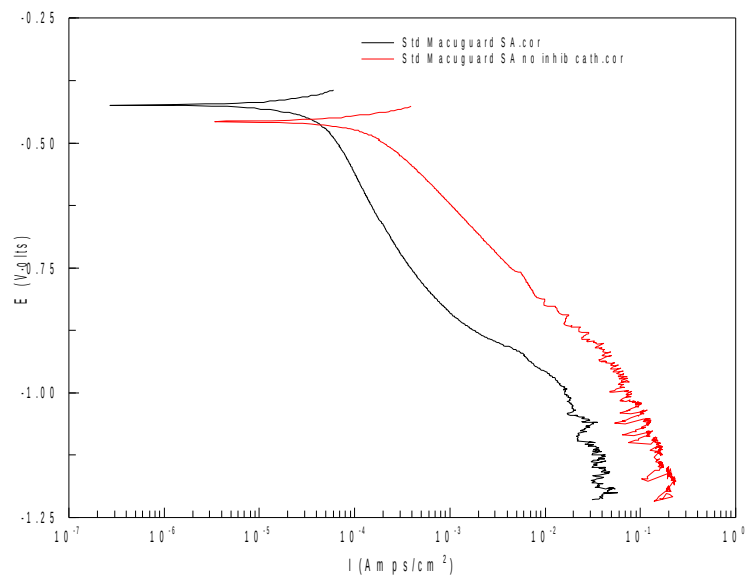
The corrosion current density can be calculated from the following equation:

$$i_{\text{corr}} = B/R_p \quad \text{Where } B = (\beta_a\beta_c)/2.3(\beta_a + \beta_c)$$

**Figure 1 Potentiodynamic Scan of Anodic Branch**



**Figure 2 Potentiodynamic scan of Cathodic Branch**



**Table 1 Tafel Coefficients and Corrosion Current Densities**

Type of Solution	$\beta_a$ (mV)	$\beta_c$ (mV)	B (mV)	$R_p$ ( $\Omega/\text{cm}^2$ )	$i_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ )
No Inhibitor	36.5	60.12	9.88	230	43
With Inhibitor	39.5	154.17	13.67	1677	8.1

Having calculated the corrosion current density, we now know the rate at which hydrogen is produced during the mechanical processing operation. If we assume a time of 30 minutes during which the Macuguard solution is in contact with the steel (this is longer than usual and also the 5% concentration that we tested the solution at is also somewhat more concentrated than would be used in practice), then we can calculate the total amount of hydrogen generated from the number of coulombs utilised in the corrosion reaction as follows:

Uninhibited acid:

$$\text{Number of Coulombs} = 4.3 \times 10^{-5} \times 1800 = 0.0774 \text{ C}$$

Inhibited acid:

$$\text{Number of Coulombs} = 8.1 \times 10^{-6} \times 1800 = 0.0146 \text{ C}$$

We can now calculate the amount of atomic hydrogen generated during the mechanical plating operation (in moles) by dividing the number of coulombs used to generate hydrogen by the Faraday constant (96500 C/equiv):

Moles of Hydrogen generated per square centimetre:

Uninhibited acid:

$$\text{Moles of atomic hydrogen}/\text{cm}^2 = 0.0774/96500 = 8.02 \times 10^{-7}$$

Inhibited acid:

$$\text{Moles of atomic hydrogen}/\text{cm}^2 = 0.01458/96500 = 1.51 \times 10^{-7}$$

If we assume that all of the hydrogen generated at the surface is absorbed into the substrate and none leaves as hydrogen gas (again a “worst case” scenario), and we further assume that the hydrogen diffuses to a depth of 1mm and no further (also a worst case scenario, in practice diffusion of hydrogen would continue), then we can calculate the maximum hydrogen concentration within that volume of steel. Lovicu et al<sup>(1)</sup> determined the diffusion coefficient for hydrogen permeation of steel as  $6 \times 10^{-7} \text{ cm}^2\text{s}^{-1}$  at ambient temperature and referenced other literature giving similar values. Applying Fick's second law of diffusion, we can state that:

$$C(x, t) = C_0 \left[ 1 - 2 \left( \frac{x}{2\sqrt{Dt\pi}} \right) \right]$$

Where :

$C(x, t)$  is the concentration at distance X from the surface at time t  
 $C_0$  is the concentration at the surface

D is the diffusion coefficient of the diffusing species

This assumes a constant concentration of hydrogen at  $C_0$  and this would not happen in practice, but it does give a useful estimation of the rate of diffusion. Applying the values of 6 hours for time (21600 seconds) and a distance of 1mm and a diffusion coefficient of  $6 \times 10^{-7} \text{ cm}^2\text{s}^{-1}$ , it can be determined that after 6 hours, the concentration of hydrogen at a distance of 1mm below the surface would be 99.7% of the concentration at the surface. This calculation gives a good degree of confidence that the first millimetre of steel would have an approximately homogeneous concentration of hydrogen after a storage time of 6 hours or longer, and agrees with the paper produced by Lovicu et al<sup>(1)</sup>. We can now calculate the hydrogen concentration in the first millimetre of steel as follows:

Volume of steel =  $0.1 \text{ cm}^3$  for every square centimetre of area.

Density of steel =  $7.873 \text{ g/cm}^3$

Weight of steel 1mm thick  $1\text{cm}^2$  area =  $0.7873 \text{ g}$

Atomic weight of iron =  $55.85 \text{ g/mol}$

Moles of iron =  $0.7873/55.85 = 0.0141$

Assuming that the hydrogen concentration in the first mm of steel is homogeneous and that all of the hydrogen has been absorbed in the first mm, we can now calculate the hydrogen concentration in atomic ppm and weight ppm:

Molar ratio of hydrogen to iron in uninhibited acid =  $8.02 \times 10^{-7} / 0.0141 = 5.69 \times 10^{-5}$

In terms of number of atoms, this is a concentration of 56.9 appm

In terms of weight ppm, it corresponds to a value of  $56.9/55.85 = 1.02 \text{ wppm}$

Molar ratio of hydrogen to iron in inhibited acid =  $1.51 \times 10^{-7} / 0.0141 = 1.07 \times 10^{-5}$

In terms of number of atoms, this is a concentration of 10.7 appm

In terms of weight ppm, it corresponds to a value of  $10.7/55.85 = 0.19 \text{ wppm}$

## 2. Discussion

The results of the calculation show that in a correctly functioning mechanical plating operation, the amount of hydrogen present in the top layer of steel after a 6 hour storage period would not be expected to exceed 0.2 ppm by weight of hydrogen taking the worst case scenario where no hydrogen escapes from the steel into the atmosphere. Lovicu et al<sup>(1)</sup> performed extensive testing on the effects of hydrogen embrittlement on high tensile steels and determined the critical concentration for hydrogen at which embrittlement commenced. The most susceptible steels to hydrogen embrittlement were hardened Martensitic steels. The critical hydrogen concentration was found to be 1 wppm for M1400 steel and 4 wppm for M1200 steel. Various steels were tested at a hydrogen concentration of 0.4 wppm and no hydrogen embrittlement was found in any of these instances, even with the hardest steels. They concluded that a concentration of 0.4 wppm or less of hydrogen was likely to be safe for any hardened steel. As the calculated value for the mechanical plating operation is well below this threshold, it is very unlikely that the mechanical plating operation would give rise to any hydrogen embrittlement unless the processed bolts were tensioned immediately after plating. The results show the importance of using the correct inhibitors during the mechanical plating operation.

## **Conclusions**

1. The maximum amount of hydrogen in the surface of steel substrates during mechanical plating was calculated to be 0.19 wppm using the Macuguard process and 1.02 wppm using uninhibited acid.
2. The maximum concentration of hydrogen when using the Macuguard process is below the safe threshold of 0.4 wppm suggested by Lovicu et al.
3. From the results of the calculation, it would not be expected that the mechanical plating process would cause hydrogen embrittlement issues.

## **References**

1. "Hydrogen Embrittlement of Automotive Advanced High Strength Steels" Lovicu et al. Metallurgical and Materials Transactions 43A November 2012 4075-4087

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