

# **Effect of Surface Processing Variables and Coating Characteristics on Hydrogen Embrittlement of Steel Fasteners**

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Coating processes applied to industrial fasteners were sampled and tested by incremental step load testing in accordance with ASTM F1940. The purpose was to rank the processes for the propensity to cause internal hydrogen embrittlement. The results showed that coating permeability has a first order effect, while the quantity of hydrogen introduced by the process has a second order effect. Pure zinc electroplating processes, alkaline and acid, were found to be the most embrittling, owing to the low permeability of zinc. The least embrittling processes were zinc-nickel, alkaline and acid, owing to the high permeability of Zn-Ni coatings. Non-electrolytic processes, namely phosphating, mechanical galvanising, Dacromet<sup>®</sup> and Magni 555<sup>®</sup> were found to be non-embrittling. Preliminary characterization of the coatings is underway to determine the parameters that influence permeability.

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## INTRODUCTION

The overall objective of this research is to quantify the risk of embrittlement caused by residual hydrogen from coating processes commonly utilised to coat high strength mechanical fasteners. More specifically, the effects of coating process variables and certain coating characteristics, such as thickness and permeability are investigated. The principal investigative technique used is incremental step loading (ISL) in accordance with test method ASTM F1940.<sup>1</sup> In brief, this approach consists of performing a mechanical test on standardised specimens that have been coated along with actual fasteners as “witness” samples. The test measures the fracture threshold by subjecting the specimen to an incrementally increasing loading sequence that allows for the time dependant nature of hydrogen embrittlement to evolve. Under standardised test conditions, the measured drop in fracture strength is a function of the amount of residual hydrogen introduced by the coating process.

This paper discusses the findings pertaining electroplating processes, and also to a number of non-electrolytic coating processes commonly used in the fastener industry. The processes are ranked by their propensity to cause internal hydrogen embrittlement (IHE), which in turn is a function of: (i) the amount of hydrogen they introduced into the test specimens, and (ii) the ability of each coating to act as a barrier to hydrogen absorption or effusion, also characterised as its hydrogen permeability.

## BACKGROUND

Hydrogen embrittlement (HE) causes permanent loss of ductility in a metal or alloy over a period of time.<sup>2</sup> In order for HE to occur, three elements must be present in sufficient quantities: (i) hydrogen, (ii) stress, and (iii) material susceptibility.<sup>3</sup> There are three possible sources of hydrogen: steelmaking, processing, and the service environment. There are also three sources of stress: applied stress, residual stress from plastic deformation (e.g., cold heading or welding), and residual stress from heat treatment. Hydrogen embrittlement is classified into two broad categories based on the source of hydrogen: internal hydrogen embrittlement (IHE) and environmental hydrogen embrittlement (EHE).<sup>4</sup> Internal hydrogen embrittlement, the topic of this study, is caused by residual hydrogen from steelmaking or from processing steps such as pickling and electroplating. The risk of IHE increases with material strength (e.g., high strength steel fasteners). The delayed nature of this type of hydrogen embrittlement suggests that it is controlled by the rate of diffusion of hydrogen or its entrapment within the matrix. Internal hydrogen embrittlement is usually reversible, meaning that ductility can be restored provided microcracks have not been initiated.<sup>2</sup> Restoration of ductility can be achieved by moderately heating the

material for a pre-defined number of hours (e.g., 200 °C for 4h). This process is commonly referred to as “baking.”

Many studies have found that electroplating is a high risk process with respect to IHE. Electrochemical reactions that occur in the process promote the adsorption and absorption of hydrogen. Hydrogen charging is most elevated before the build-up of the coating layer, which acts as a barrier that slows down hydrogen absorption, but can also trap hydrogen in the metal. Specific hydrogen charging conditions will vary with each plating bath, and the surface cleaning process applied before plating. Zinc, zinc alloys, nickel, chromium, and cadmium are the most common electroplated metals on fasteners. The requirements for electroplated coatings on fasteners are specified in ASTM F1941 and F1941M.<sup>5,6</sup>

## EXPERIMENTAL

The general methodology consisted of a series of sequential sampling events whereby the “witness” test specimens were coated with actual production parts in industrial coating processes. The coated specimens were tested in bending by the incremental step load method using the test protocol (i.e., load/strain increments and hold times) specified in ASTM F1940. The load at which the specimen fractures is known as its *notch fracture strength* (NFS).

“Pristine” (uncoated) test specimens were tested in the same manner to establish the baseline notch fracture strength. The ratio of the fracture strength for each witness over the baseline represents the *percent notch fracture strength* (NFS%). The NFS% ratio, when statistically validated, represents a measure of the embrittling potential of a coating process.

$$NFS\% = \frac{NFS_{(W)F1940}}{NFS_{(B)}} \times 100 \quad (1)$$

where:

NFS% = Percent notch fracture strength  
NFS<sub>(B)</sub> = Notch fracture strength of “pristine” specimen  
NFS<sub>(W)F1940</sub> = Notch fracture strength of coated “witness” specimen

The standard test specimens are designed to simulate conditions of extreme material susceptibility, or “worst case scenario.” Specimens used in this research were notched square bars, manufactured using 4340 steel, quench and

tempered to a hardness of 51 to 53 HRC, in accordance with ASTM F519 type 1e.<sup>7</sup>

The duration of each test cycle ranged from 8 to 20 hours and was dependent upon the degree of embrittlement of the specimen. The ASTM F1940 loading protocol is defined as follows: five one-hour steps at 10% increments of the baseline notch fracture strength, followed by four one-hour steps at 5% increments, followed by five one-hour steps at 2% increments, and finally six one-hour steps at 5% increments (i.e., [5 x 1h @ 10%] + [4 x 1h @ 5%] + [5 x 1h @ 2%] + [6 x 1h @ 5%]).<sup>1</sup>

The test equipment used for this investigation consisted of an RSL<sup>®</sup> loading frame, manufactured by Fracture Diagnostics Inc. An RSL<sup>®</sup> loading frame, shown in figure 1, is a computer-controlled four-point bend displacement control frame that is capable of holding a displacement within  $\pm 0.13 \mu\text{m}$  and reaching target loads within  $\pm 1.78 \text{ N}$  (0.4 lb). The load readings were generated by a calibrated load cell having a maximum capacity of 2.224 kN (500 lb). The tests were automatically halted at a 5% drop in load, which was taken to indicate the onset of cracking.

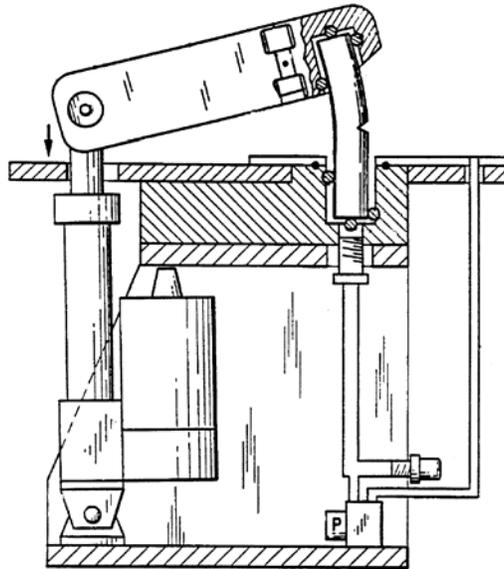


Figure 1 – Schematic of RSL<sup>®</sup> loading frame illustrating the bending motion being applied to a test specimen<sup>8</sup>

## RESULTS

The ISL test results are organised in the first order by *process codes* that are unique to each sampling event (e.g., P1). The process code identifies the sampling conditions and the process parameters at the time of sampling. In the second order, the results are organised in groups based on defined variable(s) that correspond to a specific theme of interest. The ISL test results are presented as bar charts summarising the data by process code (e.g., P1). As a rule, each coded condition comprised five test specimens. The individual bars show the average, standard deviation, and minimum/maximum values.

### Electroplating Processes

#### *Zinc – acid chloride*

Zinc acid chloride process data are divided into three groups. In Group 1, three conditions were sampled: (i) “full process” (P6) which included alkaline degreasing and pickling in hydrochloric acid at 13 wt% for 14 minutes, (ii) “no surface cleaning – not activated” (P2) which consisted of exposing the specimens only to the electroplating step, and (iii) “no surface cleaning – activated” (P1) which was the same as the previous condition, except that the specimen surfaces were activated manually in dilute hydrochloric acid for 30 seconds prior to electroplating. As expected, the “full process” resulted in the lowest NFS% average at 44.7%. This is explained by the fact that the specimens were exposed to hydrogen both from pickling and electroplating. The elimination of pickling in conditions P2 and P1 resulted in notable improvements, up to 49.1% and 64.2% respectively. It is interesting to note that surface activation resulted in the least amount of embrittlement. It is conceivable that surface activation leads to a more permeable coating morphology that offers hydrogen an easier escape path. (Fig. 2)

Group 2 consists of a repetition of the same conditions on the same plating line as Group 1, but several weeks later. These were the only sampling events where the effect of surface activation was tested. The average current density was 6.7 mA/cm<sup>2</sup> as compared to 8.5 mA/cm<sup>2</sup> for Group 1. This difference was due to the smaller size of production parts being plated. The trends in Group 1 are also observed in Group 2, where in addition, the lower current density seemed to result in decreased embrittlement of the specimens that were not pickled.

Group 3 consists of an attempt to assess the impact of baking time on embrittlement. Three conditions were sampled: (i) “full process without baking” (P1001) which included alkaline degreasing and pickling in hydrochloric acid at 13 wt% for 10 minutes, (ii) “full process followed by a 12 hour bake at 204 °C”

(P1002), and (iii) “full process followed by a 24 hour bake at 204 °C” (P1003). The current density for Group 5 was 8.2 mA/cm<sup>2</sup>. The first observation is that “full process without baking” (P1001) resulted in similar NFS<sub>%</sub> values (~44%) as in the previous groups. This seems to indicate that the zinc acid chloride process is generally a high risk process. The second observation is that the average NFS<sub>%</sub> value after 12 hours of baking had increased to 66.2%. The large data scatter for this condition (43 percentage points) can be explained by the fact that in this region, small changes in hydrogen concentration can result in large changes of NFS<sub>%</sub>.<sup>1</sup> Finally, the average NFS<sub>%</sub> value after 24 hours of baking had increased to 95%, meaning that ductility had been fully restored. This finding is encouraging as it validates the theory regarding the reversibility of IHE. On the other hand, full recovery required 24 hours of baking time, which is six times greater than the 4 hour baking time specified in most industry standards. It must be emphasised that these observations are limited to the acid chloride zinc plating process.

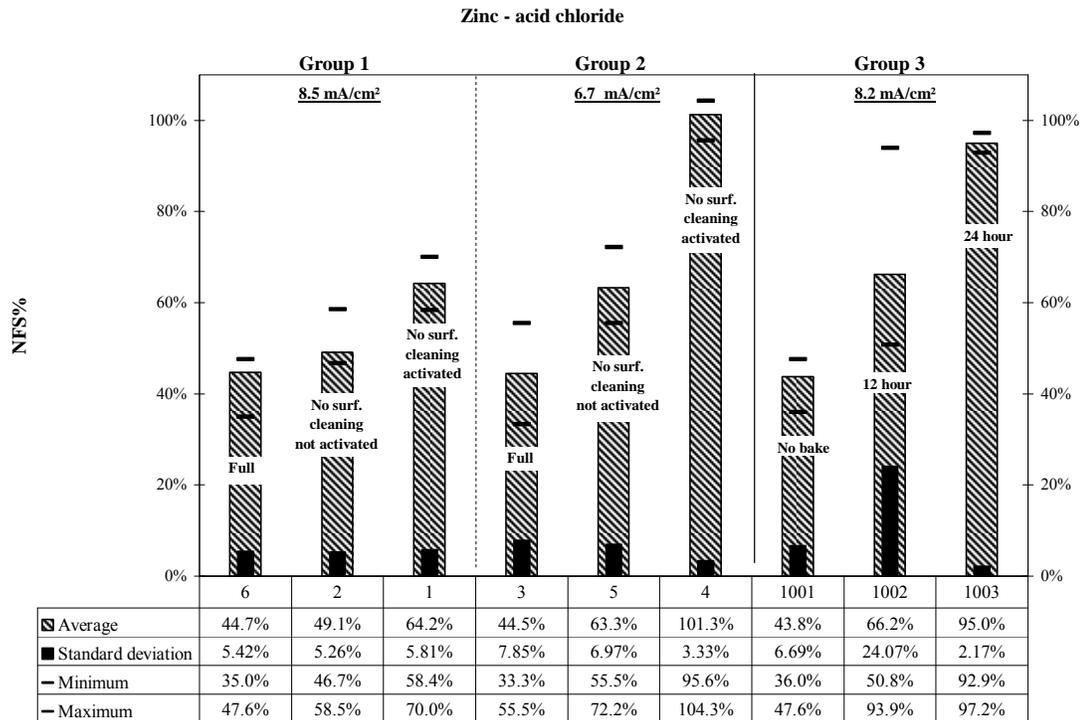
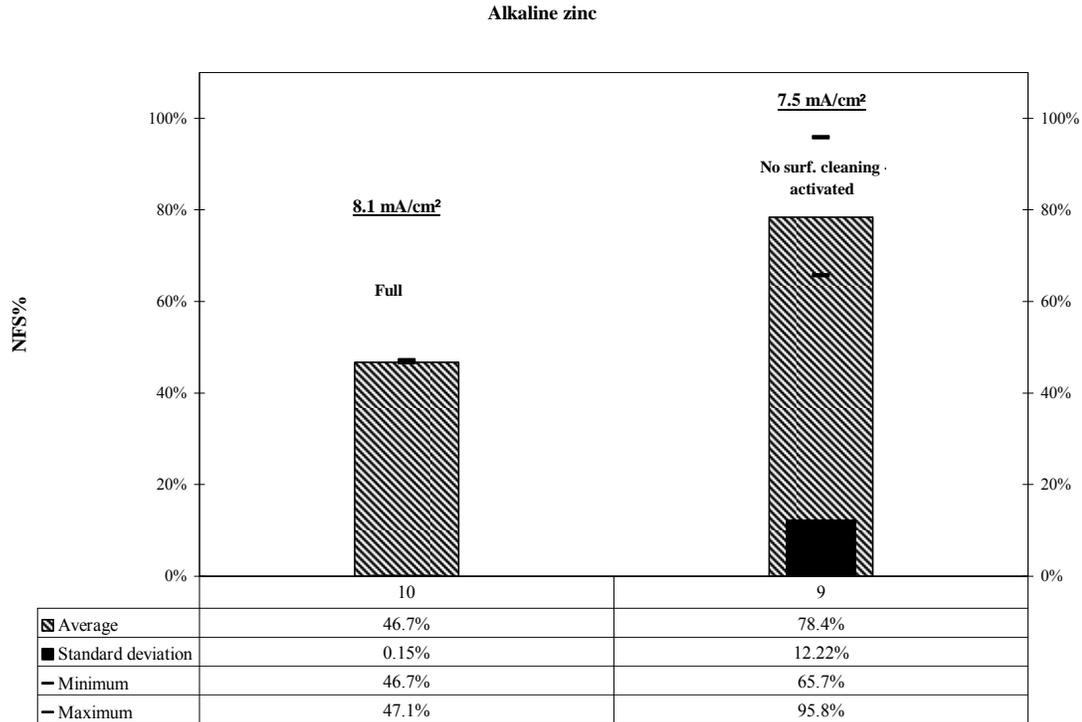


Figure 2 – Zinc – acid chloride, percent fracture strength (NFS<sub>%</sub>) by process condition

### Zinc – alkaline non cyanide

One alkaline non cyanide zinc barrel process was sampled under two conditions: (i) “full process” (P10) which included alkaline degreasing and pickling in hydrochloric acid at 13 wt% for 7 minutes, and (ii) “no surface

cleaning – activated” (P9) which is the same as the previous condition, except that the specimen surfaces were activated manually in dilute hydrochloric acid for 30 seconds prior to electroplating. In both cases the plating time was 120 minutes. Current densities were 7.5 mA/cm<sup>2</sup> for P10 and 8.1 mA/cm<sup>2</sup> for P9. (Fig. 3)



*Figure 3 – Zinc – alkaline non cyanide, percent fracture strength (NFS<sub>%</sub>) by process condition*

As was anticipated, the “full process” (P10) resulted in lower NFS<sub>%</sub> values, with an average of 47.7% as compared to 78.4% for P9. Again, this can be attributed to the hydrogen contribution of acid pickling. When comparing P9 to the acid chloride process in P1, both of which do not include pickling, it is interesting to note at roughly the same current density but twice the plating time, the alkaline zinc process still yielded higher NFS<sub>%</sub> values, with an average of 78.4% as compared to 64.2% for P1. This result seems to indicate that alkaline non cyanide zinc is less embrittling than acid chloride zinc.

#### *Zinc nickel – acid chloride*

One acid chloride zinc nickel barrel process was sampled under two conditions: (i) “full process” (P12) which included alkaline degreasing and pickling in hydrochloric acid at 17 wt% for 5 minutes, and (ii) “no surface

cleaning – activated” (P11) which is the same as the previous condition, except that the specimen surfaces were activated manually in dilute hydrochloric acid for 30 seconds prior to electroplating. Both conditions were plated at 5.2 mA/cm<sup>2</sup> for 60 minutes. Both conditions were found to be non-embrittling with average NFS% values of 92.1% for P12 and 99.8% for P11. The lower result in the case of P12 can once again be attributed to the hydrogen contribution of acid pickling. (Fig. 4)

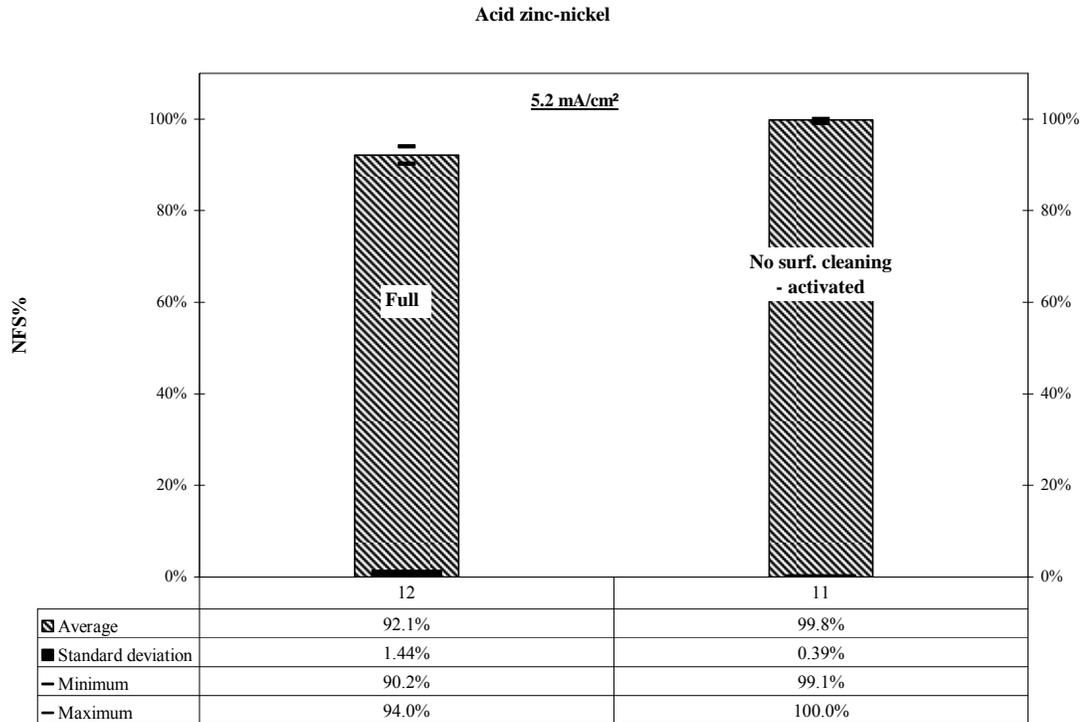


Figure 4 – Zinc nickel – acid chloride, percent fracture strength (NFS%) by process condition

#### Zinc nickel – alkaline non cyanide

Three alkaline zinc nickel processes were sampled. Group 1 was a barrel process sampled under two conditions: (i) “full process” (P8) which included alkaline degreasing and pickling in hydrochloric acid at 12 wt% for 10 minutes, and (ii) “no surface cleaning – activated” (P7) which is the same as the previous condition, except that the specimen surfaces were activated manually in dilute hydrochloric acid for 30 seconds prior to electroplating. Both conditions were plated at 5.4 mA/cm<sup>2</sup> for 90 minutes. Both conditions were non-embrittling with average NFS% values around 100%. (Fig. 5)

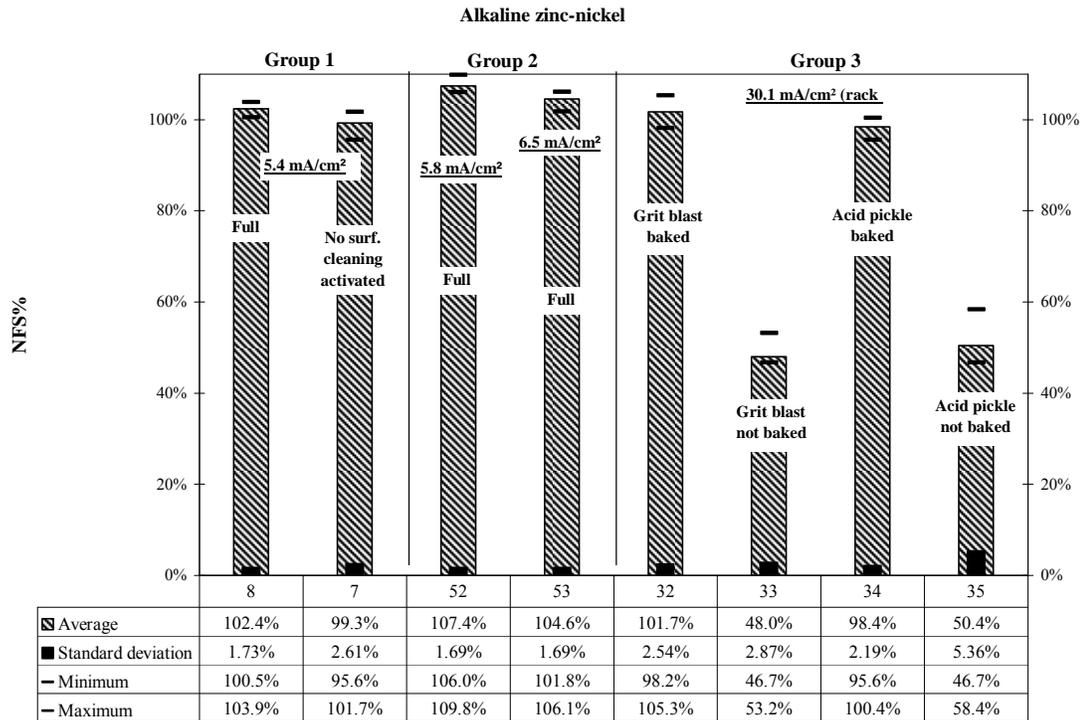


Figure 5 – Zinc nickel – alkaline non cyanide, percent fracture (NFS%) by process condition

Group 2 was another barrel process sampled under two conditions, both classified as “full process” with the following distinction: (i) P52 included pickling in hydrochloric acid at 18.2 wt% for 4 minutes, and plating current density of 5.8 mA/cm<sup>2</sup>, while (ii) P53 comprised pickling in hydrochloric acid at 18.2 wt% for 10 minutes, and plating current density of 6.5 mA/cm<sup>2</sup>. P53 was to be the high risk condition with maximum exposure to acid for this particular process. P53 was also plated at a slightly higher current density than P52. Both conditions were found to be non-embrittling with average NFS% values in excess of 100%.

Groups 3 consists of a rack process sampled under four separate conditions. The conditions were selected to separately test the effects of baking, and mechanical surface preparation (versus acid pickling). The four conditions are as follows: (i) “grit blast – baked” (P32), (ii) “grit blast – not baked” (P33), (iii) “acid pickle – baked” (P34) and, (iv) “acid pickle – not baked” (P35). Acid pickling was performed in hydrochloric acid at 25 wt% for 3 minutes. Baking was performed at 191 °C for 24 hours. In all cases, the oil on the specimens was removed using a commercial solvent. Also, all the specimens were rack plated at 30.1 mA/cm<sup>2</sup>, which is five to six times greater than the plating current density in a typical barrel process.

From the results it can be seen that in the absence of baking this process resulted in significant embrittlement of the specimens with average NFS<sub>%</sub> values between 40 and 50%. This is most likely due to the high current density in comparison to Groups 1 and 2. When considering the effect of mechanical surface preparation versus acid pickling, no significant difference was observed in Group 3, with average NFS<sub>%</sub> values of 48.0% for P33 and 50.4% for P35. In Group 4, the acid pickled condition P39 had a higher average NFS<sub>%</sub> value (51.4%) than the grit blasted condition P37 (42.2%). Due to the relatively high standard deviations, 4.98% and 6.35%, this difference may not be significant. When considering the effect of baking, the results clearly point to full recovery following the lengthy baking time of 24 hours with average NFS<sub>%</sub> values nearing 100%. Once again, this observation is consistent with the theory of reversibility of IHE.

*Zinc iron – alkaline non cyanide – rack*

One alkaline non cyanide zinc iron barrel process was sampled under two conditions (Fig. 6). The first condition “full process” (P14) included alkaline degreasing and pickling in hydrochloric acid at 17 wt% for 5 minutes, and the second condition “no surface cleaning – activated” (P13) is the same as the previous condition, except that the specimen surfaces were activated manually in dilute hydrochloric acid for 30 seconds prior to electroplating. Both conditions were plated at a current density of 12.4 mA/cm<sup>2</sup> for 50 to 55 minutes. Both conditions were found to be moderately embrittling with average NFS<sub>%</sub> values of 81.7% for P14 and 86.0% for P13. The slightly lower result in the case of P14 may be attributed to the hydrogen contribution of acid pickling. However, considering the standard deviations in the order of 5 to 7%, this difference may not be statistically significant.

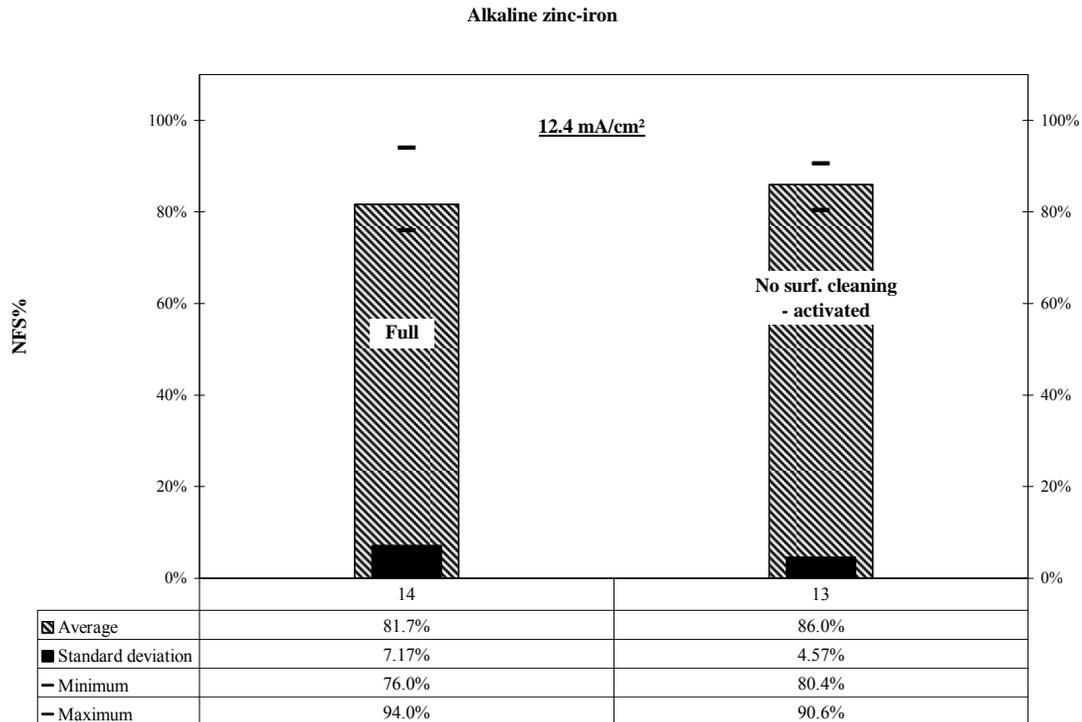


Figure 6 – Zinc iron – alkaline non cyanide, percent fracture (NFS%) by process condition

### Cadmium – cyanide

One bright cyanide cadmium rack process was sampled under two conditions: (i) “not baked” (P41) which comprised alkaline degreasing, no pickling, and manual activation in dilute hydrochloric acid for 30 seconds prior to electroplating, and (ii) “baked” (P41) which is the same as the previous condition, except that the specimen was baked at 204 °C for 4 hours. Both conditions were plated in two phases, first a strike at 86.1 mA/cm<sup>2</sup> current density for 45 seconds, followed by plating at 21.5 mA/cm<sup>2</sup> current density for 20 minutes, both in the same bath. The initial high current density strike prior to plating is an industrial practice designed to minimise hydrogen penetration by rapidly creating a barrier on the surface of the workpiece before starting the actual plating process.

The un-baked condition P41 resulted in an average NFS<sub>%</sub> value of 92.1%, which is considered non-embrittled by the ASTM F1940 standard. This result may have been achieved thanks to the initial high current density strike, although this hypothesis must be validated by testing the same condition with and without the strike. The addition of baking in P40 increased the average NFS<sub>%</sub> value to 102.8%, signifying full recovery after only four hours baking time. (Fig. 7)

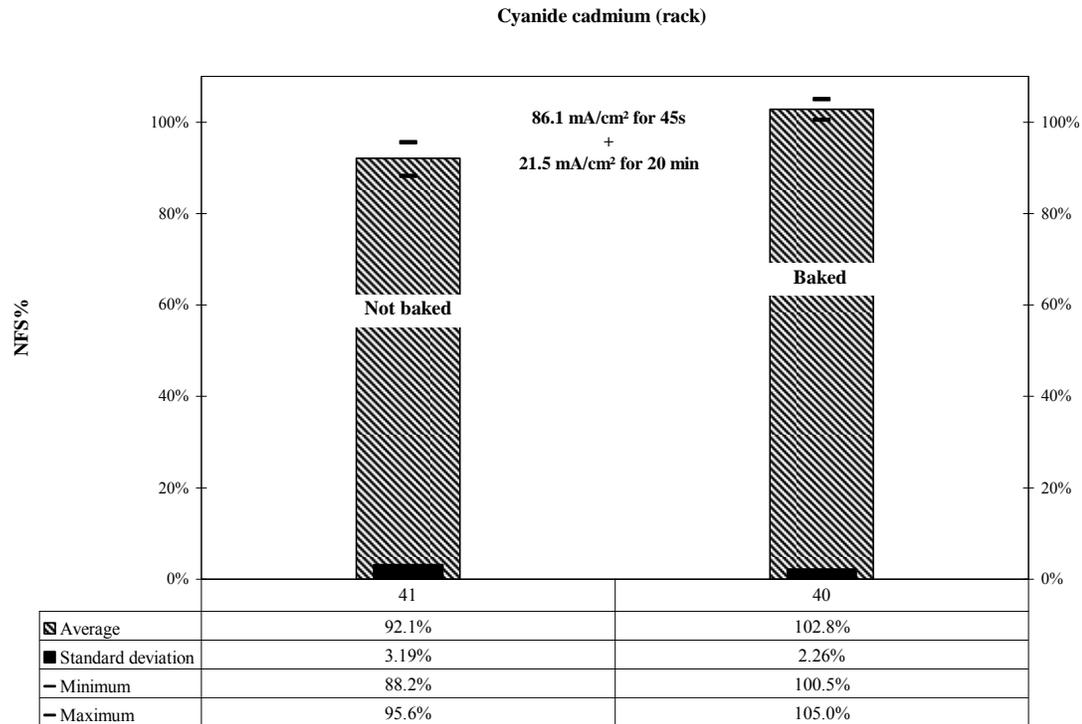


Figure 7 – Cadmium – bright cyanide, percent fracture strength (NFS<sub>%</sub>) by process condition

## Non-Electrolytic Processes

### Acid dip – laboratory

The conditions for acid dipping are divided into three groups designed to illustrate the effect of immersion time, concentration and time before testing. Group 1 comprised of immersion in 9 wt% HCl for 20 minutes (P21). This condition was found not to be non-embrittling. Conditions for Group 2 consisted of: immersion in 18 wt% HCl for (i) 30 minutes, and (ii) 70 minutes. Both conditions are represented in the same bar.

The doubling of both immersion time and acid concentration from Group 1 was designed to generate an extreme case of acid exposure. The average NFS<sub>%</sub> value obtained was 97.7%. In Group 3, wait times ranging from 24 to 72 hours were imposed before ISL testing. Once again the results showed no sign of specimen embrittlement, with NFS<sub>%</sub> values around 100%. All of these data seem to indicate that even the most severe acid pickling conditions will not cause embrittlement in the absence of a barrier to prevent hydrogen escaping. (Fig.8)

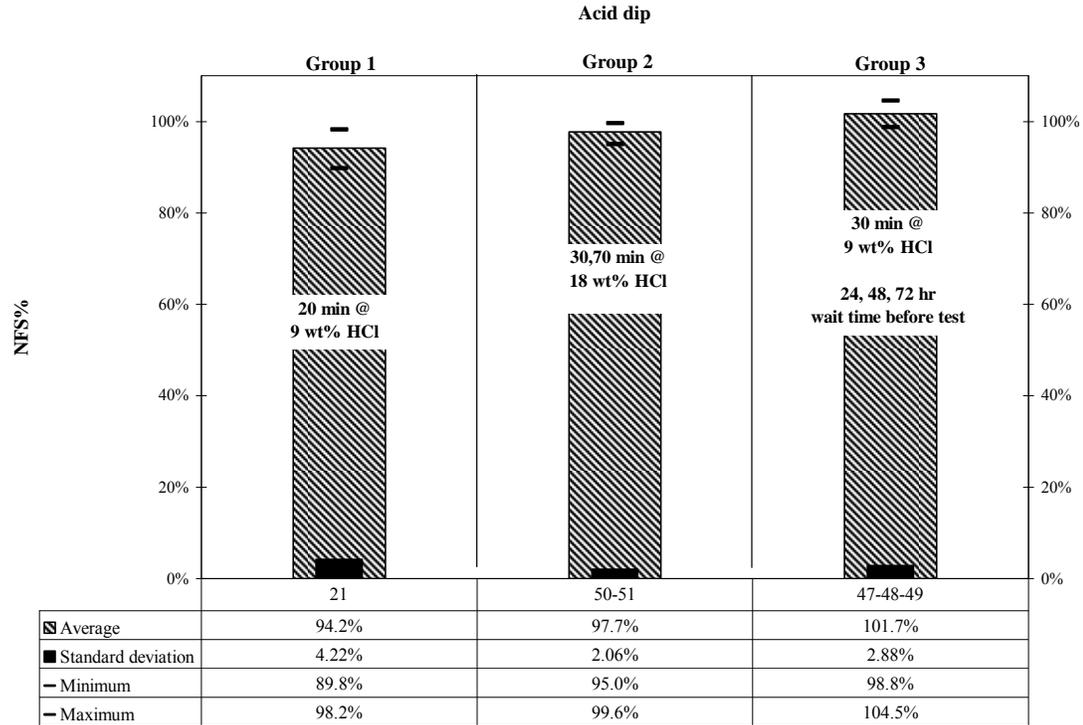


Figure 8 – Acid dip, percent fracture strength (NFS%) by process condition

### Mechanical zinc – bulk drum

The mechanical zinc process was sampled under two conditions: (i) P17 at eight minutes of pickling time, which was the maximum pickling time for this process, and (ii) P18 at one minute of pickling time. Hydrochloric acid at 5 wt% was used for both conditions. The resulting NFS% values in both cases exceeded 100%. These results are consistent with the literature which holds that mechanical zinc is a non-embrittling process. (Fig. 9)

### Zinc phosphate – barrel

The zinc phosphate process sampled (P20) included 10 minutes of pickling time in 10% v/v sulphuric acid. As expected, the average NFS% value was 100%. This result is consistent with the literature which holds that phosphating is a non-embrittling process. (Fig. 9)

### Zn/Al Flake Coatings – Dacromet® & Magni 555® – bulk dip spin

The Dacromet<sup>®</sup> process (P1007) resulted in an average NFS<sub>%</sub> value of 92.7%. This marginal reduction in fracture load is not thought to be related to hydrogen embrittlement phenomena. Rather, it is explained by a parallel reduction of specimen hardness resulting from the 15 minute curing cycle at 320 °C, which significantly exceeds the specimen tempering temperature of 220 °C. The specimen hardness measured after processing was 48.1 HRC, instead of 51 HRC originally. The Magni 555<sup>®</sup> process (P19) resulted in an average NFS<sub>%</sub> value of 99.5%, indicating no embrittlement, despite some exposure to acid during phosphating. Similar to Dacromet<sup>®</sup> the process includes a curing cycle, but at a significantly lower temperature of at 225 °C for 18 minutes. Although this is slightly higher than the 220 °C at which the specimens were tempered, it did not have a significant effect on fracture strength. The specimen hardness measured after processing was 50.4 HRC, instead of 51 HRC originally. These results confirm that both Dacromet<sup>®</sup> and Magni 555<sup>®</sup> are non-embrittling. (Fig. 9)

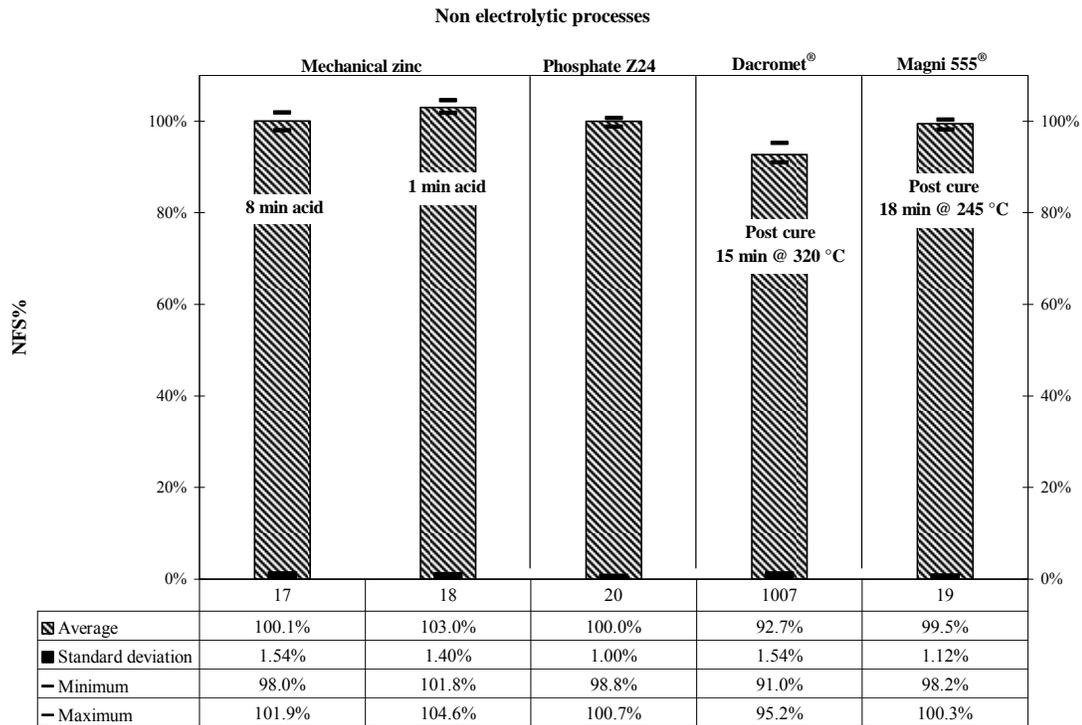


Figure 9 – Non electrolytic processes, percent fracture strength (NFS<sub>%</sub>) by process

## Fractography

A thorough examination and mapping of a sampling of fracture surfaces of test specimens was performed by scanning electron microscopy (SEM). The electrolytically coated specimens that ruptured at high fracture strength exhibited

a mix of ductile dimples and some brittle transgranular (cleavage) fracture morphology. In comparison, specimens with low fracture strengths exhibited intergranular fracture morphology, but only in the area below the notch where stress, and therefore hydrogen concentration were highest. Interestingly, a specimen from P1003 (zinc plated, 24 hr bake) exhibited almost entirely ductile and transgranular morphology. A sample from P1002 (zinc plated, 12 hour bake) had evidence of intergranular morphology below the notch area, and a predominance of ductile and transgranular morphology elsewhere. In comparison, non-electrolytically coated test specimens consistently showed a mix of ductile dimples and some brittle transgranular (cleavage) fracture morphology. This observation was consistent with the fact that all the specimens had ruptured at high fracture strengths, indicating no embrittlement.

## DISCUSSION

The results obtained with electrolytic processes support the assertion that the multitude of complex processing variables and coating characteristics can be grouped into two basic parameters affecting IHE: (i) the amount of hydrogen introduced by the process, and (ii) the permeability of the coating. It will be shown that coating permeability has a first order effect, while the quantity of hydrogen introduced by the process has a second order effect.

The results of the acid dip tests and the phosphating process showed that in the absence of a coating barrier, hydrogen had a tendency to freely “out-gas” or escape, rather than be attracted to areas of stress concentration. The data seem to indicate that this statement can hold true even with the most severe acid pickling. This finding is consistent with the literature and industry standards that do not require phosphated parts to be baked, owing to the highly porous nature of phosphate coatings.

When a coating barrier is present, the effect of permeability is evident when comparing Zn-Ni coatings to other coatings. The Zn-Ni coated specimens plated at the same current density as Zn coated specimens were not embrittled. This result is thought to be related to the porosity of the Zn-Ni coating.<sup>9</sup> Although this point will be thoroughly investigated in future work, preliminary characterisation by electron microscopy showed the Zn-Ni coatings to be considerably more fractured than pure zinc coatings, thus allowing hydrogen easier escape paths (Fig. 10-12).<sup>10</sup> These results highlight the relationship between the coating metal and permeability. The results of the cadmium process showed the reverse effect of coating permeability. In this process, the application of an impermeable layer at the start of plating was used to prevent additional hydrogen being absorbed during plating build-up.

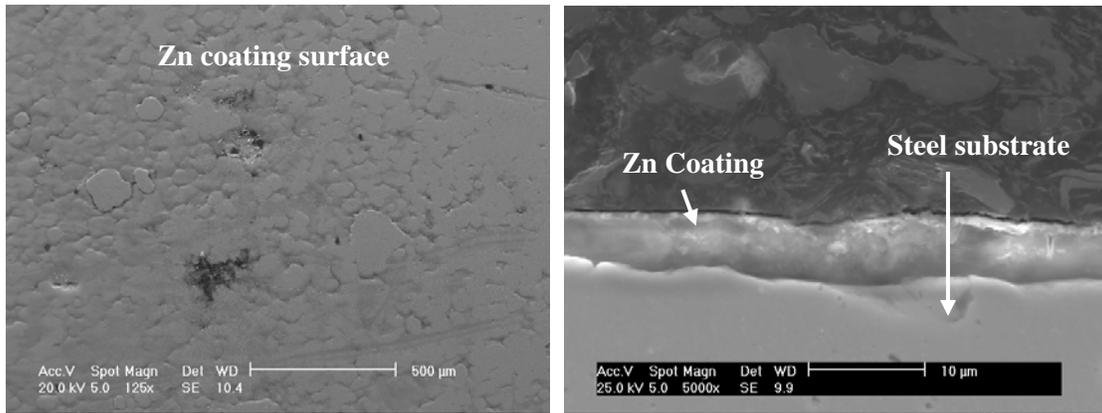


Figure 10 – Surface and cross section views of pure Zn electrodeposited coating<sup>10</sup>

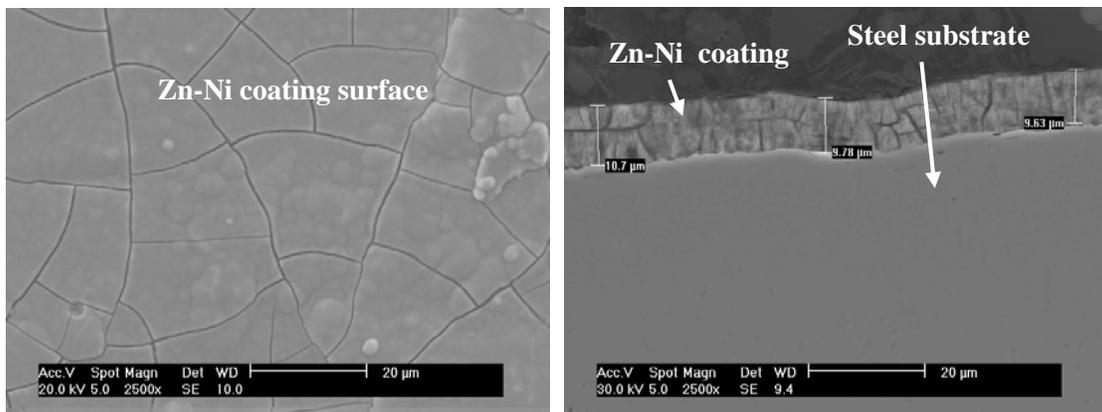


Figure 11 – Surface and cross section views of Zn-Ni electrodeposited coating<sup>10</sup>

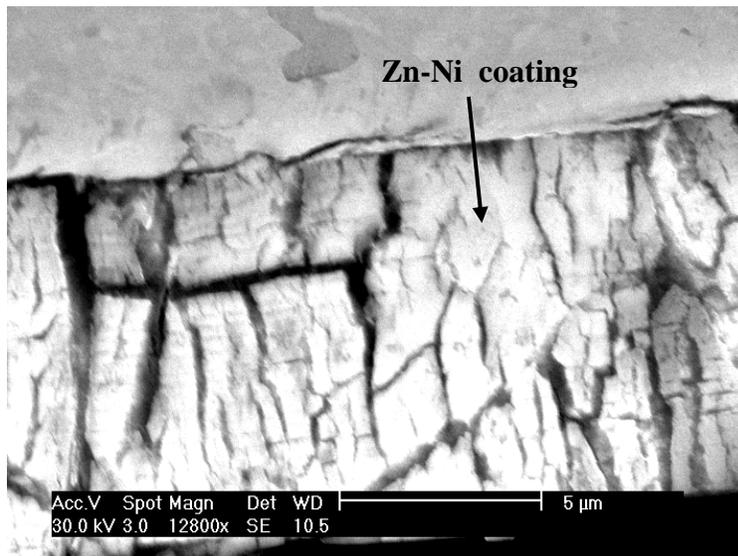


Figure 12 – High magnification cross section view of Zn-Ni electrodeposited coating highlighting fractured morphology, presumably allowing for H transport pathways<sup>10</sup>

Quantity of hydrogen is a function of electrolytic parameters (i.e., current density and plating time), and acid exposure conditions (i.e., acid type, concentration, and pickling time). The effect of current density was most evident when comparing Zn-Ni rack plating to barrel plating. The current densities were as much as six times greater and fracture strengths as low as 45% for the rack process as compared to 100% for barrel processes.

The hydrogen contribution of acid pickling was evident when comparing the results of the “full process” conditions to the “no surface cleaning” conditions. The latter consistently produced higher fracture strength results than the former. The effect of acid pickling was most evident in the acid-chloride zinc process, which is thought to produce the least permeable coating. Conversely, the effect of acid pickling was least evident for the Zn-Ni processes which are thought to produce the most permeable coatings.

Although conventional wisdom supported by theory has always held that high efficiency baths are less embrittling because they generate less hydrogen, there was no apparent effect of bath efficiency on ISL results. It may be that the effect of bath efficiency is minor in relation to current density/time and pickling concentration/time. It is also possible that the limiting current density  $i_L$  is not readily achieved in the course of an industrial plating process.

In summary, the results of ASTM F1940 testing showed that the zinc acid chloride process was the most embrittling process (i.e., highest risk) because it consistently produced the lowest NFS% results. Next in the order of risk, the alkaline zinc process was found to be slightly less embrittling with higher NFS% values, even at twice the plating time. These results are attributed to low permeability of pure zinc coatings. The fact that the acid zinc chloride bath is an acidic medium might explain its slightly more embrittling nature versus the alkaline zinc bath. Pure zinc processes were followed by the alkaline zinc-iron process, which at 86% fracture strength was classified as moderately embrittling. This result reflects the mixed effects of coating permeability and hydrogen contribution. The least embrittling processes were zinc-nickel, both alkaline and acid. In barrel processes, where plating current densities were in the range of 6 mA/cm<sup>2</sup>, the zinc-nickel processes produced no measurable embrittlement. In a rack process where plating current density was five times greater, embrittlement had occurred, but ductility was fully restored after 24 hours of baking at 191 °C. These results are attributed to the permeability of Zn-Ni coatings.

The cyanide cadmium plating process cannot be ranked against the others because the coating was applied in two steps: (i) a quick high current density

“strike” followed by, (ii) lower current density plating. Despite being applied at a relatively high current density ( $\sim 22 \text{ mA/cm}^2$ ), the initial strike evidently succeeded in preventing subsequent hydrogen absorption. This assertion is supported by the fracture strength result of roughly 92%, obtained without the benefit of baking. The technique of creating an impermeable absorption barrier prior to plating is not widespread in the general plating industry. However, it is used by some electroplaters specialising in the coating of high strength and ultrahigh strength components for the aerospace industry.

It must be emphasised that results obtained for electroplating processes are only a measure of the potential for internal hydrogen embrittlement. Ultimately, whether or not hydrogen embrittlement will occur depends upon the degree of susceptibility of parts being plated. If a process is deemed “high-risk” by this method, it may still be suitable for plating parts that have low susceptibility. On the other hand, if a process is deemed non-embrittling or “safe” by this method, then there is no risk of embrittlement, regardless of the susceptibility of parts being plated. The only exception to this rule is if the hardness of the production parts exceeds that of the test specimens. In very rare cases, non-standard ultrahigh strength parts, or in some cases surface hardened parts may exceed a hardness of 52 HRC. Under such circumstances, non-embrittling coating processes should be used.

When considering the effect of baking, fracture strength results supported by fractographic analysis showed that ductility can be fully restored by baking at temperatures ranging from 190 to 204 °C. This finding is significant because it not only validates the theory regarding the reversibility of IHE, but it also signifies that baking can be used as an effective countermeasure for preventing IHE related failures. Current industrial standards overwhelmingly, although not exclusively, specify a “one size fits all” approach for baking electroplated high strength fasteners. The typical approach comprises four hours of baking at 204 °C. However, this study demonstrated that baking response depends upon the permeability of the coating and, therefore, varies with coating type. Zinc plating, which is the most widespread electroplated coating applied to fasteners, achieved full recovery only after 24 hours of baking at 204 °C.

Clearly, the fact that IHE related failures are relatively rare with zinc plated fasteners has little to do with the effectiveness of baking practice. Instead, the absence of failures is a consequence of the low hydrogen embrittlement susceptibility of most fastener materials. The findings of this research warrant a comprehensive revision of industrial baking standards and practices. The resulting scenario would be one where a considerably smaller quantity of parts would be baked for longer periods.

## CONCLUSIONS

The primary objective of this research was to quantify the risk of embrittlement from residual hydrogen (i.e., IHE) from coating processes commonly utilised to coat high strength mechanical fasteners. The effects of coating process variables and certain coating characteristics were investigated, principally by the incremental step loading (ISL) technique, in accordance with test method ASTM F1940. This methodology was used to rank a number of industrial coating processes for their propensity to cause internal hydrogen embrittlement. The following conclusions were derived from this study.

1. Fractographic evidence supported the causal relationship between the presence of residual hydrogen from processing and the reduction of fracture strength, which is the premise upon which the ASTM F1940 test method is based.
2. The results supported the assertion that the multitude of complex processing variables and coating characteristics can be grouped into two basic parameters affecting IHE: (i) the amount of hydrogen introduced by the process, and (ii) the permeability of the coating. Coating permeability had a first order effect, while the quantity of hydrogen introduced by the process had a second order effect.
3. In the absence of a coating barrier, hydrogen had a tendency to freely “out-gas” or escape, rather than be attracted to areas of stress concentration, even with the most severe acid pickling. In the presence of a coating, the first order effect of permeability was evident with phosphate and Zn-Ni coatings, both of which are porous.
4. The results of the cadmium process showed the reverse effect of coating permeability, where the application of an impermeable layer by high current density strike at the start of plating was used to prevent additional hydrogen being absorbed during plating build-up.
5. Quantity of hydrogen introduced was affected by: (i) electrolytic parameters (i.e., current density and plating time), and (ii) acid exposure conditions (i.e., acid type, concentration, and pickling time). There was no apparent effect of bath efficiency on hydrogen contribution.
6. The process qualification results can be summarised as follows. The zinc acid chloride process was the most embrittling, and therefore the highest risk process. Next in the order of risk, the alkaline zinc process was found to be slightly less embrittling as it produced higher NFS% values, even at twice the

plating time. This was followed by the alkaline zinc-iron process, which at 86% fracture strength was classified as moderately embrittling. The least embrittling processes were zinc-nickel, both alkaline and acid.

7. Baking can fully restore ductility at temperatures ranging from 190 to 204 °C, at times between 4 and 24 hours depending on the coating. This finding validating the theory of reversibility of IHE. Baking response depends upon the permeability of the coating. Therefore, baking time must be adapted to the coating type. Zinc plating, which is the most widespread electroplated coating applied to fasteners, achieved full recovery only after 24 hours of baking. The “standard” four hour bake time had no beneficial effect.
8. All four of the non-electrolytic processes tested, mechanical zinc, zinc phosphate, Dacromet<sup>®</sup>, and Magni 555<sup>®</sup> were found to be non-embrittling. In the cases of phosphate and mechanical zinc, the results were attributed to the permeability of the coating.

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