An IFI Research Report

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# Influence of Phosphorus on Fastener Integrity

Advancing
Fastener
Application
Engineering

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## SCOPE

This study was established to investigate the effect of the presence of a full or partial zinc-phosphate raw material coating on the integrity and performance of high tensile metric screws processed to Property Class 8.8, 10.9 and 12.9, respectively.

In this test program, the test method found in ASTM F1624, *Standard Test Method for Measurement of Hydrogen Embrittlement Threshold in Steel by the Incremental Step Loading Technique*, is used to correlate any reduction in fracture strength of the fasteners with the presence of a purported embrittling agent, namely phosphorus. Both the residual hydrogen in the fastener from processing and then the effect of the phosphorus modified surface finishes on the threshold stress required to induce subcritical crack growth under an imposed cathodic charging voltage were measured.

The ASTM F1624 Test Method measures the threshold stress for the onset of hydrogen induced subcritical crack growth, which when tested in air, quantifies the amount of residual hydrogen retained in a fastener from processing as a reduction in its fracture strength. When tested under an imposed hydrogen charging potential in an aqueous solution, the threshold stress required to induce subcritical cracking is measured.

## SUMMARY

The application of the rising step load test method established in ASTM F1624 indicates that fasteners manufactured with a phosphate coating and subsequently heat treated did not show any reduction in fastener load carrying capability. Cleaning methods prior to heat treating for phosphate removal were only partially effective. No difference in load carry capability between those subjected to cleaning and those which were not cleaned was discernible.

## BACKGROUND

Historically, zinc phosphate coating of wire and rod is a common practice in the cold forming process that is used to produce all types of mechanical fasteners and special cold formed, non-fastener parts. Zinc phosphate is the vehicle that retains various lubricants on the surface of the wire or rod to protect the surfaces of the tool and work piece against damage during the various steps in the cold forming and extrusion processes.

This vehicle for lubricants is not easily removed from the rod, wire, or cold-formed part that is produced. While acid is used to remove some of the zinc phosphate, experience has shown that it is difficult, if not impossible, to completely remove all phosphate from the product surfaces prior to heat treatment. A task group of ASME B18 Subcommittee 4 examined this issue when it was raised in ISO/TC 2 working group discussions and was unable to identify any supplier of cleaning equipment that would guarantee the capability to achieve 100% removal.

In 1988, ISO/TC 2 published a revision of ISO 898-1 which included a note that said: *"A metallographically detectable white phosphorous enriched layer is not permitted for property class 12.9 on surfaces subjected to tensile stress."* A major European auto manufacturer claimed the failure of a bolt because of the presence of phosphorus. However, subsequent review of that paper by Craig Hood, a world-renowned expert in fastener metallurgy, indicated the paper was not conclusive and only speculated on the impact of phosphorus. (See ISO/TC 2/SC 1 ad hoc N14, May 1999, Appendix IV.) In 1993, Ford Worldwide Standard WX 100 was released, which required the removal of <u>all</u> phosphate prior to heat treatment of Property Class 8.8 (>M16), 9.8, 10.9, and 12.9. IFI advised its members to seek waivers for this requirement for the following reasons:

1.) No technology exists that can guarantee the 100% removal of phosphorus from the surface of bolts, screws, or cold formed parts in the manufacturing process. Further, the methods for detection of its presence are not reliable and, in fact, can be misleading. (See N64 of ISO/TC 2/SC 1/WG 9, October 2001, Appendix V.)

2.) Significant quantities of bolts and screws that have a zinc phosphate coating present during heat treatment are installed annually and the fastener industry can report with a high degree of certainty that it has not experienced failures attributable to the presence of phosphorus.

3.) No known organized investigation, until now, has ever been carried out to evaluate the impact of phosphorus on threaded fasteners. (Proprietary research may have been done, but the results are not generally available.)

4.) Because zinc phosphate is a coating often used on cold forming materials and because it cannot be completely removed with current technology, its continued use should be permitted until such time as research would demonstrate that a change in this practice was technically justified.

5.) While other coatings exist, issues with alternate coatings include their ability to carry a lubricant as effectively, and the ability to provide sufficient corrosion protection, which relates to a shorter shelf life for the raw material.

In 2002, Textron Fastening Systems (TFS), in concert with Ford Motor Company, completed a study involving 15 test lots to seek information concerning the behavior of zinc phosphate coatings on fasteners. These were heat treated to Property Class 8.8, 10.9, and 12.9, respectively. They were then tested in air, and under an imposed galvanic potential that electrochemically simulated the addition of a subsequent zinc coating. This report will review the Textron study and discuss the findings.

## TEST PROCEDURE

### Test Product

An M12 X 1.75 X 100 mm hex flange screw (Figure 1) was selected for this study with all samples being manufactured by the Shamrock Fastener Division of Textron Fastening Systems. In order to achieve uniformity of product, the screws were manufactured in successive forming operations using the same cold heading machine, thread roller, and tooling.

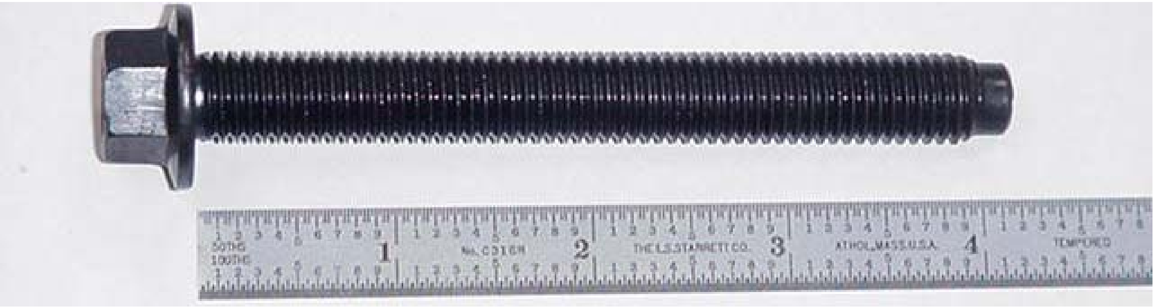


Figure 1

All screws, for each property class were traceable to their respective single mill heat of material. The raw materials used for each of the three property classes were as follows:

| Material | Property Classes Produced |
|---|---|
| 10B21 | Property Class 8.8 and 10.9 |
| 1541 | Property Class 8.8, 10.9, and 12.9 |
| 4037 | Property Class 8.8, 10.9, and 12.9 |

Each property class was furnished in three different surface finishes including:

- zinc phosphate applied to the wire prior to heading, and not removed prior to heat treatment
- lime applied to the wire prior to heading, and not intentionally removed prior to heat treatment
- zinc phosphate intentionally removed after heading, prior to heat treatment

Thus a total of 24 lots of fasteners were produced.

The parts subjected to phosphate removal were placed in a stainless steel apparatus, which is subdivided into four compartments to provide four stages of cleaning. The fasteners were transported using a horizontal screw driven conveyor with the compartments alternately cleaning then rinsing such that 2 cleanings and 2 rinses are sequenced. The cleaning solution was a 10% by volume alkaline solution with a potassium hydroxide (KOH) base. The fasteners were in each stage for six minutes. The first stage was at 170°F and the second at 190°F. The third stage was a hot rinse with no temperature control and the fourth stage was a dryer at 350°F.

All parts were heat treated toward the upper limit of the specification hardness for their respective property class: 8.8 to 32 HRC, 10.9 to 39 HRC, and 12.9 to 44 HRC. (See ASTM F568M or ISO 898-1 for a complete delineation of the respective property classes.) It was determined that Property Class 10.9 lots would be tested first to determine the need for testing Property Class 8.8, since Property Class 10.9 represented the worst case scenario between the two property classes in terms of higher hardness and strength. The lots of Property Class 12.9 subjected to phosphate removal prior to heat treatment were heat treated at a different time period than the other Property Class 12.9's, and it was noted that they were measured to be at a slightly lower hardness (2 HRC points lower) than the Property Class 12.9 lots that were not subject to removal of the phosphate prior to heat treatment.

The heat treatment process alters the finish on the surface of the fastener, but it does not change the susceptibility of the core fastener material to hydrogen induced stress cracking. The susceptibility is a material property that is strongly dependent on the hardness or strength of the fastener. Therefore, modifying the surface finish affects the permeability of hydrogen into the fastener. For example, with a surface finish of copper, which is impervious to hydrogen diffusion, no degradation in strength will be measured even while imposing an aggressive hydrogen-charging cathodic potential; i.e. the modified surface finishes act as a barrier to the infusion of hydrogen into the steel fastener.

## Test Method

In accordance with an agreement with Ford representatives, Textron used an incremental step load method to test the lots of flange screws. The test method is established in ASTM F1624, *Standard Test*

*Method for Measurement of Hydrogen Embrittlement Threshold in Steel by the Incremental Step Loading (ISL) Technique*. These tests may be performed in air or in a controlled environment. The test method determines the threshold stress for the onset of hydrogen induced subcritical crack growth with an incrementally increasing step loading profile on the fastener.

Heading, and subsequent heat treatment of the fastener, alters the surface finish, resulting in a change in the electrochemical kinetics on the surface of the screw when immersed in a salt water solution. First, the incremental step load test conducted in air is a measure of the residual hydrogen in the steel due to the heading and heat treatment on the surface finish. The incremental step load test was then conducted in an aqueous environment (3.5% NaCl solution) under a hydrogen-charging cathodic potential of –1.2 volts referenced against a Saturated Calomel Electrode (–1.2Vsce) to electrochemically simulate the application of a zinc coating to the altered surfaces after the forming and heat treat processes. The quantitative measure for the susceptibility of the fastener with the modified surface treatment is the threshold stress or the ratio of the threshold stress to the Fast Fracture Strength.

The evidence provided in the ISO N14 document that suggests that phosphorus or the phosphorus enriched delta-ferrite seam and zone of phosphorus diffusion during heat treatment caused the intergranular cracks only illustrates that the applied stress exceeded the threshold stress for the surface generated by the coating and thermal mechanical processing that was employed, but this was in a raw state and not with a zinc coating subsequently applied. See Appendix VI for more information.

Using the above fastener lots and test method, testing was begun at the Textron facilities in Rockford, Illinois on April 11, 2002. The test equipment and setup is shown in Photos 1-3, Appendix III. ASTM F1624 utilizes an initial four point bending method in air at ASTM E8 loading rates to establish the Fast Fracture Strength (FFS) of a given lot of screws. Five samples from each lot were used to establish the FFS for each respective lot as indicated in Column 6 of the tables in Appendix I and Appendix II. The lots were then tested using the ASTM F1624 method in air, then in a 3.5% saline solution at an electrochemical potential measurement value of –1.2Vsce as a hydrogen charging potential, simulating the addition of a zinc coating that electrochemically provides a worst case scenario for the tested fasteners. Each of the Property Class 10.9 fasteners was tested over a 24-hour period using 5% of FFS as the increment increase in load for a one-hour duration per step, which corresponds to the loading profile of ASTM F1940, *Standard Test Method for Process Control Verification to Prevent Hydrogen Embrittlement in Plated or Coated Fasteners*.

It should be noted that the Ford designated and approved contractor for cleaning, i.e., removal of the phosphate, did not successfully remove 100% of the zinc phosphate from the fastener surfaces as currently required by Ford specifications. In fact, it was also discovered that phosphorus existed on the surface of the screws where the wire was coated with lime (no zinc phosphate) as well as those in which the zinc phosphate was simply “removed.” This seems to confirm the evaluation of current cleaning technology by the ASME B18 Subcommittee 4 task group.

## Test Results

An examination of the test results from the 45 Property Class 10.9 screws reveals the following: 38 samples or 84.4% equaled or exceeded the FFS (fast fracture strength). The ISL fracture strength of the remaining seven test samples are within 1.9% of the FFS.

An examination of Property Class 10.9 fasteners reveals the following:

1.) Zinc phosphate coated fasteners processed to Property Class 10.9 and ISL tested in air averaged 104% FFS = 250-265 lbs., which converts to a hardness of 39-40 HRC.

2.) Fasteners subjected to attempts to remove the zinc phosphate coating prior to heat treatment and then ISL tested in air averaged 103.5% FFS = 250-265 lbs., which converts to a hardness of 39-40 HRC.

3.) Lime coated fasteners processed to Property Class 10.9 and ISL tested in air resulted in an average of 102.7% FFS = 250-265 lbs., which converts to a hardness of 39-40 HRC.

4.) The air test results substantiate the fact that no residual hydrogen was introduced during processing that would cause any degradation in mechanical properties of the P.C. 10.9 fasteners.

5.) Zinc phosphate coated fasteners ISL tested in a saline solution with a –1.2 Vsce current had an average of 101.2% FFS = 250-265 lbs., which converts to a hardness of 39-40 HRC.

6.) Fasteners subjected to attempts to remove zinc phosphate coating and ISL tested in a saline solution with a –1.2 Vsce current had an average of 104.1% FFS = 250-265 lbs., which converts to a hardness of 39-40 HRC.

7.) Lime coated fasteners ISL tested in a saline solution with a –1.2 Vsce current had an average of 100.4% FFS = 250-265 lbs., which converts to a hardness of 39-40 HRC.

8.) The environmental test results substantiate the fact that under aggressive hydrogen charging conditions that electrochemically simulate the addition of a zinc coating, the threshold stress equaled or exceeded the FFS of the 10.9 fasteners, regardless of the altered surface conditions.

9.) In summary, no matter the material, coating, or test environment, none of the Property Class 10.9 test screws failed prematurely. Therefore, none of the three surface conditions caused any degradation in strength from processing or from environmental conditions that duplicated subsequent coating with zinc (Vsce = –1.2 volts).

10.) Based on the Property Class 10.9 results, a decision was made by TFS in consultation with Ford that the Property Class 8.8 fasteners need not be tested. Therefore, the 24 test lots were reduced to 15 test lots including nine lots of P.C. 10.9's and six lots of P.C. 12.9's.

An examination of Property Class 12.9 fasteners reveals the following:

1.) Zinc phosphate coated fasteners processed to Property Class 12.9 and ISL tested in air averaged 97.4% FFS = 320 lbs., which converts to a hardness of 46 HRC.

2.) Fasteners subjected to attempts to remove the zinc phosphate coating and then ISL tested in air averaged 100.5% FFS = 285-290 lbs., which converts to a hardness of 43 HRC.

3.) Lime coated fasteners processed to Property Class 12.9 and ISL tested in air resulted in an average of 98.7% FFS = 320 lbs., which converts to a hardness of 46 HRC.

4.) The air test results substantiate the fact that no residual hydrogen was introduced during processing that would cause any degradation in mechanical properties of the P.C. 12.9 fasteners.

5.) The twelve samples of Property Class 12.9 ISL tested in a saline solution with a –1.2 Vsce current had a threshold stress that averaged 72.3% or 26% less than when tested in air.

6.) The P.C. 12.9's with zinc phosphate removed and ISL tested in a saline solution with a –1.2 Vsce current achieved a higher threshold stress prior to fracture (82-90% FFS) than the lime coated or zinc phosphate coated fasteners (45-75% FFS) tested in the same solution. This difference can be attributed to the fact that the fasteners with the ZnP coating removed had a measured lower hardness of about 2 points HRC than the other two lots. This difference was consistent with the hardness conversion from the FFS that showed the fasteners with the ZnP coating removed to be 3 points HRC lower than the other two lots. Taking into account the difference in hardness, the degradation in strength of the 12.9 fasteners can be considered to be about the same for all three surface finishes.

7.) NOTE: 50% FFS in bending corresponds to the ASTM E8 Tensile Strength of 1200 MPa (~ 175 ksi). In bending of highly ductile steels, the limit load is about twice the ASTM E8 material Tensile Strength or ASTM F606M axial tensile strength. Therefore, the degradation in strength in bending from the three surface finishes, still meets or exceeds the axial tensile strength in tension.

8.) The environmental test results substantiate the fact that under aggressive hydrogen charging conditions that electrochemically simulate the addition of a zinc coating, the threshold stress of the P.C. 12.9 fasteners is less than the bend fracture strength in air, but is essentially the same for all three surface finishes on an equivalent hardness scale and meets or exceeds the axial tensile strength of the M12 fastener when tested in tension.

## Conclusions

**1.) The air test results substantiate the fact that no residual hydrogen was introduced during processing that would cause any degradation in mechanical properties of the 10.9 fasteners, regardless of the initial surface finish.**

**2.) The environmental test results substantiate the fact that under aggressive hydrogen charging conditions that electrochemically simulate the addition of a zinc coating, the threshold stress of the P.C. 10.9 fasteners exceeds the FFS, regardless of the altered surface conditions; i.e., they are immune to environmentally induced hydrogen stress cracking, regardless of the initial surface finish.**

**3.) The air test results substantiate the fact that no residual hydrogen was introduced during processing that would cause any degradation in mechanical properties of the P.C. 12.9 fasteners, regardless of the initial surface finish.**

**4.) The environmental test results substantiate the fact that under aggressive hydrogen charging conditions that electrochemically simulate the addition of a zinc coating, the threshold stress of the P.C. 12.9 fasteners is less than the bend fracture strength in air, but is essentially the same for all three surface finishes on an equivalent hardness scale, which meets or exceeds the axial tensile strength of the M12 fastener when tested in tension.**

5.) **It is clear that the Property Class 12.9 screws ISL tested in air did not experience a reduction in fracture load. The presence of the phosphorus after heading, prior to heat treatment or zinc plating, does not introduce any residual hydrogen that would cause any premature, time-delayed brittle failure.**

## Recommendations for Future Work

P.C. 12.9 fasteners ISL tested in a hydrogen-charging environment that electrochemically simulates the addition of a zinc coating did not experience a reduction in fracture load at stresses below the ASTM F606M axial tensile strength. In bending, surface tensile stresses in excess of the axial tensile strength are attainable up to a factor of 2X Ultimate Tensile Strength in tension at the limit load. This leads to the conclusions:

1.) The ISL test (ASTM F1624 Test Method) in bending is capable of quantifying the influence of surface finishes on the susceptibility of fasteners to environmentally induced hydrogen embrittlement. The susceptibility of the core material is not altered with various surface finishes. The different conditions of the surface only alter the hydrogen being generated on the surface, with the more active cell requiring a lower threshold stress for the onset of subcritical crack growth.

2.) The ASTM F1624 Test Method should be utilized as specified by continually decreasing the ISL loading rate until an invariant value of the threshold is obtained. Only in this way can the influence of the surface treatments on the relative susceptibility be accurately measured.

3.) The Open Circuit Corrosion Potential (OCP) of the three surface conditions should be measured to electrochemically quantify their differences.

4.) Metallographic photomicrographs should be utilized in subsequent test programs to correlate the OCP to the presence of surface substances and internal structures.

5.) To circumvent any confusion regarding specimen comparison, a program should be alternately outlined that uses bare, coated, heat treated, and zinc plated specimens instead of fasteners. Machined studs should be used for the bare specimen as in the ISO study.

# APPENDIX I

## SUMMARY OF ISL TESTING FOR FORD (PHOSPHATE EMBRITTLEMENT STUDY) P.C. 10.9

🟩 Equal to or greater than 75%
🟨 Between 50% and 75%
🟥 Less than 50% Fast Fracture Strength
⬜ Part did not fail (machine bottomed out) - 17 of 45

| 1 CLASS | 2 COATING | 3 MATERIAL | 4 TEST DESCRIPTION | 5 LOAD (lbs.) | 6 FFS (lbs.) | 7 %FS | 8 TEST DATE | |
|---|---|---|---|---|---|---|---|---|
| 10.9 | Zn-P | 4037 | 24steps/5%FFS/1hour steps in air | 264.7 | 265 | 99.9% | 04/11/02 | 1 |
| 10.9 | Zn-P | 4037 | 24/5/1 in air | 263.3 | 265 | 99.4% | 04/23/02 | 2 |
| 10.9 | Zn-P | 4037 | 24/5/1 in air | 264.4 | 265 | 99.8% | 04/24/02 | 3 |
| 10.9 | Zn-P | 4037 | 24/5/1 @ -1.2 volts | 264.9 | 265 | 100.0% | 04/15/02 | 4 |
| 10.9 | Zn-P | 4037 | 24/5/1 @ -1.2 volts | 264.2 | 265 | 99.7% | 05/01/02 | 5 |
| 10.9 | Zn-P | 1541 | 24/5/1 in air | 261.8 | 250 | 104.7% | 04/11/02 | 6 |
| 10.9 | Zn-P | 1541 | 24/5/1 in air | 263.5 | 250 | 105.4% | 04/23/02 | 7 |
| 10.9 | Zn-P | 1541 | 24/5/1 in air | 299.9 | 250 | 120.0% | 04/24/02 | 8 |
| 10.9 | Zn-P | 1541 | 24/5/1 @ -1.2 volts | 255.0 | 250 | 102.0% | 04/24/02 | 9 |
| 10.9 | Zn-P | 1541 | 24/5/1 @ -1.2 volts | 258.6 | 250 | 103.4% | 05/03/02 | 10 |
| 10.9 | Zn-P | 10B21 | 24/5/1 in air | 258.7 | 255 | 101.5% | 04/25/02 | 11 |
| 10.9 | Zn-P | 10B21 | 24/5/1 in air | 260.0 | 255 | 102.0% | 04/25/02 | 12 |
| 10.9 | Zn-P | 10B21 | 24/5/1 in air | 266.9 | 255 | 104.7% | 04/29/02 | 13 |
| 10.9 | Zn-P | 10B21 | 24/5/1 @ -1.2 volts | 255.1 | 255 | 100.0% | 04/29/02 | 14 |
| 10.9 | Zn-P | 10B21 | 24/5/1 @ -1.2 volts | 260.1 | 255 | 102.0% | 05/30/02 | 15 |
| 10.9 | Zn-P removed | 4037 | 24/5/1 in air | 270.1 | 265 | 101.9% | 05/10/02 | 16 |
| 10.9 | Zn-P removed | 4037 | 24/5/1 in air | 267.2 | 265 | 100.8% | 05/12/02 | 17 |
| 10.9 | Zn-P removed | 4037 | 24/5/1 in air | 260.0 | 265 | 98.1% | 05/13/02 | 18 |
| 10.9 | Zn-P removed | 4037 | 24/5/1 @ -1.2 volts | 278.3 | 265 | 105.0% | 05/14/02 | 19 |
| 10.9 | Zn-P removed | 4037 | 24/5/1 @ -1.2 volts | 261.7 | 265 | 98.8% | 05/21/02 | 20 |
| 10.9 | Zn-P removed | 1541 | 24/5/1 in air | 268.7 | 250 | 107.5% | 05/10/02 | 21 |
| 10.9 | Zn-P removed | 1541 | 24/5/1 in air | 259.6 | 250 | 103.8% | 05/12/02 | 22 |
| 10.9 | Zn-P removed | 1541 | 24/5/1 in air | 269.1 | 250 | 107.6% | 05/13/02 | 23 |
| 10.9 | Zn-P removed | 1541 | 24/5/1 @ -1.2 volts | 263.2 | 250 | 105.3% | 05/20/02 | 24 |
| 10.9 | Zn-P removed | 1541 | 24/5/1 @ -1.2 volts | 262.8 | 250 | 105.1% | 05/23/02 | 25 |
| 10.9 | Zn-P removed | 10B21 | 24/5/1 in air | 259.8 | 255 | 101.9% | 04/30/02 | 26 |
| 10.9 | Zn-P removed | 10B21 | 24/5/1 in air | 264.4 | 255 | 103.7% | 04/30/02 | 27 |
| 10.9 | Zn-P removed | 10B21 | 24/5/1 in air | 270.3 | 255 | 106.0% | 04/30/02 | 28 |
| 10.9 | Zn-P removed | 10B21 | 24/5/1 @ -1.2 volts | 268.0 | 255 | 105.1% | 04/30/02 | 29 |
| 10.9 | Zn-P removed | 10B21 | 24/5/1 @ -1.2 volts | 268.1 | 255 | 105.1% | 06/01/02 | 30 |
| 10.9 | Lime | 4037 | 24/5/1 in air | 284.9 | 265 | 107.5% | 04/11/02 | 31 |
| 10.9 | Lime | 4037 | 24/5/1 in air | 267.8 | 265 | 101.1% | 04/23/02 | 32 |
| 10.9 | Lime | 4037 | 24/5/1 in air | 260.9 | 265 | 98.5% | 04/24/02 | 33 |
| 10.9 | Lime | 4037 | 24/5/1 @ -1.2 volts | 265.3 | 265 | 100.1% | 04/23/02 | 34 |
| 10.9 | Lime | 4037 | 24/5/1 @ -1.2 volts | 265.0 | 265 | 100.0% | 05/02/02 | 35 |
| 10.9 | Lime | 1541 | 24/5/1 in air | 253.0 | 250 | 101.2% | 05/10/02 | 36 |
| 10.9 | Lime | 1541 | 24/5/1 in air | 267.9 | 250 | 107.2% | 05/12/02 | 37 |
| 10.9 | Lime | 1541 | 24/5/1 in air | 252.1 | 250 | 100.8% | 05/13/02 | 38 |
| 10.9 | Lime | 1541 | 24/5/1 @ -1.2 volts | 250.1 | 250 | 100.0% | 05/19/02 | 39 |
| 10.9 | Lime | 1541 | 24/5/1 @ -1.2 volts | 250.5 | 250 | 100.2% | 05/22/02 | 40 |
| 10.9 | Lime | 10B21 | 24/5/1 in air | 265.9 | 255 | 104.3% | 04/25/02 | 41 |
| 10.9 | Lime | 10B21 | 24/5/1 in air | 258.4 | 255 | 101.3% | 04/29/02 | 42 |
| 10.9 | Lime | 10B21 | 24/5/1 in air | 261.2 | 255 | 102.4% | 04/29/02 | 43 |
| 10.9 | Lime | 10B21 | 24/5/1 @ -1.2 volts | 255.1 | 255 | 100.0% | 04/25/02 | 44 |
| 10.9 | Lime | 10B21 | 24/5/1 @ -1.2 volts | 260.9 | 255 | 102.3% | 05/31/02 | 45 |

# APPENDIX II

## SUMMARY OF ISL TESTING FOR FORD (PHOSPHATE EMBRITTLEMENT STUDY)

## P.C. 12.9

| | |
|---|---|
| 🟩 | Equal to or or greater than 75% |
| 🟨 | Between 50% and 75% |
| 🟥 | Less than 50% Fast Fracture Strength |
| ▢ | Part did not fail (machine bottomed out) - 0 of 30 |

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | |
|---|---|---|---|---|---|---|---|---|
| **CLASS** | **COATING** | **MATERIAL** | **TEST DESCRIPTION** | **LOAD (lbs.)** | **FFS (lbs.)** | **%FS** | **TEST DATE** | |
| 12.9 | Zn-P | 4037 | 24 steps/5%FFS/1 hour steps in air | 314.7 | 320 | 98.3% | 05/06/02 | 1 |
| 12.9 | Zn-P | 4037 | 24/5/1 in air | 315.6 | 320 | 98.6% | 05/07/02 | 2 |
| 12.9 | Zn-P | 4037 | 24/5/1 in air | 311.1 | 320 | 97.2% | 05/09/02 | 3 |
| 12.9 | Zn-P | 4037 | 24/5/1 @ -1.2 volts | 240.1 | 320 | 75.0% | 05/08/02 | 4 |
| 12.9 | **Zn-P** | 4037 | **24/5/1 @ -1.2 volts** | 144.3 | 320 | 45.1% | 05/12/02 | 5 |
| 12.9 | Zn-P | 1541 | 24/5/1 in air | 311.7 | 320 | 97.4% | 05/07/02 | 6 |
| 12.9 | Zn-P | 1541 | 24/5/1 in air | 308.2 | 320 | 96.3% | 05/08/02 | 7 |
| 12.9 | Zn-P | 1541 | 24/5/1 in air | 309.9 | 320 | 96.8% | 05/09/02 | 8 |
| 12.9 | **Zn-P** | 1541 | **24/5/1 @ -1.2 volts** | 160.3 | 320 | 50.1% | 05/06/02 | 9 |
| 12.9 | **Zn-P** | 1541 | **24/5/1 @ -1.2 volts** | 224.1 | 320 | 70.0% | 05/11/02 | 10 |
| 12.9 | Zn-P removed | 4037 | 24/5/1 in air | 298.8 | 285 | 104.8% | 05/15/02 | 11 |
| 12.9 | Zn-P removed | 4037 | 24/5/1 in air | 280.2 | 285 | 98.3% | 05/15/02 | 12 |
| 12.9 | Zn-P removed | 4037 | 24/5/1 in air | 281.3 | 285 | 98.7% | 05/16/02 | 13 |
| 12.9 | Zn-P removed | 4037 | 24/5/1 @ -1.2 volts | 256.1 | 285 | 89.9% | 05/16/02 | 14 |
| 12.9 | Zn-P removed | 4037 | 24/5/1 @ -1.2 volts | 242.7 | 285 | 85.2% | 05/18/02 | 15 |
| 12.9 | Zn-P removed | 1541 | 24/5/1 in air | 296.7 | 290 | 102.3% | 05/15/02 | 16 |
| 12.9 | Zn-P removed | 1541 | 24/5/1 in air | 290.3 | 290 | 100.1% | 05/16/02 | 17 |
| 12.9 | Zn-P removed | 1541 | 24/5/1 in air | 286.1 | 290 | 98.7% | 05/16/02 | 18 |
| 12.9 | Zn-P removed | 1541 | 24/5/1 @ -1.2 volts | 240.1 | 290 | 82.8% | 05/15/02 | 19 |
| 12.9 | Zn-P removed | 1541 | 24/5/1 @ -1.2 volts | 246.6 | 290 | 85.0% | 05/17/02 | 20 |
| 12.9 | Lime | 4037 | 24/5/1 in air | 317.4 | 320 | 99.2% | 05/06/02 | 21 |
| 12.9 | Lime | 4037 | 24/5/1 in air | 315.2 | 320 | 98.5% | 05/07/02 | 22 |
| 12.9 | Lime | 4037 | 24/5/1 in air | 317.3 | 320 | 99.2% | 05/08/02 | 23 |
| 12.9 | **Lime** | 4037 | **24/5/1 @ -1.2 volts** | 224.1 | 320 | 70.0% | 05/09/02 | 24 |
| 12.9 | **Lime** | 4037 | **24/5/1 @ -1.2 volts** | 224.0 | 320 | 70.0% | 05/13/02 | 25 |
| 12.9 | Lime | 1541 | 24/5/1 in air | 310.6 | 320 | 97.1% | 05/06/02 | 26 |
| 12.9 | Lime | 1541 | 24/5/1 in air | 318.2 | 320 | 99.4% | 05/08/02 | 27 |
| 12.9 | Lime | 1541 | 24/5/1 in air | 315.3 | 320 | 98.5% | 05/09/02 | 28 |
| 12.9 | Lime | 1541 | 24/5/1 @ -1.2 volts | 240.1 | 320 | 75.0% | 05/07/02 | 29 |
| 12.9 | **Lime** | 1541 | **24/5/1 @ -1.2 volts** | 224.1 | 320 | 70.0% | 05/10/02 | 30 |

# APPENDIX III


Photo 1 - RSL™ Test System


Photo 2 - RSL™ test in air

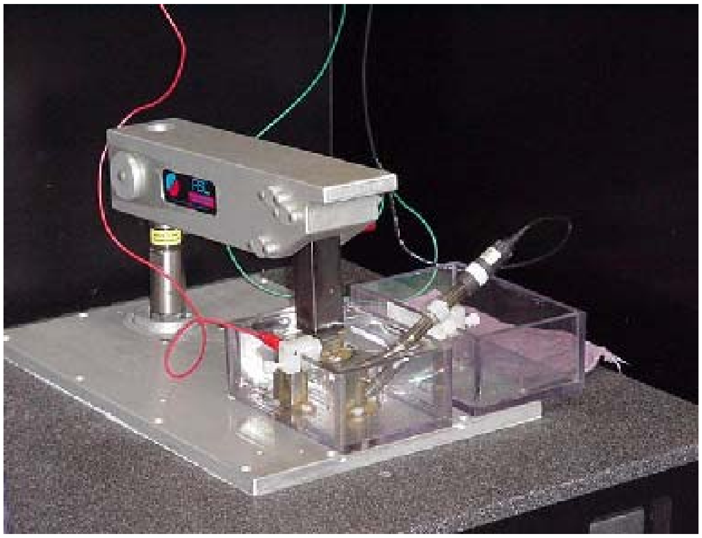
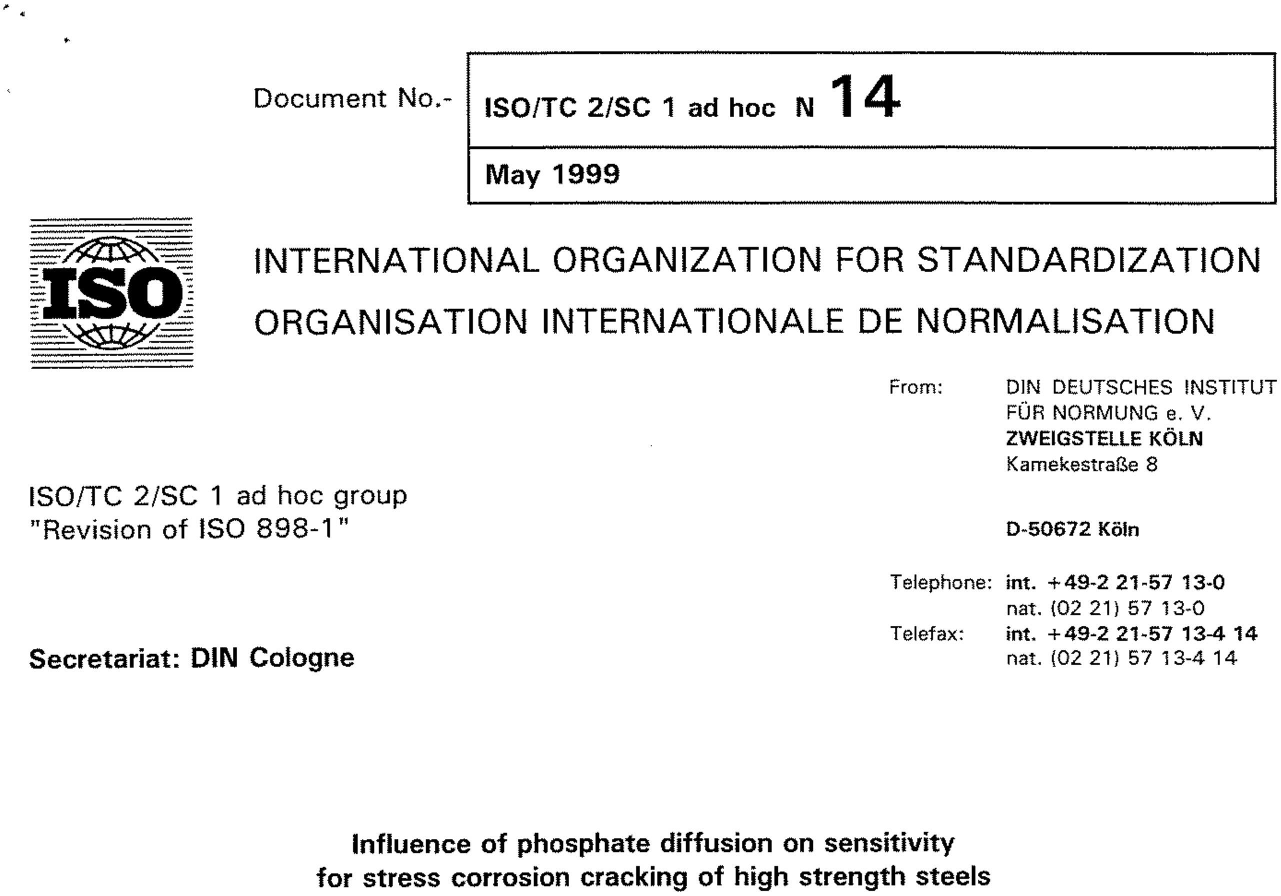


Photo 3 - RSL™ test in 3.5% NaCl solution

# APPENDIX IV



Document No.- **ISO/TC 2/SC 1 ad hoc N 14**

**May 1999**

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION
ORGANISATION INTERNATIONALE DE NORMALISATION

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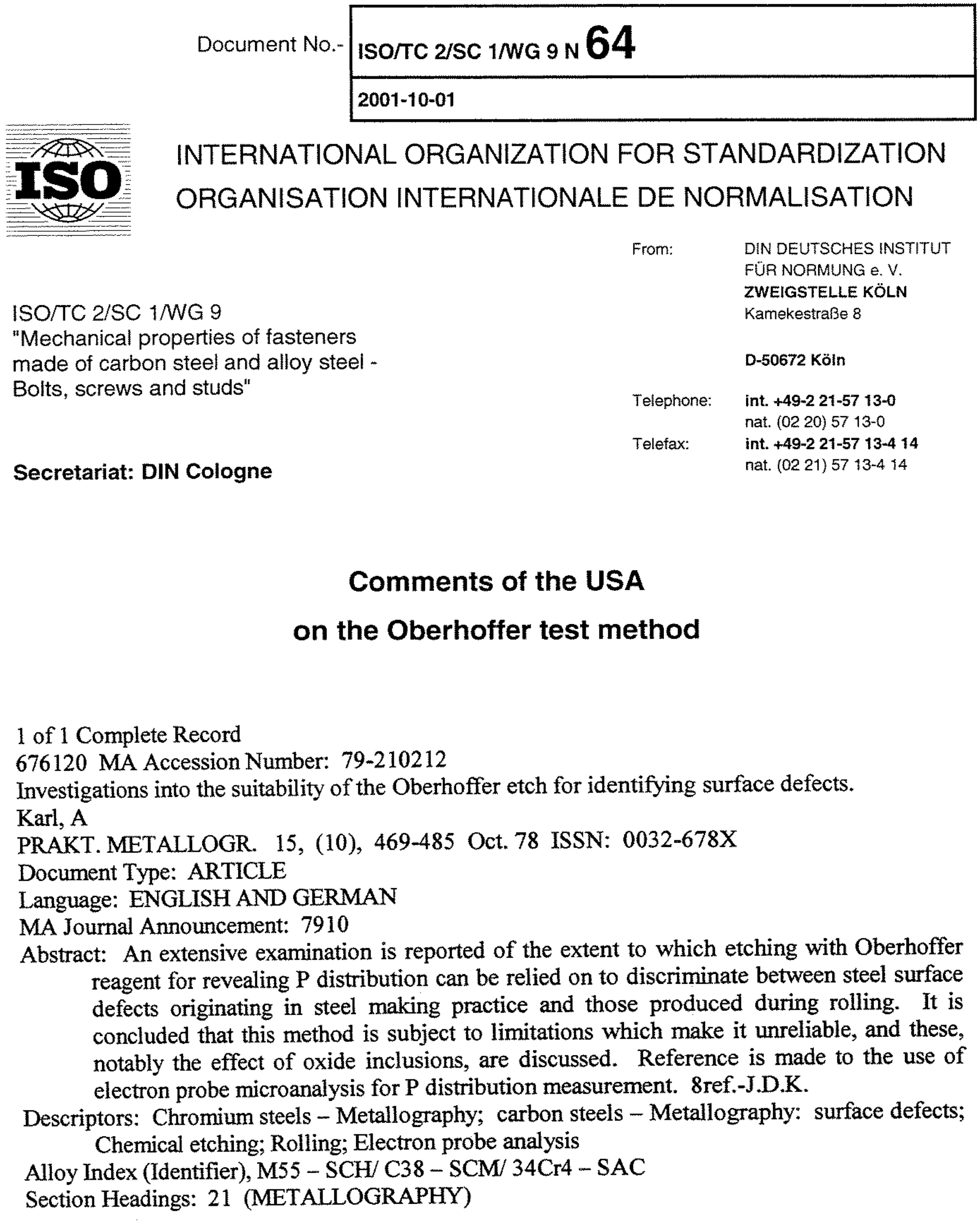
ISO/TC 2/SC 1 ad hoc group
"Revision of ISO 898-1"

**Secretariat: DIN Cologne**

## Influence of phosphate diffusion on sensitivity for stress corrosion cracking of high strength steels

# APPENDIX V



Document No.- **ISO/TC 2/SC 1/WG 9 N 64**

**2001-10-01**

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ISO/TC 2/SC 1/WG 9
"Mechanical properties of fasteners made of carbon steel and alloy steel - Bolts, screws and studs"

**Secretariat: DIN Cologne**

## Comments of the USA on the Oberhoffer test method

1 of 1 Complete Record
676120 MA Accession Number: 79-210212
Investigations into the suitability of the Oberhoffer etch for identifying surface defects.
Karl, A
PRAKT. METALLOGR. 15, (10), 469-485 Oct. 78 ISSN: 0032-678X
Document Type: ARTICLE
Language: ENGLISH AND GERMAN
MA Journal Announcement: 7910
Abstract: An extensive examination is reported of the extent to which etching with Oberhoffer reagent for revealing P distribution can be relied on to discriminate between steel surface defects originating in steel making practice and those produced during rolling. It is concluded that this method is subject to limitations which make it unreliable, and these, notably the effect of oxide inclusions, are discussed. Reference is made to the use of electron probe microanalysis for P distribution measurement. 8ref.-J.D.K.
Descriptors: Chromium steels – Metallography; carbon steels – Metallography: surface defects; Chemical etching; Rolling; Electron probe analysis
Alloy Index (Identifier), M55 – SCH/ C38 – SCM/ 34Cr4 – SAC
Section Headings: 21 (METALLOGRAPHY)

# APPENDIX VI

## Comments and Independent Tests
## by
## Dr. Louis Raymond*

I conducted a test program with ASTM F1940 test specimens of 4340 steel, tempered back to 45 HRC and 39 HRC to provide supplementary data for direct measurement of the threshold stress for hydrogen induced stress cracking of bare specimens; i.e., specimens that never have been exposed to a ZnP coating. These specimens were then compared to the data located in the Annex to ASTM F1940 for M12 screws at 45 HRC and 39 HRC. In addition, the corrosion potential was measured on remnants of specimens from a supplier that had been alkaline cleaned, acid cleaned, or had no cleaning prior to heat treatment.

The results and conclusions are summarized a follows:

1.) A modified surface, after a ZnP coating on some M12 screws, no matter how obtained, alkaline cleaned, acid cleaned, or no cleaning prior to heat treatment, always had a stress corrosion threshold at the zinc corrosion potential that was higher than uncoated (bare) ASTM F1940 4340 steel specimens at the same hardness. This means that all three of the residual surface conditions acted as a barrier to the infusion of hydrogen due to galvanic coupling to zinc, when exposed to water, i.e., they were more effective than a bare metal, tempered martensite steel surface.

2.) The measured corrosion potential of all three of these surfaces is located between zinc and steel, which means it electrochemically behaves the same as zinc, but produces less hydrogen that is available for infusion into the steel, when exposed to aqueous conditions.

3.) Complete removal of the ZnP coating before zinc plating makes the steel screw more susceptible to hydrogen embrittlement than with the residual sub-surface from the ZnP coating.

4.) The work performed in Appendix IV was conducted on the as-heat treated surfaces of ZnP or MnP coated specimens and not on the surfaces after they were subsequently plated with zinc. The interpretation of the test results that were generated in the report (Appendix IV) that led to the requirement for removal of the ZnP coating prior to heat treatment and subsequent zinc plating, misrepresent the influence of the residual surfaces with a ferritic layer infused with phosphorous under actual service conditions. Tested at the zinc corrosion potential, the threshold stress for the onset of hydrogen induced stress cracking was found to be higher than the uncoated F1940 steel specimens at the same hardness; therefore, the residuals on the surfaces from the ZnP result in a barrier to hydrogen induced stress cracking. The FoMoCo/TFS testing program had the results distorted because of a significant drop in hardness of the specimens with the ZnP "apparently" but not "actually" removed from the M12 fasteners prior to heat treatment. The most certain method to circumvent the problem of testing a contamination free surface is to start with bare metal specimens instead of rolled fasteners, as performed in the ISO report.

Reference:
Appendix IV: ISO Document N14 Paper "Influence of Phosphate Diffusion on Sensitivity of SCC of High Strength Steels

* Recipient of the IFI 2006 Roy P. Trowbridge Technology Award (www.LouRaymond.com).

## Expansion on “Conclusion”

In reviewing the work that has been done, it is my opinion that the main problem in arriving at the conclusion to remove the ZnP coating prior to heat treatment is based on the results of a mixture of data that does not represent actual service conditions. In the ISO Report, the subsequent addition of a zinc coating is ignored; and in the Ford study, no comparison is made to bare metal specimens that are pristine, i.e., have never been exposed to ZnP. It is never clear as to the surface condition of the samples being tested. The major issue being that the specimens with the “ZnP removed” still had residual contamination from the ZnP coating.

Conclusion: The results of my study show that a bare steel sample that has not been exposed to any ZnP coating prior to heat treatment is more susceptible to hydrogen induced stress cracking than the steel that has been ZnP coated prior to heat treatment, regardless of any attempt to remove the ZnP coating prior to heat treatment, because all of the attempted treatments to date have resulted in residual deposits of phosphate in one form or another. The presence of the residual phosphates after a subsequent coating inhibits the subsequent diffusion of hydrogen into the steel; i.e., acts as a barrier after being plated.

Obviously, the interpretation of the test results that were generated in the report (Appendix IV) that led to the requirement for removal of the ZnP coating prior to heat treatment and subsequent zinc plating are misleading, because they do not represent the actual service conditions that have the surface zinc coated after heat treatment. No one uses the ZnP coating after heat treating without a subsequent coating process. In ISO Document N14, the samples were tested after heat treatment with no subsequent coating process. They should have tested their samples after exposure to a subsequent coating process such as zinc.

The susceptibility of a steel such as 34Cr4 to hydrogen induced stress cracking is a function of hardness, independent of the surface condition. The surface condition affects crack initiation. Because dissimilar metal by-products are formed on the surface during the heat treating process, galvanic cells that result in salt water generate hydrogen at the surface. For this reason, it is not surprising that the specimens in the ISO Document N14 failed after heat treatment and then subsequent exposure to salt water and then stress. The bare metal samples had no dissimilar metal surface conditions and therefore had no hydrogen generation cells on the surface. Had they zinc plated the samples after heat treatment with the ZnP coating present, they would have found the samples with the dissimilar metal ZnP by-products on the surface to be more resistant to hydrogen induced stress cracking than the zinc plated bare steel specimen.

Reference:
Appendix IV: ISO Document N14 Paper “Influence of Phosphate Diffusion on Sensitivity of SCC of High Strength Steels

**SUMMARY TABLE from ASTM F1940:** The hydrogen susceptibility ratio (HSR) in terms of % Fast Fracture Strength (%FFS) in bending (B) was measured at a loading rate of 20 steps/5% FFS/1hr. in a 3.5% salt water solution under hydrogen charging condition of –1.2 Vsce (Saturated Calomel Electrode), which is equivalent to galvanic coupling at the open circuit corrosion potential of zinc. That generates a galvanic hydrogen charging potential on the specimen of about 0.5 Vsce on a steel specimen.

Included in ASTM STD F 1940, FIG. X1.1 and FIG. X1.2 is data comparing test results at –1.2 Vsce on 4340 steel at 52 HRC to M10 fasteners at 45 HRC (12.9) and 39 HRC (10.9). The Type 4037 M10 fasteners were ZnP coated before heat treatment.

I conducted a supplementary test program with some F1940 test specimens that were tempered back to 45 HRC and 39 HRC to provide data for direct comparison to the lower hardness fasteners.

The bare F1940 specimens at 45 HRC and 39 HRC were found to have a threshold of 45% FFS and > 85% FFS, respectively, which in both cases is below the threshold of the M12 fasteners at the same hardness. Since the M12 fasteners did not have the ZnP coating removed prior to heat treatment, these results imply that the bare metal surfaces are more susceptible to hydrogen induced stress cracking than the ZnP coated samples, or conversely, the ZnP coating provides a barrier to the infusion of hydrogen into the steel.

**Data from ASTM F1940**

| Steel | HRC | Specimen | %FFS(B) | Surface |
|---|---|---|---|---|
| 4340 | 50-52 | F1940* | 30 | Bare |
| | | | | |
| 4340 | 45 | F1940* | 45 | Bare |
| 4037 | 45 | M10 (12.9) | 60 | ZnP |
| | | | | |
| 4340 | 39 | F1940* | > 85 | Bare |
| 4037 | 39 | M10 (10.9) | 100 | ZnP |

* Specimens per ASTM F1940.

**Conclusion from ASTM F1940 Comparison:**

- The resistance to environmental hydrogen induced stress cracking (HISC) increases with a decrease in hardness.
- At $\leq$ 39 HRC, no measurable degradation in strength occurs in either bare or coated samples in a hydrogen charging environment that generates a galvanic hydrogen charging potential of about 0.5Vsce.
- On 12.9 screws, a delta ferrite layer resulting from the heat treatment of the ZnP coated screws acts as a barrier to hydrogen that results in a higher threshold stress for the onset of hydrogen induced stress cracking; i.e., 60% FFS(B) vs. 45% FFS(B). In effect, at the same sample hardness, the phosphate layer increased the resistance to HISC above that of a specimen with a bare metal surface.

**Corrosion Potential:** The Open Circuit Corrosion Potential **(OCP)** in a 3.5% salt-water solution of processed ZnP screws was measured. Bare Type 4340 steel, by comparison, is slightly cathodic to all four surface conditions of the ZnP coated samples. Conversely, all of the residual phosphate surfaces are anodic to the bare steel; therefore, it is not surprising in Ref. #1 that these surfaces initiated pitting sites, resulting in a more susceptible surface condition relative to stress corrosion cracking. With the addition of a zinc coating, the residual surfaces inhibit the entry of hydrogen into the steel.

**OCP in a 3.5% NaCl Solution vs. Saturated Calomel Electrode**

| Steel | Surface Condition | OCP (V vs. SCE) |
|---|---|---|
| SAE 4340 | Bare Metal Surface | -0.62 **(cathode)** |
| SAE 1541 | 4B (Patchy $P_2O_5$) | -0.689 |
| SAE 1541 | 2B (Acid Clean, delta-ferrite) | -0.723 |
| SAE 1541 | 1B ($P_2O_5$) | -0.728 |
| SAE 1541 | 3B (Alkaline Clean, delta-ferrite) | -0.739 |
| Cd-plated | cadmium | -0.85 |
| Zn-plated | zinc | -1.1 **(anode)** |

An IFI Research Report

IFI RR-3

# Influence of Phosphorus on Fastener Integrity

Advancing
Fastener
Application
Engineering

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## SCOPE

This study was established to investigate the effect of the presence of a full or partial zinc-phosphate raw material coating on the integrity and performance of high tensile metric screws processed to Property Class 8.8, 10.9 and 12.9, respectively.

In this test program, the test method found in ASTM F1624, *Standard Test Method for Measurement of Hydrogen Embrittlement Threshold in Steel by the Incremental Step Loading Technique*, is used to correlate any reduction in fracture strength of the fasteners with the presence of a purported embrittling agent, namely phosphorus. Both the residual hydrogen in the fastener from processing and then the effect of the phosphorus modified surface finishes on the threshold stress required to induce subcritical crack growth under an imposed cathodic charging voltage were measured.

The ASTM F1624 Test Method measures the threshold stress for the onset of hydrogen induced subcritical crack growth, which when tested in air, quantifies the amount of residual hydrogen retained in a fastener from processing as a reduction in its fracture strength. When tested under an imposed hydrogen charging potential in an aqueous solution, the threshold stress required to induce subcritical cracking is measured.

## SUMMARY

The application of the rising step load test method established in ASTM F1624 indicates that fasteners manufactured with a phosphate coating and subsequently heat treated did not show any reduction in fastener load carrying capability. Cleaning methods prior to heat treating for phosphate removal were only partially effective. No difference in load carry capability between those subjected to cleaning and those which were not cleaned was discernible.

## BACKGROUND

Historically, zinc phosphate coating of wire and rod is a common practice in the cold forming process that is used to produce all types of mechanical fasteners and special cold formed, non-fastener parts. Zinc phosphate is the vehicle that retains various lubricants on the surface of the wire or rod to protect the surfaces of the tool and work piece against damage during the various steps in the cold forming and extrusion processes.

This vehicle for lubricants is not easily removed from the rod, wire, or cold-formed part that is produced. While acid is used to remove some of the zinc phosphate, experience has shown that it is difficult, if not impossible, to completely remove all phosphate from the product surfaces prior to heat treatment. A task group of ASME B18 Subcommittee 4 examined this issue when it was raised in ISO/TC 2 working group discussions and was unable to identify any supplier of cleaning equipment that would guarantee the capability to achieve 100% removal.

In 1988, ISO/TC 2 published a revision of ISO 898-1 which included a note that said: *"A metallographically detectable white phosphorous enriched layer is not permitted for property class 12.9 on surfaces subjected to tensile stress."* A major European auto manufacturer claimed the failure of a bolt because of the presence of phosphorus. However, subsequent review of that paper by Craig Hood, a world-renowned expert in fastener metallurgy, indicated the paper was not conclusive and only speculated on the impact of phosphorus. (See ISO/TC 2/SC 1 ad hoc N14, May 1999, Appendix IV.) In 1993, Ford Worldwide Standard WX 100 was released, which required the removal of <u>all</u> phosphate prior to heat treatment of Property Class 8.8 (>M16), 9.8, 10.9, and 12.9. IFI advised its members to seek waivers for this requirement for the following reasons:

1.) No technology exists that can guarantee the 100% removal of phosphorus from the surface of bolts, screws, or cold formed parts in the manufacturing process. Further, the methods for detection of its presence are not reliable and, in fact, can be misleading. (See N64 of ISO/TC 2/SC 1/WG 9, October 2001, Appendix V.)

2.) Significant quantities of bolts and screws that have a zinc phosphate coating present during heat treatment are installed annually and the fastener industry can report with a high degree of certainty that it has not experienced failures attributable to the presence of phosphorus.

3.) No known organized investigation, until now, has ever been carried out to evaluate the impact of phosphorus on threaded fasteners. (Proprietary research may have been done, but the results are not generally available.)

4.) Because zinc phosphate is a coating often used on cold forming materials and because it cannot be completely removed with current technology, its continued use should be permitted until such time as research would demonstrate that a change in this practice was technically justified.

5.) While other coatings exist, issues with alternate coatings include their ability to carry a lubricant as effectively, and the ability to provide sufficient corrosion protection, which relates to a shorter shelf life for the raw material.

In 2002, Textron Fastening Systems (TFS), in concert with Ford Motor Company, completed a study involving 15 test lots to seek information concerning the behavior of zinc phosphate coatings on fasteners. These were heat treated to Property Class 8.8, 10.9, and 12.9, respectively. They were then tested in air, and under an imposed galvanic potential that electrochemically simulated the addition of a subsequent zinc coating. This report will review the Textron study and discuss the findings.

## TEST PROCEDURE

### Test Product

An M12 X 1.75 X 100 mm hex flange screw (Figure 1) was selected for this study with all samples being manufactured by the Shamrock Fastener Division of Textron Fastening Systems. In order to achieve uniformity of product, the screws were manufactured in successive forming operations using the same cold heading machine, thread roller, and tooling.

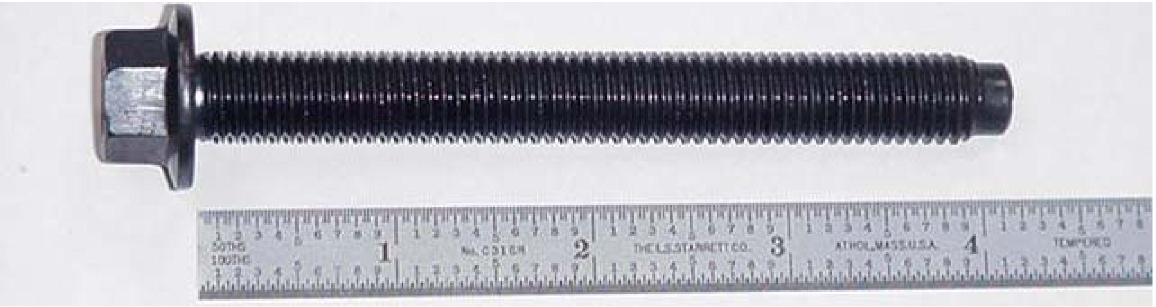


**Figure 1**

All screws, for each property class were traceable to their respective single mill heat of material. The raw materials used for each of the three property classes were as follows:

| Material | Property Classes Produced |
|---|---|
| 10B21 | Property Class 8.8 and 10.9 |
| 1541 | Property Class 8.8, 10.9, and 12.9 |
| 4037 | Property Class 8.8, 10.9, and 12.9 |

Each property class was furnished in three different surface finishes including:

- zinc phosphate applied to the wire prior to heading, and not removed prior to heat treatment
- lime applied to the wire prior to heading, and not intentionally removed prior to heat treatment
- zinc phosphate intentionally removed after heading, prior to heat treatment

Thus a total of 24 lots of fasteners were produced.

The parts subjected to phosphate removal were placed in a stainless steel apparatus, which is subdivided into four compartments to provide four stages of cleaning. The fasteners were transported using a horizontal screw driven conveyor with the compartments alternately cleaning then rinsing such that 2 cleanings and 2 rinses are sequenced. The cleaning solution was a 10% by volume alkaline solution with a potassium hydroxide (KOH) base. The fasteners were in each stage for six minutes. The first stage was at 170°F and the second at 190°F. The third stage was a hot rinse with no temperature control and the fourth stage was a dryer at 350°F.

All parts were heat treated toward the upper limit of the specification hardness for their respective property class: 8.8 to 32 HRC, 10.9 to 39 HRC, and 12.9 to 44 HRC. (See ASTM F568M or ISO 898-1 for a complete delineation of the respective property classes.) It was determined that Property Class 10.9 lots would be tested first to determine the need for testing Property Class 8.8, since Property Class 10.9 represented the worst case scenario between the two property classes in terms of higher hardness and strength. The lots of Property Class 12.9 subjected to phosphate removal prior to heat treatment were heat treated at a different time period than the other Property Class 12.9's, and it was noted that they were measured to be at a slightly lower hardness (2 HRC points lower) than the Property Class 12.9 lots that were not subject to removal of the phosphate prior to heat treatment.

The heat treatment process alters the finish on the surface of the fastener, but it does not change the susceptibility of the core fastener material to hydrogen induced stress cracking. The susceptibility is a material property that is strongly dependent on the hardness or strength of the fastener. Therefore, modifying the surface finish affects the permeability of hydrogen into the fastener. For example, with a surface finish of copper, which is impervious to hydrogen diffusion, no degradation in strength will be measured even while imposing an aggressive hydrogen-charging cathodic potential; i.e. the modified surface finishes act as a barrier to the infusion of hydrogen into the steel fastener.

## Test Method

In accordance with an agreement with Ford representatives, Textron used an incremental step load method to test the lots of flange screws. The test method is established in ASTM F1624, *Standard Test*

*Method for Measurement of Hydrogen Embrittlement Threshold in Steel by the Incremental Step Loading (ISL) Technique*. These tests may be performed in air or in a controlled environment. The test method determines the threshold stress for the onset of hydrogen induced subcritical crack growth with an incrementally increasing step loading profile on the fastener.

Heading, and subsequent heat treatment of the fastener, alters the surface finish, resulting in a change in the electrochemical kinetics on the surface of the screw when immersed in a salt water solution. First, the incremental step load test conducted in air is a measure of the residual hydrogen in the steel due to the heading and heat treatment on the surface finish. The incremental step load test was then conducted in an aqueous environment (3.5% NaCl solution) under a hydrogen-charging cathodic potential of –1.2 volts referenced against a Saturated Calomel Electrode (–1.2Vsce) to electrochemically simulate the application of a zinc coating to the altered surfaces after the forming and heat treat processes. The quantitative measure for the susceptibility of the fastener with the modified surface treatment is the threshold stress or the ratio of the threshold stress to the Fast Fracture Strength.

The evidence provided in the ISO N14 document that suggests that phosphorus or the phosphorus enriched delta-ferrite seam and zone of phosphorus diffusion during heat treatment caused the intergranular cracks only illustrates that the applied stress exceeded the threshold stress for the surface generated by the coating and thermal mechanical processing that was employed, but this was in a raw state and not with a zinc coating subsequently applied. See Appendix VI for more information.

Using the above fastener lots and test method, testing was begun at the Textron facilities in Rockford, Illinois on April 11, 2002. The test equipment and setup is shown in Photos 1-3, Appendix III. ASTM F1624 utilizes an initial four point bending method in air at ASTM E8 loading rates to establish the Fast Fracture Strength (FFS) of a given lot of screws. Five samples from each lot were used to establish the FFS for each respective lot as indicated in Column 6 of the tables in Appendix I and Appendix II. The lots were then tested using the ASTM F1624 method in air, then in a 3.5% saline solution at an electrochemical potential measurement value of –1.2Vsce as a hydrogen charging potential, simulating the addition of a zinc coating that electrochemically provides a worst case scenario for the tested fasteners. Each of the Property Class 10.9 fasteners was tested over a 24-hour period using 5% of FFS as the increment increase in load for a one-hour duration per step, which corresponds to the loading profile of ASTM F1940, *Standard Test Method for Process Control Verification to Prevent Hydrogen Embrittlement in Plated or Coated Fasteners*.

It should be noted that the Ford designated and approved contractor for cleaning, i.e., removal of the phosphate, did not successfully remove 100% of the zinc phosphate from the fastener surfaces as currently required by Ford specifications. In fact, it was also discovered that phosphorus existed on the surface of the screws where the wire was coated with lime (no zinc phosphate) as well as those in which the zinc phosphate was simply “removed.” This seems to confirm the evaluation of current cleaning technology by the ASME B18 Subcommittee 4 task group.

## Test Results

An examination of the test results from the 45 Property Class 10.9 screws reveals the following: 38 samples or 84.4% equaled or exceeded the FFS (fast fracture strength). The ISL fracture strength of the remaining seven test samples are within 1.9% of the FFS.

An examination of Property Class 10.9 fasteners reveals the following:

1.) Zinc phosphate coated fasteners processed to Property Class 10.9 and ISL tested in air averaged 104% FFS = 250-265 lbs., which converts to a hardness of 39-40 HRC.

2.) Fasteners subjected to attempts to remove the zinc phosphate coating prior to heat treatment and then ISL tested in air averaged 103.5% FFS = 250-265 lbs., which converts to a hardness of 39-40 HRC.

3.) Lime coated fasteners processed to Property Class 10.9 and ISL tested in air resulted in an average of 102.7% FFS = 250-265 lbs., which converts to a hardness of 39-40 HRC.

4.) The air test results substantiate the fact that no residual hydrogen was introduced during processing that would cause any degradation in mechanical properties of the P.C. 10.9 fasteners.

5.) Zinc phosphate coated fasteners ISL tested in a saline solution with a –1.2 Vsce current had an average of 101.2% FFS = 250-265 lbs., which converts to a hardness of 39-40 HRC.

6.) Fasteners subjected to attempts to remove zinc phosphate coating and ISL tested in a saline solution with a –1.2 Vsce current had an average of 104.1% FFS = 250-265 lbs., which converts to a hardness of 39-40 HRC.

7.) Lime coated fasteners ISL tested in a saline solution with a –1.2 Vsce current had an average of 100.4% FFS = 250-265 lbs., which converts to a hardness of 39-40 HRC.

8.) The environmental test results substantiate the fact that under aggressive hydrogen charging conditions that electrochemically simulate the addition of a zinc coating, the threshold stress equaled or exceeded the FFS of the 10.9 fasteners, regardless of the altered surface conditions.

9.) In summary, no matter the material, coating, or test environment, none of the Property Class 10.9 test screws failed prematurely. Therefore, none of the three surface conditions caused any degradation in strength from processing or from environmental conditions that duplicated subsequent coating with zinc (Vsce = –1.2 volts).

10.) Based on the Property Class 10.9 results, a decision was made by TFS in consultation with Ford that the Property Class 8.8 fasteners need not be tested. Therefore, the 24 test lots were reduced to 15 test lots including nine lots of P.C. 10.9's and six lots of P.C. 12.9's.

An examination of Property Class 12.9 fasteners reveals the following:

1.) Zinc phosphate coated fasteners processed to Property Class 12.9 and ISL tested in air averaged 97.4% FFS = 320 lbs., which converts to a hardness of 46 HRC.

2.) Fasteners subjected to attempts to remove the zinc phosphate coating and then ISL tested in air averaged 100.5% FFS = 285-290 lbs., which converts to a hardness of 43 HRC.

3.) Lime coated fasteners processed to Property Class 12.9 and ISL tested in air resulted in an average of 98.7% FFS = 320 lbs., which converts to a hardness of 46 HRC.

4.) The air test results substantiate the fact that no residual hydrogen was introduced during processing that would cause any degradation in mechanical properties of the P.C. 12.9 fasteners.

5.) The twelve samples of Property Class 12.9 ISL tested in a saline solution with a –1.2 Vsce current had a threshold stress that averaged 72.3% or 26% less than when tested in air.

6.) The P.C. 12.9's with zinc phosphate removed and ISL tested in a saline solution with a –1.2 Vsce current achieved a higher threshold stress prior to fracture (82-90% FFS) than the lime coated or zinc phosphate coated fasteners (45-75% FFS) tested in the same solution. This difference can be attributed to the fact that the fasteners with the ZnP coating removed had a measured lower hardness of about 2 points HRC than the other two lots. This difference was consistent with the hardness conversion from the FFS that showed the fasteners with the ZnP coating removed to be 3 points HRC lower than the other two lots. Taking into account the difference in hardness, the degradation in strength of the 12.9 fasteners can be considered to be about the same for all three surface finishes.

7.) NOTE: 50% FFS in bending corresponds to the ASTM E8 Tensile Strength of 1200 MPa (~ 175 ksi). In bending of highly ductile steels, the limit load is about twice the ASTM E8 material Tensile Strength or ASTM F606M axial tensile strength. Therefore, the degradation in strength in bending from the three surface finishes, still meets or exceeds the axial tensile strength in tension.

8.) The environmental test results substantiate the fact that under aggressive hydrogen charging conditions that electrochemically simulate the addition of a zinc coating, the threshold stress of the P.C. 12.9 fasteners is less than the bend fracture strength in air, but is essentially the same for all three surface finishes on an equivalent hardness scale and meets or exceeds the axial tensile strength of the M12 fastener when tested in tension.

## Conclusions

**1.) The air test results substantiate the fact that no residual hydrogen was introduced during processing that would cause any degradation in mechanical properties of the 10.9 fasteners, regardless of the initial surface finish.**

**2.) The environmental test results substantiate the fact that under aggressive hydrogen charging conditions that electrochemically simulate the addition of a zinc coating, the threshold stress of the P.C. 10.9 fasteners exceeds the FFS, regardless of the altered surface conditions; i.e., they are immune to environmentally induced hydrogen stress cracking, regardless of the initial surface finish.**

**3.) The air test results substantiate the fact that no residual hydrogen was introduced during processing that would cause any degradation in mechanical properties of the P.C. 12.9 fasteners, regardless of the initial surface finish.**

**4.) The environmental test results substantiate the fact that under aggressive hydrogen charging conditions that electrochemically simulate the addition of a zinc coating, the threshold stress of the P.C. 12.9 fasteners is less than the bend fracture strength in air, but is essentially the same for all three surface finishes on an equivalent hardness scale, which meets or exceeds the axial tensile strength of the M12 fastener when tested in tension.**

5.) **It is clear that the Property Class 12.9 screws ISL tested in air did not experience a reduction in fracture load. The presence of the phosphorus after heading, prior to heat treatment or zinc plating, does not introduce any residual hydrogen that would cause any premature, time-delayed brittle failure.**

## Recommendations for Future Work

P.C. 12.9 fasteners ISL tested in a hydrogen-charging environment that electrochemically simulates the addition of a zinc coating did not experience a reduction in fracture load at stresses below the ASTM F606M axial tensile strength. In bending, surface tensile stresses in excess of the axial tensile strength are attainable up to a factor of 2X Ultimate Tensile Strength in tension at the limit load. This leads to the conclusions:

1.) The ISL test (ASTM F1624 Test Method) in bending is capable of quantifying the influence of surface finishes on the susceptibility of fasteners to environmentally induced hydrogen embrittlement. The susceptibility of the core material is not altered with various surface finishes. The different conditions of the surface only alter the hydrogen being generated on the surface, with the more active cell requiring a lower threshold stress for the onset of subcritical crack growth.

2.) The ASTM F1624 Test Method should be utilized as specified by continually decreasing the ISL loading rate until an invariant value of the threshold is obtained. Only in this way can the influence of the surface treatments on the relative susceptibility be accurately measured.

3.) The Open Circuit Corrosion Potential (OCP) of the three surface conditions should be measured to electrochemically quantify their differences.

4.) Metallographic photomicrographs should be utilized in subsequent test programs to correlate the OCP to the presence of surface substances and internal structures.

5.) To circumvent any confusion regarding specimen comparison, a program should be alternately outlined that uses bare, coated, heat treated, and zinc plated specimens instead of fasteners. Machined studs should be used for the bare specimen as in the ISO study.

# APPENDIX I

## SUMMARY OF ISL TESTING FOR FORD (PHOSPHATE EMBRITTLEMENT STUDY) P.C. 10.9

🟩 Equal to or greater than 75%
🟨 Between 50% and 75%
🟥 Less than 50% Fast Fracture Strength
□ Part did not fail (machine bottomed out) - 17 of 45

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | |
|---|---|---|---|---|---|---|---|---|
| **CLASS** | **COATING** | **MATERIAL** | **TEST DESCRIPTION** | **LOAD (lbs.)** | **FFS (lbs.)** | **%FS** | **TEST DATE** | |
| **10.9** | Zn-P | 4037 | 24steps/5%FFS/1hour steps in air | 264.7 | 265 | 99.9% | 04/11/02 | 1 |
| **10.9** | Zn-P | 4037 | 24/5/1 in air | 263.3 | 265 | 99.4% | 04/23/02 | 2 |
| **10.9** | Zn-P | 4037 | 24/5/1 in air | 264.4 | 265 | 99.8% | 04/24/02 | 3 |
| **10.9** | Zn-P | 4037 | 24/5/1 @ -1.2 volts | 264.9 | 265 | 100.0% | 04/15/02 | 4 |
| **10.9** | Zn-P | 4037 | 24/5/1 @ -1.2 volts | 264.2 | 265 | 99.7% | 05/01/02 | 5 |
| **10.9** | Zn-P | 1541 | 24/5/1 in air | 261.8 | 250 | 104.7% | 04/11/02 | 6 |
| **10.9** | Zn-P | 1541 | 24/5/1 in air | 263.5 | 250 | 105.4% | 04/23/02 | 7 |
| **10.9** | Zn-P | 1541 | 24/5/1 in air | 299.9 | 250 | 120.0% | 04/24/02 | 8 |
| **10.9** | Zn-P | 1541 | 24/5/1 @ -1.2 volts | 255.0 | 250 | 102.0% | 04/24/02 | 9 |
| **10.9** | Zn-P | 1541 | 24/5/1 @ -1.2 volts | 258.6 | 250 | 103.4% | 05/03/02 | 10 |
| **10.9** | Zn-P | 10B21 | 24/5/1 in air | 258.7 | 255 | 101.5% | 04/25/02 | 11 |
| **10.9** | Zn-P | 10B21 | 24/5/1 in air | 260.0 | 255 | 102.0% | 04/25/02 | 12 |
| **10.9** | Zn-P | 10B21 | 24/5/1 in air | 266.9 | 255 | 104.7% | 04/29/02 | 13 |
| **10.9** | Zn-P | 10B21 | 24/5/1 @ -1.2 volts | 255.1 | 255 | 100.0% | 04/29/02 | 14 |
| **10.9** | Zn-P | 10B21 | 24/5/1 @ -1.2 volts | 260.1 | 255 | 102.0% | 05/30/02 | 15 |
| **10.9** | Zn-P removed | 4037 | 24/5/1 in air | 270.1 | 265 | 101.9% | 05/10/02 | 16 |
| **10.9** | Zn-P removed | 4037 | 24/5/1 in air | 267.2 | 265 | 100.8% | 05/12/02 | 17 |
| **10.9** | Zn-P removed | 4037 | 24/5/1 in air | 260.0 | 265 | 98.1% | 05/13/02 | 18 |
| **10.9** | Zn-P removed | 4037 | 24/5/1 @ -1.2 volts | 278.3 | 265 | 105.0% | 05/14/02 | 19 |
| **10.9** | Zn-P removed | 4037 | 24/5/1 @ -1.2 volts | 261.7 | 265 | 98.8% | 05/21/02 | 20 |
| **10.9** | Zn-P removed | 1541 | 24/5/1 in air | 268.7 | 250 | 107.5% | 05/10/02 | 21 |
| **10.9** | Zn-P removed | 1541 | 24/5/1 in air | 259.6 | 250 | 103.8% | 05/12/02 | 22 |
| **10.9** | Zn-P removed | 1541 | 24/5/1 in air | 269.1 | 250 | 107.6% | 05/13/02 | 23 |
| **10.9** | Zn-P removed | 1541 | 24/5/1 @ -1.2 volts | 263.2 | 250 | 105.3% | 05/20/02 | 24 |
| **10.9** | Zn-P removed | 1541 | 24/5/1 @ -1.2 volts | 262.8 | 250 | 105.1% | 05/23/02 | 25 |
| **10.9** | Zn-P removed | 10B21 | 24/5/1 in air | 259.8 | 255 | 101.9% | 04/30/02 | 26 |
| **10.9** | Zn-P removed | 10B21 | 24/5/1 in air | 264.4 | 255 | 103.7% | 04/30/02 | 27 |
| **10.9** | Zn-P removed | 10B21 | 24/5/1 in air | 270.3 | 255 | 106.0% | 04/30/02 | 28 |
| **10.9** | Zn-P removed | 10B21 | 24/5/1 @ -1.2 volts | 268.0 | 255 | 105.1% | 04/30/02 | 29 |
| **10.9** | Zn-P removed | 10B21 | 24/5/1 @ -1.2 volts | 268.1 | 255 | 105.1% | 06/01/02 | 30 |
| **10.9** | Lime | 4037 | 24/5/1 in air | 284.9 | 265 | 107.5% | 04/11/02 | 31 |
| **10.9** | Lime | 4037 | 24/5/1 in air | 267.8 | 265 | 101.1% | 04/23/02 | 32 |
| **10.9** | Lime | 4037 | 24/5/1 in air | 260.9 | 265 | 98.5% | 04/24/02 | 33 |
| **10.9** | Lime | 4037 | 24/5/1 @ -1.2 volts | 265.3 | 265 | 100.1% | 04/23/02 | 34 |
| **10.9** | Lime | 4037 | 24/5/1 @ -1.2 volts | 265.0 | 265 | 100.0% | 05/02/02 | 35 |
| **10.9** | Lime | 1541 | 24/5/1 in air | 253.0 | 250 | 101.2% | 05/10/02 | 36 |
| **10.9** | Lime | 1541 | 24/5/1 in air | 267.9 | 250 | 107.2% | 05/12/02 | 37 |
| **10.9** | Lime | 1541 | 24/5/1 in air | 252.1 | 250 | 100.8% | 05/13/02 | 38 |
| **10.9** | Lime | 1541 | 24/5/1 @ -1.2 volts | 250.1 | 250 | 100.0% | 05/19/02 | 39 |
| **10.9** | Lime | 1541 | 24/5/1 @ -1.2 volts | 250.5 | 250 | 100.2% | 05/22/02 | 40 |
| **10.9** | Lime | 10B21 | 24/5/1 in air | 265.9 | 255 | 104.3% | 04/25/02 | 41 |
| **10.9** | Lime | 10B21 | 24/5/1 in air | 258.4 | 255 | 101.3% | 04/29/02 | 42 |
| **10.9** | Lime | 10B21 | 24/5/1 in air | 261.2 | 255 | 102.4% | 04/29/02 | 43 |
| **10.9** | Lime | 10B21 | 24/5/1 @ -1.2 volts | 255.1 | 255 | 100.0% | 04/25/02 | 44 |
| **10.9** | Lime | 10B21 | 24/5/1 @ -1.2 volts | 260.9 | 255 | 102.3% | 05/31/02 | 45 |

# APPENDIX II

# SUMMARY OF ISL TESTING FOR FORD (PHOSPHATE EMBRITTLEMENT STUDY)

## P.C. 12.9

| | |
|---|---|
| 🟩 | Equal to or or greater than 75% |
| 🟨 | Between 50% and 75% |
| 🟥 | Less than 50% Fast Fracture Strength |
| ⬜ | Part did not fail (machine bottomed out) - 0 of 30 |

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | |
|---|---|---|---|---|---|---|---|---|
| CLASS | COATING | MATERIAL | TEST DESCRIPTION | LOAD (lbs.) | FFS (lbs.) | %FS | TEST DATE | |
| 12.9 | Zn-P | 4037 | 24 steps/5%FFS/1 hour steps in air | 314.7 | 320 | 98.3% | 05/06/02 | 1 |
| 12.9 | Zn-P | 4037 | 24/5/1 in air | 315.6 | 320 | 98.6% | 05/07/02 | 2 |
| 12.9 | Zn-P | 4037 | 24/5/1 in air | 311.1 | 320 | 97.2% | 05/09/02 | 3 |
| 12.9 | Zn-P | 4037 | 24/5/1 @ -1.2 volts | 240.1 | 320 | 75.0% | 05/08/02 | 4 |
| 12.9 | **Zn-P** | 4037 | **24/5/1 @ -1.2 volts** | 144.3 | 320 | 45.1% | 05/12/02 | 5 |
| 12.9 | Zn-P | 1541 | 24/5/1 in air | 311.7 | 320 | 97.4% | 05/07/02 | 6 |
| 12.9 | Zn-P | 1541 | 24/5/1 in air | 308.2 | 320 | 96.3% | 05/08/02 | 7 |
| 12.9 | Zn-P | 1541 | 24/5/1 in air | 309.9 | 320 | 96.8% | 05/09/02 | 8 |
| 12.9 | **Zn-P** | 1541 | **24/5/1 @ -1.2 volts** | 160.3 | 320 | 50.1% | 05/06/02 | 9 |
| 12.9 | **Zn-P** | 1541 | **24/5/1 @ -1.2 volts** | 224.1 | 320 | 70.0% | 05/11/02 | 10 |
| 12.9 | Zn-P removed | 4037 | 24/5/1 in air | 298.8 | 285 | 104.8% | 05/15/02 | 11 |
| 12.9 | Zn-P removed | 4037 | 24/5/1 in air | 280.2 | 285 | 98.3% | 05/15/02 | 12 |
| 12.9 | Zn-P removed | 4037 | 24/5/1 in air | 281.3 | 285 | 98.7% | 05/16/02 | 13 |
| 12.9 | Zn-P removed | 4037 | 24/5/1 @ -1.2 volts | 256.1 | 285 | 89.9% | 05/16/02 | 14 |
| 12.9 | Zn-P removed | 4037 | 24/5/1 @ -1.2 volts | 242.7 | 285 | 85.2% | 05/18/02 | 15 |
| 12.9 | Zn-P removed | 1541 | 24/5/1 in air | 296.7 | 290 | 102.3% | 05/15/02 | 16 |
| 12.9 | Zn-P removed | 1541 | 24/5/1 in air | 290.3 | 290 | 100.1% | 05/16/02 | 17 |
| 12.9 | Zn-P removed | 1541 | 24/5/1 in air | 286.1 | 290 | 98.7% | 05/16/02 | 18 |
| 12.9 | Zn-P removed | 1541 | 24/5/1 @ -1.2 volts | 240.1 | 290 | 82.8% | 05/15/02 | 19 |
| 12.9 | Zn-P removed | 1541 | 24/5/1 @ -1.2 volts | 246.6 | 290 | 85.0% | 05/17/02 | 20 |
| 12.9 | Lime | 4037 | 24/5/1 in air | 317.4 | 320 | 99.2% | 05/06/02 | 21 |
| 12.9 | Lime | 4037 | 24/5/1 in air | 315.2 | 320 | 98.5% | 05/07/02 | 22 |
| 12.9 | Lime | 4037 | 24/5/1 in air | 317.3 | 320 | 99.2% | 05/08/02 | 23 |
| 12.9 | **Lime** | 4037 | **24/5/1 @ -1.2 volts** | 224.1 | 320 | 70.0% | 05/09/02 | 24 |
| 12.9 | **Lime** | 4037 | **24/5/1 @ -1.2 volts** | 224.0 | 320 | 70.0% | 05/13/02 | 25 |
| 12.9 | Lime | 1541 | 24/5/1 in air | 310.6 | 320 | 97.1% | 05/06/02 | 26 |
| 12.9 | Lime | 1541 | 24/5/1 in air | 318.2 | 320 | 99.4% | 05/08/02 | 27 |
| 12.9 | Lime | 1541 | 24/5/1 in air | 315.3 | 320 | 98.5% | 05/09/02 | 28 |
| 12.9 | Lime | 1541 | 24/5/1 @ -1.2 volts | 240.1 | 320 | 75.0% | 05/07/02 | 29 |
| 12.9 | **Lime** | 1541 | **24/5/1 @ -1.2 volts** | 224.1 | 320 | 70.0% | 05/10/02 | 30 |

# APPENDIX III

Photo 1 - RSL™ Test System

Photo 2 - RSL™ test in air

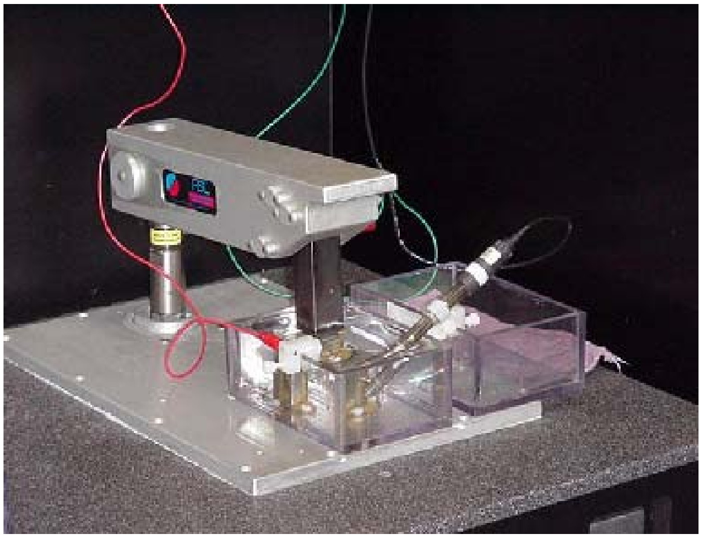
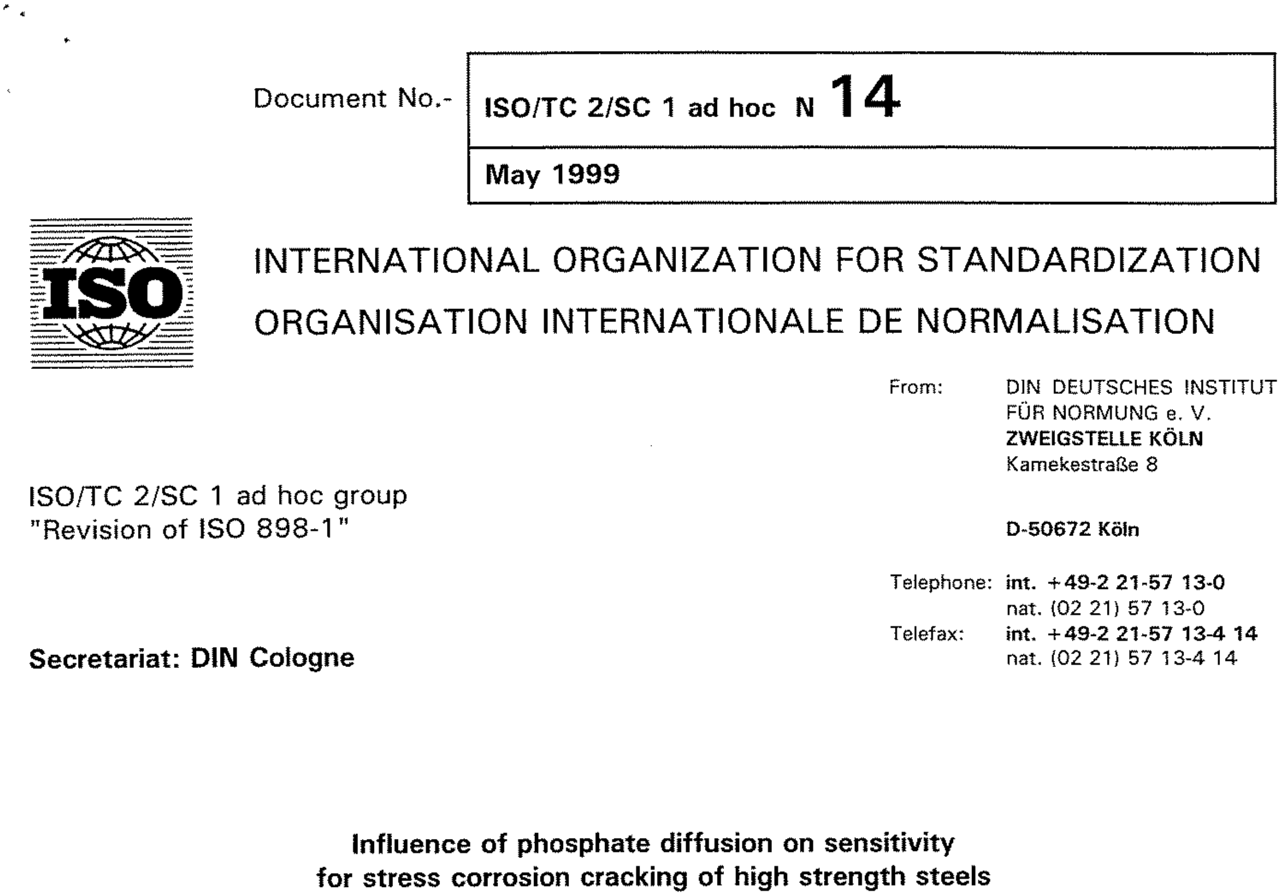


Photo 3 - RSL™ test in 3.5% NaCl solution

# APPENDIX IV



Document No.- **ISO/TC 2/SC 1 ad hoc N 14**

**May 1999**

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION
ORGANISATION INTERNATIONALE DE NORMALISATION

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ISO/TC 2/SC 1 ad hoc group
"Revision of ISO 898-1"

**Secretariat: DIN Cologne**

## Influence of phosphate diffusion on sensitivity for stress corrosion cracking of high strength steels

# APPENDIX V

Document No.- **ISO/TC 2/SC 1/WG 9 N 64**

**2001-10-01**

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION
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ISO/TC 2/SC 1/WG 9
"Mechanical properties of fasteners
made of carbon steel and alloy steel -
Bolts, screws and studs"

**Secretariat: DIN Cologne**

## Comments of the USA
## on the Oberhoffer test method

1 of 1 Complete Record
676120 MA Accession Number: 79-210212
Investigations into the suitability of the Oberhoffer etch for identifying surface defects.
Karl, A
PRAKT. METALLOGR. 15, (10), 469-485 Oct. 78 ISSN: 0032-678X
Document Type: ARTICLE
Language: ENGLISH AND GERMAN
MA Journal Announcement: 7910

Abstract: An extensive examination is reported of the extent to which etching with Oberhoffer reagent for revealing P distribution can be relied on to discriminate between steel surface defects originating in steel making practice and those produced during rolling. It is concluded that this method is subject to limitations which make it unreliable, and these, notably the effect of oxide inclusions, are discussed. Reference is made to the use of electron probe microanalysis for P distribution measurement. 8ref.-J.D.K.

Descriptors: Chromium steels – Metallography; carbon steels – Metallography: surface defects; Chemical etching; Rolling; Electron probe analysis
Alloy Index (Identifier), M55 – SCH/ C38 – SCM/ 34Cr4 – SAC
Section Headings: 21 (METALLOGRAPHY)

# APPENDIX VI

## Comments and Independent Tests
## by
## Dr. Louis Raymond[*]

I conducted a test program with ASTM F1940 test specimens of 4340 steel, tempered back to 45 HRC and 39 HRC to provide supplementary data for direct measurement of the threshold stress for hydrogen induced stress cracking of bare specimens; i.e., specimens that never have been exposed to a ZnP coating. These specimens were then compared to the data located in the Annex to ASTM F1940 for M12 screws at 45 HRC and 39 HRC. In addition, the corrosion potential was measured on remnants of specimens from a supplier that had been alkaline cleaned, acid cleaned, or had no cleaning prior to heat treatment.

The results and conclusions are summarized a follows:

1.) A modified surface, after a ZnP coating on some M12 screws, no matter how obtained, alkaline cleaned, acid cleaned, or no cleaning prior to heat treatment, always had a stress corrosion threshold at the zinc corrosion potential that was higher than uncoated (bare) ASTM F1940 4340 steel specimens at the same hardness. This means that all three of the residual surface conditions acted as a barrier to the infusion of hydrogen due to galvanic coupling to zinc, when exposed to water, i.e., they were more effective than a bare metal, tempered martensite steel surface.

2.) The measured corrosion potential of all three of these surfaces is located between zinc and steel, which means it electrochemically behaves the same as zinc, but produces less hydrogen that is available for infusion into the steel, when exposed to aqueous conditions.

3.) Complete removal of the ZnP coating before zinc plating makes the steel screw more susceptible to hydrogen embrittlement than with the residual sub-surface from the ZnP coating.

4.) The work performed in Appendix IV was conducted on the as-heat treated surfaces of ZnP or MnP coated specimens and not on the surfaces after they were subsequently plated with zinc. The interpretation of the test results that were generated in the report (Appendix IV) that led to the requirement for removal of the ZnP coating prior to heat treatment and subsequent zinc plating, misrepresent the influence of the residual surfaces with a ferritic layer infused with phosphorous under actual service conditions. Tested at the zinc corrosion potential, the threshold stress for the onset of hydrogen induced stress cracking was found to be higher than the uncoated F1940 steel specimens at the same hardness; therefore, the residuals on the surfaces from the ZnP result in a barrier to hydrogen induced stress cracking. The FoMoCo/TFS testing program had the results distorted because of a significant drop in hardness of the specimens with the ZnP “apparently” but not “actually” removed from the M12 fasteners prior to heat treatment. The most certain method to circumvent the problem of testing a contamination free surface is to start with bare metal specimens instead of rolled fasteners, as performed in the ISO report.

Reference:
Appendix IV: ISO Document N14 Paper “Influence of Phosphate Diffusion on Sensitivity of SCC of High Strength Steels

[*] Recipient of the IFI 2006 Roy P. Trowbridge Technology Award (www.LouRaymond.com).

## Expansion on “Conclusion”

In reviewing the work that has been done, it is my opinion that the main problem in arriving at the conclusion to remove the ZnP coating prior to heat treatment is based on the results of a mixture of data that does not represent actual service conditions. In the ISO Report, the subsequent addition of a zinc coating is ignored; and in the Ford study, no comparison is made to bare metal specimens that are pristine, i.e., have never been exposed to ZnP. It is never clear as to the surface condition of the samples being tested. The major issue being that the specimens with the “ZnP removed” still had residual contamination from the ZnP coating.

Conclusion: The results of my study show that a bare steel sample that has not been exposed to any ZnP coating prior to heat treatment is more susceptible to hydrogen induced stress cracking than the steel that has been ZnP coated prior to heat treatment, regardless of any attempt to remove the ZnP coating prior to heat treatment, because all of the attempted treatments to date have resulted in residual deposits of phosphate in one form or another. The presence of the residual phosphates after a subsequent coating inhibits the subsequent diffusion of hydrogen into the steel; i.e., acts as a barrier after being plated.

Obviously, the interpretation of the test results that were generated in the report (Appendix IV) that led to the requirement for removal of the ZnP coating prior to heat treatment and subsequent zinc plating are misleading, because they do not represent the actual service conditions that have the surface zinc coated after heat treatment. No one uses the ZnP coating after heat treating without a subsequent coating process. In ISO Document N14, the samples were tested after heat treatment with no subsequent coating process. They should have tested their samples after exposure to a subsequent coating process such as zinc.

The susceptibility of a steel such as 34Cr4 to hydrogen induced stress cracking is a function of hardness, independent of the surface condition. The surface condition affects crack initiation. Because dissimilar metal by-products are formed on the surface during the heat treating process, galvanic cells that result in salt water generate hydrogen at the surface. For this reason, it is not surprising that the specimens in the ISO Document N14 failed after heat treatment and then subsequent exposure to salt water and then stress. The bare metal samples had no dissimilar metal surface conditions and therefore had no hydrogen generation cells on the surface. Had they zinc plated the samples after heat treatment with the ZnP coating present, they would have found the samples with the dissimilar metal ZnP by-products on the surface to be more resistant to hydrogen induced stress cracking than the zinc plated bare steel specimen.

Reference:
Appendix IV: ISO Document N14 Paper “Influence of Phosphate Diffusion on Sensitivity of SCC of High Strength Steels

**SUMMARY TABLE from ASTM F1940:** The hydrogen susceptibility ratio (HSR) in terms of % Fast Fracture Strength (%FFS) in bending (B) was measured at a loading rate of 20 steps/5% FFS/1hr. in a 3.5% salt water solution under hydrogen charging condition of –1.2 Vsce (Saturated Calomel Electrode), which is equivalent to galvanic coupling at the open circuit corrosion potential of zinc. That generates a galvanic hydrogen charging potential on the specimen of about 0.5 Vsce on a steel specimen.

Included in ASTM STD F 1940, FIG. X1.1 and FIG. X1.2 is data comparing test results at –1.2 Vsce on 4340 steel at 52 HRC to M10 fasteners at 45 HRC (12.9) and 39 HRC (10.9). The Type 4037 M10 fasteners were ZnP coated before heat treatment.

I conducted a supplementary test program with some F1940 test specimens that were tempered back to 45 HRC and 39 HRC to provide data for direct comparison to the lower hardness fasteners.

The bare F1940 specimens at 45 HRC and 39 HRC were found to have a threshold of 45% FFS and > 85% FFS, respectively, which in both cases is below the threshold of the M12 fasteners at the same hardness. Since the M12 fasteners did not have the ZnP coating removed prior to heat treatment, these results imply that the bare metal surfaces are more susceptible to hydrogen induced stress cracking than the ZnP coated samples, or conversely, the ZnP coating provides a barrier to the infusion of hydrogen into the steel.

**Data from ASTM F1940**

| Steel | HRC | Specimen | %FFS(B) | Surface |
|---|---|---|---|---|
| 4340 | 50-52 | F1940* | 30 | Bare |
| | | | | |
| 4340 | 45 | F1940* | 45 | Bare |
| 4037 | 45 | M10 (12.9) | 60 | ZnP |
| | | | | |
| 4340 | 39 | F1940* | > 85 | Bare |
| 4037 | 39 | M10 (10.9) | 100 | ZnP |

* Specimens per ASTM F1940.

**Conclusion from ASTM F1940 Comparison:**

- The resistance to environmental hydrogen induced stress cracking (HISC) increases with a decrease in hardness.

- At ≤ 39 HRC, no measurable degradation in strength occurs in either bare or coated samples in a hydrogen charging environment that generates a galvanic hydrogen charging potential of about 0.5Vsce.

- On 12.9 screws, a delta ferrite layer resulting from the heat treatment of the ZnP coated screws acts as a barrier to hydrogen that results in a higher threshold stress for the onset of hydrogen induced stress cracking; i.e., 60% FFS(B) vs. 45% FFS(B). In effect, at the same sample hardness, the phosphate layer increased the resistance to HISC above that of a specimen with a bare metal surface.

**Corrosion Potential:** The Open Circuit Corrosion Potential **(OCP)** in a 3.5% salt-water solution of processed ZnP screws was measured. Bare Type 4340 steel, by comparison, is slightly cathodic to all four surface conditions of the ZnP coated samples. Conversely, all of the residual phosphate surfaces are anodic to the bare steel; therefore, it is not surprising in Ref. #1 that these surfaces initiated pitting sites, resulting in a more susceptible surface condition relative to stress corrosion cracking. With the addition of a zinc coating, the residual surfaces inhibit the entry of hydrogen into the steel.

**OCP in a 3.5% NaCl Solution vs. Saturated Calomel Electrode**

| Steel | Surface Condition | OCP (V vs. SCE) |
|---|---|---|
| SAE 4340 | Bare Metal Surface | -0.62 **(cathode)** |
| SAE 1541 | 4B (Patchy $P_2O_5$) | -0.689 |
| SAE 1541 | 2B (Acid Clean, delta-ferrite) | -0.723 |
| SAE 1541 | 1B ($P_2O_5$) | -0.728 |
| SAE 1541 | 3B (Alkaline Clean, delta-ferrite) | -0.739 |
| Cd-plated | cadmium | -0.85 |
| Zn-plated | zinc | -1.1 **(anode)** |