THE DRIVE OFF ROAD

NEWSLETTER

TOPIC

THE EFFECTIVE PREVENTION OF

HYDROGEN EMBRITTLEMENT

PICKLANE

THE TECHNOLOGY

PRETREATMENT OF HARDENED STEEL

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1 TESTING HYDROGEN EMBRITTLEMENT IN PICKLING SOLUTIONS

Per common industry standards it is the obligation of the plater and of the plating process supplier to evaluate and control the risk of hydrogen embittlement during the plating of high-strength steel parts.[1]
Main elements for eliminating the risk of hydrogen embrittlement in manufacturing are the choice of the right process sequence, the choice of the right process chemistry, definition of control parameters and thorough bath maintenance and documentation. In addition to those measures, it was proposed to perform tank side embrittlement testing of parts plated in the process to make sure the parameters are in line and the risks minimized. For that purpose a simple test using retaining rings (C-rings) was developed in the early 2000s.[2]

Over time this test was used in various studies and proved to have certain informative value.[3] However, it was found that there were a number of flaws in the testing method. Inconsistency (batch to batch variation) of the hardening process, non-representative shape and material of the parts[4], and handling (rings need to be over stretched for mounting on the glass rod for the quick test). The issue of inconsistent hardness of the parts was addressed in a subsequent study and a batch qualification method was proposed.[5] Due to the remaining deficiencies, the test was not generally accepted as a control tool in the industry. A new revision of DIN 50969-2[6] mentions the C-ring test and points out that the method is not applicable for part specific suitability tests. Also, the issue of plastic deformation of the rings is addressed - a defined widening of the rings using a controlled pulling device is required. Those pulling devices are also used in scientific studies that utilize the C-ring method for comparative tests.[3,7]

Generally accepted and global industry standards use real bolts[8] or representative test parts[9,10] to qualify processes for the absence of internal hydrogen embrittlement (IHE). Scientific studies are also using those accepted test methods to quantify and compare the hydrogen embrittlement risk of different processes.[11]

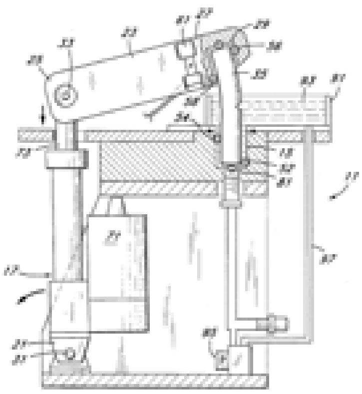

Fig. 1: RSL®Fig. 1: RSL®Loading Frame by Fracture Diagnostics Inc. as described in [1] (Image from US5585570)

COVENTYA, as an associate member of the German Fastener Association (Deutscher Schraubenverband e.V.) is actively involved in current efforts to provide the fastener industry with better test methods to mitigate the risk of hydrogen embrittlement in plating operations.

2 EFFECT OF THE COMPOSITION OF PICKLING SOLUTIONS

The desired removal of metal oxides and other acid-soluble surface impurities during the pickling process goes along with hydrogen formation (cathodic process) and base metal dissolution (anodic process). Those undesired side-reactions can be drastically slowed down by the use of inhibitors which adsorb on metal (iron) surfaces to block active sites for the cathodic process.[12] In addition to the deceleration of side reactions to prevent the formation of hydrogen, pickling additives also have a minor impact on hydrogen embrittlement by removing the formed hydrogen gas from the surface (e.g. through wetting agents). This secondary effect, however, is also depending on part geometry and bath agitation. The substances used as inhibitors in pickling solutions can be of the same group as inhibitors used for the temporary rust prevention of steel, acting on the cathodic or anodic reaction of the natural corrosion process.[13] Some of those substances can, when used in a strongly acidic pickling solution, accelerate the cathodic reaction (Promoters) and hence are not suitable as pickling additives for hardened steel.[2,14]

A study of different pickling inhibitors[3] reveals that a product based on thiourea leads to a high occurrence (~50%) of fracture failures already in parts with a hardness of 486 HV10. It is important to mention that a hardness of over 450 HV is significantly higher than the average hardness of fasteners of property class 12.9. This observation is in line with an electrochemical study of different inhibitors[14] that proposes a mechanism in which sulfur containing substances, otherwise acting as effective corrosion inhibitors, promote the absorption of hydrogen into steel.

PICKLANE 50 from COVENTYA, which is recommended as an inhibitor to effectively prevent hydrogen embrittlement, is of another inhibitor type evaluated in study [3] which causes 0% fracture failures even at 580 HV. PICKLANE 50 does not contain organic sulfur compounds like thiourea or mercaptobenzimidazole.

COVENTYA conducted a study to quantify the inhibiting effect of PICKLANE 50 in different pickling acid solutions. Both, the cathodic as well as the anodic part of the iron dissolution reaction, were evaluated by acid consumption analysis and weight loss of steel test panels respectively (Table 1).

Pickling Acid	PICKLANE 50 [%]	Temp. [°C]	Time [h]	Weight Loss Steel Panel [g]	Acid Consumpti-on [%]	Acid Consumption per 24h [L/m^2]	Dissolved Iron per 24h [g/m^2]
HCl 30%	0	20	24	1,3	3,8	1,4	100
	1	20	24	0,04	0,1	< 0,05	3
H_2SO_4 20%	0	20	24	14,0	2,6	1,0	1050
	1	20	24	0,11	0,1	0,05	8,5
H_2SO_4 17%	0	50	2	8,4	1,6	7,2	7500
	1	50	2	0,12	0,1	0,12	110

Table 1: Inhibiting Effect of PICKLANE 50 (from [15])

It can be seen that PICKLANE 50 is an effective inhibitor which retards both, acid consumption (hydrogen formation) and iron dissolution, in the same way and does not promote one of the partial reactions.

3 DETERMINATION OF THE INHIBITION VALUE

The Inhibition Value is the characteristic measure for the fast determination of inhibitor effectiveness. The most common method to test a pickling additive regarding its suitability as an inhibitor consists of measuring the metal dissolution in an ***inhibited*** and ***non inhibited*** acid. Over a defined time period and at a fixed temperature, the Inhibition Value is calculated according to the following equation:

An Inhibition Value of > 85% indicates that the additive has a sufficient inhibition effect.

Inhibition Value [%] = V_O-V_H) / V_O * 100

V_O: Metal dissolution in not inhibited acid
V_H: Metal dissolution in inhibited acid

Parameters for this trial:

- Steel Panel: Material No. 1.0332 after EN 10111 (contains 0,2% Mn; 0,005% C)
- Hydrochloric Acid (technical grade, 31%) 1:1
- Temperature: 23°C
- Pickling Time: 30 min

Product in HCl (31%) 1:1	Additive Concentration [%]	Inhibition Value [%]
PICKLANE 50	**0,5**	**96**
	2,0	**98**
PICKLANE INH 96	2,0	95
	5,0	95
PICKLANE 40	2,0	75
	5,0	80
PICKLANE 39 S	2,0	19
	5,0	48

4 C-RING EMBRITTLEMENT TEST WITH PICKLANE 50

Above and beyond the quantifiable inhibiting effect of PICKLANE 50 shown right, COVENTYA conducted a study on the effect on hydrogen embrittlement using this inhibitor. For this test a C-ring pickling test was conducted according to the method described in [18]:

Ten (10) C-rings of the highest hardness class of nominally 580 HV were pickled for 10 minutes in a pickling solution of 30% analytical grade hydrochloric acid with and without the addition of 5 mL/L of PICKLANE 50. The C-rings were subsequently washed with water, acetone, air dried and then mounted in the test frame to apply a maximum tensile stress of 1500 MPa. The inhibition effect is illustrated visually in the image below where the lack of hydrogen evolution in the inhibited pickling solution (right) contrasts greatly with the uninhibited solution (left)

After a test period of ca. 1h it was noted that 9 of the 10 C-rings which were exposed to the un-inhibited pickling solution are fractured, whereas no ring which was exposed to the inhibited pickle exhibited the failure.

Fig. 2: Hydrogen evolution in a pickling solution without (left) and with (right) the addition of PICKLANE 50

Fig. 3: Fractures after application of tensile stress to C-rings exposed to a pickling solution with (upper) and without (lower) the addition of PICKLANE 50

SEM investigation of the fractured surfaces from a hydrogen induced fracture of the described test in comparison to a mechanical fracture of the same kind of C-ring that was not pickled demonstrates the high brittleness (low elasticity) of the material even without hydrogen exposure.

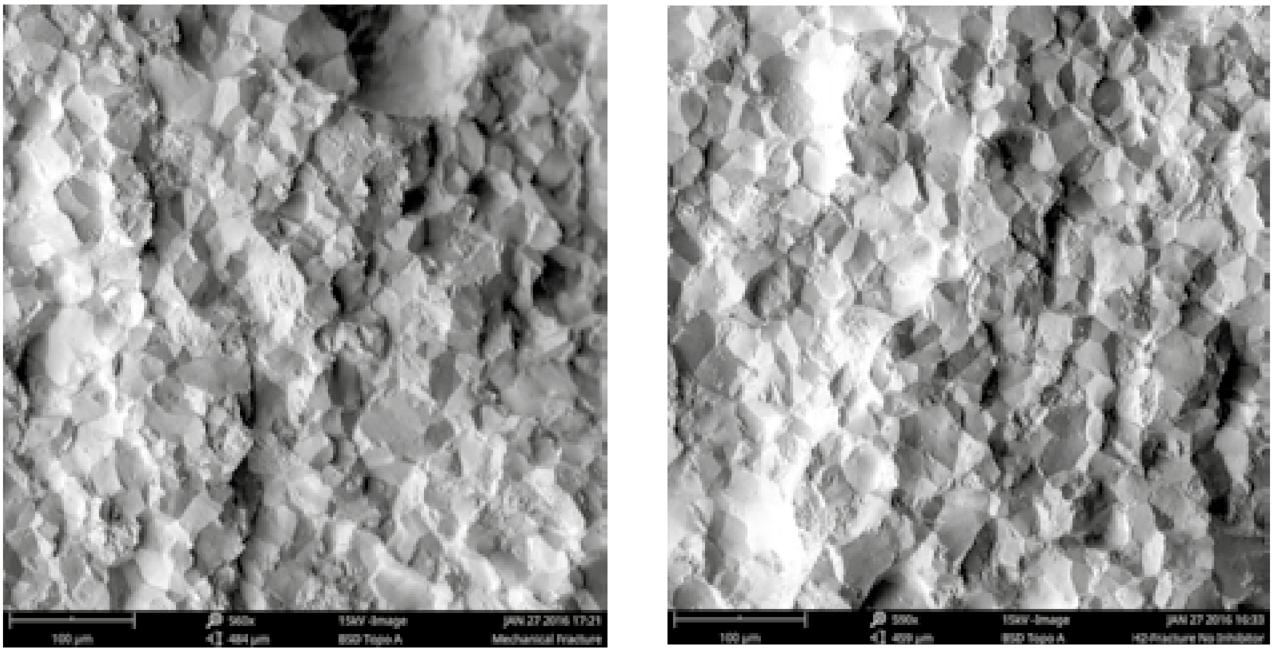

Fig. 4: SEM images of fractured surfaces of C-rings from a hydrogen induced fracture (right) vs. a mechanical fracture (left)

5 CONCLUSION

In order to avoid hydrogen embrittlement during the pre-treatment of hardened steel parts it is necessary to choose the right plating sequence and parameters (**no** cathodic cleaning step, **short** pickling time), to select – of the right additive for the pickling step (inhibitor) and to control and maintain the pickling solution during production.

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