

Avoidance of Hydrogen Embrittlement During Rust Removal with Vapro VBCI 812

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Abstract

This article documents the avoidance of hydrogen embrittlement during rust removal process. It also documents the difference between Vapro VBCI MRST 812 and Magna 114 a conventional acid-based rust remover. It features the advantages of using Vapro VBCI MRST (Molecular Reaction Surface Technology) during rust removal process [1] over the conventional acid-based rust remover.

Commercially, Sulfuric, Hydrochloric and Phosphoric acids are common acids used in rust removal process. Sulfuric acid shows lower hydrogen embrittlement rates at lower temperatures but it has low rust removing capability, thus it is typically used at around 60°C. At this temperature, sulfuric acid shows hydrogen embrittlement rate similar to that of hydrochloric acid. Phosphoric acid is also similar [2].

The embrittlement of a metal or alloy by atomic hydrogen involves the ingress of hydrogen into a component, an event that can seriously reduce the ductility and load-bearing capacity, cause cracking and catastrophic brittle failures at stresses below the yield stress of susceptible materials. Hydrogen embrittlement occurs in a number of forms but the common features are an applied tensile stress and hydrogen dissolved in the metal [3]. Examples of hydrogen embrittlement are cracking of weldments or hardened steels when exposed to conditions which inject hydrogen into the component.

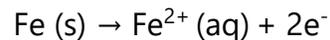
Presently this phenomenon is not completely understood and hydrogen embrittlement detection, in particular, seems to be one of the most difficult aspects of the problem. Hydrogen embrittlement does not affect all metallic materials equally. The most vulnerable are high-strength steels, titanium alloys and aluminium alloys [4,5]. Using strong acid-based rust removal will result in corrosion [6] after rust removal process affecting the tensile strength of the metal.

Introduction

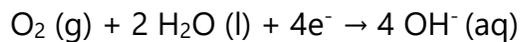
Corrosion is a chemical process that takes place in metals, which deteriorates the metal due to the interaction between metal surface and the environment. Most metals, ferrous or non-ferrous, are prone to corrosion, which eventually leads to rusting on the surfaces.

Pure iron is rarely found in nature, since it is reactive towards oxygen and water in the air. Under these conditions, over time, a reaction known as rusting occurs. [8,9] Rusting is a type of electrochemical reaction where iron undergoes oxidation to form different iron oxides, with the main oxides of rust consisting of hydrated iron (III) oxide and iron (III) hydroxide. [10,11]

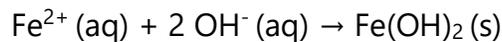
Iron reacts with oxygen and moisture in the air to form iron (II) hydroxide in the chemical equations below:



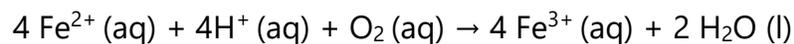
From the equation, iron undergoes oxidation and gains an oxidation state of 2+ and loses 4 electrons.



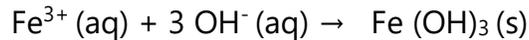
Oxygen is reduced to form hydroxide ions. [3]



Hydroxide ions react with ferrous ions to form ferrous hydroxide, or iron (II) hydroxide. Iron (III) hydroxide is a type of rust which is green in colour and insoluble in water. Iron (II) hydroxide is further oxidised to iron (III) hydroxide from the chemical equations below:



Ferrous ions are converted to ferric ions after reacting with oxygen and hydrogen ions.



Lastly, ferric ions and hydroxide ions react to form iron (III) hydroxide. [5] Iron (III) hydroxide, or $\text{Fe}(\text{OH})_3$, is brown in colour and one of the main components of rust, the other being iron (III) oxide.

When iron begins to rust, it will puff up and expose clean metal to the open air, allowing rust to continue to the depths of the metal. Many methods can be used to remove rust: Sand Blasting or Bead Blasting-this method of removing rust from metals will also remove some good metal. Plastic beads blasting is used for more delicate parts. Immediately after any blasting, the metal surface is clean and exposed; so it is essential to rust proof it.

Sandpaper and steel wool will also remove rusting, but they don't get into tiny crevices. Rubber abrasive sanding blocks are good at removing a thin coat of rust and can also remove rust from minute pores in the metal.

Phosphoric acid has a unique property of dissolving hydrated iron oxide (i.e. rust) quickly while etching iron very slowly (by removing molecules of water from it). This means that metal can be left in the acid for much longer time than necessary with very little damage.

However, the acid will attack bare metal slowly and will start the process of hydrogen embrittlement, hence the minimum etch time that removes all rust should be used. Another advantage of phosphoric acid is that it leaves a fine coating of iron phosphate behind. (iron phosphate prevents rust) and leaves a hard, bright metal finish – this is because it will etch the surface slightly, exposing new, bare metal. Other Acids (e.g. H_2SO_4 , HCl and oxalic acid) will etch rust, but not as selectively. These acids will etch rust quickly, but if metal is left in them a bit too long, they will attack significant amount of metal. Also, the acids do not leave a protective film behind.

The corrosion rate of iron in different concentrations of sulphuric acid ranging from 0.5 N to 3 N for exposure time of 60 minutes has been determined by weight loss method

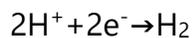
at 25.0 °C to 40.0 °C. It is observed that iron corrodes in different concentration of sulphuric acid because there is considerable decrease in original weight of the specimen. Similar results were obtained in case of nitric acid. However, the weight loss was more pronounced in nitric acid as compared to sulphuric acid. This may be due to

powerful oxidizing action of nitric acid which causes violent attack on Iron [7]. Vapro VBCI 812 was developed to solve the said problems and a study between the acid-based rust remover and Vapro VBCI was then carried out [12].

Hydrogen Embrittlement

When acids react with metals, they produce a salt and hydrogen gas. Most metals react with acids. The general equation that describes the chemical reaction between an acid and metal is metal + acid = salt + hydrogen gas.

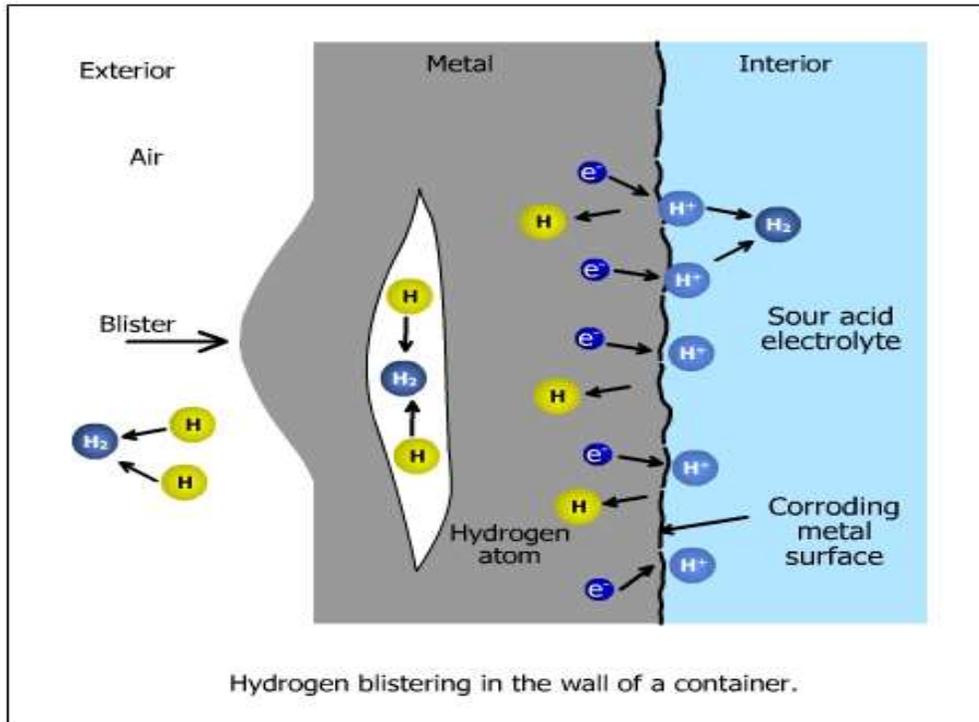
Example: Iron + hydrochloric acid = iron chloride and hydrogen gas ($\text{Fe} + 2\text{HCl} = \text{FeCl}_2 + \text{H}_2$) Acids contain H^+ ions. They tend to grab electrons and form hydrogen gas,



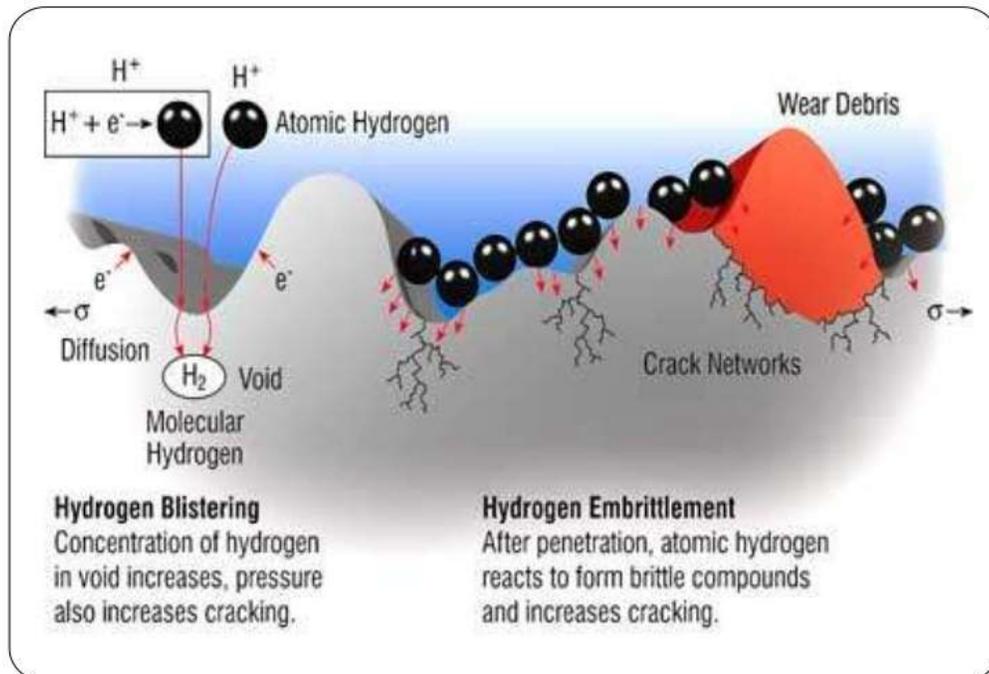
All acids contribute some hydrogen to the metal structure by a process called hydrogen embrittlement – this weakens iron or steel. Embrittlement is a phenomenon that causes loss of ductility in a material, thus making it brittle. There are a number of different forms including: Environmentally Induced Cracking, Stress Corrosion Cracking, Hydrogen Embrittlement, Corrosion Fatigue, Liquid Metal Embrittlement [13].

Hydrogen is the most common element in the world and many acidic and oxidation reactions with steel will liberate hydrogen in various amounts depending on the specific chemical reaction. Nearly nine out of every ten atoms in the universe are hydrogen atoms [14,15].

Hydrogen embrittlement can occur whenever atomic or protonic hydrogen is produced from a reaction [16,17] e.g. acid pickling can react iron and hydrochloric acid to diffuse hydrogen in iron. During acid pickling hydrogen can be diffused into the iron. Electroplating is another process to introduce hydrogen into a metal in both the acid pickle and the plating processes (see pictorial 1 & 2) below.



Pictorial 1



Pictorial 2

Internal hydrogen embrittlement is the more common form of hydrogen embrittlement and can occur any time atomic hydrogen is absorbed into the fastener from any chemical process before exposure to an externally applied stress.

Frequently, hydrogen is introduced to the metal during the electroplating process or rust removal process [19,20]. In these cases, the hydrogen is absorbed into the metal during the acid cleaning or descaling process and is then trapped in the part by the plating.

One of the methods for combating hydrogen embrittlement during rust removal process is to use a neutral based rust remover such as Vapro VBCI 812. Vapro VBCI 812 is an organic rust remover with a neutral pH. Vapro VBCI 812 removes rust on ferrous and non-ferrous metals through the chelation of ferrous ions on the surface of the metal. Vapro VBCI 812 is biodegradable and safe for the environment, humans and the metal. Furthermore, Since, it is neutral pH, Vapro VBCI 812 does not cause hydrogen embrittlement, which is a form of corrosion that is induced due to the absorption of hydrogen by the metal surface. Vapro VBCI 812 is a fully organic solution and is an ideal replacement for common rust removers in cases where chemical waste disposal is unavoidable. Usage of Vapro VBCI 812 does not require further rinsing or neutralisation after application.

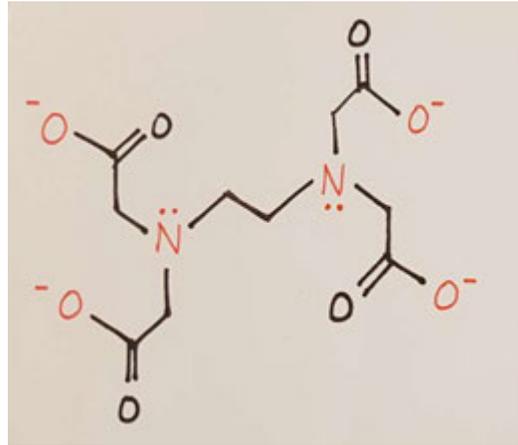
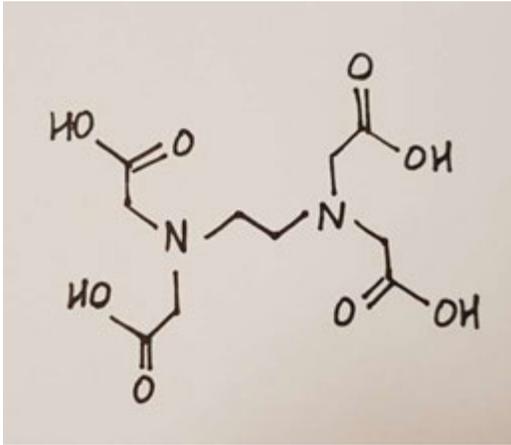
Mechanism of Vapro VBCI 812

The application of MRST in Vapro VBCI 812 is in the reaction of iron (Fe^{3+}) ions in the stable oxide complex (rust) and the rust remover.

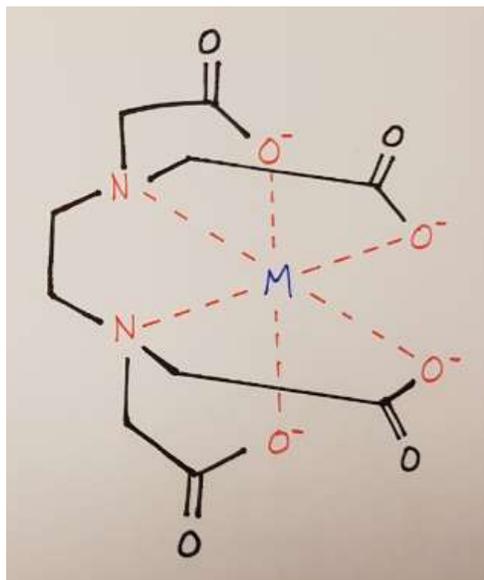
Vapro VBCI 812 is a chelating agent which removes rust from the surface of the ferrous metal by chelation of Fe^{3+} ions from $\text{Fe}(\text{OH})_3$. The chemical structure of Vapro VBCI 812 binds to the Fe^{3+} ion to form a six-membered ring chelate suspended in solution. Vapro VBCI 812 attacks only Fe^{3+} ions which can only be found on the surface of the metal in $\text{Fe}(\text{OH})_3$, hence avoiding any loss of metal through unwanted reaction with the metal itself.

Chelating agents are compounds that are able to bind to metal ions through multiple bonds to form chelates, which are complex ring-like structures. Chelating agents consist of either bidentate or polydentate ligands which are able to bind to the metal ion at multiple sites to form ring structures that include the metal ion and the ligand atoms involved in bonding. This process of chelation extracts the metal ion into the solution of chelating agent by binding the metal ion to form a new complex. [21,22]

An example to illustrate the reaction mechanism of a polydentate chelating agent is used to explain how Vapro VBCI 812 works to remove rust.



Ethylenediaminetetraacetic Acid (EDTA) produces EDTA⁴⁻ ions, which are polydentate ligands that bind to metal ions at the atoms that are highlighted in red [23]. There is a total of 6 binding sites, like Vapro VBCI 812. As EDTA⁴⁻ attacks a metal ion and bonds with it, it creates a metal-EDTA complex that has a 6-membered ring structure, as seen by the bonds highlighted in red. Vapro VBCI 812 works in a very similar way to remove Fe³⁺ ions from rust on the surface of the metal, specifically targeting only the Fe³⁺ ions due to its polydentate characteristic which prevents it from reacting with other forms of iron ions.



Comparison Between Vapro VBCI 812 and Conventional Acid-Based Magna114 Rust Remover

Tests were conducted on two different rust removers: Vapro VBCI 812 and Magna 114. Vapro VBCI 812 utilises MRST mechanism while Magna 114 is a conventional acid-based rust remover. Metal specimens were prepared and left to rust until severe corrosion was observed on the surface of the specimens.

Preparation of Sample

Standard steel bars were cut and grinded to a consistent surface finish. After which, the steel specimens were placed in a salt spray machine under moderate humidity to accelerate corrosion. The specimens were taken out and left in the open for complete surface corrosion. The experiment proceeded once a consistent layer of rust was obtained on the specimens.

The specimens were labelled as such:

A1	To be treated with Vapro 812
A2	
B1	To be treated with Magna 114

Testing of Rust Removers

Similar specimens were selected to be used for further experimentation. Specimen B1 was completely submerged in Magna 114 while specimen A1 was submerged in Vapro VBCI 812. The specimens were left in the beakers and monitored constantly until complete rust removal was observed.

Once it was deemed that all rust had been removed from the specimen surface, the specimens were taken out and dried. Extra caution was taken to ensure that any layer

formed on the surface of the specimens were not wiped off during drying. The specimens were then left on a table top and constantly monitored for any flash rusting.

The beaker containing Vapro VBCI 812 was reused for a second (A2) and specimen the relevant steps were repeated.

Other Actions Taken

When the specimens were dried, specimen A1 and B1 were wrapped in paper towels to completely remove all liquid from the surface of the metal. The layer of dark coloured precipitate on specimen A1 was not wiped off. For specimens A2, the precipitate layer was washed off and the specimen was then cleaned dry. This meant that the surfaces of the specimens were completely clear of any precipitate which exposes the original surface of the metal to the surroundings

Specimens (Before Treatment)



A1



B1



A2

Specimens (After Treatment with Vapro VBCI 812)

A1:



After 2 hours



Immediately after drying



After 7 days with Vapro VBCI 812

A2: After treatment with Vapro VBCI 812 with rinsing



After 24 hours



Immediately after drying

B1: After rust removal with Magna 114 acid based rust remover



Immediately after drying



After 2 hours



After 5 hours



After 24 hours



Vapro 812 before use



Vapro 812 after use

Discussion

Comparing the surfaces of the specimens treated with Magna 114 and Vapro VBCI 812, it is seen that the specimen treated with Magna 114 had a shiny surface, most possibly due to the etching effect of the acid. Specimens A1 and A2 had relatively duller surfaces, with what seems like a dark coloured precipitate on the surface of the metals. This is result of chelation by Vapro VBCI 812 on the Fe^{3+} ions in the layer of rust, which produces a chelate precipitate in the solution and on the metal surface.

Rust began to form on Specimen B1 within hours after treatment with the acid-based Magna 114. The specimens treated with Vapro 812 did not experience any corrosion in the first few days of treatment, this shows that the surface of the metal has been passivated by the solution and protected against after treatment corrosion. It is seen however that corrosion still occurred after a few days.

The change in colour of the solution from colourless to dark brown-black indicates that the Fe^{3+} ions have been chelated into the solution, which results in the darkening of the solution. This is proof that Vapro VBCI 812 has effectively removed rust from the surface of the metal and has held the Fe^{3+} ions in suspension without interacting with the metal itself. Upon each use of the solution, the solution also became less effective and was no longer able to completely remove rust from the specimen. It was also observed that the

dark coloured precipitate on the surface of the metal was not removable by washing, which could mean that the chelate formed by the removal of rust could no longer dissolve in the solution. The solution was considered to have reached saturation and is no longer effective in removing rust.

Conclusion

Based on the observations made throughout the present study, it is evident that Vapro VBCI 812 is superior to an acid-based rust remover. Due to the fully organic composition of Vapro VBCI 812, it is also safer to dispose of after use with lessened environmental impact. Further studies can be done to ascertain the environmental effects of Vapro VBCI 812 during usage and disposal, as well as the effect of Vapro VBCI 812 on the surface of the metal.

It is also advised to not wash off the layer of precipitate on the metal surface after treatment. Observations show that the dark precipitate layer on the metal surface provides added corrosion protection after treatment. Hence, to provide maximum protection against corrosion after rust removal, the precipitate layer should not be washed off.

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