VCI Paper Guidance

Ver. 1

ADCOAT CO., LTD.

Preface

This handout gives a brief explanation of VCI paper, “Why do metals rust / corrode?” “How can we use VCI paper to prevent rust / corrosion?” “What are the cautions to take when using VCI paper?” etc. The main purpose is about commonly how to use VCI paper, so our brand “adpack®” is not described, but it is an explanation of VCI paper in commonly, including other companies' products.

“Rust prevention oil”, “rust prevention agent (rust / corrosion inhibitors)”, “rust prevention film”, “desiccant”, etc., which are often compared with VCI paper, which is a packaging material. However, these do not been explained in this handout.

ADCOAT CO., LTD.
Technical Division

Contents

Definition

- Rust

  Oxide or hydroxide of “Iron”

- Corrosion

  Phenomenon that general metal such iron or copper erodes or deteriorates.

- VCI Paper

  Combination of Volatile Corrosion inhibitors and paper such kraft paper.
  Alias: anti-corrosion (anti-rust) paper

- Corrosion Inhibitors

  The chemicals of “Simple substance” or “Mixture” with protecting of metals from corrosion/rust, and it may vaporize at room temperature.

- Moisture-Proof Paper

  Packing material of combination with polyethylene (PE) etc. and paper.
  Protect from outside moisture.

- Acid-free Paper

  PH of paper is neutral region.
  Common kraft paper is acid region, acid paper.

- Crepe Paper

  Wrinkled paper.

Reference）
JIS Z 1535:2014
JIS Z 0103:1996
JIS Z 0108:2012
JIS P 0001:1998

2-1. Saturated Vapor Pressure

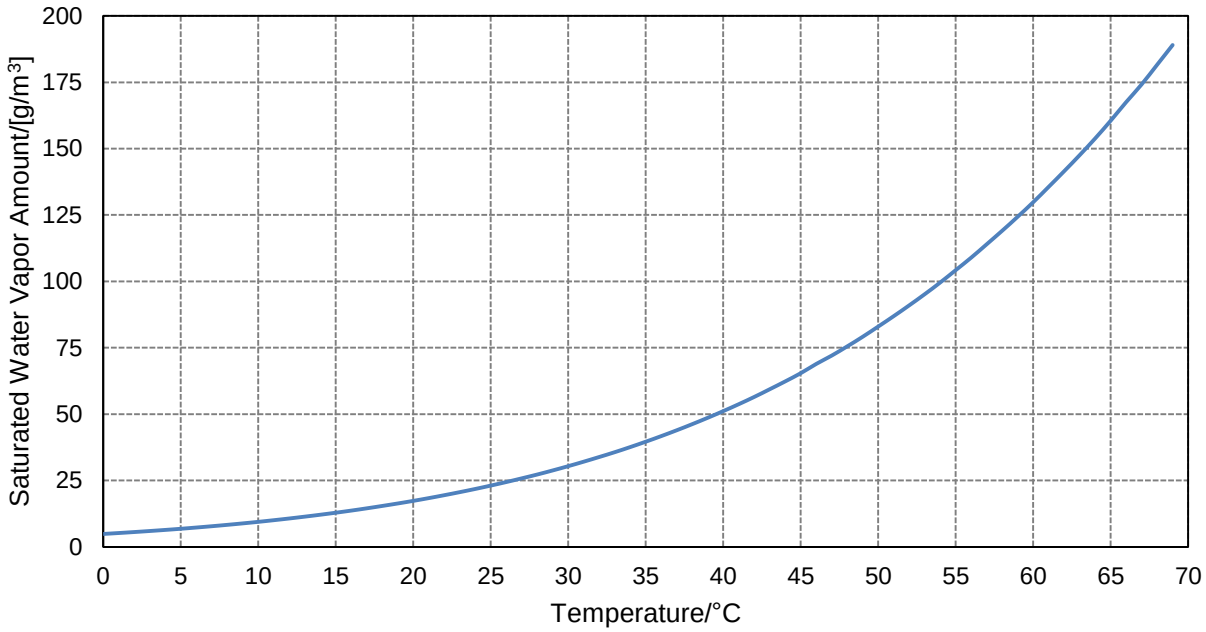


Fig 1. Saturated water vapor curve in the atmosphere

Table 1. Saturated water vapor amount in the atmosphere [g/m^3]

˚C	0.	1.	2.	3.	4.	5.	6.	7.	8.	9.
0.	4.85	5.20	5.57	5.96	6.37	6.80	7.27	7.76	8.28	8.83
10.	9.41	10.03	10.68	11.37	12.09	12.85	13.65	14.50	15.40	16.33
20.	17.31	18.35	19.45	20.60	21.80	23.07	24.40	25.80	27.24	28.78
30.	30.39	32.08	33.84	35.65	37.58	39.60	41.71	43.91	46.21	48.61
40.	51.12	53.73	56.46	59.36	62.32	65.41	68.89	72.04	75.51	79.13
50.	82.98	86.90	90.96	95.16	99.56	104.23	108.94	113.98	119.07	124.35
60.	129.81	135.62	141.50	147.56	153.85	160.53	167.53	174.22	181.62	189.04

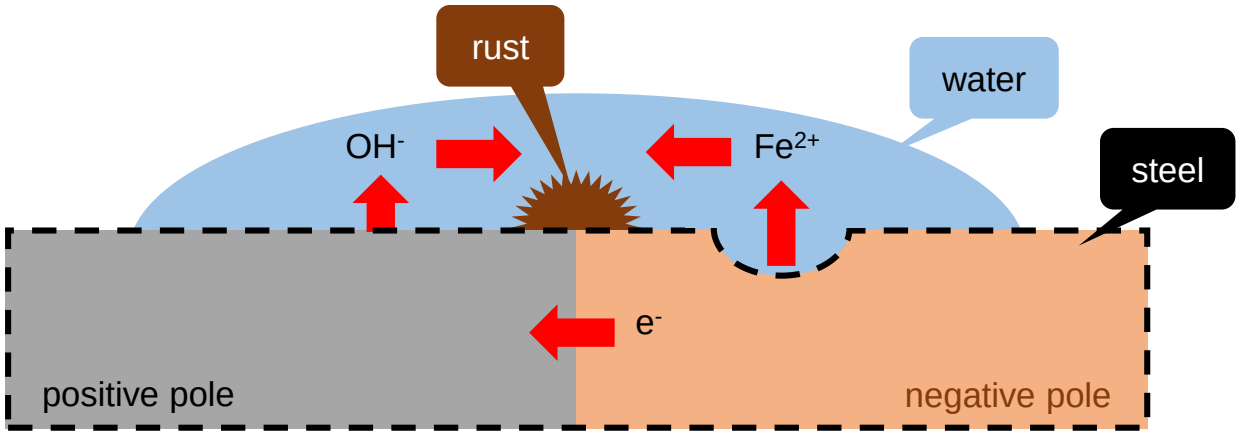
The upper limit amount of contained water vapor in atmosphere is fixed. For example, in the air at 30˚C is 30.39 g/m^3 is upper limit amount (Saturated water vapor amount). Humidity of at this condition is 100%. Water vapor amount cannot exceed the upper limit amount. So, “Temperature 30˚C, Water vapor amount 35.00 g/m^3” does not exist.

If temperature 30˚C / Water vapor amount 30.39 g/m^3 [Humidity 100%] rises temperature 40˚C, the humidity is 59% [= “30.39 g/m^3” ÷ “51.12 g/m^3” × 100] because saturated water vapor amount at 40˚C is 51.12 g/m^3.

On the other hand, if temperature drop to 20˚C, the humidity is 100%. However, 13.08 g/m^3 [= “30.39 g/m^3” − “17.31 g/m^3”] is dew condensation (water) because saturated water vapor amount at 20˚C is 17.31 g/m^3.

2-2. Theory

Main cause of rust / corrosion is oxygen in the air dissolves in the water layer on the metal surface, and three substances, “metal + water + oxygen”, react. On the other hand, There is also corrosion such as silver that is not reacted with water and oxygen. This rust / corrosion reaction is an "electrochemical reaction". As we call "electrochemical”, weak electricity flows on the metal surface, and formed “battery cell”. The following figure is an example of iron rust / corrosion. Other reactions may occur depending on the environment state.



1st Step

$Fe \rightarrow Fe^{2+} + 2e^-$ Oxidation Reaction

$1/2\ O_2 + H_2O + 2e^- \rightarrow 2OH^-$ Reduction Reaction

2nd Step

$Fe^{2+} \rightarrow Fe^{3+} + e^-$ Oxidation Reaction

$1/4\ O_2 + 1/2\ H_2O + e^- \rightarrow OH^-$ Reduction Reaction

$Fe \rightarrow Fe^{2+} + 2e^-$

(Iron) (Iron ion) (Electron)

$O_2 + 2H_2O + 2e^- \rightarrow 4OH^-$

(Oxygen) (Water) (Hydroxide ion)

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$

(Iron(II) hydroxide, White color)

$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4FeO(OH)\cdot nH_2O$

(Iron(III) hydroxide, Red color)

Fig 2. Example of iron rust / corrosion reaction

Rust / Corrosion

The word “battery” is written on the previous page, if you have a good intuition, you will be thinking there are positive and negative pole (charge). The answer is “Yes”. This positive and negative pole (charge) forms a battery on the metal surface, and rust / corrosion occurs when electricity flows. The reason why there are positive and negative charge is that common metal materials are multi-elements, so the charge is generated due to the difference in the properties of the elements. For example, in the case of stainless steel, the main elements are iron (Fe), and elements such as chromium (Cr) and nickel (Ni) are also containing. The positive and negative charge are generated by the difference in the properties of individual elements.

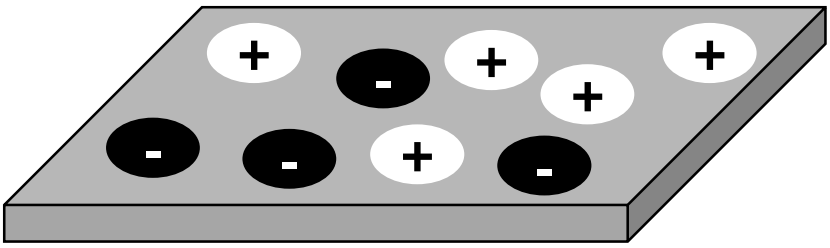


Fig 3. local-action cells on the metal surface

Following tables 2 and 3 show the relationship between the corrosion resistance of various metals depending on pH.

Table 2. Corrosion resistance of various metals on pH

pH	0	2	4	6	8	10	12	14
Steel	Corrosion (acid)			Corrosion (oxygen)			Passivation	
Stainless	Corrosion (acid)				Passivation			
Zinc		Corrosion (acid)				Passivation		Corrosion
Aluminum	Corrosion (acid)			Passivation			Corrosion	

Table 3. Relationship between various metals and solutions

	Concentrated nitric acid or sulfuric acid	Hydrochloric acid Dilute sulfate	Acidity (pH3 - 5)	Neutral*1	Seawater	Alkalinity
Zinc	Corrosion	Corrosion	Corrosion	Protective Film	Protective Film	Corrosion*3
Copper	Corrosion	Stability*2	Protective Film	Protective Film	Protective Film	Protective Film
Aluminum	Passivation	Corrosion	Corrosion	Passivation	Passive Film (Pitting Corrosion)	Corrosion*4
Stainless	Passivation	Corrosion	Passivation	Passivation	Passive Film (Pitting Corrosion)	Passivation
Chrome	Passivation	Corrosion	Passivation	Passivation	Passivation	Passivation
Carbon Steel	Passivation	Corrosion	Corrosion	Corrosion	Corrosion	Passivation

*1 Trace amount of chloride ion *2 Corrosion: Dissolved oxygen *3 Corrosion: pH13< *4 Corrosion: pH8.5<

Reference）

R. Winston Revie; Herbert H. Uhling. Corrosion and Corrosion Control: An Introduction to Corrosion Science and Engineering, 4th Edition, Wiley InterScience, 2008.

Matsushima; 腐食防食の実務知識, Ohmsha, 2002.

2-3. Type of Corrosion

There are various types of rust / corrosion depending on the mechanism of rust / corrosion. The differences are occurred by the combination of the type of metal and the usage environmental. Typical corrosions are as follows.
There are different types of rust / corrosion, and the factors that cause them are different, so the prevention methods are also different. For example, "oil staining" is caused by oxidation of oil such as applied rust preventive oil, so is given as this countermeasure "removal and reapply oil regularly", "use no oil, and use another anti-rust wrapping materials", etc.

1. General Corrosion
2. Local Corrosion
3. Pitting Corrosion
4. Crevice Corrosion
5. Galvanic Corrosion
6. Dealloying
7. Intergranular Corrosion
8. Erosion-corrosion
9. Cavitation Damage
10. Fretting Corrosion
11. Stress-Corrosion Cracking [SCC]
11. Corrosion Fatigue
13. Scale
12. Oil Staining

Fig 4. Main Type of Corrosion

2-4. Type of Dirt

The following are listed in the US military handbook as types of dirt that cause rust / corrosion. This dirt are natural enemies of anti-rust /anti-corrosion packaging materials, containing VCI paper. If metal products are not properly cleaned and dried, this dirt cause rust / corrosion even if the anti-rust / anti-corrosion packaging material is used properly.

1. Body secretions [finger prints, sweat, etc.]
2. Residues during soldering, welding / Wax
3. Cutting or cooling agent
4. Abrasive
5. Metal residues of machining, polishing, etc.
6. Residues of salts for heat treatment
7. General waste from work place, etc.
8. Attachment of dust or chemicals in the atmosphere
9. Residues of ink or etching solution

Fig 5. Main Type of Dirt

Reference）
Technical Order 00-85-3, Corrosion Control for Packaging, 1963.

2-5. “Capillary Phenomenon” & “Salts of Sweat etc.”

When foreign objects adheres to the metal surface, a phenomenon called “capillary condensation” will occur. This is a phenomenon in which moisture enters a slight interspace (capillary part) between objects, and the moisture (gas) changes to water (liquid). In addition, when sweat is dried on the metal surface, salts contained in the sweat remains on the surface. In high humidity environment, these salts may absorb moisture and return to liquid. It makes easier for electric flow of rust / corrosion reactions because of salty water conducts electricity well (see pages 5 and 6).

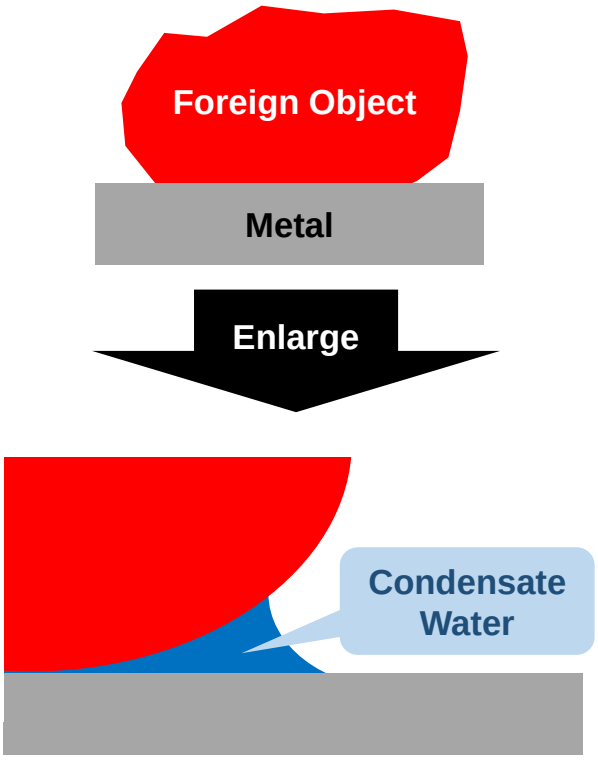


Fig 6. Capillary Phenomenon

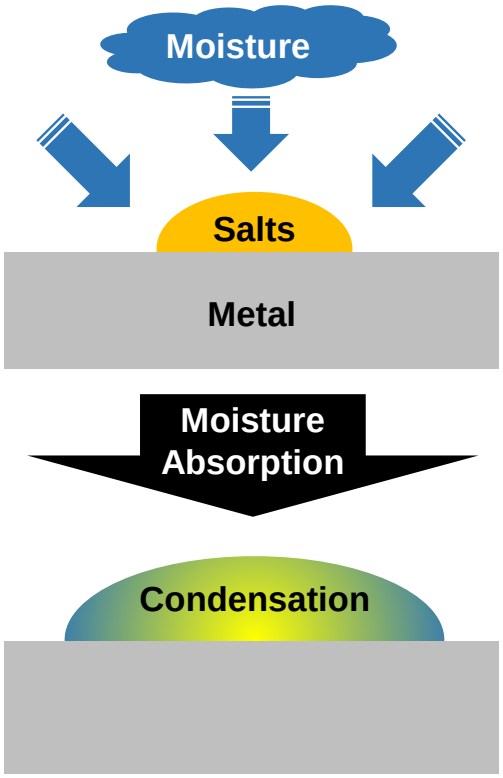


Fig 7. Salts of Sweat etc.

2-6. Others

Silver (Ag) differ the metal such as copper alloy and steel, and is not corroded by “Water" and “Oxygen". What cause?
As one of the cause, “Hydrogen sulfide (H_2S)” is. Silver react with sulfur compounds like hydrogen sulfide. If you bring the silver items at hot spring, the color of items will change to black. Hydrogen sulfide is produced from exhaust, paper and skin etc. under general life environmental, because of degradation of sulfur compounds.

$$2Ag + H_2S \rightarrow Ag_2S + H_2$$

[Black]

Reference）
V. S. SASTRI. GREEN CORROSION INHIBITORS, Wiley, 2011.

Temperature and Humidity in our factory

The following reference data of temperature and humidity are data in Japan. These data were in 2017, were recorded every 1 h in our factory. These graphs are “Highest value” and “Lowest value” in a day.

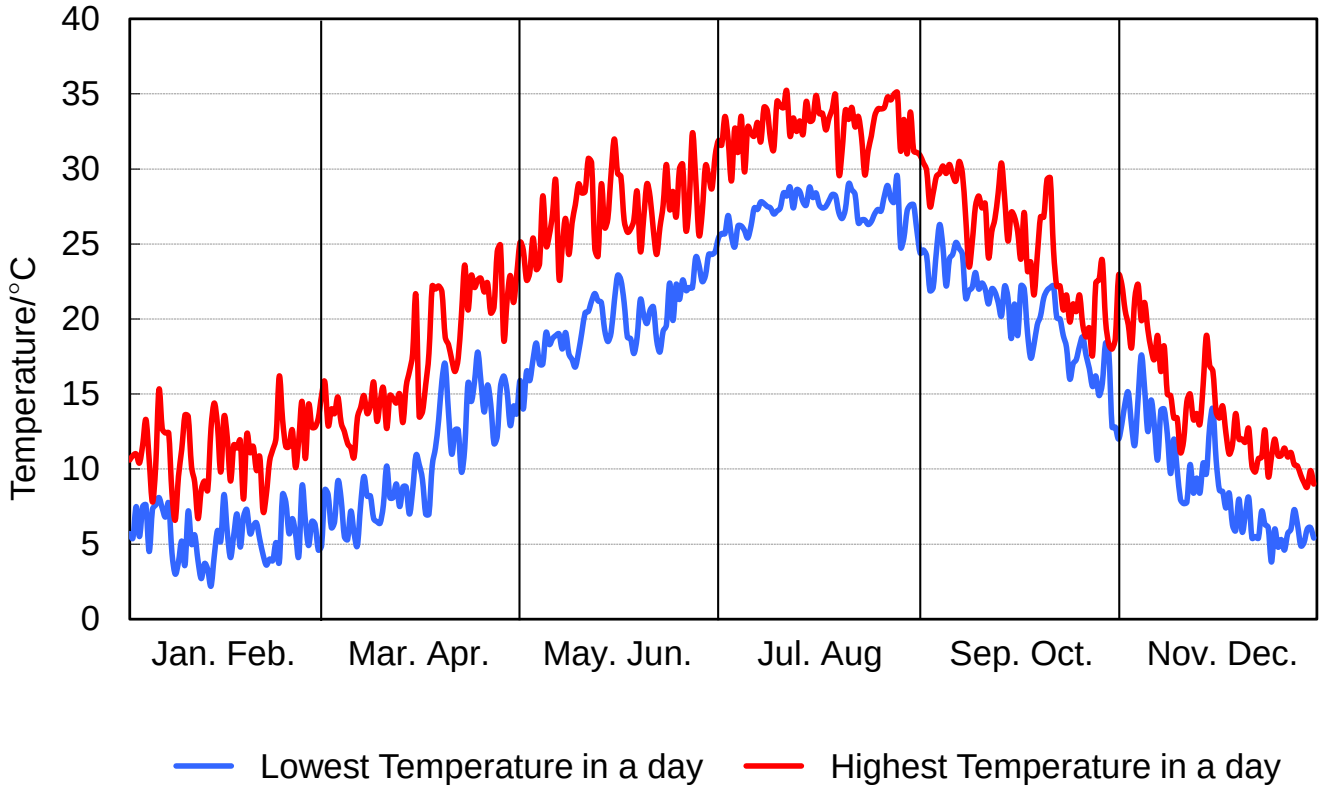


Fig 8. Highest and Lowest Temperature in a day

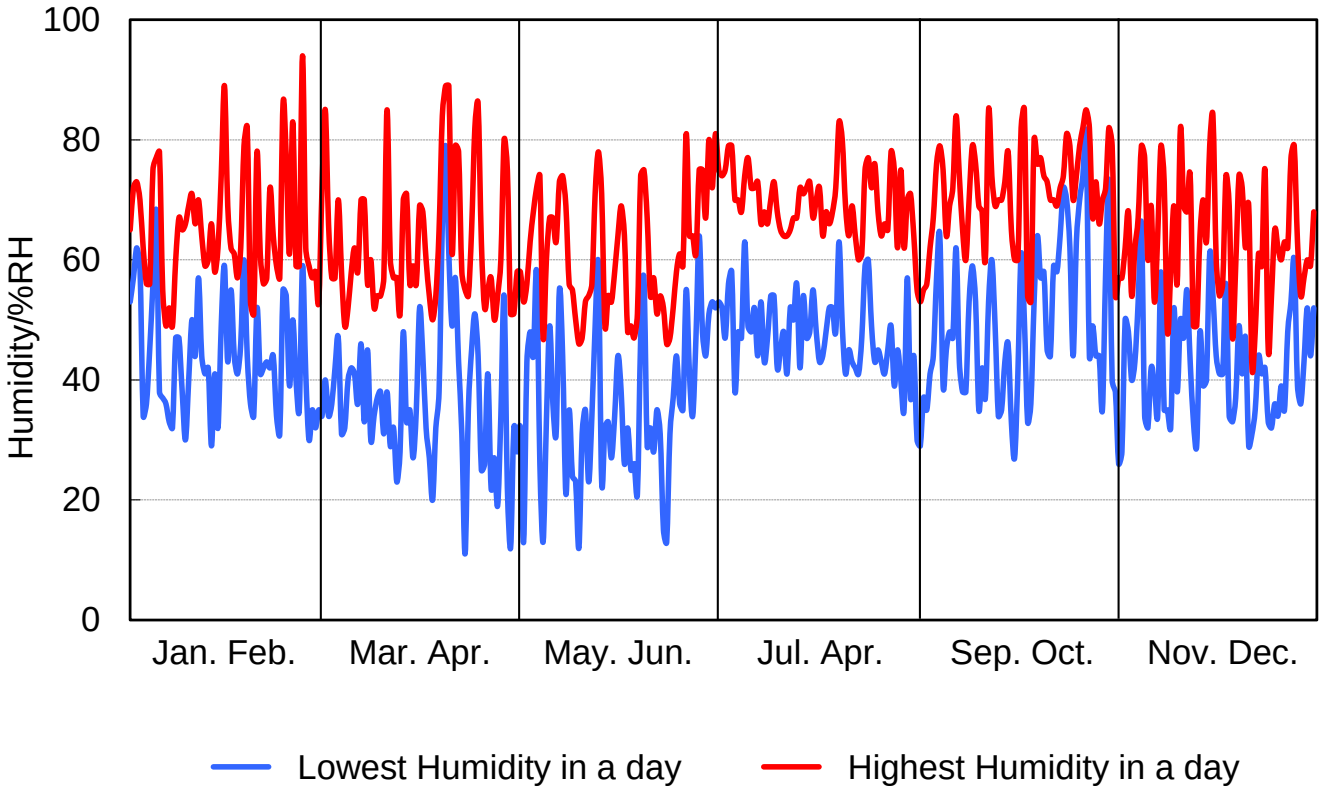


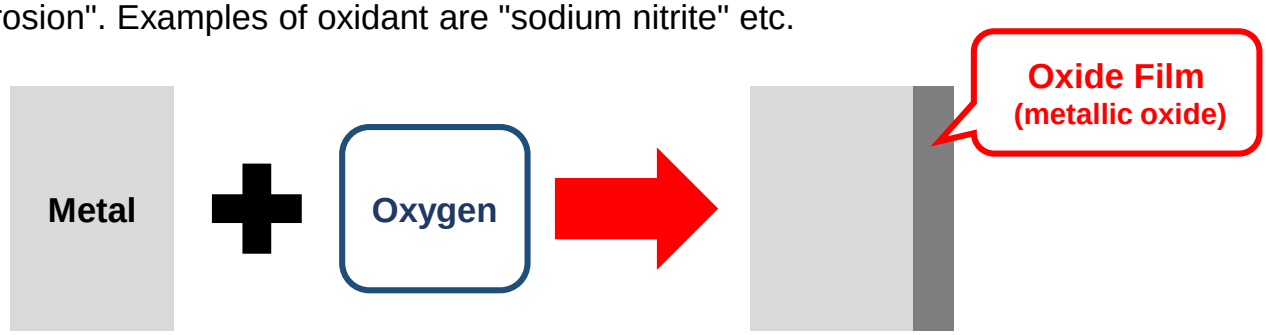
Fig 9. Highest and Lowest Humidity in a day

Mechanism of Corrosion Inhibitors

The action of the inhibitors are divided into the following three types in Japan.

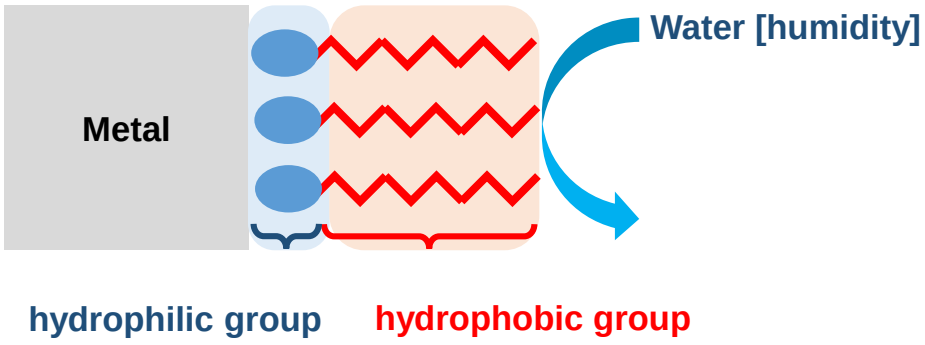
3-1. Oxide Film

Oxide film is a film formed by oxidizing the metal surface with oxidant. When a lot of people hear "oxidation", they may be reminded of "rust / corrosion". However, the oxidation state of the metal produced by the oxidant is different from the state of "rust / corrosion". Examples of oxidant are "sodium nitrite" etc.



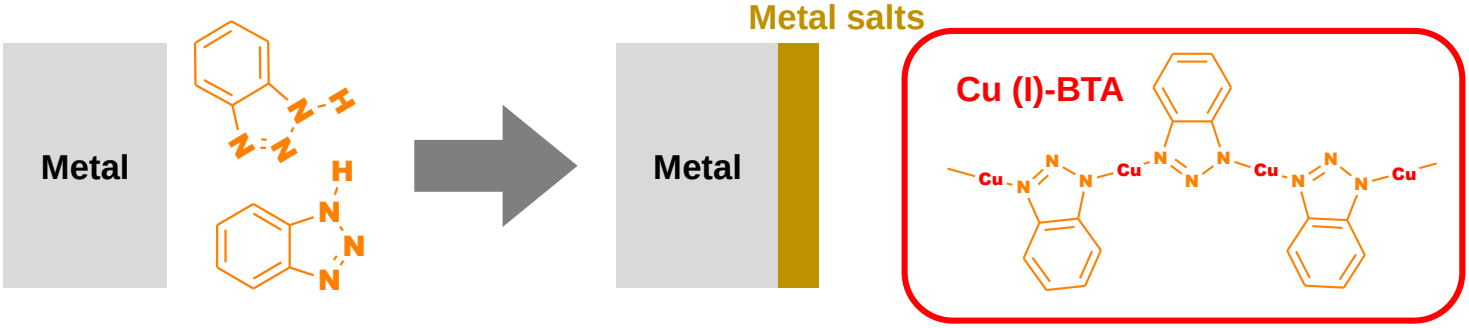
3-2. Adsorption Film

This is a film of “Inhibitor for iron and steel”. A substance having both “hydrophilic group” and “hydrophobic group” adsorb onto the metal surface, and the film is formed. At this time, the hydrophilic group contact with the metal surface. The bonding of the inhibitor and the metal surface is not strong. Therefore, the inhibitor can evaporate naturally or be wiped off with a solvent. Examples are “amines" etc.



3-3. Complex Film

This is a film of “Inhibitor for copper and copper alloy”. A bonding of the inhibitor and the metal surface is strong. Usually, the film can not be removed unless polishing etc. Examples are “triazole compounds" etc.



VCI Paper

4-1. Constitution

The basic construction of VCI paper is "paper + inhibitors".

VCI paper is not “oil paper”. Oil paper is applied oil to paper, and moisture-proof better. And the oil paper is not contained inhibitors. Popular VCI paper with moisture-proof better is PE (polyethylene) is coated on the one side. Some companies have been using wax instead of PE.
Base paper of VCI paper is usually using “acid-free paper / neutral paper”. The acid-free paper is controlled from neutral to alkaline of pH region. Since normal paper is acid, metal is easy to rust.
Inhibitors used are 2 type, impregnated type: inhibitors is between paper fibers, coated type: mixed inhibitors and adhesive and they are coating on the paper surface. Popular type is “impregnated type”, but DHICAN (Dicyclohexylammonium nitrite) of one of inhibitors is difficult to dissolve in water. So, it mix with adhesive and water, and coat on the paper surface.
In the case of steel like cut sheet or coil, the base paper of VCI paper uses paper with cloth sheet of PE. This type of paper is stronger than kraft paper of paper with PE. And, wrinkle processing type is also. This type is called “Crepe paper”. This crepe paper stretches, can use like bandage.

4-2. Type

Types of VCI paper mainly have “for iron and steel”, “for copper and copper alloys” and “for ferrous and non-ferrous” depending on the target metal.

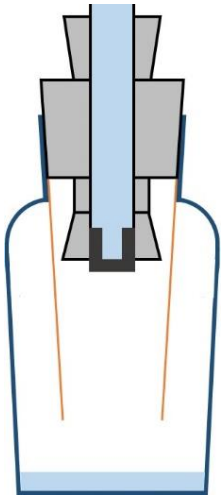
Just as individual metals differ the properties, so compatibility with inhibitors and metals. Therefore, we have to change the inhibitors depending on the target metal.
For example, sodium nitrite is famous as common inhibitor, this formed oxide film on the metal surface. However, if this was used for copper / copper alloys, the color of copper / copper alloys will change darker, because the thickness of oxide film of copper / copper alloys increase. On the other hand, in the case of use it for iron, the color is almost unchanged even if the oxide film becomes thicker.

It is necessary to select VCI paper suitable for use from the combination of "type of VCI" and "type of paper".
For example, if you use VCI paper on the bottom or top of a container, it is not necessary to use a PE laminated type (moisture-proof type). However, in the case of packaging of heavy products, if there is no paper strength, such as a type without PE cross sheet, there is a risk of tearing during packaging or transportation.

4-3. Evaluation Test according to JIS (Japanese Industrial Standards)

JIS of VCI paper are the below 2 types (As of 2019).
・JIS Z 1535 [Review: 2014]: Corrosion inhibitor treated papers for iron and steel
・JIS Z 0321 [Issue: 1997]: Volatile corrosion inhibitor paper for copper and copper alloys
(There are not test about JIS of the other metals like aluminum.)

There are 2 types, “Volatile Test” and “Contact Test”.
In addition to these JIS tests, the products are actually packaged, and using an environmental testing machine. The products are promoted rust / corrosion under the specific temperature and humidity, and we evaluate them.

<table>
<tr><th></th><th>JIS Z 1535</th><th>JIS Z 0321</th></tr>
<tr><td>Volatile Test</td><td> 
Steel (SGD3)

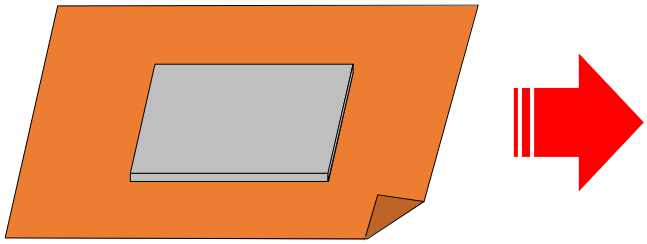
VCI paper:
30 mm × 130 mm,
2 sheets

Temperature: 20°C
(Using cool water)

Humidity: 90%RH</td><td> 
Copper / Brass / Phosphor bronze [plate]

VCI paper:
71.5 mm × 280 mm

Temperature cycle:
30°C / R.T. / 5°C / 50°C / 5°C / 50°C /

Humidity: 100%RH</td></tr>
<tr><td rowspan="2">Contact Test</td><td colspan="2"> 
Bottom
Top</td></tr>
<tr><td>Steel (SPCC)

Temperature 50°C
Humidity 100%RH</td><td>Copper / Brass / Phosphor bronze [plate]

Temperature 50°C
Humidity 95%RH</td></tr>
<tr><td>Evaluation</td><td>・Volatile Test (Pass)
Type S: Not Rust
Type H: Not Rust
Type EL: Rust prevention rate, 50%≤

・Contact Test (Pass)
Not Rust</td><td>Grade A: Not Change
Grade B: Slightly Discoloration
Grade C: A Little Discoloration
Grade D: Discoloration
Grade E: Terrible Discoloration / Corrosion

Grade A and B are Pass.</td></tr>
</table>

4-4. Usage

1. VCI in VCI paper is finite.
   ⇒ If keep expose of VCI paper (for days), VCI will gradually vaporize from VCI paper, reducing the total amount of VCI. As a result, the performance of VCI paper reduce. When not in use, store it in a plastic bag or container.

2. You can leave VCI paper exposed during working (about half a day).
   ⇒ Generally used VCI paper is that the VCI contained in VCI paper gradually vaporizes, but the amount of vaporization loss during working (about half a day) is a very small amount, the performance of VCI paper does not reduce.

3. Use with the printed side or PE laminated side outward.
   ⇒ VCI is impregnated/coated on the kraft paper side.

4. The storage location is preferably “cold dark place”.
   ⇒ This is to prevent product deterioration.

5. It is safe to touch the product with bare hands.
   ⇒ The base material is paper, and the behavior and content of the contained VCI is small, making it harder to rough skin than rust preventive oil (base material is oil), which is often compared. However, since VCI is often not edible, you should wash your hands after touching VCI paper.

6. Can be used in combination with rust preventive oil/desiccant/rust preventive film.
   ⇒ There are no companies that recommend VCI paper and these combinations, but some customers used in combination. In rare cases, it may cause some chemical reactions with VCI, and the causes of discoloration and foreign objects.

7. If the packaging form is moisture-proof, the rust-proof period will be extended.
   ⇒ Moisture is prevented from entering the packaging, and VCI vaporized from VCI paper hardly become to go outside the packaging.

8. Mainly VCI paper is only effective against dew condensation.
   ⇒ If there are many corrosive factors (foreign objects) on the metal surface due to insufficient cleaning, etc., it may be impossible to anti-rust with VCI paper.

9. The rust-proof period is not constant.
   ⇒ For example, if “The rust-proof period is less than 6 months” is written on the document, the products do not rust/corrosive reliably even after the storage period 6 months. The rust-proof period change by the condition of the packaging and metal and the storage environmental.

10. The disposal method is the same as that for general paper (in Japan).
    ⇒ Follow the relevant laws/ordinances of each country and region.

11. The size of VCI paper used for packaging must be changed according to the situation.
    ⇒ There is the rough indication size of each company, but it is necessary to change the size according to the usage environment. If the size is smaller than the rough indication size, it is necessary to test with the actual packaging. There is not generally formula of the determine size.

Example of Using

Conditions for rust-proof packaging with VCI paper are: **“Metal products are not rusted”, “Metal product surface are clean”, “VCI paper is properly stored”, “Do not reuse VCI paper / disposable”, “Type of VCI paper and target metal combination is appropriate”**. The most common trouble cases are “Products are already rusted / dirtied before using VCI paper”.

The required size of VCI paper differs depending on "metal type / surface treatment method of metal / storage environment / etc.", so it can not be determined with one formula. Also, even if the metal is the same manufacturer and the same standard, the corrosion resistance may change if the production lot is different.
Since only VCI paper is effective, "rust prevention oil" and "desiccant" are not required.

Packaging “A” Wrapping by kraft paper (not moisture-proof) type


1


2

It is sufficient if the metal product is packaged, and it is not necessary to seal with tape as in packaging "B".

Packaging “B” Wrapping by PE laminated paper (moisture-proof) type


1


2

Close the gap with tape to prevent outside air from entering.

Example of Using

Packaging “C” PE bag + kraft paper (not moisture-proof) type


1


2

Close the opening of the PE bag to prevent outside air from entering.
It is not necessary to pack the metal product with VCI paper like packaging "A" and "B".

Both of packing "B" and "C" are moisture-proof packaging, and the evaporated VCI hardly disappaers from in the packaging, so it becomes a packaging form for long-term storage.

Packaging “D” Container [VCI paper only on the bottom]


1


2


3

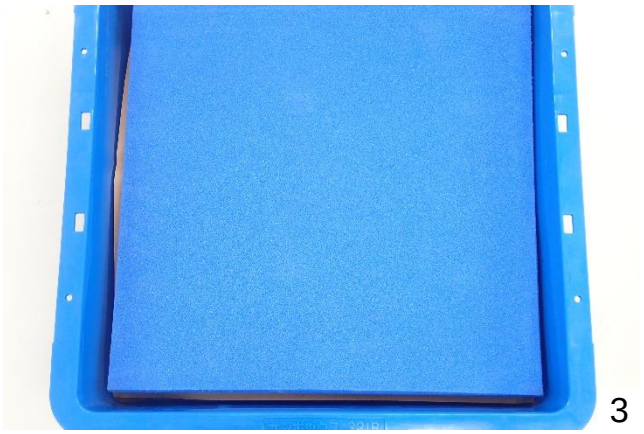
Put another container or a lid on the container containing the products.
The smaller the gap, the better for long-term storage.

Example of Using

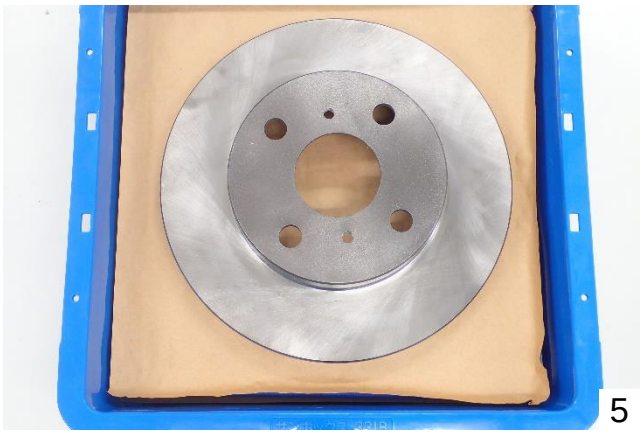
Packaging “E” Container [multilayer]


1


2


3


4


5


6

If the board is divided into multiple layers, the vaporized VCI does not diffuse uniformly into the container with only VCI paper 1 sheet, so it is necessary to place VCI paper in each layer.

After sandwiching the metal product with VCI paper 2 sheets and making a layer with the board, put the metal product and VCI paper in the same way.

Example of Using

Packaging “F” Container [interim storage, VCI paper instead of lid]

1

2

When using as a lid, cover whole the products so that they do not get dusty.

Packaging “G” Big container

Since it is necessary to consider the reach (effective range) of the VCI, it is necessary to place VCI paper on the top, middle and/or bottom.

Packaging “H” Crepe paper type of VCI paper

Can use like bandage.

VCI Paper Trouble Cases and the Solutions

Problem 1

Metal rusted / corroded / had some foreign objects.

Cause 1

- The products are dirty. [Reusing cleaning solution. The work tools are dirty.]
  ⇒ Use clean cleaning solution and work tools.
- Cutting solution and cleaning solution remain and on the metal (react with VCI)
  ⇒ Wash / dry cleanly. Change the cutting solution/cleaning solution to another type.
- VCI paper size is small.
  ⇒ Use large size.
- Sealing is low, Moisture enters the packaging, VCI vaporized goes out of the packaging.
  ⇒ Increase sealing of the packaging.
- Rusted before packaging.
  ⇒ VCI does not have removing rust effect, and not stop rust growth effect also.
- Mistaking the combination of the VCI paper type and the metal type.
  ⇒ Package in the correct combination.
- VCI paper has deteriorated due to reuse and inappropriate storage environment.
  ⇒ Not reuse VCI paper. Correct storage environmental.
- There is PE sheet between products and VCI paper.
  ⇒ VCI paper is required between products and PE because VCI vaporized does not reach onto the product surface.
- In the case of PE laminated VCI paper type, PE side is touching the products.
  ⇒ The direction is reversed. PE side is outside.

Problem 2

The plating cracked.

Cause 2

- There are the foreign objects under plating layer, base metal was rusted by them.
  ⇒ Plating after removing foreign objects. It is the phenomenon in which VCI paper can not be involved.

Problem 3

Resin, plastic or rubber discolored.

Cause 2

- Some VCI types have negative effects for them.
  ⇒ Change VCI paper type.

Issue Date: Dec. 13, 2019
Revision Date: -

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