ThreeBond
TECHNICAL NEWS

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Volatile Corrosion Inhibitor (VCI)

1. Introduction

Trade dispute by export surplus has come up in the newspaper. Trading, especially export, is essential to Japan economy, whereas it is said that economical loss caused by corrosion in the export activity is about 2,000,000,000,000 yen.

We at Three Bond have released a variety of volatile corrosion inhibitors as ThreeBond 1870 series when we considered these circumstances. Volatile corrosion inhibitors have been codified technically, but they took an auxiliary part only in rust prevention due to their relatively shallow history.

In this issue, we will provide you with VCI's features that it should be the mainstream in the future rust prevention packaging, and also introduce a new method as well.

Contents

2. What is Volatile Corrosion Inhibitor (VCI)?

Volatile corrosion inhibitor is referred to metal corrosion inhibitor that has a volatile property at normal temperature regardless of solid or liquid.

Typically volatile corrosion inhibitor is a compound or mixture that is vaporized slowly at normal temperature such as nectarine, camphor, paradichlorobenzene that are used in a home as a mothproofing agent. The vaporized gas can prevent metal corrosion, that absorbs to a metallic surface chemically and physically and reacts with that surface or that forms an atmosphere that prevents metal corrosion.

Volatile corrosion inhibitor is often called as VCI (Volatile Corrosion Inhibitor) or VRI (Volatile Rust Inhibitor).

3. Positioning of Volatile Corrosion Inhibitors

Volatile Corrosion Inhibitor is classified into “packaging” category in the rust prevention or rust prevention field as apparently shown in Figure 1.

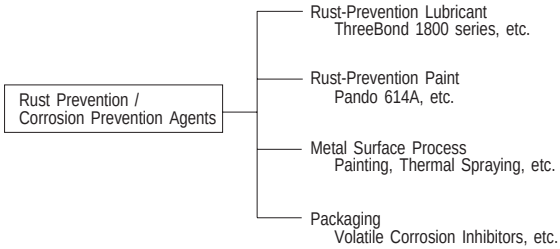


Figure 1. Classification of Rust Prevention or Corrosion Prevention Agents

4. Shape of Volatile Corrosion Inhibitors

Products that use volatile corrosion inhibitors are as follows:

(1) Powder
(2) Tablet
(3) Rust-inhibiting oil
(4) Water-soluble rust inhibitor
(5) Rust-inhibiting paper
(6) Device
(7) Emitter
(8) Tape
(9) Film
(10) Others

5. Type of Volatile Corrosion Inhibitors

(1) Volatile Corrosion Inhibitors for Steel

- Nitrite of amines
- Carboxylate of amines
- Chromate of amines
- Ester of carboxylic acid
- These mixture

It often uses a quick volatile benzoic acid monoethanolamine salt together for steel.

(2) Volatile Rust Inhibitor for Coppers and Copper Alloys

- Hetero cyclic compounds

  Triazole ring

  Pyrole ring

  Pyrazole ring

  Thiazole ring

  Compounds with imidazole ring
- Thiourea ring
- Compounds with mercapto group

6. Typical Volatile Corrosion Inhibitors

1 BTA	:Benzo triazole
2 TTA	:Tolyl triazole (Methyl benzotriazole)
3 DICHAN	:Dicyclohexyl ammonium nitrite
4 DICHA•SA	:Dicyclohexyl ammonium salicylate
5 MEA•BA	:Monoethanolamine benzoate
6 DICHA•BA	:Dicyclohexyl ammonium benzoate
7 DIPA•BA	:Diisopropyl ammonium benzoate
8 DIPAN	:Diisopropyl ammonium nitrite
9 CHC	:Cyclohexylamine carbamate
10 NITAN	:Nitro naphthalene ammonium nitrite

11 CHA•BA :Cyclohexylamine benzoate

12 DICHA•CHC :Dicyclohexyl ammonium cyclohexanecarboxylate

13 CHA•CHC :Cyclohexylamine cyclohexane carboxylate

14 DICHA•AA :Dicyclohexyl ammonium acrylate

15 CHA•AA :Cyclohexylamine acrylate

16 Others

7. Structure of Typical Volatile Corrosion Inhibitors

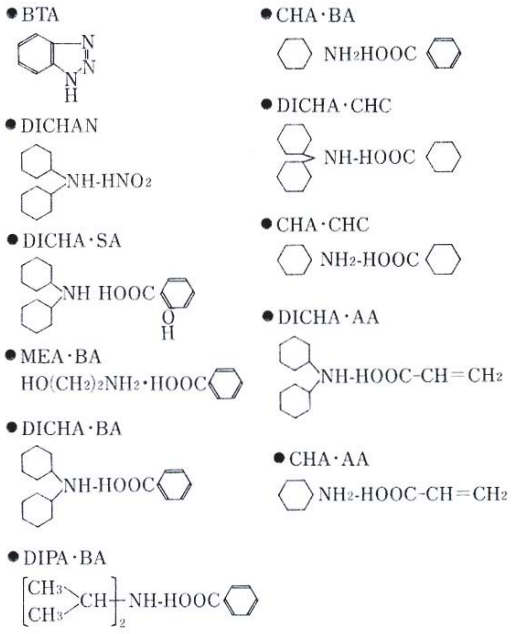


Figure 2. Structure of Typical Volatile Corrosion Inhibitors

8. Structure of Typical Volatile Corrosion Inhibitors

Table 1. Rust Prevention Effect for Various Metals

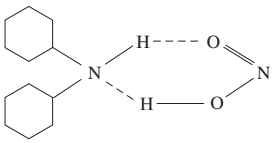
Rust Prevention Agents / Metals	BTA	DICHAN	DICHA•SA	MEA•BA	DICHA•BA	DIPA•BA	CHA•BA	DICHA•CHC	CHA•CHC	DICHA•AA	CHA•AA
Copper	◎	◎	○	○	△	◎	◎	◎	○	○	○
Phosphor bronze	△	△	◎	×	◎	◎	◎	○	○	◎	◎
Brass	○	○	◎	◎	△	◎	◎	◎	◎	○	◎
Aluminum	△	○	○	◎	◎	◎	×	◎	△	○	○
Corrosion resistant aluminum	◎	◎	×	×	×	◎	◎	◎	◎	◎	×
Zinc die casting	○	○	○	◎	○	○	○	◎	◎	○	○
Duralumin	◎	○	◎	◎	○	×	△	○	◎	◎	○
Magnesium alloy	◎	△	○	◎	○	◎	○	○	○	◎	○
Alumite	×	×	◎	×	◎	◎	◎	◎	◎	◎	◎
Gloss chrome plating	○	◎	×	○	◎	◎	◎	◎	○	◎	◎
Hard chrome plating	○	◎	◎	○	○	◎	◎	◎	◎	◎	◎
Gloss zinc chrome plating	×	◎	◎	◎	◎	◎	○	◎	◎	◎	◎
Gloss zinc plating	◎	○	◎	◎	◎	○	○	○	○	○	○
Hot-dip zinc plating	△	△	◎	◎	○	◎	○	◎	◎	△	○
Silver plating	△	○	×	◎	◎	△	○	◎	○	○	◎
Nickel plating	△	○	◎	◎	○	○	◎	◎	◎	◎	○
Solder plating	○	○	○	○	○	○	○	◎	◎	○	○
Tin plating	○	○	×	○	◎	◎	◎	○	○	◎	◎
Cadmium plating	×	◎	◎	◎	◎	×	◎	◎	×	×	×

Evaluation ◎ : It has rust prevention capability, and is excellent rust prevention capability.
○ : It has weak rust prevention capability compared to others.
△ : It has no rust prevention capability, or adverse effect.
× : It has no rust prevention capability, or adverse effect (accelerated corrosion).
Condition Temperature: 50°C, Humidity: 90RH%, Period: 70 days

9. Corrosion Inhibitor Mechanism of Volatile Corrosion Inhibitors

(1) For Steels

a. Nitrite (DICHAN)



Vaporization state of DICHAN

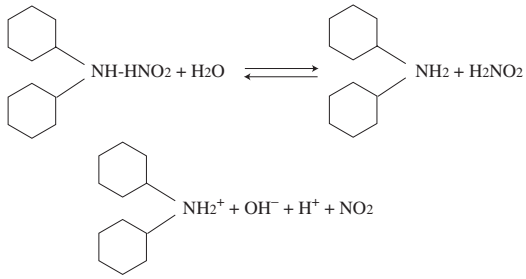
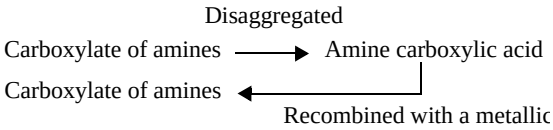


Figure 3. Nitrite

If moisture in the air is condensed into a metallic surface, this slowly vaporized DICHAN is dissolved into the condensation water to prevent oxygen and liquid water that react with a metal from corroding.

b. Carboxylate of amines

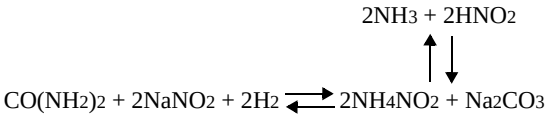


In this case, carboxylate of amines was disaggregated into amine and carboxylic acid, and they were recombined in a metal surface back into the carboxylate of amines, which prevents metal corrosion.

c. Mixed system

Even corrosion inhibitors without characteristics to vaporize alone are hydrolyzed and evaporated in mixture system by absorbing atmospheric moistures.

In case of sodium nitrite and urea



(2) Coppers and Copper Alloys

Corrosion inhibition mechanism, inclulding BTA and TTA, for coppers and copper alloys is considered not due to simple absorption or forming complex compounds films, but due to forming benzotriazole copper salt coating by reacting as follows:

$$Cu + \tfrac{1}{2}O_2 + 2C_6H_4N_2{\bullet}NH \rightarrow (C_6H_4N_2{\bullet}N)_2{\bullet}Cu + H_2O$$

On the other hand, polymer-like compounds are formed by copper ionic states shown in Figure 4 and Figure 5.

Thickness of protective films shown in Figure 4 and Figure 5 is about 50Å to 2000Å, and they are a multiple film composed by Cu_2O and Cu-BTA, as well as a film by simple Cu-BTA.

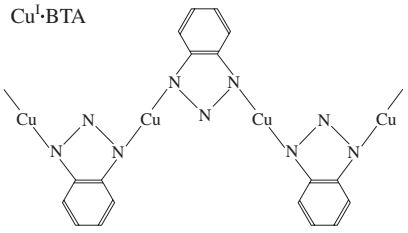


Figure 4. In case of Cu^{I}•BTA

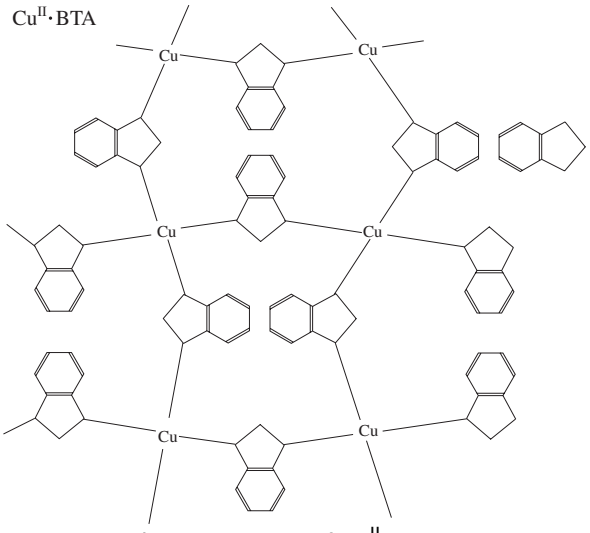
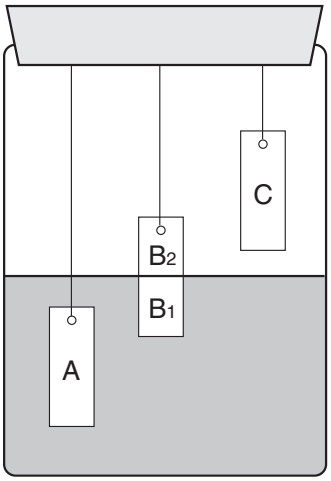


Figure 5. In case of Cu^{II}•BTA

10. Corrosion Inhibition Effect of Volatile Corrosion Inhibitors

(1) Effect in Solution

A solution that volatile corrosion inhibitors are dissolved obtains rust prevention effects. Results that steel test pieces grinded as shown in Figure 6 are examined in each concentration are shown in Table 2. From this result, valid threshold concentration in distilled water of DICHAN is found as 0.01wt% or so.



Condition Test piece: SAE-1020
Temperature: 37.8°C
Time: 500h

Figure 6. Corrosion prevention capability test equipment for solutions

Table 2. Corrosion prevention effects in DICHAN distilled water solution

Test piece / Concentration(wt%)	A	B		C
		B_1	B_2	
0	×	×	×	×
0.01	△	△	×	×
0.10	○	○	×	×
1.00	○	○	×	×
2.00	○	○	○	○
3.00	○	○	○	○

× : Rusting △ : Slightly Rusting
○ : Complete Corrosion Prevented

(2) Effect in Gas Phase

It is clear that volatile corrosion inhibitors should show rust prevention effects in gas phase, but every corrosion prevention materials don't show the effects immediately. Initial effect variation is great due to steam pressure and the like, and the typical examples are shown in Table 3.

Table 3. Initial effect in the typical volatile corrosion inhibitors (20±1°C)

Time (h)	DICHAN	DIPAN	CHC
1/4	×	○	◎
1/2	×	◎	◎
1	×	◎	◎
2	△	◎	◎
3	○	—	—
4	◎	—	—
5	◎	—	—
16	◎	—	—
20	◎	—	—

(Criteria in volatile corrosion inhibitors)

Criteria	Indication	Result
No rusting; Passed in specified codes completely	◎	Passed
Some rusting; Rejected in specified codes, but effects are recognized definitely	○	Rejected
Rusting but a little effects are recognized compared with blank tests	△	Rejected
Rusting same as blank tests; no effects are recognized	×	Rejected

On the other hand, rust prevention effects in gas phase greatly depend on minimum requirements or concentrations along with initial effects. The results are shown in Table 4. As shown in the table, the minimum requirement is found 5mg/l or so as a rough standard.

Table 4. Minimum requirements of typical volatile corrosion inhibitors

(20±1°C, 20h)

VCH(mg/)	DICHAN	DIPAN	CHC
50	◎	◎	◎
40	◎	◎	◎
30	◎	◎	◎
20	◎	◎	◎
10	◎	◎	◎
5	◎	◎	◎
4	△	△ – ○	◎
3	× – △	△	△ – ○
2	×	×	×
1	×	×	×

(Criteria and indication are same as Table 3.)

11. Toxicity of Volatile Corrosion Inhibitors

Representative volatile corrosion inhibitor, DICHAN, is safe without toxicity and accumulation functions unless it is drunk much in ordinary usage. However, some bitterness is felt in mouth and nasal mucosa are stimulated so that use of mask, etc. is recommended when much DICHAN must be always handled. For your information, summary of a bulletin at the Department of Pharmaceutical Chemistry in the University of California is shown in Table 5 and Table 6.

12. General Considerations on Applying Volatile Corrosion Inhibitor (VCI)

(1) VCI amount of standard usage is referred to Table 7, and follow the instructions from the manufacture.

(2) Evaporation gas travels at within about 30cm so that it must be not kept away 30cm or more. Also in case of rust prevention paper, use the internal side, which a chemical is applied.

(3) Evaporation gas is heavier than air so that VCI must be used at the possible top of the space that requires rust prevention.

(4) VCI must be used at 100°C or less with the status that is as possible almost neutral, and it must be stored in the cool, dark, dry place without direct sunlight.

(5) Consider enough before using VCI when nonferrous metal and nonmetallic material are combined.

(6) Pretreatment should be performed completely. In case of longterm-rust prevention, preserve it in fully sealing or the like.

Table 5. Peroral administration test for volatile corrosion inhibitors

Name of chemical		Target animal	LD_{50} (mg/kg)
DICHAN		Laboratory mouse	205±15
		Marmot	350±50
		House rabbit	440±20
BTA	Purity 95%	Laboratory mouse	500
	Purity 98%	Laboratory mouse	937±28
TTA		Laboratory mouse	675

Note: DICHAN only reported on the bulletin at the Department of Pharmaceutical Chemistry in the University of California

Table 6. Animal testing values in related substances (Laboratory mouse)

Name of chemical	LD_{50} (mg/kg)
Dicyclohexylamine	500
Cyclohexylamine	710
Diisopropylamine	550 to 770
Monoethanolamine	15,000 to 770
Morpholine	1,050
Benzoic acid	1,700
Urea	12,000 or more
Sodium nitrite	180 to 277
Formic acid	1,210
Acetic acid	4,960

Table 7. Amount of standard usage in volatile corrosion inhibitor

Form	Amount of standard usage
Powder	1g/$(30cm)^3$
Solution	Concentration of 0.5% for steel use
Rust prevention paper	Rust prevention paper of $(30cm)^2$ or appearance surface area and the like of an object $(30cm)^3$

13. Three Bond's Volatile Corrosion Inhibitors

(1) ThreeBond 1871

This is a product that contains a volatile corrosion inhibitor into a sponge of 35mm long and 55mm in diameter and that makes a space of one 1001 rust prevention atmosphere. This is effective for several metals: steel, copper, aluminum, corrosion resistance aluminum, alumite, zinc die casting, hard chrome plating, gloss zinc chromate plating, duralumin, silver plating, solder plating.

On the other hand, it affects phosphor bronze, brass, zinc, gloss zinc plating, dissolving zinc plating, gloss chrome plating, magnesium alloy, cadmium plating, tin plating. You must be careful enough when using it. As an application, it is expected as a rust prevention packaging material for transport and storage.

(2) ThreeBond 1872

This is a volatile corrosion inhibitor for all metals. It is contained into a sponge, and it is impregnated into the sponge, and it can be used for various applications.

(3) ThreeBond 1873, ThreeBond 1873B (volatile rust prevention sheet)

These are products that a volatile corrosion inhibitor is impregnated into a non-woven fabric. ThreeBond 1873 is for all metals. ThreeBond 1873B is for ferrum. Raw fabric of 1cm wide × 100m long and roll fablic of 25cm wide × 30m long (perforation processed) are lined up, and they can be used as mold inner rust inhibitor provided with both packaging small components and cushion functions.

(4) ThreeBond 1874 (volatile rust prevention bag)

This is a product that a volatile corrosion inhibitor is impregnated into a special non-woven fabric for all metals, and then the fabric with sheets that laminate impermeable films is bag-made. Standard sizes are 5 types: 100 × 150, 150 × 200, 150 × 250, 200 × 350, 250 × 300. Other sizes can be also supported as special use.

The application is for rust prevention package for bits and pieces or small components. Because this product uses special materials for non-woven fabrics and films, heat sealing is available after packaging and sealing status is maintained, and rust prevention effect lasts more.

The other side of the bag is transparent so that contents in the bag can be distinguished easily as well as a plastic bag used from before.

On the other hand, if these technical methods are redeployed, the following products can be developed and distributed.

To store leisure and sports goods. For example, fusion-cutting an iron head of golf crabs can be iron rust prevention and damage prevention cushion medium during transporting crabs.Also by bag-making continuous length, an application as a rust inhibitor of edges and bindings of ski during the off-season can be expected.

(5) ThreeBond 1875, ThreeBond 1875B

ThreeBond 1875	Aerosol product of volatile corrosion inhibitors for all metals. Rust inhibitor used in the coexisted system by many kinds of metals such as ferrum, copper especially.
ThreeBond 1875B	Aerosol product of volatile corrosion inhibitors for ferrum.

Effectiveness for various metals of volatile corrosion inhibitors series above mentioned is summarized as follows.

14. Rust Prevention Effect for Three Bond's Volatile Corrosion Inhibitors

Table 8. Rust prevention effect for various metals

Rust Inhibitors / Metal	TB1871	TB1872	TB1873	TB1873B	TB1874	TB1875	TB1875B
Copper	◎	◎	◎	◎	◎	◎	◎
Phosphor bronze	△	○	○	△	○	○	△
Brass	△	◎	◎	○	◎	◎	○
Aluminum	◎	◎	◎	○	◎	◎	○
Corrosion resistant aluminum	◎	◎	◎	◎	◎	◎	◎
Zinc die casting	◎	◎	◎	○	◎	◎	○
Duralumin	◎	○	○	○	○	○	○
Magnesium alloy	△	○	○	△	○	○	△
Alumite	◎	◎	◎	×	◎	◎	×
Gloss chrome plating	○	◎	◎	◎	◎	◎	◎
Hard chrome plating	◎	◎	◎	◎	◎	◎	◎
Gloss zinc chrome plating	◎	◎	◎	◎	◎	◎	◎
Gloss zinc plating	×	○	○	○	○	○	○
Hot-dip zinc plating	△	◎	◎	△	◎	◎	△
Silver plating	◎	◎	◎	○	◎	◎	○
Nickel plating	○	◎	◎	○	◎	◎	○
Solder plating	◎	◎	◎	○	◎	◎	○
Tin plating	○	○	○	○	○	○	○
Cadmium plating	×	◎	◎	◎	◎	◎	◎
Steel	◎	◎	◎	◎	◎	◎	◎

Evaluation ◎ : It has rust prevention capability and excellent rust prevention capability
○ : It has weaker rust prevention capability compared with others.
△ : It has no rust prevention capability, or adverse effect.
× : It has no rust prevention capability, or adverse effect (accelerated corrosion).

Condition Temperature: 50°C, Humidity: 90RH%, Period: 70 days

Note: TB is an acronym of Three Bond.

On the other hand, because such a volatile corrosion inhibitor is contained into a sponge or is impregnated into non-woven fabric, it is difficult to confirm effectiveness of the volatile corrosion inhibitor in normal usage state. However, we at Three Bond have devised a new method to confirm the effectiveness of these volatile corrosion inhibitors visually and consider for practical use.

We provide the outline at next page.

15. How to Confirm the Effectiveness of Volatile Corrosion Inhibitors

We have considered how to confirm (the indicator of) the effectiveness of volatile corrosion inhibitors. As a result, we are confident in practical use so that we provide the outline below.(Patent Applied For)

(1) Present situation and necessity of development

Valid period of volatile corrosion inhibitors differs from that of other products such as aromatic and deodorant. When active principle is run out, advantage to use rust inhibitors is lost and furthermore it may cause rusting adversely. Today, however, there have been no indicators for valid period of these volatile corrosion inhibitors. Thus, we also think that every company's products were used as an auxiliary rusting prevention.

Therefore, we have considered that this indicator is important to develop new products as well as level up of existing volatile corrosion inhibitors, and developed the indicator technology. We provide the outline as follows.

(2) About indicator technology

As for indicators, three of the following are conceivable.

(a) Indicator that adopts electron donative coloration substances and phenolic hydroxyl group containing compounds

Note: With vaporization of volatile corrosion inhibitors, electron donative coloration substances react with phenolic hydroxyl group containing compounds and develop color.

(b) Indicator that adopts acid-base indicators and strong acid

Note: Color is developed by PH change generated with vaporization of volatile corrosion inhibitors.

(c) Indicator that adopts cobalt chloride

Note: Color is developed by increased moisture content with vaporization of volatile corrosion inhibitors.

We considered above three methods, and recognized that method (a) had the highest possibility as practical use. We provide the outline of the method (a).

(3) Components to develop color

Electron donative coloration substances include crystal violet lactone, malachite green lactone, rhodamine B lactam; phenolic hydroxyl group containing compounds include bisphenol A, P-hydroxybenzoic acid benzil; volatile corrosion inhibitors include DICHAN (dicyclohexyl ammonium nitrite), CHA•CHC (carboxylate cyclohexylamine cyclohexane) and etc.

(4) Chemical mechanism

Color development mechanism of CVL and phenolic hydroxyl group is as follows.

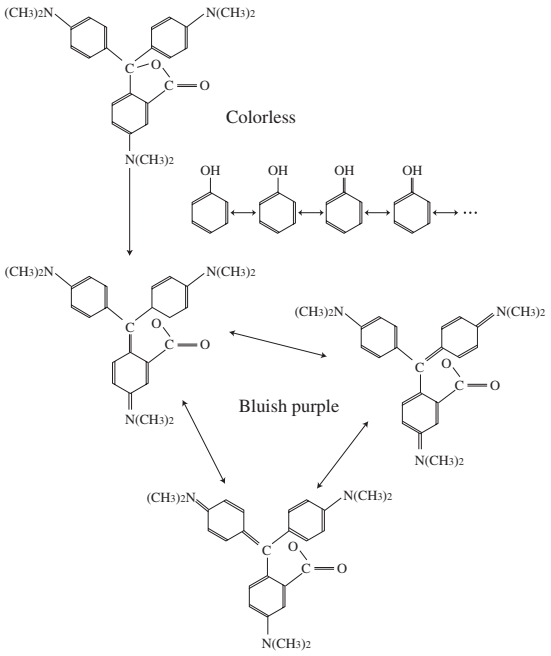


Figure 7. Color development mechanism of CVL and phenolic hydroxyl group

When CVL reacts with acid developer (phenolic hydroxyl group containing compounds), electron transfer is generated in a molecular, and lactone ring cleaves, and then color is developed by taking ionic resonance structure.

(5) Quantitation of the color development degree

Visual color development degree includes errors and cannot be quantified. Thus, color development changes in our tests are computed with color stimulus specification (L value, a value, b value). As to colors, their three properties (three primary colors of light) red, green, bluish purple are applied to the following formula with color stimulus specification X (red), Y (green), Z (bluish purple) respectively.

$$L = 10\sqrt{Y}$$

$$a = 17.5(1.02 - Y) / \sqrt{Y}$$

$$b = 7.0(Y - 0.847Z) / \sqrt{Y}$$

When there are any objects, color difference between source and target objects is applied to the following Hunter's color difference formula to compute delta E.

$$\Delta E = \sqrt{(L_0 - L_1)^2 + (a_0 - a_1)^2 + (b_0 - b_1)^2}$$

- Hunter's color difference formula

(6) Relationship between amount of volatilization in volatile corrosion inhibitors and color difference

By adopting volatile corrosion inhibitors DICHAN and CHA•CHC, non-woven fabric is impregnated with volatile corrosion inhibitor / coloring agent = 100, forced vaporization was performed at 60°C constant temperature, and color development changes accompanied with it were computed. Amount of volatile corrosion inhibitor vaporization (%) - delta E curve can be obtained shown in Figure 8.

(7) Relationship among amount of volatile corrosion inhibitor vaporization (%), color development degree and rust prevention capability

We have examined the following experiments for relationship between color development degree and rust prevention capability accompanied with vaporization of non-woven fabric impregnated with DICHAN.

Impregnated volume	1.94g/m^2
Test piece for rust prevention	JIS-G3141 SPCC-SB Surface grinding by calcium carbonate
Humidifying condition	40°C × 90RH% 500h
Test method	Figure 9

<Result>

Table 9. Vaporization volume and color development degree, rust prevention test result

VCI vaporization %*1	Color development degree *2	Rust prevention test result
Blank	L = +51.0 a = -0.1 b = -2.7	Rusting
0.0	L = +56.2 a = -1.1 b = -3.1	OK
6.2	L = +55.7 a = -0.8 b = -2.7	OK
15.6	L = +55.3 a = -0.8 b = -5.0	OK
16.9	L = +54.2 a = -0.8 b = -4.5	OK
35.1	L = +53.7 a = -0.8 b = -6.0	OK
43.8	L = +54.1 a = -0.8 b = -4.6	OK
74.0	L = +48.5 a = +0.1 b = -9.6	OK
93.2	L = +41.1 a = +4.1 b = -22.9	Rusting
100.0	L = +41.1 a = +39.0 b = -23.0	Rusting

*1 It was made by forced vaporization of 60°C
*2 Average at n=3

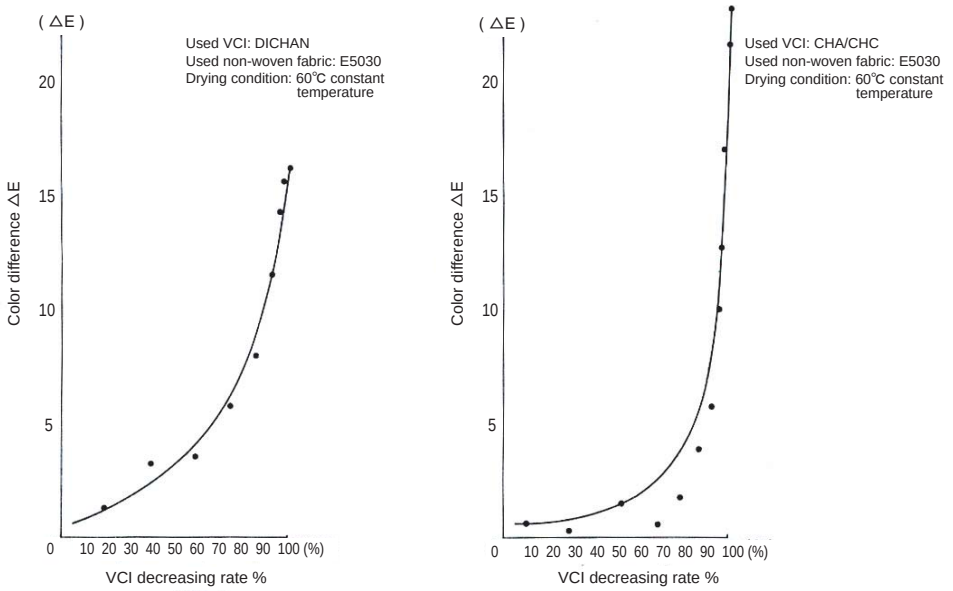


Figure 8. VCI decreasing rate and color difference

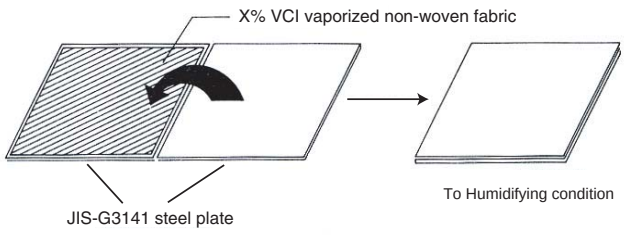


Figure 9. Making test piece

(8) Discussion

Rusting are found in blank and VCI decreasing rate 93.2% and 100%, but rusting are not found in VCI decreasing rate ranged 0 to 74 %.

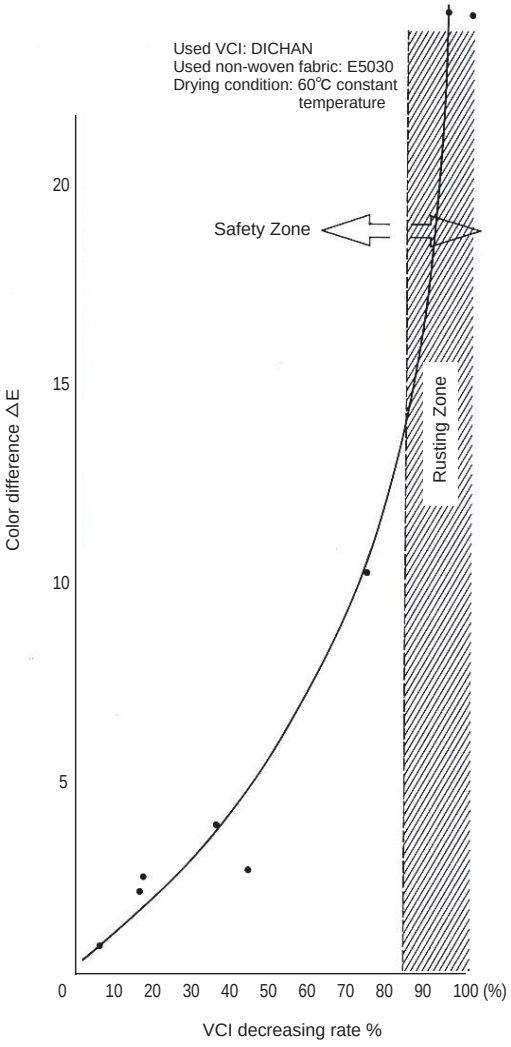


Figure 10. VCI decreasing rate and color difference, rusting zone

As known from color difference, delta E, that is computed with L, a, b values, color development accompanied with vaporization becomes remarkable at the time that vaporization proceeded than 74%. This method is available as non-woven fabric impregnated indicator.

(9) Summary

We have researched and developed the indicator in this way. We expect that this technology can be applied and deployed into volatile rust prevention sheet (for mold rust prevention and others) and volatile rust prevention bag (for parts storage and others). In other words, without previously using the method to pass color samples, it is expected to compute safety margin by the following technique. For example, as of this color development reaction, more phenolic hydroxyl group containing compound is contained in a single volume, color is developed before VCI vaporization. Thus, when a solvent, that phenolic hydroxyl group containing compound is dissolved, is stamped into the previously-impregnated indicator non-woven fabric, only the stamped portion is color-developed. And then when color development is advanced by VCI vaporization, no border between the first stamped portion and other portions will be existed. This allows application limits to be set.

16. Conclusion

Volatile corrosion inhibitor is a unfamiliar term so far so that it played second fiddler in the rust prevention field. However, as above mentioned, there are many kinds and shapes of volatile corrosion inhibitor so that it can play primary fiddler by devising the indicator and the like.

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Laboratory of sealing, rust prevention, lubricants

Sakae Amamiya

ThreeBond TECHNICAL NEWS

THREE BOND CO., LTD.

1456 Hazama-cho, Hachioji-shi, Tokyo 193-8533, Japan
Tel: 81-426-61-1333