Vappro VBCI MBP 3000 Masterbatch Powder Compounding Nitrite Free VCI Masterbatch Polyethylene Resin

Nelson Cheng[1] PhD (Honoris Causa), Patrick Moe[1] BSc, Grad Dip, MSc.
[1]Magna International Pte Ltd Singapore, 10 H Enterprise Road, Singapore 629834

Dr Benjamin Valdez Salas[2], Dr Michael Schorr[2] Dr Nicola Nedev[2]
[2]Autonomous University of Baja California

Abstract

The main objective of this article is to promote the compounding of VCI Masterbatch Polyethylene Resin by eliminating the formation of N-Nitrosamine, using nitrites free Vappro VBCI MBP 3000 masterbatch powder. Carcinogenic nitrosamines are formed from the reaction of Sodium Nitrite with Amines under acidic conditions (such as occurs in the human stomach).

Nitrosamines form a large group of genotoxic chemical carcinogens which occur in the human diet and other environmental media, and can be formed endogenously in the human body. N-Nitroso compounds can induce cancer in experimental animals [1,2,3,4,5,6]. Cancer causing chemicals are widely used in the production of VCI Masterbatch Polyethylene Resins. Due to economy reason, Nitrites, heavy metals and its' derivatives are commonly used in the production of VCI Masterbatch resins. Nitrites and its derivatives can lead to the formation of potentially cancer-causing (carcinogenic) chemicals such as N-nitroso-compounds (NOC) and polycyclic aromatic hydrocarbons. [1,2,3]. Among carcinogens, the N-nitroso compounds are the most broadly acting and among the most potent [7].

Magna International [8] together University of Baja California (UABC) [9,10] promotes the safe manufacturing process for production VCI Masterbatch Resins and the extrusion of VCI film with Vappro VBCI (vapor bio corrosion inhibitor) by using Nitrite free raw materials.

Vappro VBCI MBP 3000 VCI masterbatch powder is specially developed as an additive for the production of masterbatch P.E. thermo-plastic resin with a high load of pigment. It is also used as a corrosion inhibitor additive for making masterbatch resin for extruding into VCI Film. Polyethylene Film extruded with the color masterbatch resin

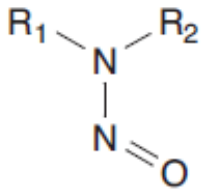
fortified with Vappro VBCI MBP 3000 masterbatch powder will provide excellent corrosion inhibitions properties. Vappro VBCI MBP 3000 masterbatch powder additive enhances the performance of your product line and does not contain heavy metals, nitrates or nitrites which can lead to the formation of potentially cancer-causing (carcinogenic) chemicals such as N-nitroso-compounds (NOC) and polycyclic aromatic hydrocarbons.

Keywords

N-Nitrosamine, Carcinogens, Nitrites, Carboxylates, Masterbatch P.E Resins. VBCIs, VCIs.

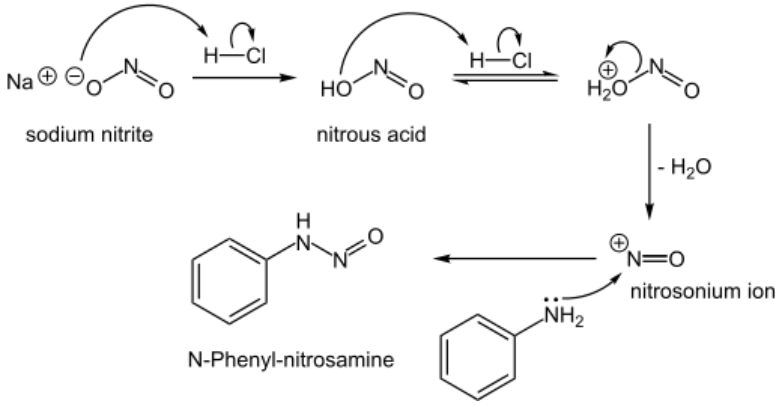
Introduction

N-Nitrosamines are a class of chemical compounds with the general structure shown below. The essential feature of N-nitroso compounds is the N–N=O structure; the R1 and R2 groups attached to the amine nitrogen may range from a simple hydrogen (H) atom to more complex chemical substituents (including ring structures that incorporate the nitrogen atom) [11,12].



Generic N-nitrosamine structure R_1-N(-R_2)-N=O

Nitrosamines are produced from nitrites and secondary amines, which often occur in the form of proteins [13]. Their formation can occur only under certain conditions, including strongly acidic conditions such as that of the human stomach. High temperatures, as in frying, can also enhance the formation of nitrosamines. The mechanism of the formation of N-Phenyl-nitrosamine is shown below.



Formation of an N-Phenyl-nitrosamine

$$NO_2^- + 2\ H^+ \rightarrow NO^+ + H_2O$$
$$R_2NH + NO^+ \rightarrow R_2N\text{-}NO + H^+$$

N-Nitrosamine, arise from the reaction of nitrite sources with amino compounds, which can happen during the curing of meat. Typically, this reaction proceeds via attack of nitrosonium electrophile on an amine

Mechanism of reaction from Sodium Nitrite to Cancer cell in Stomach.

Carcinogenic nitrosamines can also be formed from the reaction of **Sodium Nitrite** with **Amines** under acidic conditions (such as occurs in the human stomach).

R_2NH (amines) + $NaNO_2$ (sodium nitrite) → $R_2N\text{-}N{=}O$ (nitrosamine)

In the presence of acid (such as in the stomach), nitrosamines are converted to **diazonium ions.**

$R_2N\text{-}N{=}O$ (nitrosamine) + (acid or heat) → $R\text{-}N_2^+$ (diazonium ion)

Diazonium ion form carbocations (R^+) and react with biological **nucleophiles (such as DNA or an enzyme)** in the cell.

$R\text{-}N_2^+$ (diazonium ion) → R^+ (carbocation) + N_2 (leaving group) + :Nu (biological nucleophiles)

→ R-Nu

If this **nucleophilic substitution** reaction occurs at a crucial site in a biomolecule, it can disrupt normal cell functioning and leading to cancer or cell death [32].

In foods, the nitrosating agent is usually nitrous anhydride, formed from nitrite in acidic, aqueous solution. Ascorbic acid and sulfur dioxide are used to inhibit nitrosamine formation in foods [14,15].

The presence of nitrosamines may be identified by the Liebermann nitroso reaction [19, 20] (not to be confused with the Lieberman reagent which reacts red or blue in the presence of phenols) [16,17,18].

Under acidic conditions the nitrite forms nitrous acid (HNO_2), which is protonated and splits into the nitrosonium cation $N{\equiv}O^+$ and water:

$$H_2NO_2^+ \rightarrow H_2O + NO^+.$$

The nitrosonium cation then reacts with an amine to produce nitrosamine. These processes lead to significant levels of nitrosamines in many foodstuffs, especially beer, fish, and fish byproducts, and also in meat and cheese products preserved with nitrite compounds. The U.S. government established limits on the

amount of nitrites used in meat products in order to decrease cancer risk in the population [21].

The chemical class of N-nitroso compounds includes the N-nitrosamines, N-nitrosamides and N-nitrosamidines, many of which have been demonstrated to be carcinogenic, mutagenic and teratogenic in various animal species [22]. The N-nitrosamides are unstable at physiological pH and decompose non-enzymatically to a reactive intermediate capable of reacting with cellular macromolecules. The N-nitrosamines are, however, stable at physiological pH and are metabolized by microsomal mixed function oxidases. Human, rat, monkey and trout liver possess the capacity to metabolize DNA and, in most cases, a lower metabolic capacity is observed in extrahepatic tissues, with a few notable exceptions [23].

In response to the need for greater industrial environmental responsibility and safety of the applicators, Magna Group has expanded a new range VCI products to include a new series of Vappro Bio-based Corrosion Inhibitors (VBCIs), which are organic, biodegradable and essentially non-toxic.

Vappro VBCI MBP 3000 is a class of masterbatch vapor corrosion inhibiting compounds with a finite vapor pressure where the inhibitors are transported to the target metal through space to condense on the metal surface to form a protective film, lowering the corrosion rate of the metal itself. Factors that determine the efficiency of VCIs are the concentration of VCI compounds, the period of exposure and vapor pressure.

VCI products fortified with **Vappro VBCI MBP 3000** can effectively protect both ferrous and non-ferrous metals against corrosion by inhibiting the reaction between metals and corrosive mediums. Vappro VBCIs act by adsorbing either ions or molecules onto the metal surface, reducing the corrosion rate by blocking anodic and/or cathodic reactions.

Vappro revolutionary VBCI technology is an environmentally safe alternative to traditional formulations of corrosion inhibitors. It's RoHs Compliant [24], RoHS stands for Restriction of Hazardous Substances. RoHS, also known as Directive 2002/95/EC, originated in the European Union and restricts the use of specific hazardous materials found in electrical and electronic products. All applicable products in the EU market after July 1, 2006 must pass RoHS compliance [23].

The development of **Vappro VBCI MBP 3000** VCI masterbatch powder is specially developed as an additive for the production of masterbatch thermo-plastic resin with a high load of pigments. It is also used as a corrosion inhibitor additive for making color masterbatch resin. Polyethylene Film extruded with the color masterbatch resin fortified with **Vappro VBCI MBP 3000** will provide corrosion inhibitions properties.

Vappro VBCI MBP 3000 can be compounded into your masterbatch pigment resin to give corrosion protection capabilities. Vappro VBCIs are self-replenishing allowing for uninterrupted protection through vapor phase, interphase and direct contact protection. It gives your products added market value without drastically increasing your cost. It has the properties to protect both ferrous and non-ferrous metals, simply by adding the masterbatch pigment resin into the polyethylene resin for the extrusion of PE film. The special features of Vappro VBCI MBP 3000 as follows:
It eliminates the formation of N-Nitrosamine. It enhances the performance of your product line. Environmentally friendly, Uninterrupted Protection through Vapor phase, Interphase and direct contact protection. Gives your products added market value. Cost-effective additive. Added value additive helps to generate sales and create inroads to untapped markets. Broad-ranging industrial applications.
VCI films and bags extruded from Vappro VBCI MBP 3000 masterbatch powder will conform to US MIL-PRF-22019 E TYPE I, Bags are MIL-DTL-22020 [25,26] and NATO Stock Number 6850-32-086-9421 [27,28,29].

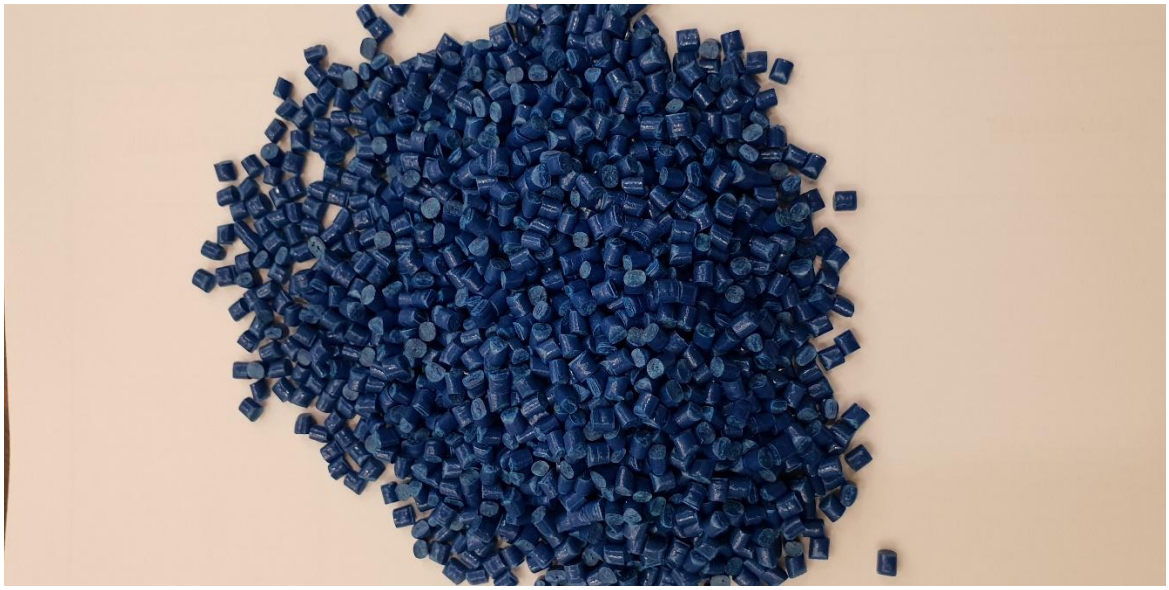
Vappro VBCI MBP 3000 Masterbatch Powder can be formulated into VCI masterbatch pigment resin to give corrosion protection capabilities. VCI Films and bags extruded from the said masterbatch resins are self-replenishing allowing for uninterrupted protection through vapor phase, interphase and direct contact protection. It gives your products added market value without drastically increasing your cost. It can be used as it is for compounding VCI Masterbatch Resin with or without grinding. (see pictorial 1 & 2).

Pictorial 1 Vappro VBCI MBP 3000 Masterbatch Powder

Pictorial 2-Vappro VBCI MBP 3000 Powder Ground into 400 mesh

Masterbatch Resin producers worldwide are looking for new ways to add or create new value to their masterbatch pigment resins, the **Vappro VBCI MBP 3000** Masterbatch Powder is an ideal source for adding value to their current Masterbatch Pigment Resins.

Many established Masterbatch Resins manufacturers worldwide have started using **Vappro VBCI MBP 3000** as their anti-corrosion additives.
It can be compounded into VCI Masterbatch resins in strands and cut into the beads or die-cut into oval shape resins (see pictorial 3 and 4).



Pictorial 3-Masterbatch Resins in Strand-cut compounded with Vappro VBCI 3000

Pictorial 4- Masterbatch Resin in Oval Shape compounded with Vappro VBCI 3000

VCI Polyethylene (PE) Film, Shrink Film and Stretch Film extruded from VCI Masterbatch Resins compounded from Vappro VBCI MBP 3000 Powder Masterbatch, are used widely for packaging for both ferrous and non-ferrous metallic substrates, for different types machinery and equipment.

They are extruded into roll film with different length and thickness (see pictorial 5,6,7) below.

Pictorial 5- Vappro VCI Polyethylene Film extruded from masterbatch resin compounded with Vappro VBCI 3000

Pictorial 6- Vappro VCI Stretch Film extruded from masterbatch resin compounded with Vappro VBCI 3000

Pictorial 7- Vappro Shrink Film extruded from masterbatch resin compounded with Vappro VBCI 3000

The above said films extruded from VCI Masterbatch Resins with Vappro VBCI MBP 3000 Masterbatch Powder at a dosage rate of 3-5% by weight will pass the German Test Method TL 81305-002 [30] for its' Vapor Inhibition Ability (VIA). The details of the test are herein described below:

Method for Ascertaining Vapor Corrosion Inhibition Ability Properties of PE VCI Film Extruded from Masterbatch PE Resin fortified with Vappro VBCI MBP 3000 Masterbatch Powder using German TL 8135-002 Test Method [30] as follows:

Volatile corrosion inhibitor (VCI) provides protection for metal surfaces. VCI Ions attach themselves to metal. The usage of VBCI/ VCI PE film, Shrink Film and Stretch Film to protect equipment and metallic parts from corrosion during storage or shipping has been globally accepted now than ever before. Corrosion is a multi-billion dollars problem globally, as such, ascertaining the vapor corrosion inhibition properties of VCI film is of paramount importance to all manufacturers.

In view of the above, a reliable test method is of paramount importance. The German TL 8135-002 test method has been adopted to ascertain the vapor inhibition corrosion

properties of 3mils thick Vappro 826 VCI Film extruded from Vappro Masterbatch P.E. resin fortified with Vappro VBCI MBP 3000.

Purpose of Using German Test Method TL8135-002

To evaluate the corrosion protection properties of the Vappro VBCI 826 film extruded from Vappro VBCI MBR 1000 Masterbatch Resin fortified with Vappro VBCI MBP 3000

Test Method Used

German test method TL 8135-002. This method is used to determine the corrosion protection effect of VCI papers and films on a defined test object of constructional steel.

Principle of the test method

A test sample with a high degree of sensitivity to corrosion through condensation water is packed together with a VCI auxiliary packing material in a vessel, which is then tightly closed. Condensation is then forced on the surface of the test sample. By means of a blank trial – that is, a trial structure of the same type, but without VCI auxiliary packing material – it is determined whether the conditions of the trial are sufficient to cause corrosion to appear on the unprotected test sample.

Test object

4 pieces of unalloyed, solid construction steel.

Test Sample

Vappro 826 VCI film was cut into 6 strips of 2.5 cm x 15 cm of VCI film.

Test solution

10 ml freshly prepared glycerine/water mixture with a density of 1.076 g/cm^3 at (23±2) °C, which is intended to produce approximately 90% Relative Humidity in the jar.

Test Equipment and Material

For each test, 4 test sets are necessary. A test set consists of the following parts

(1) Test Jar, 1 L, wide-necked.

(2) Rubber stopper, 54 mm Æ, with longitudinal through hole

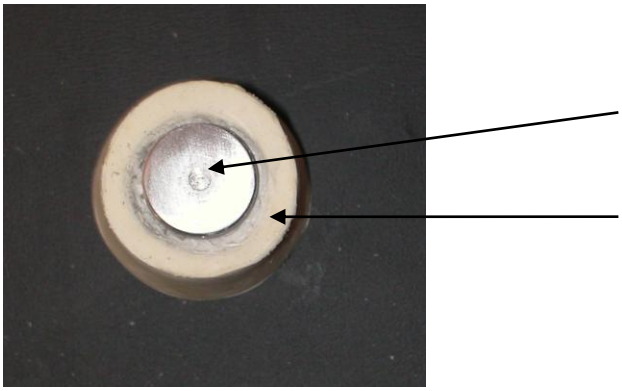
(3) Test sample of unalloyed, solid construction steel

(4) 10 millilitres freshly prepared glycerin/water mixture with a density of 1.076 g/cm3 at (23± 2) °C (glycerin/water mass ratio about 1:2)
(5) Ethanol

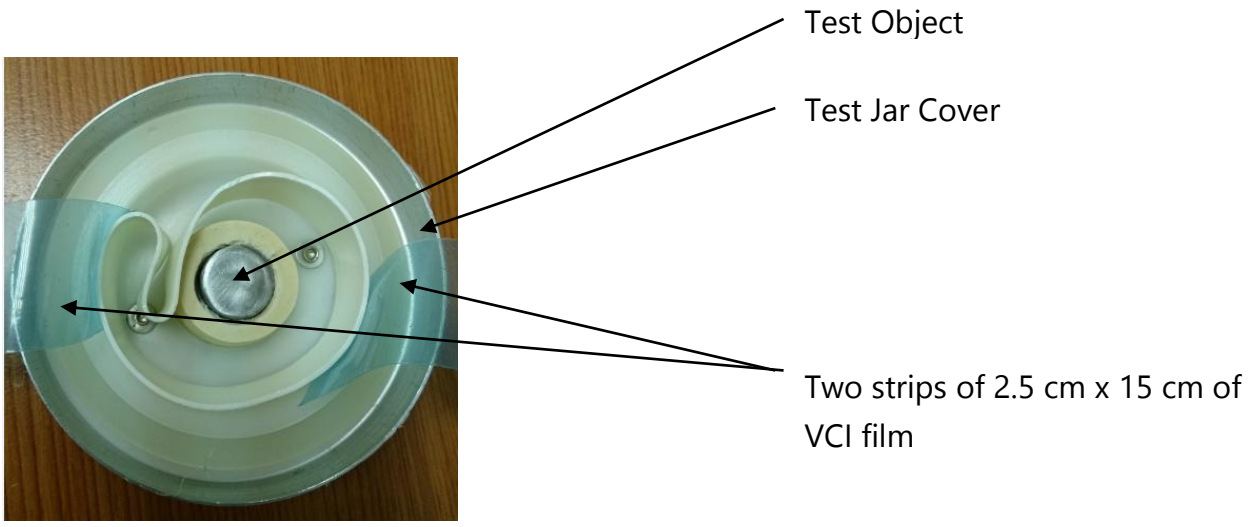
Procedure of the test

Four test objects were polished with 320 grit abrasive paper to remove all the grit and rust. Rinsed with ethanol and dried them.

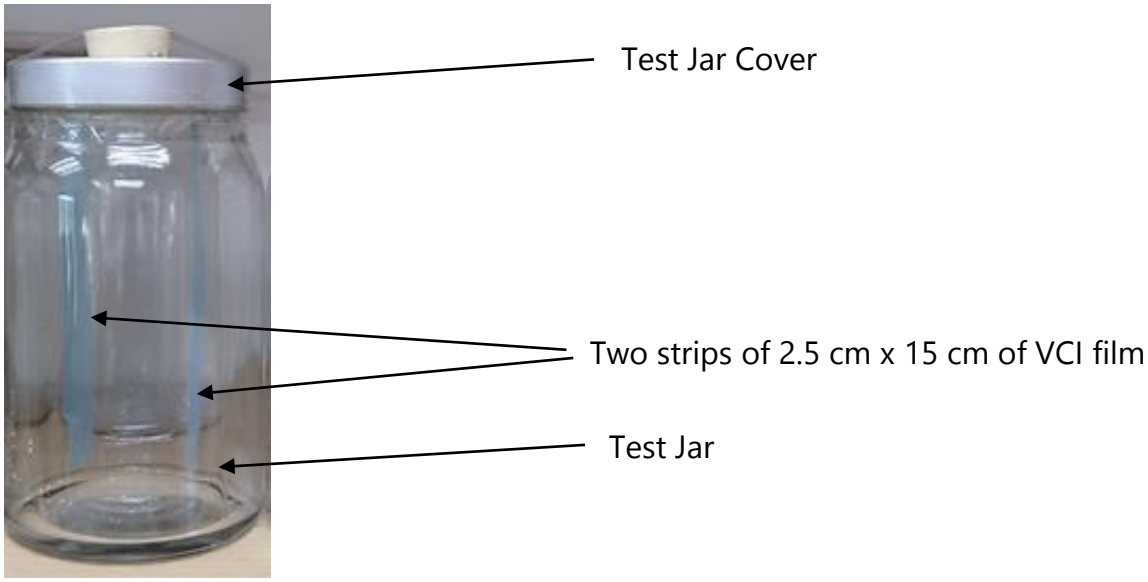
Polished test object was inserted in the rubber stopper. Please see below picture.



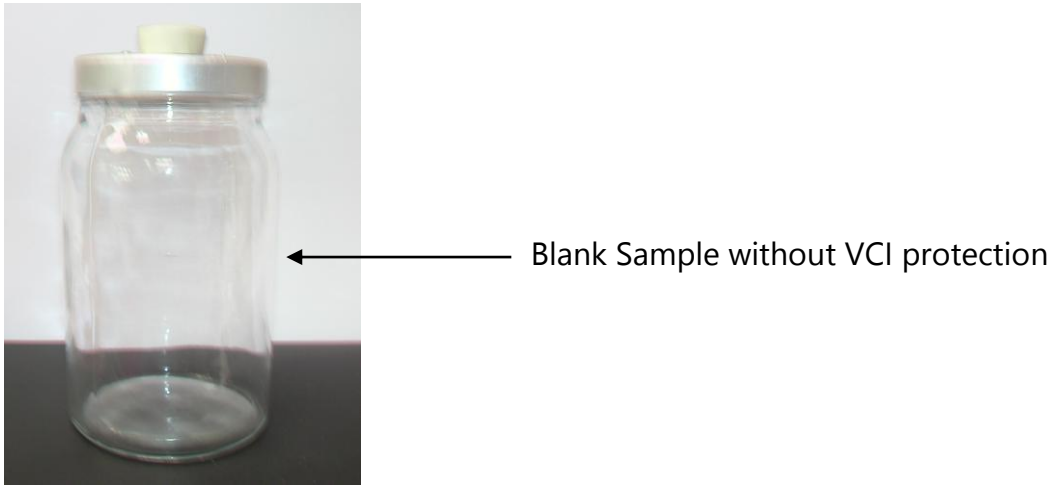
Then rubber stopper was inserted to the test jar cover. Two strips of 2.5 cm x 15 cm of test samples were attached with test jar cover. Please see below picture.



The test jar was closed with jar cover. Please see below picture.



For blank sample, test jar was sealed without inserting two strips of test samples. It had no VCI chemicals and it is only used as a control/ yardstick for the experiment. Please see below picture.

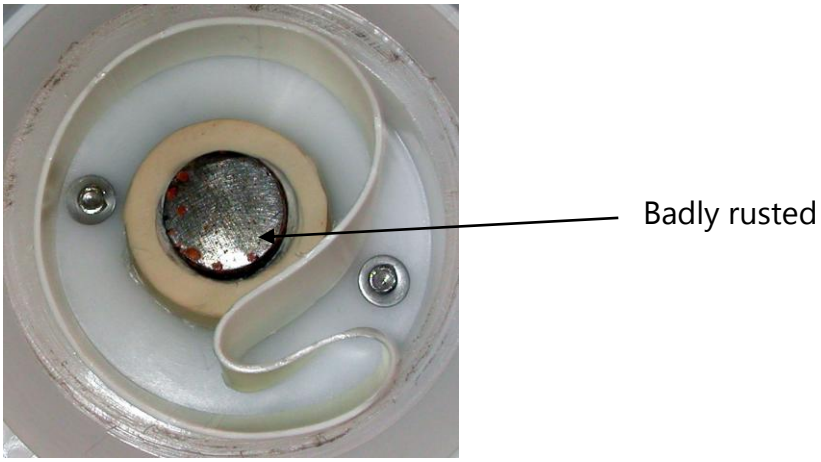


The four test sets were stored for a period of (20±0.5) hours at a room temperature. At the end of the storage period, the jar covers were removed from the test jars, the freshly prepared 10 ml of test solution, glycerine/water mixture, was poured into each jar immediately after opening, and the jars were immediately closed again

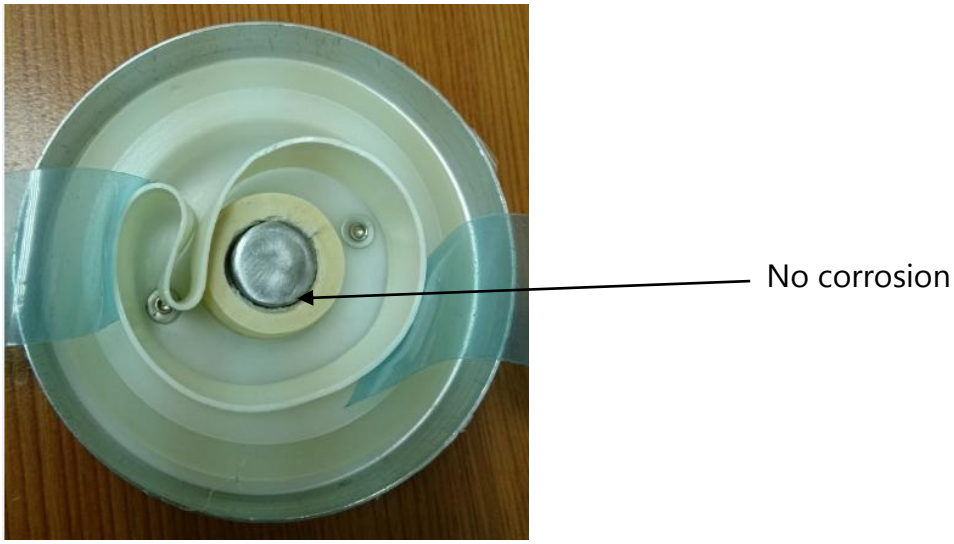
After an additional 2 hours ± 10 minutes, the test jars were stored for a period of 2 hours ± 10 minutes in the heating chamber at temperature 40°C to create 90% Relative Humidity in the both test jars.
On conclusion of storage in the heating chamber, the test objects were disassembled from test jars and dried with warm air. Then inspected any sign of corrosion on the sanded surface of the test objects from the four jars.

Test Result

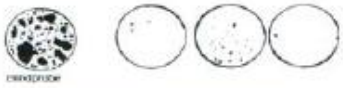
Sanded surface of the test object from blank sample was badly rusted. Please see below picture.



No sign of corrosion was found on three test objects protected with Vappro 826 VCI film. Please see below picture.



Requirement of TL 8135-0002 for the corrosion protection effect:

Evaluation of the test objects	Corrosion protection effect	
 Keine korrosionsschützende Wirkung	**None**	(Grade 0)
 Geringe korrosionsschützende Wirkung	**Slight**	(Grade 1)
 Mittlere korrosionsschützende Wirkung	**Middle**	(Grade 2)
 Gute korrosionsschützende Wirkung	**Good**	(Grade 3)

Conclusion:

Blank Sample (Without VCI Film)	Protected samples with Vappro 826 VBCI film extruded from Vappro VBCI MBR 1000 Resin.
	
Badly Rusted	No visible corrosion was found on all three test objects

Based on above the test result, Vappro VBCI 826 Film extruded from Vappro VBCI MBR 1000 Resin fortified with Vappro VBCI MBP 3000 passed the Grade 3 German test method TL 8135-0002.

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About the Authors

Nelson Cheng

NELSON CHENG PhD (Honoris Causa) is the founder and chairman of Magna Group, consisting of Magna International; Magna F.E. Chemical Pte. Ltd.; Magna Chemical Canada Ltd.; Magna Australia Pvt. Ltd.; and Lupromax International Pte. Ltd. Nelson Cheng received a Doctor honoris causa from the Universidad Autonoma de Baja California, Mexico. He graduated as a marine engineer under the United Nations Development Program (UNDP) Scholarship. He is recognized as Singapore's leading inventor and the Singaporean with highest number of patents from the Intellectual Property Office of Singapore. He is the inventor of several technologies for corrosion protection including, Vappro VCIs (Vapour Corrosion Inhibitors), Vappro VBCIs (Vapour Bio Corrosion Inhibitors) and Vappro CRI (Concrete Rebar Inhibitor), Molecular Reaction Surface Technology (MRST), Colloidal corrosion inhibitors (CCI) and Heat Activated Technology (HAT). He is a member of Society of Tribologists and Lubrication Engineers (STLE), American Chemical Society (ACS) World Corrosion Organization (WCO) and European Federation of Corrosion (EFC).

Patrick Moe

Patrick Moe is the senior technical manager of Magna International Pte. Ltd. He has a BSc in Industrial Chemistry, Grad. Dip and MSc in Environmental Engineering. His key responsibilities at Magna International as follows: assisting the CEO in research and development of new products, finding out customers' needs and develop customized new products, helping in synthesizing new compounds by making appropriate modifications of known methods, recommending and implementing methods to increase the quality of products and service, management of hazardous raw materials. He is a member of National Association Corrosion Engineers (NACE) and World Corrosion Association (WCA).

Professor Benjamin Valdez Salas

Benjamin Valdez Salas was the director of the Institute of Engineering (2006-2013), Universidad Autonoma de Baja California, Blvd. Benito Juarez y calle de la Normal s/n, Colonia Insurgentes Este, 21280 Mexicali, Baja California, Mexico. He has a B.Sc. in chemical engineering, a M.Sc. and Ph.D. in chemistry, and is a member of the Mexican Academy of Science and the National System of Researchers in Mexico. He was the guest editor of Corrosion Reviews, in which he produced two special issues on corrosion control in geothermal plants and the electronics industry. He is a full professor at the University of Baja California. His activities include corrosion research, consultancy, and control in industrial plants and environments. He has published more than 350 publications with almost 1000 citations. He received a NACE Distinguished Service

Award. He has been a member of NACE for 26 years. He is the current Technical Advisor of Magna Group of Companies.

Professor Michael Schorr Weiner

Michael Schorr is a professor (Dr. honoris causa) at the Institute of Engineering, Universidad Autonoma de Baja California. He has a BSc in chemistry and an MSc in materials engineering from the Technion-Israel Institute of Technology. From 1986 to 2004, he was an editor of *Corrosion Reviews*. He is acquainted with the appreciation of VCI in industrial environments. In addition, M. Schorr was a corrosion consultant and professor in Israel, USA, Latin America, and Europe. He has published 410 scientific and technical articles on materials and corrosion.

Professor Nicola Nadev

Dr. Nicola Nedev received the Ph.D. degree in physics from the Institute of Solid State Physics, Bulgarian Academy of Sciences, in 1990. He is a Professor of Semiconductor Physics and head of the laboratory Semiconductors, Microelectronics and Nanotechnology with the Institute of Engineering, Autonomous University of Baja California, Mexico. His research interests include nanostructured materials, semiconductors and semiconductor device technologies. He authored and coauthored more than 90 refereed papers and collaborates with the semiconductor and automobile industry in Mexico. Dr. Nedev is member of the Mexican Academy of Sciences and Mexican National System of Researchers.