

## VCI containing package material – mode of functioning

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### Abstract

I. L. Rozenfeld was one of the pioneers in the field of corrosion research and the application of vapor phase corrosion inhibitors (VCIs, volatile corrosion inhibitors). He found that no substance can sufficiently inhibit the corrosion by its own, what is reflected on conventional corrosion protection schemes. Nowadays, three strategies are established in the field of iron protection to reach a passive state:

1. the installation of buffer systems (combination of a weak acid with its corresponding base) to keep the pH value of the surface electrolyte layer constant in the alkaline range;
2. the combination of anodic and cathodic inhibitors to achieve a synergistic effect;
3. the supply of (at least one) oxidizing agent in the present of oxygen in the atmosphere or already dissolved in the surface electrolyte layer.

In general, polymer based packaging materials are used in order to protect metallic equipment (mostly made of iron materials) during transport and storage against atmospheric corrosion. This temporary corrosion protection is achieved by incorporation of VCI in the polymer film, whereby the packaging material functions as a VCI source. Protection is necessary especially during the time of wetness, where the metal surface can corrode due to the formation of a thin electrolyte layer on the surface. The efficiency of a selected combination of VCI compounds mainly depends on three parameters:

1. their vapor pressure (more exactly: their tendency to sublime) under atmospheric conditions are high enough allowing significant vapor phase transport of the compounds within an enclosed space to the metal surface;
2. their adsorption strength on the oxide covered metal surface (directly or after dissolving in the condensed water film) inhibiting the metal corrosion during storage and transport by interaction with the surface;
3. the achieved mixture of different VCIs on the metal surface to cover different strategies of corrosion protection

Within this paper calculations should be presented to estimate the minimum need of VCI in dependence of the package volume, the surface roughness of the goods and the exposed temperature. Further, the transport of the VCI in the atmosphere of a densely closed package by diffusion and natural convection should be discussed. These findings can be used to approximate the conditioning time. In the second part results of electrochemical measurements like the measuring of the free corrosion potential and recording of electrochemical impedance spectra should be presented characterizing the interaction of

different VCIs with oxide covered metal surfaces in the presence of a condensed air saturated water film. Thereby, mechanisms of action (e.g. passivation, adsorption and/or formation of insoluble salts to seal defects in the oxide layer) shall be derived from the data and compared to the concept of isoelectric points of metal oxides covered the metal surfaces (IEPS). Finally, the efficiency of VCI containing package materials should be demonstrated by self- developed climatic tests according to DIN EN 60068-2-30.

**Key words:** *corrosion inhibitors, packaging materials, volatile inhibitors.*

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## Introduction

In due to the first contact with the oxygen in the surrounding atmosphere all common metals (except gold) and alloys form a natural oxide layer on the interface metal/ air. Based on the kind of material and the composition of the atmosphere this so called primary oxide layer (POL) is more or less stable leading to a passive behavior under moderate conditions. But as well microscopic effects like the formation of different phases and grain boundaries (especially in steels and alloys) as macroscopic effects due to mechanical treatment and finishing interfere homogeneous growth or bring a local damaging of the POL. Because of this, a temporary prevention is necessary during the period of a (oversea) shipment or storage to avoid a chemical and/or mechanical decay of the POL.

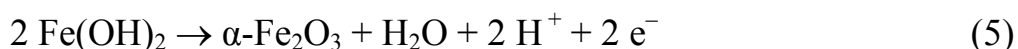
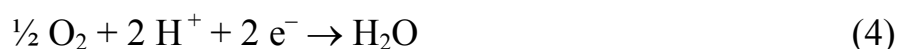
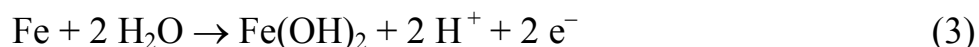
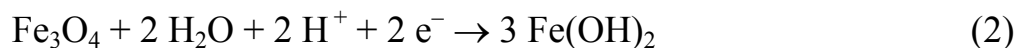
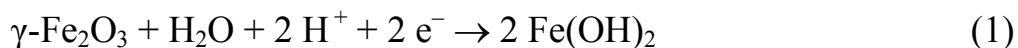
The use of package material containing systems of volatile corrosion inhibitors (VCI) is a conventional method to conserve or to repair (up to a certain point) the POL inside a densely closed package allowing a development of a VCI-saturated atmosphere. A stabilized POL and the defense of chemical attacks by corrosion promoting ingredients of the vapor phase ensure the retention of the passive behavior meaning an active way of corrosion protection. Therefore, suitable corrosion inhibitors are required possessing a moderately high vapor pressure, to form another volatile substance, or such as water vapor or urea has to be used as carrier. VCIs are transferred to the metal surface by diffusion through the gas room. They act at the metal site by means of adsorption or formation of precipitates [1–4].

The following paper describes the common protection mechanisms and explains a concept for the appropriate choice of VCI systems with respect to the protolytic characteristics of the POL, which has to be protected. Further, a simplified way is presented to calculate and set up packages with commercial available VCI package materials, including a test program for the evaluation of the provided protection effect.

## Choice of appropriate VCI systems

Volatile corrosion inhibitors can be divided into passivation, adsorption and precipitation type inhibitors with respect to their main inhibition mechanism. The so called **passivating inhibitors** e.g. nitrite evolve a good protection effect especially on iron materials by forming a passive layer in cooperation with oxygen. This kind of open circuit passivation

is unique for these materials. Thereby, nitrite acts as sufficiently strong oxidizing and easy reducible agent to counter the corrosion of the bulk metal by means of autoxidation, and through the reconstruction of the POL using the available oxygen. The autoxidation process according to the Equations (1) to (6) starts with dissolution of the Iron(III) containing oxides magnetite ( $\text{Fe}_3\text{O}_4$ ) and  $\gamma\text{-Fe}_2\text{O}_3$  in the presence of a surface electrolyte film with a respective thickness, which is realized at r.H. > 60% or in the case of condensed water formation below the dew temperature (Eq. 1 and 2).



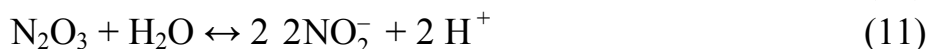
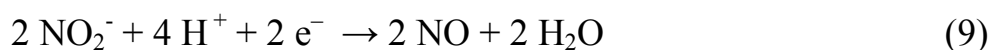
High portions of available oxygen (dissolved in the surface electrolyte layer) support the cathodic part reaction (Eq. 4) accelerating the whole process. In this way the visible corrosion products  $\alpha\text{-Fe}_2\text{O}_3$  (Hematite) and  $\alpha\text{-FeOOH}$  (Goethite) are formed by the oxidation of Iron(II)-hydroxide  $\text{Fe}(\text{OH})_2$  (Eq. 5 and 6).

Independent of the use of VCI containing material wet air should be excluded as good as possible by the packaging design, regulation of the storage conditions as well by avoiding of wrapping hot and wet parts. Because of the poor feasibility in the practice suitable conditions (adequate inhibitor amounts in the presence of needed small amounts oxygen) must be realized for iron materials allowing a passivation. This meets the spirit of Rozenfeld, who said in the general sense: “The presence of oxygen must be accepted, but it is an art to enable the oxygen acting as passivator and not as accelerator of the cathodic part reaction of the corrosion.”

It is well known that the POL of iron materials consist of the sequence  $\text{Fe}/\text{Fe}_3\text{O}_4$ ,  $\gamma\text{-Fe}_2\text{O}_3$ . Therefore, the oxidation potential of the available oxygen has to be high enough to reach the passive state in accordance to the Pourbaix Diagram. In this case the redox process is described with the Equations (7) and (8):



Under these conditions the nitrite acts as catalyst of oxygen reduction according to the following mechanism (Equations 9 to 13):

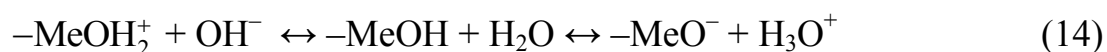


With that the reaction (Equation 13) is suppressed, which delivers a too low oxidation potential:

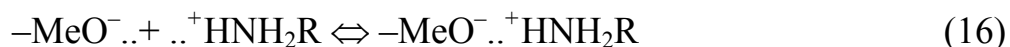
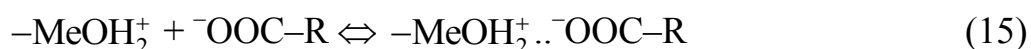


However, passivating inhibitors have little effect on non-ferrous metals such as Zinc, Aluminum and Magnesium with the main purpose to prevent dissolution of the POL. Note, in the case of copper materials the single use of such inhibitors can lead to an undesired tarnishing [5, 6].

The protection mechanisms of the **adsorption and precipitation type inhibitors** can be divided into 3 groups. In all 3 groups the adsorption strength of VCI components on the different POLs depends on the pH value of the surrounding electrolyte, because every POL is characterized by an isoelectric point (IEPS = **i**soelectric **p**oint of the surface covering oxide) due to the dissociative adsorption of one water layer resulting in surface hydroxide groups. According to Equation 14 an equilibrium exists, which can be shifted to both sites depending on the concentration of  $\text{H}^+$  or  $\text{OH}^-$  in the surrounding electrolyte.



According to this the surface is charged positively or negatively. At the IEPS the surface charge is zero. Due to the surface charging negative or positive charged species or molecule segments can interact attractively (Equations 15 and 16). Table 1 summarizes the IEPS of the common surface oxides [7, 8].



**Table 1.** IEPS at room temperature of common surface oxides.

Oxide	IEPS (RT)	Oxide	IEPS (RT)
$\gamma\text{-Fe}_2\text{O}_3$	$6.7 \pm 0.2$	$\text{Cu}_2\text{O}$	6.8
$\text{Fe}_3\text{O}_4$	$6.5 \pm 0.2$	$\text{CuO}$	$9.5 \pm 0.4$
$\gamma\text{-FeOOH}$	$7.4 \pm 0.2$	$\text{SiO}_2$	2.1
$\alpha\text{-Fe}_2\text{O}_3$	$8.6 \pm 0.3$	$\text{MnO}_2$	4.5
$\text{ZnO}$	$9.0 \pm 0.3$	$\text{SnO}_2$	4.7
$\text{Al}_2\text{O}_3$	6.6.....9.2	$\text{TiO}_2$	5.3
$\alpha\text{-AlOOH}$	9.1	$\text{Cr}_2\text{O}_3$	7.0
$\text{Al(OH)}_3$	9.25	$\text{MgO}$	12.4

### Adsorption leading to open circuit passivation

Here, the still existing POL becomes stabilized by adsorption of cathodic inhibitors on the oxide and/or anodic inhibitors into the defects. In the case of small defects a plugging by a precipitation shows an anodic effect. Synergistic effects can be achieved by suitable combinations of cathodic and anodic acting inhibitors.

In the presence of high humidity similar conditions should be realized as mentioned above enabling the oxygen operating as passivator. With that small defects in the POL are repaired. In solutions (condensed water layer CWL on the metal surface) of salts from weak acids open circuit passivation is possible above a critical pH value ( $\text{pH}_{\text{crit}}$ ), which can be calculated according Equation 17:

$$\text{pH}_{\text{crit}} = \log c_s - \log c_{\text{ox}} + \text{p}K_a + D^* \quad (17)$$

With  $D$  values for  $\text{O}_2$  and  $\text{FeOH}^+$  as well  $c_{\text{ox}}$  in air-saturated solutions at  $25^\circ\text{C}$  the Equation 17 can be transformed into Equation 18:

$$\text{pH}_{\text{crit}} = \log c_s + \text{p}K_a + 2.96 \quad \text{with } \text{pH}_{\text{crit}} \geq (\text{p}K_a + 1) \quad (18)$$

Table 2 shows the  $\text{pH}_{\text{crit}}$  values of some carboxylates as a function of the concentration  $c_s$  of salts which are often used as adsorption type inhibitors [9, 10].

**Table 2.**  $\text{pH}_{\text{crit}}$  values of some carboxylates in dependence of the salt concentration.

Salt	$\text{p}K_a$	$\text{pH}_{\text{crit}}$ $c_s = 0.1 \text{ M}$	$\text{pH}_{\text{crit}}$ $c_s = 0.01 \text{ M}$
Benzoate	4.2	6.2	(5.16)
Isononanoate	4.6	6.6	(5.6)
Caprylate	4.85	6.8	(5.8)

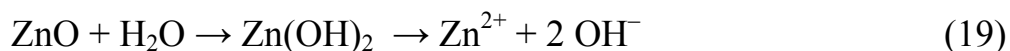
It should be mentioned that the salt and not the corresponding (weak) acid is needed. Therefore, alkaline VCI components like listed in Table 3 within VCI systems are used to generate the anions  $\text{R-COO}^-$ . In this way a plenty of combinations consisting of volatile weak acids and weak bases can be realized, which lead with the dissolved oxygen in the CWL on iron materials to an open circuit passivation.

**Table 3.** Alkaline VCI components and their  $\text{p}K_b$  values.

VCI substance	$\text{p}K_b$ (RT)
2-Aminobutanol	3.2
Amino-Methyl-Propanol (AMP)	3.8
2-Amino-Ethanol	4.5
Ammonia	4.75
Tri-Ethanol-Amine (TEA)	6.2

Another strategy is the establishing of a pH buffer system additionally to the use of adsorbing species. Here, the solubility of the POL shall be reduced by stabilization of a suitable pH value in accordance to the Pourbaix diagram of the respective metal or alloy.

For example an adsorption layer on Zinc (galvanized steel) is not sufficiently resistant against wet air or condensed water. After the dissolution of the POL the corrosion of the bulk occurs according the Equation (19) and (21):



With the dissolution of the POL the adsorbed acid (HA) and alkaline (BOH) components accumulates in the CWL. In this way pH values near the IEPS can be realized resulting in a (desired) minimum of dissolution. With the help of buffer systems the stabilization of  $\text{pH}_{\text{CWL}} \approx \text{IEPS}$  is possible. Suitable is a combination of a weak acid and its corresponding salt (S-salt) with a strong base, where the buffered pH value is determined by Equation (22) (*e.g.* strong base + benzoic acid/ benzoate):

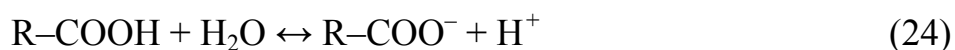
$$\text{pH} = \text{p}K_{\text{a}} - \log c_{\text{HA}}^0 / c_{\text{S-Salt}}^0 \quad (22)$$

Another (rather seldom) concept consist of a combination of a weak base BOH and its salt (B-salt) with strong acid (*e.g.* strong acid + ammonia/ ammonium chloride), where the buffered pH value is determined by Equation (23):

$$\text{pH} = \text{p}K_{\text{w}} - \text{p}K_{\text{b}} - \log c_{\text{B-Salt}}^0 / c_{\text{BOH}}^0 \quad (23)$$

Especially in the regions, where the metal is in direct contact with the VCI-containing package material, installed pH buffer systems are an effective way of corrosion inhibition.

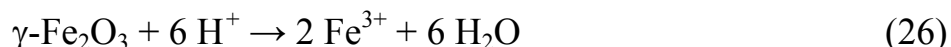
It is possible that volatile weak acids are dissolved in the CWL only. If alkaline components (*e.g.* alkaline cleaner ingredients) are absent, the  $\text{pH}_{\text{CWL}}$  is always below the  $\text{p}K_{\text{a}}$  value of the respective acid leading to dissolution of the POL. In Table 4 the  $\text{p}K_{\text{a}}$  values of often used volatile weak acids are listed together with the achieved pH value in solutions containing 0.1 and 0.01 M acid. Additionally, the dissociation degree  $\alpha$  for 25°C is mentioned belonging to the dissociation equilibrium of the acids according Equation (24). In all cases  $\alpha$  is obviously smaller than 1. With the help of these data and Equation (22) the pH value and the needed amount of the strong base can be calculated.



**Table 4.** Properties of volatile weak acids.

Acid	pK <sub>a</sub>	$\alpha$ (0.1M)	pH (0.1M)	$\alpha$ (0.01M)	pH (0.01M)
Benzoic acid	4.2	0.025	2.6	0.08	3.1
Isononanoic acid	4.6	0.016	2.8	0.07	3.2
Caprylic acid	4.85	0.012	2.9	0.04	3.4
Nitrous acid (HNO <sub>2</sub> )	3.3	0.07	2.1	0.22	2.7

Although the POL of iron materials is attacked by the solely solution of weak acids in the CWL, an inhibition effect is observed in short-term experiments (climatic tests and electrochemistry). The explanation of this paradox behavior is the quick formation of an invisible, thin but porous conversion layer consisting of hardly soluble products of the precipitation reaction between iron ions (especially Fe<sup>3+</sup>) and the anions R–COO<sup>−</sup> of the weak acids. The Equations (25) and (26) describe the dissolution of the POL under acid conditions delivering the needed metal ions.



In the literature the following components of such conversion layers are mentioned:

Caprylate	[Fe(CH <sub>3</sub> –(CH <sub>2</sub> ) <sub>6</sub> –COO) <sub>3</sub> ]
Benzoate	[Fe(C <sub>6</sub> H <sub>5</sub> –COO) <sub>x</sub> ](OH) <sub>3–x</sub>
Sebacate	[Fe(OOC–(CH <sub>2</sub> ) <sub>8</sub> –COOH)](OH) <sub>2</sub>
Borate	{FeOH[B(OH) <sub>4</sub> ] <sub>2</sub> }

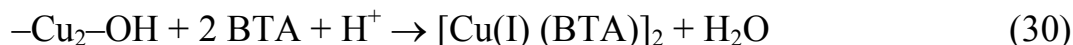
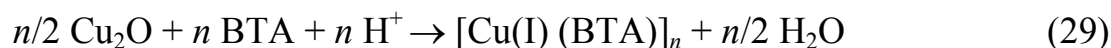
In wet atmospheres the dissolution of the POL according Equation (25) and (26) is accompanied by a hydrogen-type of corrosion attacking the bulk metal according to Equation (27) and (28):



The formed hydrogen (Equation 28) is the reason of the porous characteristic of such conversion layers. This effect is also observed at phosphate conversion coatings. Therefore, a long-term corrosion protection cannot be realized with this kind of conversion layers. Besides them, a risk of hydrogen embrittlement exists. In practice the protection of phosphate conversion coatings with systems consisting a strong base is even recommend in the Technical data sheets of respective media [11–14].

### ***Adsorption and formation of conversion layers***

Here, the POL becomes stabilized by adsorption, too. But unlike the case above, the POL becomes converted into a thin, homogeneous and insulating layer in the presence of humidity. Such behavior was observed up to now for copper-based materials only. Here, immersion of a combination consisting of a weak acid and benzotriazole (BTA) leads to formation of an invisible adherent conversion layer according the Equations (29) and (30):



Although the resulting layer is porous, the  $\text{H}^+$  ions do not attack the bulk copper in the pores, because these regions are more noble than hydrogen [15, 16].

On the brasses Cu10Zn and Cu40Zn the following composition was analyzed:  $\text{Cu}_2\text{O}$ ,  $\text{ZnO}$ ,  $[\text{Cu(I)(BTA)}]_n$ ,  $[\text{Zn(II)(BTA)}]_n$ .

According to this, zinc oxide and zinc ions are able to form solid and insoluble complexes. The suggested mechanism is (Equations 31 to 33) [17]:



On “pure” zinc surfaces (see also galvanized steel) the resulting conversion layers are porous and do not possess a remarkable barrier effect. The bulk metal at the bottom of the pores is less noble than hydrogen and because of this the corrosion keeps on. Therefore, this kind of conversion layers provides a sufficient protection for copper and brass only.

### ***Adsorption, formation of a conversion layer and/or inhibition of the hydrogen evolution occurring in the pores of the POL or conversion layer***

The stabilization of the still existing POL by adsorption is also here the first step of protection. In the presence of humidity and acid substances ( $\text{CO}_2$ , but also acidic VCI components) a hydrogen-type corrosion gets started, either in the pores only or leading to a uniform conversion of the POL into a not visible, thin and porous layer. Both results in a corrosion of the bulk metal into the pores demonstrated here on zinc (Equations 34 and 35).



Here, the inhibition of the cathodic part reaction (the hydrogen evolution according Equation 15) by increasing the hydrogen overvoltage using suitable VCI reduces the corrosion rate.



## VCI combinations – Mode of functioning

Within this paper the way of two typical VCI components, benzoic acid (HBzO) and benzotriazole (BTA), should be described from the release of the source (*e.g.* VCI containing packaging papers or polymer films), over their transport via vapor phase to the adsorption and action on the metal surface of cleaned mild steel. This combination belongs to the group of adsorption and precipitation inhibitors, which needs the assistance of a strong base to achieve in the CWL a pH  $\approx$  IEPS to reach the open circuit passivation (see above) for a long-term protection effect [10].

HBzO and BTA can sublime at room temperature, meaning a phase transition from solid to gaseous. The sublimation is characterized by the vapor pressure under saturated conditions  $p_{\text{sat}}$  and the molar enthalpy of sublimation  $\Delta H_{\text{sub}}$ , the difference between the enthalpy of melting and the enthalpy of vaporization. Further  $p_{\text{sat}}$  depends on the temperature  $T$  according to the equation of Clausius and Clapeyron (Equation 36) [1].

$$\frac{dp_{\text{sat},T}}{dT} = \frac{\Delta H_{\text{sub}}}{T \cdot \Delta V} \quad (36)$$

For calculation the following simplification can be made: The change of the volume  $V$  mentioned in Equation 36 corresponds to the volume of the gaseous phase meaning here the volume of the atmosphere inside the densely closed package. Assuming that the sublimated substances behave like ideal gases and the molar enthalpy of sublimation  $\Delta H_{\text{sub}}$  is independent of the temperature the differential equation can be solved leading to Equation 37:

$$p_{\text{sat},T} = p_{\text{sat},298\text{K}} \cdot \exp \left\{ \frac{\Delta H_{\text{sub}}}{R} \cdot \left( \frac{1}{298\text{K}} - \frac{1}{T} \right) \right\} \quad (37)$$

The values of  $p_{\text{sat}}$  and  $\Delta H_{\text{sub}}$  for HBzO and BTA are given in Table 5.

**Table 5.** Physical properties for sublimation of HBzO and BTA.

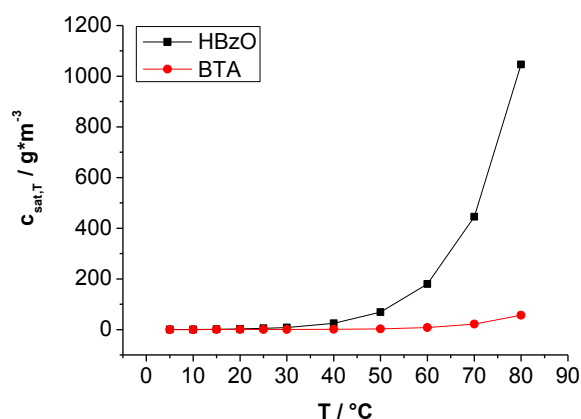
Substance	$M$ [g/mol]	$p_{\text{sat}}$ (25°C) [Pa]	$\Delta H_{\text{sub}}$ (25°C) [kJ/mol]
Benzoic acid	122.12	0.093 [18]	89.00 [19]
Benzotriazole	119.13	0.003 [20]	98.15 [21]

With the known values of  $p_{\text{sat}}$  for each temperature one can calculate nearly the concentration of saturation for the sublimated substances in the gaseous phase using Equation (38).

$$c_{\text{sat},T} = \frac{M \cdot p_{\text{sat},T}}{T \cdot R} \quad (38)$$

This equation is analogous to the calculation of the concentration of saturation for water vapour. Figure 1 shows the concentration of saturation for HBzO and BTA in between 5 and

80°C (278 K and 353 K) covering the typical temperature range occurring during global transports. It is obvious in the diagram that at room temperature the concentration of saturation increases strongly for HBzO meaning a rapid release from donator, while only small amounts of BTA are set free. Otherwise, BTA is available as VCI also at higher temperatures. Therefore, inhibitors with different release behavior should be combined to ensure corrosion protection for a wide temperature range. In the literature it is described that the gas permeability of VCIs can be estimated at elevated temperatures from vaporization rates measured using a simple thermo-gravimetric method [22].



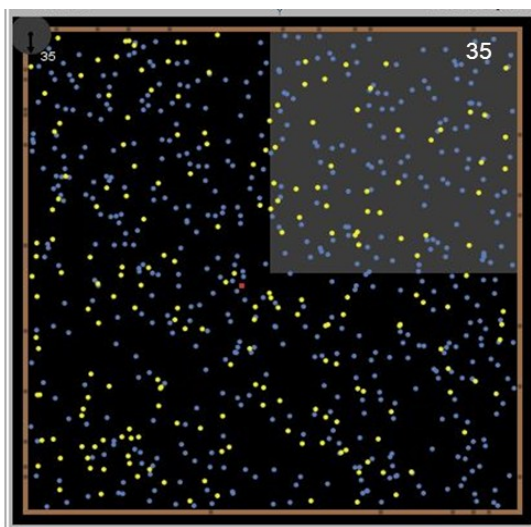
**Figure 1.** Concentration of saturation: temperature-dependence.

We used an experimental setup consisting of a sublimation device and a gas cleaning bottle to trap the released VCIs (Figure 2). Thereby, a sample of VCI containing PE film (260 cm<sup>2</sup>, approx. 2.5 g) is exposed in the closed sublimation oven. During the experiment, the temperature inside is adjusted to 80°C, an air stream is blowing over the sample. After this the air stream is guided into a gas cleaning bottle containing 35 ml methanol. The amount of VCI dissolved in methanol after 2 h was analyzed by means of HPLC again. The measurement revealed that after 2 hours at 80°C the whole amount HBzO and BTA each was released from the film. The same experiment was performed but instead of methanol 100 ml water was used. The pH value of the water measured after 2 h amounted between 5.8 and 6.



**Figure 2.** Sublimation device.

Released VCIs cannot return into the source or leave the inner atmosphere of a package except the “barrier” is damaged or insufficient closed. The distribution follows Fick’s second law, when natural and forced convection are excluded. Although the calculation were made for perfume molecules, the simulation on the website of J. Kottonau from the ETH Zurich [23] demonstrate in an illustrative way the VCI distribution. Within this simulation a sub-volume is marked transferred to the topic of the paper it can be identified with the metal part to protect (Figure 3). The first molecules quickly reach the sub-volume, while still arrived molecules disappear as long an equilibrium is adjusted. Metonymic, the time to adjust the equilibrium (at dry surfaces it is an adsorption/desorption equilibrium; in the present of a hydrate film it is a solution equilibrium) is the so-called conditioning time. After this time the optimal corrosion protection effect is installed, while the inhibitor molecules still act as soon the critical concentration is exceeded.



**Figure 3.** Distribution of VCI (yellow dots) in a gaseous phase filled with air (blue dots); grey = sub-volume.

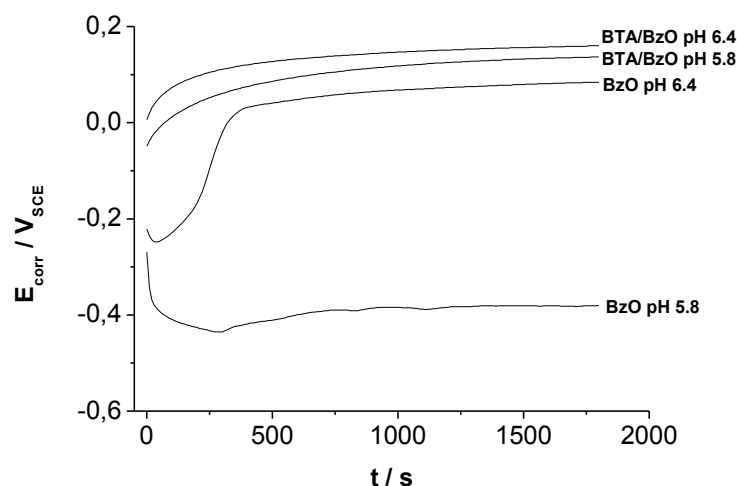
The amount of inhibitor to exceed the critical concentration can be estimated by two models. Both models deliver comparable values. The first way is assuming the formation of a mono-molecular layer. As maximum surface coverage values between  $1 \cdot 10^{-9}$  and  $1 \cdot 10^{-10}$  mol/cm<sup>2</sup> are mentioned in the literature [24]. According to this model, between 0.12 and 1.22 mg/m<sup>2</sup> of both selected substances are needed to cover 1 m<sup>2</sup>.

In another literature [25] the amounts of water are published, which are attached on the metal surface in dependence on the relative humidity. The values are in the range of 0.01 and 0.1 g/m<sup>2</sup>. For comparison the estimated quantity of water on a metal surface covered by dew can amount to 10 g/m<sup>2</sup>. Here, the mass of the inhibitor can be calculated based on known critical concentrations, which are for both substances approx.  $1 \cdot 10^{-3}$  mol/l. The values are shown in Table 6.

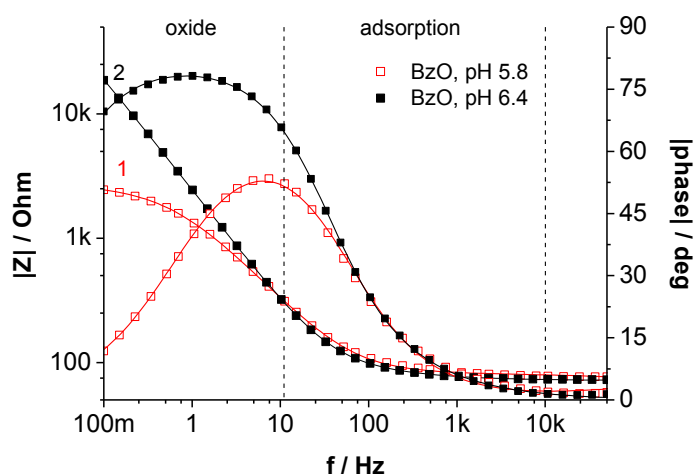
**Table 6.** Minimum amount of HBzO and BTA in mg/m<sup>2</sup> as a function the mass of adsorbed water per m<sup>2</sup>.

	0.01 g	0.1 g	10 g
Benzoic acid	0.001	0.012	1.220
Benzotriazole	0.001	0.012	1.190

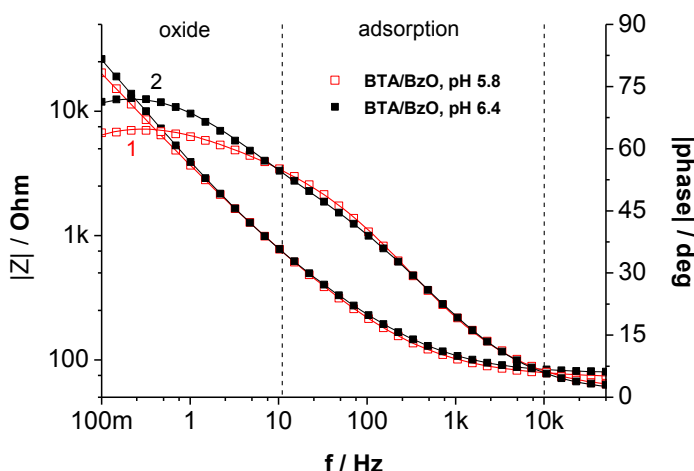
Electrochemical measurements can be used to investigate the efficiency of several inhibitors and inhibitor mixtures to protect mild steel in moist air under different ambient conditions like oxygen concentration or pH value. Within this presentation the results for HBzO and BTA should be discussed exemplary. Measurements of the free corrosion potential  $E_{\text{corr}}$  (Figure 7) and recorded electrochemical impedance spectra (Figure 6) prove the passivation of mild steel through oxygen in the presence of benzoate above the critical pH value (here:  $\text{pH}_{\text{crit}} = 6.2$  (*cf.* [9])). The effectiveness of benzoate in near neutral air saturated solution can be increased if a mixture of benzoate and BTA is used (Figures 4 and 5).

**Figure 4.**  $E_{\text{corr}}$  curves of mild steel recorded in air saturated 0.1 M benzoate solution without BTA at pH 5.8 and pH 6.4 and with 0.1M BTA at the same pH values.

It is assumed that benzoate acts primarily on the rate of iron dissolution by plugging the pores in the air formed oxide layer with insoluble ferric benzoate complexes, whereas BTA is strongly adsorbed on the oxide layer. The synergistic effect in the corrosion protection is due to a more favorable adsorption of BTA compared with benzoate. The air saturated benzoate/BTA solution provides protection to mild steel also below the critical pH value. As described in chapter 2 the protection effect at  $\text{pH}_{\text{CWL}} < \text{pH}_{\text{crit}}$  is measurable but limited. Besides them, an addition of BTA not only enhanced the corrosion protection of mild steel, but provides also a multi-metal protection up to a certain point.



**Figure 5.** Bode plots of mild steel in air saturated 0.1 M benzoate solution after 1 h exposure at pH 5.8 (1) and at pH 6.4 (2).



**Figure 6.** Bode plots of mild steel in air saturated 0.1 M benzoate with 0.1 M benzotriazole solution after 1 h exposure at pH 5.8 (1) and at pH 6.4 (2).

### Dimensioning of VCI containing package materials

Knowing the concentration of saturation the vapor phase and the amount of inhibitors to exceed the critical concentration on the metal surfaces the minimum need of several VCIs can now be estimated. Therefore, the following data have to be available:

- the volume of the package
- the filled volume of the package
- the size of the metal surface to protect (consisting of geometric surface and a factor of roughness)
- the average temperature

Figures 7a and 7b show the minimum need for HBzO and BTA at 25°C, when a package of 1 m<sup>3</sup> is filled by  $x\%$ . Thereby, the size of the metal surface to protect depends on the grade of filling. Technical surfaces (factor of roughness  $\approx 10$ ) were assumed. The influences of surfaces roughness and average temperature shall be discussed within the presentation.

Comparing both diagrams it is obvious that under room temperature not enough BTA is available to protect the whole surface. Therefore, BTA have to be transferred to the metal surfaces by other methods (*e.g.* via direct contact), or other active agents have to be added to the VCI mixtures *e.g.* mono-carboxylic acids [26, 27], di-carboxylic acids [28], nitrite [29, 30] and so on. The composition of effective mixtures is in most cases a business secret and belongs to know-how of the producer.

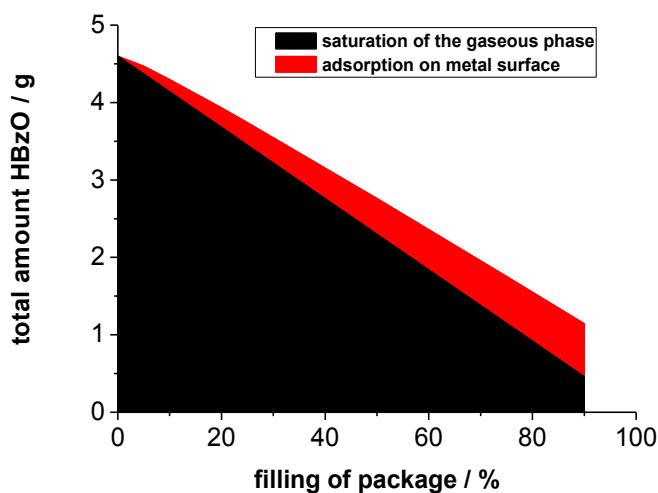


Figure 7a. Minimum need of HBzO for a package of 1 m<sup>3</sup>.

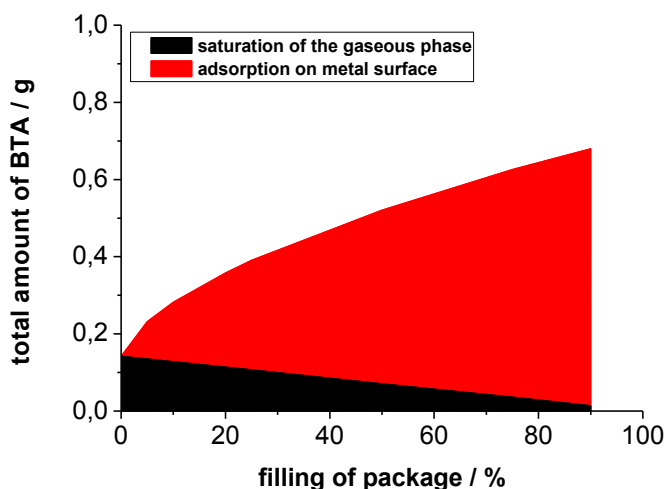


Figure 7b. Minimum need of BTA for a package of 1 m<sup>3</sup>.

### Climate tests with VCI containing package materials

The corrosion protective effect of a usual trade polyethylene (PE-LD) based VCI film was determined by means of the internal EXCOR Tests “KON” and “DIS”. This mono-extruded film had a thickness of 100  $\mu\text{m}$  and included 0.4 g sodium benzoate (correspond to 0.34 g benzoic acid) and 0.55 g benzotriazole per kg PE-film. The content of benzoic acid and benzotriazole were analyzed by means of High Performance Liquid Chromatography (HPLC) after microwave-assisted extraction with methanol (p.a.). Besides the mentioned substances the VCI film includes an alkaline VCI component in an adequate amount to achieve and stabilize a  $\text{pH}_{\text{CWL}} \geq \text{pH}_{\text{crit}}$  in the case of mild steel.

Here, the protection effect of a VCI containing polymer film is compared to a suitable reference PE-LD polymer film having the same physical and chemical properties like the film to test, but does not include any VCI. Within the KON and DIS Test model packaging were manufactured with cleaned steel panels and put in climatic cabinets for the cyclic load by the humid air-temperature alternation climate based on the standard DIN-60068-2-30.

During the KON Test the steel panels were in direct contact with the film (Figure 8). Within the DIS Test the panels were placed in spacer frames (Figure 9), which are completely wrapped in the VCI or VCI free film, respectively. The use of spacer frames ensures that the packaging material, which serves as the VCI source, is separated from the specimens by a distance of 4 cm on all sides so that the VCI components can only achieve their effect via the gas phase in accordance with the instructions for use.

The test panels are made of cold-rolled and low-alloyed steel DC 03 (referred over Q-Lab Deutschland GmbH, 66115 Saarbrücken, Germany, dimensions 50 mm  $\times$  90 mm  $\times$  0.5 mm). The KON and DIS Tests were realized as follows:

- Cleaning of the panels with methanol p.a. in an ultrasonic bath and rinsing with acetone p.a.,
- Storage of the panels for 20 hours above a desiccant (silica gel) in a desiccator to re-organize the natural oxide layer after the stress during the cleaning step;
- Preparing of the model packaging and closing of all film bags by welding with a double seam (Conditions during preparing of the model packaging: 50 % relative humidity and 23 °C),
- Storage of the model packaging for about 20 hours in dry air at room temperature to guarantee that into the VCI packaging a VCI saturated atmosphere could be formed,
- Exposing of the model packaging into climatic cabinets (VÖTSCH Industrietechnik GmbH, 72304 Balingen, Germany) (Note, VCI free and VCI containing samples have to be exposed to different climate cabinets),
- Climatic load according the standard DIN-60068-2-30, variant 1,

- Removing of 1 VCI free package after the other from the climatic cabinet after each cycle; after opening the package visual estimation of the surfaces of the test panels with rust scores according to DIN 51 802 (Table 7),
- The reference packaging failed if first corrosion signs were obvious through the film walls and/or after short opening of the package as well as both panel surfaces showed RS 1 at least Determine the dates of removing of VCI packaging; Here, when the VCI free packaging failed according to the defined failure criteria, the reached number of cycles is multiplied by 3, 4 and 5 (protection factors) to get the dates of removing,
- Removing of 3 VCI packaging of each kind simultaneously at defined 4 dates (see above), visual estimation of corrosion protective effect of the packaging (rust scores) and assessment of the test via the reached protection factor (Table 8);
- Thereby, the protective factor PF is described as follows:  

$$PF = \text{cycle number for VCI material} / \text{cycle number for VCI free material}.$$
- The evaluation of the VCI packaging differed from the assessment of VCI free references. A VCI model packaging was failed, if:
  - corrosion features visible through the transparent film walls and/or during short opening the packages and
  - the 2 panels surfaces showed corrosion and on 1 surface were RS 2 at least or on 1 of the 2 surfaces was RN 3 at least.

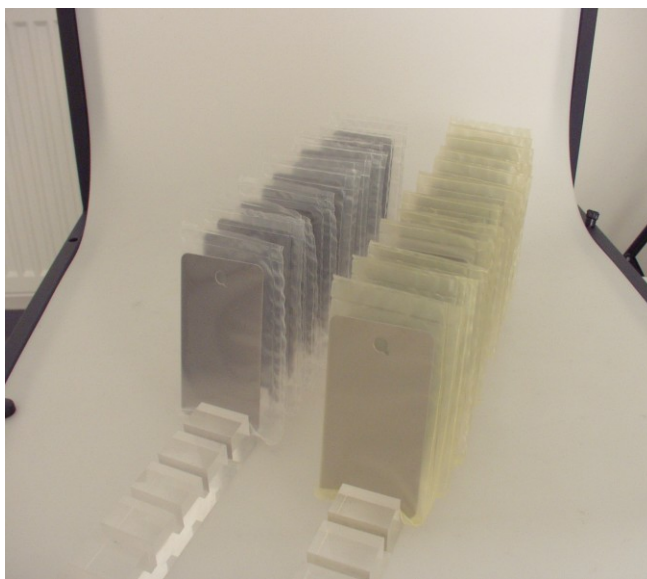
**Table 7.** Meaning of the rust scores (according to DIN 51 802).

Rust score (RS)	Meaning
0	no corrosion
1	at most 3 corroded areas, of which none has a diameter of more than 1 mm
2	slight corrosion: < 1% of the surface
3	moderate corrosion: 1 – 5% of the surface
4	severe corrosion: 5 -10% of the surface
5	very severe corrosion: > 10% of the surface

**Table 8.** Assessment of the EXCOR internal climate tests “DIS” and “KON”.

level	Protective factor PF	Rating
0	$\leq 3.0$	not worth mentioning
1	$\leq 3.5$	poor
2	$\leq 4.5$	moderate
3	$\geq 4.5$	good, VCI packaging material appropriate for overseas shipping





**Figure 8.** Model packages of the EXCOR internal “KON” test.



**Figure 9.** Model packages of the EXCOR internal “DIS” test.

Whereas electrochemical measurements show the effect of inhibitors, which have already reached the metal surfaces, the climatic tests with model packaging prove the efficiency of VCIs including the release and the transport via vapor phase in comparison to a VCI-free reference. Tables 9 and 10 summarize the results of a so-called contact test (“KON”) and a so-called distance test (“DIS”) with a VCI-containing polymer film containing among others as main components HBzO and BTA suitable for iron.

According to the defined failure criteria the VCI free packaging failed after 5 cycles of climatic load in the “DIS” test as well as in the “KON” test. These cycle numbers were taken as basis for removing the VCI model packaging out of the climatic cabinet.

After 27 cycles of climatic load the climate test was terminated. Although the test panels were more than 5 times longer exposed in the climate cabinet, no signs of corrosion were visible after opening the packages. The VCI containing polymer film tested here showed a good corrosion protective effect in direct contact as well as on distance for defined steel surfaces. Thus, this film can be recommended particularly for overseas transport.

**Table 9.** VCI-free references.

Cycles	KON	DIS
1	0 / 0	0 / 0
2	0 / 1	0 / 1
3	0 / 1	0 / 1
4	0 / 2	1 / 1
5	2 / 2	2 / 2
6	3 / 1	2 / 1
7	2 / 1	2 / 1
8	2 / 2	2 / 2
9	2 / 2	2 / 1
10	2 / 1	2 / 2
Failure of the VCI free reference film after cycles	5	5

## Conclusion

Volatile corrosion inhibitors can be divided into passivation, adsorption and precipitation type inhibitors with respect to their main inhibition mechanism. Passivating inhibitors *e.g.* nitrite evolve a good protection effect especially on iron materials by forming a passive layer in cooperation with oxygen. However, passivating inhibitors have little effect on non-ferrous metals such as Zinc, Aluminum and Magnesium with the main purpose to prevent dissolution of the POL. Note, in the case of copper materials the single use of such inhibitors can lead to an undesired tarnishing.

The protection mechanisms of the adsorption and precipitation type inhibitors can be divided into different groups. In all cases the adsorption strength of VCI components on the different POLs depends on the pH value of the surrounding electrolyte, because every POL is characterized by an isoelectric point (IEPS).

Also with a combination of suitable adsorption type inhibitor an open circuit passivation can be achieved. In the presence of high humidity conditions should realized, where the pH of the surrounding electrolyte as (condensed water layer CWL on the metal surface) is above a critical pH value ( $\text{pH}_{\text{crit}}$ ).

**Table 10.** KON and DIS test with VCI-containing polymer film.

Cycles	Protective factor PF	RS of both panels surfaces	
		KON	DIS
19	3.8	0 / 0	2 / 0
		0 / 0	1 / 0
		0 / 0	1 / 0
21	4.2	1 / 0	0 / 0
		2 / 1 *	2 / 0
		0 / 0	2 / 1 *
27	5.4	1 / 0	0 / 1
		1 / 1	0 / 1
		1 / 0	0 / 1
Failure at factor, achieved PF		~ <b>5.0</b>	> <b>5.0</b>
		good corrosion protective effect in contact	good corrosion protective effect in distance

\* packaging failed; maybe inadequacies in the sample preparation.

PF = cycle number for VCI material / cycle number for VCI free material.

Under conditions, where the POL is attacked *e.g.* by acid components, pH values near the IEPS should be realized resulting in a (desired) minimum of dissolution. With the help of buffer systems the stabilization of  $\text{pH}_{\text{CWL}} \approx \text{IEPS}$  is possible. Suitable combinations are: volatile weak acids and their corresponding salt) combined with a strong base or volatile weak bases and their salts combined with a strong acid.

In the case of copper and brass compact non-visible adherent conversion layer can be formed by immersion of a combination consisting of a weak acid and benzotriazole (BTA). Such behavior is observed up to now at copper-based materials only.

In the case of iron material porous conversion layers can be formed only, if solely volatile weak acids reach the surface, because of the formed hydrogen. This effect is also observed at phosphate conversion coatings. Therefore, a long-term corrosion protection cannot be realized with this kind of conversion layers without the assistance of a respective strong base to shift the pH value above  $\text{pH}_{\text{crit}}$ .

Within this paper the way of two typical VCI components, benzoic acid (HBzO) and benzotriazole (BTA), was described from the release of the source (*e.g.* VCI containing packaging papers or polymer films), over their transport via vapor phase to the adsorption and action on the metal surface of cleaned mild steel.

First, equations are presented to estimate the concentration of saturation of the vapor phase into a densely closed volume of package for several temperatures and the amount of inhibitors to exceed the critical concentration on the metal surfaces. Both are needed for dimensioning VCI containing package material. The calculations revealed the different

behavior of HBzO and BTA at room temperature. HBzO is strongly released from donator, while only small amounts of BTA are set free. Otherwise, BTA is available as VCI also at higher temperatures. Therefore, inhibitors with different release behavior should be combined to ensure corrosion protection for a wide temperature range.

Furthermore, an experimental setup is presented consisting of a sublimation device and a gas cleaning bottle to trap the released VCIs in methanol or water. With that, the amount of HBzO and BTA released from a usual trade polyethylene (PE-LD) based VCI film could be determined and compared with the original incorporated amounts. Here, a good accordance could be proved. Moreover, the pH value of the water eluate was amounted around 6.

The distribution of VCI inside a densely closed package follows Fick's second law, when natural and forced convection are excluded. Within this paper a simulation is presented demonstrating in an illustrative way the VCI distribution.

With the help of electrochemical measurements the efficiency of HBzO and BTA to protect mild steel in moist air was investigated at different pH values. Measurements of the free corrosion potential  $E_{\text{corr}}$  and recorded electrochemical impedance spectra prove the passivation of mild steel through oxygen in the presence of benzoate above the critical pH value (here:  $\text{pH}_{\text{crit}} = 6.2$ ). The effectiveness of benzoate in near neutral air saturated solution can be increased, if a mixture of benzoate and BTA is used. It is assumed that benzoate acts primarily on the rate of iron dissolution by plugging the pores in the air formed oxide layer with insoluble ferric benzoate complexes, whereas BTA is strongly adsorbed on the oxide layer. The synergistic effect in the corrosion protection is due to a more favorable adsorption of BTA compared with benzoate.

The corrosion protective effect of a usual trade polyethylene (PE-LD) based VCI film (containing HBzO, BTA and another alkaline VCI component) was determined by means of the internal EXCOR Tests "KON" and "DIS". Whereas electrochemical measurements show the effect of inhibitors, which have already reached the metal surfaces, the climatic tests with model packaging prove the efficiency of VCIs including the release and the transport *via* vapor phase in comparison to a VCI-free reference. The VCI containing polymer film tested here showed a good corrosion protective effect in direct contact as well as on distance for defined steel surfaces. Thus, this film can be recommended particularly for overseas transport.

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