THE DRIVE OFF ROAD NEWSLETTER

CONTENT

STATE OF THE ART

SEALANTS & TOPCOATS
State of the art
SEALANTS & TOPCOATS

Navigation
1. Introduction
2. Coating substances in electroplating technology
3. Conclusion
4. References
INTRODUCTION

Modern corrosion protection systems for metallic workpieces are modular in design and typically consist of an initial layer of zinc or zinc alloy for cathodic corrosion protection of the base metal, a Cr(III) conversion layer, and a sealant or topcoat as a final layer. It is only this final layer that comes into direct contact with the surrounding environment, which means its multifunctionality can have a significant impact on the properties of the entire corrosion protection system. This multifunctional corrosion protection is particularly essential in the case of fasteners for the automotive sector, as these are exposed to a wide range of potentially harmful stressors within their environment over the course of their life cycle. These stressors include exposure to corrosive media, thermal exposure and mechanical loads.

Over the past twenty years, the automotive industry has seen dynamic technical advances. With this has come an increased demand for high-quality surface coatings on the various automotive components. Current trends include a move towards more lightweight materials, higher corrosion protection requirements and new material combinations. This has resulted in higher material hardness, higher thermal load, and more sophisticated control of the coefficient of friction. In an environment such as this, where standards and specifications are constantly being updated, it is absolutely essential for corrosion protection systems to be in a state of continuous development. This article focuses on state of the art sealants and topcoats, highlighting their capabilities with regards to the current requirements of the automotive industry, and focusing on the key factors of corrosion protection, coefficient of friction, and resistance to external influences.

COATING SUBSTANCES IN ELECTROPLATING TECHNOLOGY

When it comes to surface treatment related to electroplating technology, a variety of different products are available for the post-treatment of passivated, zinc plated layers. Table 1 contains a list of the most common coating substances used for post treatment. This article focuses on the organic/ inorganic sealants as well as the topcoats that have been assigned to category T2 or T7 in accordance with ISO 19598:2017-04.
The terminology used in this field is not clear cut and differs according to the respective standard, country and manufacturer; however, sealant (or sealer) and topcoat are the prevailing designations used in English.

- Sealant layers are typically up to 2 µm thick and consist of Cr(VI)-free organic and/or inorganic compounds. Coatings that can be removed with cold cleaners, on the other hand, such as those with an oil, grease or wax base, are not considered sealants by this international standard.

- Topcoats are typically thicker than 2 µm and applied as Cr(VI)-free thin organic layers that often require a higher curing temperature.

Unfortunately, these definitions categorise sealants and topcoats according to their layer thickness, which is a variable coating property. This means that, according to these definitions, a thin topcoat becomes a sealant and, conversely, a thick sealant becomes a topcoat. Furthermore, topcoats should not contain any inorganic components, and sealants should not be chemically cured. It is for these reasons that those involved in using and applying these substances often hesitate when it comes to what to call – and how to use – a given coating substance. In this article, we have opted to use the terminology that is more relevant in practical applications, which is based on why and how the coating substance is used.

A sealant is used to form an inert protective layer on a workpiece to protect it from external influences. This stops corrosive media from reaching the underlying layers and therefore increases the level of corrosion protection. If the post-treatment product is formulated in a way that the top layer provides the workpiece with a multifunctional surface, then this can be referred to as a topcoat rather than a sealant. These modified surface properties may include a certain level of colouration, a certain conductivity, an increased level of corrosion resistance induced by corrosion protection inhibitors, or even a supplemental lubricant.

For the applicator, it is logical to categorize the systems based upon whether the film is physically dried or chemically cured, and whether it is an organic, inorganic, or organic/inorganic layer. It is also essential to make a distinction between water-based formulations and those based on organic solvents.

<table>
<thead>
<tr>
<th>Code</th>
<th>Type of post-treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>Use of paints, varnishes, powder coatings or similar coating substances</td>
</tr>
<tr>
<td>T2</td>
<td>Use of organic or inorganic sealing agents / sealants / sealers</td>
</tr>
<tr>
<td>T2nL</td>
<td>Sealant without integrated lubricant</td>
</tr>
<tr>
<td>T2yL</td>
<td>Sealant with integrated lubricant</td>
</tr>
<tr>
<td>T3</td>
<td>Use of organic dyes</td>
</tr>
<tr>
<td>T4</td>
<td>Use of greases, oils or other lubricants</td>
</tr>
<tr>
<td>T5</td>
<td>Waxes</td>
</tr>
<tr>
<td>T6</td>
<td>Soaps</td>
</tr>
<tr>
<td>T7</td>
<td>Topcoat</td>
</tr>
<tr>
<td>T7nL</td>
<td>Topcoat without integrated lubricant</td>
</tr>
<tr>
<td>T7yL</td>
<td>Topcoat with integrated lubricant</td>
</tr>
</tbody>
</table>

2.1 Advantages and disadvantages of water-based coatings and coatings based on organic solvents

The definition of a solvent is a substance that can dissolve or thin gases, liquids or solids without causing a chemical reaction between the dissolved substance and the solvent. The most important properties of a solvent with regard to coatings are polarity, surface tension, boiling and freezing points, and – from an environmental perspective – toxicity.

Polarity refers to the formation of separated charges caused by a charge displacement, which results in a group of atoms no longer being electrically neutral. The polarity of a molecule is measured in terms of its electric dipole moment. The dipole moment of a substance determines its solubility or its ability to act as a solvent. Alkanes are non-polar due to the small difference in electronegativity between carbon and hydrogen. Water, on the other hand, is polar due to the difference in electronegativity between hydrogen and oxygen. As a protic solvent with high polarity, water has only limited compatibility with conventional, usually non-polar binding agents. The large selection of different organic solvents allows the desired solubilities to be specifically selected by blending them. The process of forming layers can be controlled by evaporating individual solvents at different times during the coating process. A wide range of suitable binding agents are available to choose from for the formulation.

Another essential property of solvents is their surface tension and its associated wetting properties on the substrate. Unlike most organic solvents, water has an exceptionally high surface tension due to the formation of hydrogen bonds and the dipole character of the water molecules. (see Table 2).

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Surface tension at 20°C [mN/m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Pentan</td>
<td>16</td>
</tr>
<tr>
<td>Ethanol</td>
<td>22.5</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>48.4</td>
</tr>
<tr>
<td>Water</td>
<td>72.75</td>
</tr>
</tbody>
</table>

Table 2: Surface tension values in mN/m with conventional solvent 1

This high surface tension makes it difficult to wet the substrate (see Figure 1.), which can, in turn cause adhesion problems.

Figure 1:
- (above) Complete wetting of a hydrophilic substrate with water droplets.
- (below) Minimal wetting of a hydrophobic substrate with water droplets.
Even the ability to wet fillers or pigments is often inadequate, which can result in the formation of pores and thus pathways for corrosion within the coating. Furthermore, a high level of surface tension also results in pronounced edge pull-back of the coating as it dries, along with a strong tendency to foam. For each of these factors that tend to weaken the level of corrosion protection, there are suitable additives that must be considered when formulating the coating substances. Organic solvents are typically characterised by a somewhat low level of surface tension. This promotes a desirable level of substrate wetting and a low tendency towards adhesion problems or edge pull-back. In comparison to water-based formulations, the tendency to foam is also typically lower.

The most striking difference between water and organic solvents is their respective boiling/freezing points. While water-based formulations generally have boiling and freezing points of roughly 100°C and 0°C respectively, the right combination of organic solvents can be used to create the appropriate boiling points to suit each phase of the coating process. In this way, a solvent with a low boiling point can offer rapid drying properties and thereby promote the adhesion of the coating substance to the substrate. A moderate boiling point is a more favourable option for slow and even evaporation of the solvent, resulting in a uniform, pore-free surface. The use of solvents with a high boiling point, which do not disappear until the final phase of the drying process, has a positive effect on the adhesion, roughness and uniformity of the coating. At the other end of the spectrum, a freezing point below 0°C can increase storage stability in some regions.

In spite of the various advantages of using formulations with organic solvents, the industry has and continues to make significant efforts to reduce the use organic solvents. As the solvent does not form part of the final coating, it is almost completely non-recyclable and its emissions often require cost-intensive processing treatment before they can be released into the environment. Many organic solvents are also viewed negatively due to their low vapour pressure, high flammability and toxicity. The improved marketability of ‘green’ coatings is yet another essential economic driver, as the ecological and economical reasons behind reducing organic solvents go hand in hand.²
2.2 Differences between physically drying and chemically curing coatings

Another logical distinction for people to make between coating substances is whether the film formation mechanism is physically drying or chemically curing. Figure 2 a) illustrates the change in the viscosity $\eta$ and molecular weight $M_w$ during production and while applying a physically drying topcoat. The binder (1) is typically a water-based polymer emulsion comprising long-chain polymers with a relatively high molecular weight. Dilution of this binder creates a free-flowing, low-viscosity formulation (2). When this formulation is applied to a substrate and the solvent is subsequently removed by means of a drying process, it forms a continuous film (3) of entangled polymer chains on the surface of the substrate. The molecular weight of the binding agent after the applied coating corresponds to the molecular weight of the pure binding agent. The film formation process does not result in any chemical changes to the binding agent. This makes the process reversible, which can be advantageous in the event that rework is required due to incorrectly coated substrates. However, it is not possible to achieve the high solid content required to ensure a high level of mechanical and chemical resistance.

On the other hand, in the case of chemical curing, as in heat-induced cross-linking formulations, a high level of mechanical and solvent resistance can be achieved. As shown in Figure 2 b), the basic substances are low-viscosity binders (1) with a low molecular weight. In addition to being polymers, these may also be macro-molecular or molecular precursors. Chemical cured films have a low viscosity due to their low molecular weight and only a minimal amount of solvent is required to formulate the coating substance (2). During the course of the film formation process, chemical reactions take place within the binding agent and covalent bonds form between the molecules. The level of energy required to establish these stable bonds is one of the factors behind the process’ high energy requirements, the fulfilment of which is achieved by baking at high temperatures (typically 120°C – 180°C) or by using a radiation drying process. The intra- and intermolecular bonds within the coating create irreversible, closed and densely networked, high solid content films on the surface of the substrate (3).

Figure 2: Schematic representation of the change in the viscosity $\eta$ and molecular weight $M_w$ during production and while applying
a. a physically drying topcoat
b. a chemically curing topcoat
During the drying or baking phase, chemically cured topcoats, when formulated as heat cross-linked, will require a different coating application than the method used for conventional, physically drying topcoats. (see Figure 3). For the latter, drying out in a centrifuge with an air flow of roughly 80°C is sufficient to remove the solvent. Heat cross-linking coatings, on the other hand, require an oven complete with a drying zone and a zone that generates temperatures of 120–180°C to cure the coating in either batches or continuous operation.

**Figure 3: Typical process sequence of applying an industrial coating to connecting elements**

2.3 FINICOAT - The latest generation of topcoats

Figure 4 illustrates how the latest generation of heat-cured topcoats (hereafter referred to as FINICOAT) for electroplated protected surfaces fits into the development of cathodic surface protection. Before the 1990s, chromated zinc coatings from cyanide-based or acidic electrolytes were considered state of the art. As a result of environmental restrictions, Cr(VI) and cyanide were replaced by the first generation of cyanide-free electrolytes and Cr(VI)-free passivations. During this time, the use of zinc alloy, most notably zinc-iron plating electrolytes were established. In a bid to achieve the exceptional corrosion protection of the chromate coatings in a sustainable manner, the passivated zinc coatings were also protected with water-based sealants (T2) such as those in the FINIGARD product series. In addition to the excellent corrosion protection, the surfaces could then also be adapted to suit the requirements for the coefficient of friction for coating fasteners. The systems available today outperform their predecessors in many respects, but particularly in terms of their continuous development with regard to passivation and electrolytes. The zinc-nickel electrolyte with its co-deposition of 12-15% nickel found in widespread use today, represents the latest state of the art. The typical requirements of the current corrosion protection systems are able to withstand 720 hours without corrosion of the base material in a salt-spray test (SST) in accordance with DIN EN ISO 9227.
It is anticipated that these corrosion protection requirements will become even more challenging in the future. Looking to the future, it is likely the new standard requirement will require 1000 hours of salt-spray without base material corrosion, cyclical corrosion tests with temperature profiles after mechanical and heat-induced damage of the components, and high chemical resistance.

A growing trend in the requirements for the automotive industry relates to maintaining the decorative aspect of black surfaces when exposed to corrosion. The typical grey haze and white rust effect, indicating the effectiveness of the cathodic corrosion protection, is an increasingly undesirable result on black surfaces. In the past, the main focus was on the essential technical aspects of ensuring protection against base metal corrosion. The emphasis in the future, however, appears to be the ability to withstand corrosion for as long as possible without any visual changes to the surface. The ability to withstand at least 480 hours in salt spray testing without visual changes requires the cathodically active electroplated layer to be protected. This protection must be provided by the topcoat that comes into direct contact with the surrounding environment.

COVENTYA was ahead of the curve in responding to these requirements by developing the FINICOAT product series, which represents a new generation of multifunctional, heat-curing topcoats for electroplating technology. The aforementioned advantages of chemically curing topcoats was proven in a study using COVENTYA’s FINICOAT 412. This study involved zinc-nickel electroplated screws under production conditions in COVENTYA PERFORMA 285 (12–15% Ni, 8–10 µm,) and then passivated with a process containing Cr(III) (COVENTYA FINIDIP 128.3). The FINICOAT 412 topcoat was applied in a centrifuge by means of a dip-spinning process before being cured in a conveyor oven at 180°C for 30 minutes. Prior to the study, the industrially coated screws were also subjected to a certain level of mechanical load to simulate the effects of transport. The screws were
then tested in a salt-spray chamber in accordance with ISO 9227 as well as in an ACT II cyclical corrosion test in accordance with VCS 1027, 1449. Figure 5 shows the sample parts after 720 hours of salt-spray exposure, while Figure 6 shows the screws after 12 cycles of the ACT II test.

The requirements for both corrosion protection and flexibility of coefficient of friction for fasteners have increased significantly. New standards require a constant coefficient of friction even after multistage tightening processes and repeated tightening and loosening of the joints. They also call for a variety of material combinations involving steel of varying hardness, aluminium, cathodic lacquer coatings and powder coatings. Total coefficient of friction as well as individual coefficients are also clearly and precisely defined in the new standards. Noteworthy examples include the MBN 10544, Scania STD 4419 and VW 01131 standards.

COVENTYA has a forward-looking strategy in place that supports reliable delivery of products designed to meet these coefficient of friction requirements. (Figure 7). In addition to supporting the continuous development of its own products, the company’s expertise and product range have been enhanced and expanded by bringing in lubricant experts from microGLEIT Spezialschmierstoffe GmbH to the COVENTYA Group.

<table>
<thead>
<tr>
<th>Zinc System</th>
<th>Passivate</th>
<th>Topcoat</th>
<th>layer weight</th>
<th>mechanical stress</th>
<th>gray haze</th>
<th>white corrosion</th>
<th>red corrosion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc-Nickel (12-15% Ni, 8-10µm) PERFORMA 285</td>
<td>FINIDIP 128.3</td>
<td>FINICOAT 412</td>
<td>-5g/m²</td>
<td>mechanical</td>
<td>&gt;720h</td>
<td>&gt;720h</td>
<td>&gt;720h</td>
</tr>
<tr>
<td>Zinc-Nickel (12-15% Ni, 8-10µm) PERFORMA 285</td>
<td>FINIDIP 128.3</td>
<td>FINICOAT 412</td>
<td>-5g/m²</td>
<td>without</td>
<td>&gt;720h</td>
<td>&gt;720h</td>
<td>&gt;720h</td>
</tr>
</tbody>
</table>

Figure 5: Corrosion test results for the heat-cured FINICOAT 412 topcoat in a salt-spray test (SST) in accordance with ISO 9227.

Figure 6: Visual appearance of connecting elements coated with the heat-cured FINICOAT 412 topcoat in a cyclical corrosion test (ACT II, VCS 1027, 1449) after 12 cycles.
It is not always straightforward when one seeks to define whether a coating substance is a sealant or topcoat. The definitions are simply not always clear cut. Instead, it is far more important for the user to consider the functionality and properties of the finished coating. This includes differentiating between the products based on their film-formation mechanisms, as well as their correlated energy requirements and ease of application. It is also essential to make a distinction between water-based formulations and those based on organic solvents. The differences relating to physical properties such as polarity, surface tension, and the boiling and freezing point have been addressed. It is clearly preferable to minimise the use of organic solvents for environmental reasons without compromising the quality of the coating.

The increased demand for high-quality surface coatings with regard to corrosion protection and resistance to media, heat, mechanical influences and UV – in addition to the ability to adjust the coefficient of friction – calls for continuous development of the entire corrosion protection system. Since they are in direct contact with the surrounding environment, the latest generation of sealants and topcoats play a crucial role in the visual aspect of the protected components when exposed to corrosion. A primary conclusion of both our internal studies and production work in the field is that COVENTYA’S FINICOAT product line has met current and near future requirements for multifunctional, heat cured topcoats over electroplated surfaces.

**CONCLUSION**

![Figure 7: Combined expertise of COVENTYA and microGLEIT in relation to adjusting the coefficient of friction using special lubricants and corrosion protection.](image-url)
REFERENCES


CONTACT: automotive@coventya.com