

Chimia 48 (1994) 420–422
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 ISSN 0009–4293

Organic Corrosion Inhibitors

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Abstract. Organic corrosion inhibitors, which are used as additives in paints and lubricants to provide permanent corrosion protection, are briefly discussed.

1. Introduction

An inhibitor is by definition a substance which retards or slows down a chemical reaction. Thus, a corrosion inhibitor is a substance which, when added to an environment, effectively decreases or prevents the attack by the environment on a metal. Corrosion inhibitors are commonly added in small amounts to organic coatings, acids, cooling water, antifreeze fluids, metal working fluids, lubricants, and to many other systems to prevent serious corrosion [1][2].

Since several years the Additives Division of Ciba has been involved in the development of new corrosion inhibitors. Research work on new corrosion inhibitors concentrates on following topics:

- Solvent- and Water-borne Coatings
- Lubricants.

2. Corrosion Inhibitors for Coatings

Paint coatings are applied to metallic substrates for two principal reasons: 1) to protect them from corrosion; and 2) to provide a cosmetic finish. If coatings did not protect our goods, our quality of life

would most certainly be changed, for the worse (e.g., bridges would soon become unsafe to use; automobiles would rust away even faster ...). Therefore, it is extremely important that coatings provide good protection.

The development in the protection of metals against corrosion by organic coatings was focused in the past years mainly on the development of novel anticorrosive pigments, as well as on the improvement of the barrier function of the paint films [3]. The reasons for these efforts are two-fold: 1) to increase performance and durability of the paint systems; and 2) to comply with the environmental restrictions which are being placed on the use of the most effective anticorrosive pigments such as chromates or red lead.

Legislation to further restrict use of toxic materials is expected. Accordingly, demands for new solutions to environmentally safe corrosion protection are urgent, so the call for substitutes of the classical anticorrosive pigments becomes more and more audible.

In a first attempt our goal was the development of nontoxic organic corrosion inhibitors for solvent based surface coatings.

Corrosion protection by organic inhibitors can be achieved by various mechanisms. Possible mechanisms are:

- Decrease of the porosity and the permeability of the paint film for water, oxygen, and aggressive ions (→ barrier function)
- Adsorption of the inhibitor onto the metal surface (→ passivation)
- Take up of electrons which are released during the anodic dissolution of the metal or the consumption of oxygen (→ cathodic activity)
- Formation of insoluble complex salts of the inhibitor with ferrous ions (→ anodic activity)
- To enhance the adhesion (especially the wet adhesion) between the coating and the metal surface.

An approach involving adhesion improvement, adsorption onto metal surfaces, and complex formation seems to be the most suitable way to control corrosion without having a negative effect on coating properties. Therefore, an efficient corrosion inhibitor should meet the following profile:

- High efficiency at low concentrations (0.5–5%)
- Low water solubility
- No sensitivity against oxidation (aging)
- High purity
- Effective at pH 5–9
- Low toxicity (environmentally safe)
- Compatible with a wide range of resin types
- Easy incorporation, as liquid or dispersible solid, into paint systems

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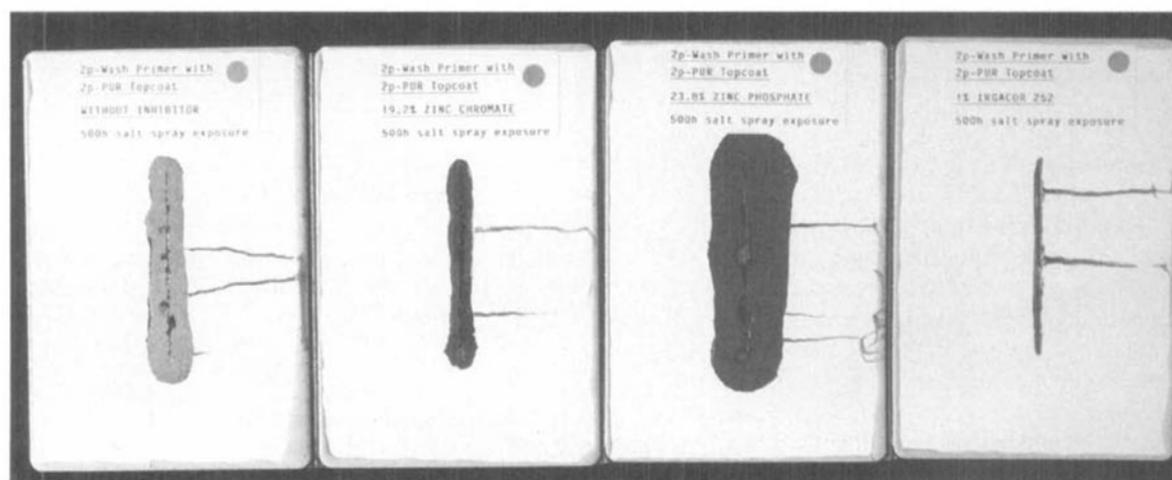


Figure. Results after 500 h salt spray exposure (ASTM B117) in Wash-Primers (with PUR topcoat). From left to right: without inhibitor, 19,2% zinc chromate, 23,8% zinc phosphate, 1% Irgacor 252.

It was found that purely organic compounds, such as (benzothiazol-2-yl)thio-succinic acid (*Irgacor 252*) and its amine salts (*Irgacor 153*) are useful as corrosion inhibitors in solvent-based coatings.

Investigations in a broad variety of resin systems for various applications have proved that this class of products can be used successfully to replace or enhance performance of the normally used anticorrosive pigments [4].

As an example, the *Figure* illustrates the high efficiency of *Irgacor 252* in a Wash-Primer. Wash-Primers are used in various application fields such as for temporary protection or in automotive applications. Replacement of zinc chromate pigments is considered difficult in such systems. Investigations involving *Irgacor 252* have shown that organic inhibitors may help to find a satisfying answer.

All application results indicate that the concept of 'organic corrosion inhibitors for coatings' opens a real chance to formulate environmentally acceptable anticorrosive paints for use in automotive and industrial applications.

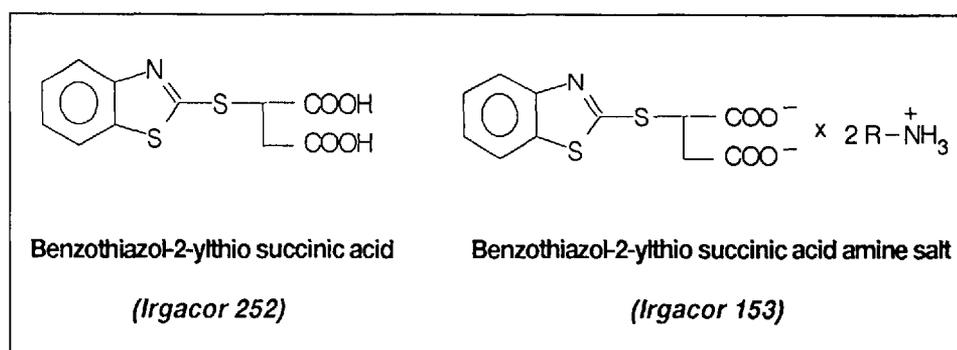
3. Corrosion Inhibitors for Lubricants

No lubricating system can fully exclude oxygen and water; the immediate consequence is oil oxidation and corrosion of metals. Most crude oils used for the refining of lubricants contain natural oxidation inhibitors such as polycyclic aromatics, and sulfur and nitrogen compounds. To a large extent, however, these compounds are removed in the refining process. For this reason, modern refined base stocks have poor stability characteristics. Usually this weakness can be more than offset by the addition of synthetic antioxidants and corrosion inhibitors.

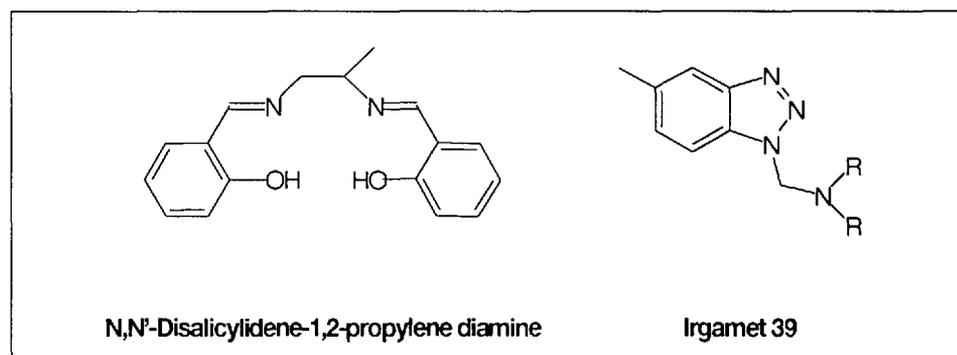
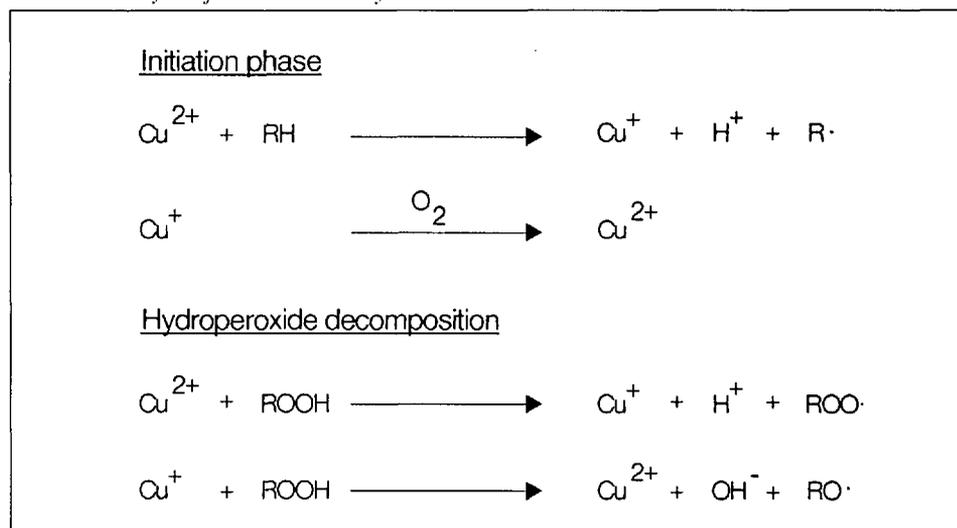
Metal corrosion and oil oxidation are closely related to one another. Acidic oil oxidation products lead to metal corrosion, whereas iron and copper ions in the lubricant considerably accelerate oil oxidation and oil polymerization through radical formation (*Scheme*). For this reason, modern lubricating formulations also include copper deactivators and iron corrosion inhibitors.

3.1. Copper Deactivators

Chelating agents react with copper ions already dissolved in the oil to form stable complexes. The latter show minimal, if any, catalytic activity in the oxidation process (radical formation, peroxide degradation). The disadvantage of chelating agents



Scheme. Catalysis of Autooxidation by Metals

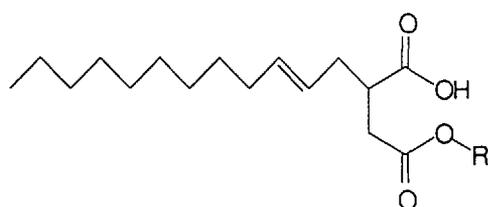


is that they do not eliminate the source of copper-ion formation, the progressive oxidation of the copper surface. An example of a typical chelator is 'disalicylidene-1,2-propylenediamine'.

By forming a passivating protective film on the copper-oxide surface, deactivators prevent both the passage of copper ions into the lubricant and the progressive oxidation of the copper surface by oxygen. An example of this type of copper deactivator is *Irgamet 39*, the Mannich condensation product of toluyl-triazole, formaldehyde, and a secondary aliphatic amine. *Irgamet 39* forms a solid film on the copper surface both with Cu₂O and CuO.

3.2. Iron Corrosion Inhibitors

On iron surfaces, a very thin oxide layer forms as a result of atmospheric oxidation. This layer is porous and can be damaged by mechanical action. In the presence of water, a localized electrochemical system forms between the metal and the oxide layer. The iron (anode) emits ferrous ions into the surrounding medium. This releases electrons, which migrate to the oxide layer (cathode) where they form hydroxide ions with oxygen and water. In the region between anode and cathode, corrosion occurs, since ferrous ions and hydroxide ions are in contact. They combine to ferric(II) hydroxide, which is fur-



Dodecyl succinic acid half ester
(Irgacor L 12)

ther oxidized by oxygen to ferrous(III) hydroxide: rust.

For rust inhibition, preferred compounds are those containing a highly polar group with a long alkyl chain. Structures of this type have a strong affinity for metal surfaces and can form dense hydrophobic protective films.

In addition to the simple fatty acids, the half ester and half amid form of dodecylsuccinic acid (Irgacor L 12) have been widely accepted as rust inhibitors.

4. Conclusions

Today, there is increasing pressure on paint manufacturers to phase out solvents and heavy metals from all types of paint. Accordingly, new corrosion inhibitors are required in order to give water-borne paints the same performance as solvent-based coatings. To fulfill these requirements, a new class of environmentally acceptable corrosion inhibitors for aqueous paint systems is under development.

The demand for lubricants with extreme maximum load and extended life time, as well as increasing legislation and control in the environmental area in recent years, has put pressure on lubricant formulators to considerably improve the quality of their products. This in turn stimulates Ciba's additive research and development efforts to fulfill the needs of their customers.

Received: July 7, 1994

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Chimia 48 (1994) 422-423
© Neue Schweizerische Chemische Gesellschaft
ISSN 0009-4293

Light Stabilizers

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Abstract. Current trends in the light stabilization of polymers and coatings are summarized, with emphasis on UV absorbers and free-radical scavengers.

1. Introduction

Light and oxygen cause photo-oxidative reactions in polymer materials and, as a consequence, a change of their visual aspect and of their physical and mechanical properties. Light stabilizers (photostabilizers, UV stabilizers) are additives which retard or prevent such detrimental processes [1][2]. Their technical and economical significance is impressive, since they do not only improve the quality of

most polymer products, but also contribute to new applications and technologies. Depending on the inherent light stability of the substrate to be stabilized and its application, light stabilizers are applied in concentrations between 0.05 and 2%. The light stabilizers are selected from the following classes:

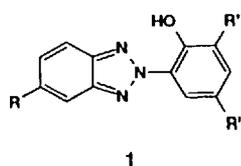
- UV absorbers and light screeners
- free-radical scavengers
- hydroperoxide decomposers
- quenchers

Light-stabilizer research at Ciba in Marly contributes to provide new solutions to industry problems by synthesizing novel photostabilizers, and by investigating theoretical and practical aspects of photodegradation and photostabilization of polymer materials under different conditions. Running projects are summarized below.

2. Synthesis and Characterization of Novel UV Absorbers

The most commonly used UV absorbers are 2-(2-hydroxyphenyl)-1,2,3-benzotriazoles (HBT) 1.

A wide range of commercial HBT is available. Collaboration with the University of Stuttgart (Prof. H.E.A. Kramer) has recently broadened theoretical insight into protection mechanisms of HBT [3]. The absorption of an UV photon leads to a singlet excited state undergoing an intramolecular proton transfer which is of fundamental importance. Internal vibrations



R = H, CH₃, Cl

R', R'' = (un)substituted alkyl

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