



Evaluation of inhibitor efficiency on corrosion of the aluminium heart exchangers and radiators in central heating

Dungall Laouali¹, François Bénérière²

¹ Université Abdou Moumouni, Faculté des Sciences, BP 10662, Niamey, Niger

² Laboratoire de Science des Matériaux (UA CNRS 804) – Université de Rennes-Beaulieu, F-35042 Rennes, France.

Received in 28 Sept 2011, Revised 19 Oct 2011, Accepted 19 Oct 2011.

Correspondence to: Dungall LAOUALI: laoualid@yahoo.fr

Abstract

Introduction of high technology in the central heating industry has been accompanied with new corrosion problem in connection with the modern concepts such as the condensation and with the choice of materials such as aluminium for the heart exchangers (boilers and radiators) and polymers (heating floors). We describe the new corrosion inhibitor specifically designed to protect the central heating circuits in those more demanding conditions, particularly when aluminium is present. The mode of action against electrochemical corrosion, pitting corrosion, flow-induced corrosion, acid corrosion, alkaline corrosion and oxygen permeation are demonstrated from a complete set of experimental results/electrochemical measurements, gravimetric tests and XPS surface analysis. The depletion of the organic and inorganic components has also been followed in 100 real installations treated to follow the behavior as a function of time.

Key words: corrosion, inhibitor, immunity, passivation.

1. Introduction

Aluminium is more and more used in the central heating industry for the fabrication of heart exchangers of gas boilers as well as radiators because of the exceptional thermal conductivity ($238 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) close to that of copper (390) and much better than stainless steel (14). This property, together with the low specific mass ($2.7 \text{ g}\cdot\text{cm}^{-3}$) is giving growing applications of aluminium in areas traditionally confined to ferrous alloys: automobile engines, central heating, etc. However, this metal is at the same time an electronegative element and a soft material ready to be corroded. Whereas the corrosion of the iron has given rise to countless studies, that of aluminium is far less understood in the condition of the central heating : use of corrosive (tap) water, elevated temperatures and intense temperature gradients, hydrodynamic fast flow and combination of many other metals (e.g. copper) and materials (e.g. plastic tubing for heating floors and heating walls). Corrosion may occur under all its possible forms: electrochemical, chemical, localized, flow induced, etc.

Most of the commercial corrosion inhibitors which were mainly intended to protect the ferrous systems failed to give an effective protection of the parts made of aluminium. The specific corrosion inhibitor (INIBAL) has been developed with the main purpose of protecting the aluminium alloys used in the central heating systems in combination with other metals. The same failures had been observed with some commercial antifreezes which used to damage aluminium boilers and aluminium radiators. The antifreezes (INIBAGEL and SANIBAGEL) were then formulated in order to combine the inhibiting properties of the inhibitor INIBAL with standard glycols.

We present in this paper a strategy to evaluate their protective effect on aluminium as well as on the other metals based on complementary experimental techniques : electrochemical measurements (polarisation curves, corrosion current, corrosion potential, polarisation resistance), gravimetric tests and surface microanalysis. We have also followed the kinetics of depletion by measuring the water composition in a number of installations treated with INIBAL and INIBAGEL from atomic absorption and high resolution NMR analysis.

2. Experimental

1.2. Composition

The present corrosion inhibitor is specifically designed to protect the central heating installations with aluminium parts. Therefore the new formulation had to fulfill the following conditions :

- Perfect protection of aluminium, particularly the heat exchangers in the condensing gas boilers, even in the most severe circumstance : a) connection of aluminium to less electropositive metals such as copper, iron, lead, tin; b) introduction of oxygen through joints, pumps, expansion vessels, plastic tubing of heating floors and c) corrosive waters from all types of water supply.
- Good protection against corrosion of other metallic parts: steel, cast iron, copper, brass, solder,...
- Good protection of the polymer parts: polymers and elastomers.
- Low toxicity, in order to be legally added to the domestic central heating circuits also producing sanitary hot water.

The basic principles of INIBAL are:

- a mixture of triazole molecules: benzotriazole, tolyltriazole and derivatives. These are all well known to be the most powerful inhibitors of copper and brass [1 – 5]. INIBAL guarantees a perfect protection of the copper and copper alloys which are practically present in all the systems of central heating. In addition, these molecules make the copper ions disappear from the water of the circuit under the form of very insoluble precipitates. This action is very beneficial also for the protection of aluminium which too easily gives pitting corrosion in presence of copper ions or other metallic ions. This indirect efficient prevention of benzotriazole on aluminium itself is of crucial importance. We have also studied the adsorption of benzotriazole on aluminium in the present work because it had been investigated [6 – 11] with controversial results.

- sodium molybdate: The molybdate ion is an anodic corrosion inhibitor greatly used for iron [12] but also for aluminium [13 – 15]. The efficiency of molybdate is reinforced by the presence of oxygen or an oxidizing agent. Some oxygen may penetrate into most installations through the plastic tubes (heating floors). However, every oxygen trace may disappear from waterproof installations because of the scavenging effect of iron. Then some NO_3^- ions may be added at a small concentration. The molybdate ion is more and more used in central heating instead of chromate, outlawed for ecological grounds in many countries. On the contrary, the toxicity of molybdate is very low [16]. Moutarlier et al. [17–20b] tried to incorporate inhibitors of corrosion at the time of the anodisation of the aluminum alloy in sulphuric media. Satisfactory results have been obtained at the time of the anodisation in presence of the molybdate ion.

- Sodium nitrate : Through its progressive release of oxygen, the nitrate ion is a good corrosion inhibitor of aluminium [21] which relies on a tight oxide film for protection [22]. It also plays a role on the protection of iron in combination of the molybdate ion. Nitrate addition, to for instance FeCl_3 solution, is a known example of pitting corrosion inhibition on mild steel [23].

- Surfactant: A soft surfactant is used at low concentration. Clean metallic surfaces free from fat sediments, grease and other debris improve the thermal efficiency of the installation. The same transfer of heat can be

obtained with lower temperatures of the circulating water. Therefore, clean surfaces decrease the danger of corrosion through erosion-cavitation. Clean surfaces also prevent the boiler noises which are associated to the implosion of steam bubbles formed on the overheated points of the heat exchanger.

- pH buffer : The pH of the tap water varies in a wide range with the origin of the water supply. Also, the pH of the antifreeze coolants tend to decrease because of the irreversible oxidation tendency of the water soluble liquid alcohol freezing point depressants (ethylene glycol, monopropylene glycol, triethylene glycol). Therefore the pH of the circulating water has to be maintained in the passivation range of the metals. Unfortunately, the respective passivation ranges of iron and aluminium do not overlap. The commercial products originally formulated for the protection of the ferrous metals impose a very high pH value of about 10 or even more due to a very alkaline buffer (like silicate or tetraborate). This indeed falls in the passivation range of iron on the Pourbaix diagramme, but at the same time in the region of intense alkaline corrosion of aluminium where Al_2O_3 is dissolved.

In the same way, whereas the organic amines [24] and particularly the fatty aliphatic amines, polyamines [25] and alcohol-amines [26] are good to prevent the pitting corrosion of steel, they may be dangerous for aluminium. Finally, we have chosen a buffer which gives a neutral solution ($6 < \text{pH} < 7.5$) in order to privilege the protection of aluminium against the chemical corrosion.

2. 2. *Electrochemical measurements*

We have used the standard cell which the working electrode is a specimen with 1 cm^2 extracted from a heat exchanger of a reknown commercial aluminium boiler, after a careful polishing and cleaning. The counter electrode is a platinum foil while the reference is a saturated calomel electrode. The polarization curves of the current density as a function of the applied voltage are measured at the speed rate of $1 \text{ mV}\cdot\text{s}^{-1}$. This is for aluminium a compromise; slow enough to be close to the stationary regime and sufficiently fast to allow a limited change of the composition and of the surface of the working electrode. The ohmic drop voltage between the working and reference electrodes is taken into account. The polarization curves are recorded as i and $\text{Ln}(i)$ -vs- E from the negative towards the positive E in the range $-2500 \text{ mV} < E < 2000 \text{ mV}$.

The measurements have been carried out for a number of inhibitors and at different water compositions as a function of the concentration, temperature and aeration.

2. 3. *Gravimetric Test ASTM-1384 [27]*

This test originally devoted to specify antifreeze coolants for automobile radiators is a screening test to evaluate the inhibitor efficiency against uniform corrosion. It is however of limited interest in case of pitting corrosion, which may dramatically destroy central heating systems without being detected by this test. It must therefore be kept in mind that the gravimetric tests should be considered only in combination with the electrochemical measurements and surface microanalyses.

2. 4. *Electron Spectroscopy for Chemical analysis (ESCA)[28-29]*

The ESCA (or XPS) technique is now widely used to investigate the chemical composition of the outer surface for all types of solids. The method is particularly adapted to identify the inhibiting mechanisms of the film-forming cathodic, anodic or mixed corrosion inhibitors [30]. It shows the nature and quality of the film over a thickness of a few hundreds of Angströms precisely where the efficiency must be verified. In addition, the method also gives the oxidation states as well as the nature of the chemical bonding of the oxygen atoms. This is extremely well suited to the specific problem of aluminium, whose protection is based on the formation of an oxide film which may take different forms (bayerite, boehmitte,...) according to the temperature, metallurgic state of aluminium and composition of water.

We have used the X-ray source of magnesium $K\alpha$ (1253.6 eV) of our instrument to produce the primary beam. The electrons emitted are focalized by a system of three transmission electrostatic lenses and they are analysed versus their energy by a retarding potential discriminator of semi-spherical symmetry. The amplification power of the detector (Channeltron) is 10^8 .

Our instrument is also equipped with a scanning ion beam (Ar^+). The diameter of the beam is $300 \mu\text{m}$ and it is possible to scan a surface of 1 cm^2 . We have used this facility to investigate the composition of the film

formed at the surface of aluminium samples as a function of the deepness by steadily sputtering the material with the argon beam.

The surface analysis as a function of the depth gives the topological nature of the passivating film which has developed from the metal. The method also allows to make the distinction between the components physically adsorbed at the surface and those really embedded inside the coating layer.

2. 5. Practical experimentations

The efficiency and modes of action of the inhibitors have been evaluated not only with the standard laboratory tests but also after the results of real utilization, which can hardly be simulated in the laboratory because of the complexity of the central heating systems.

The experimentation has been made on a sampling of one hundred systems situated in small buildings all equipped with a gas condensing boiler (GEMINOX MZ22) and 4 to 8 steel radiators. The circuits had been filled with the tap water added at the concentration of 1% of the inhibitor INIBAL. The physic-chemical properties and the chemical composition of the circulating water have been accurately analysed at regular intervals in order to measure the depletion of the individual components. This was also useful to determine the practical life time of the inhibitor.

2. 6. Concentration of the Corrosion Inhibitor

One currently observes in real circumstances large positive or negative departures from the nominal inhibitor concentration even at the beginning of the treatment. Moreover after some time, almost unavoidable readjustments of the nominal pressure of the circulating water lead to introduce additional water and, subsequently, to dilute the corrosion inhibitor. It is therefore essential that a safe inhibitor does not provoke any risk of enhanced corrosion in case of large overtitration or undertitration. This risk exists with some otherwise good inhibitors. As an example, sodium benzoate is known as a good inhibitor for iron and it's has been extensively studied. However, it has been shown that at any given pH, benzoate only inhibits the corrosion of iron over an intermediate concentration range, too low or too high a concentration leading to corrosion [30]. All such potentially dangerous inhibitors have been turned aside in the formulation of INIBAL because in the central heating circuits the concentration is very difficult to control, much more than in a vehicle where the volume is much smaller.

3. Results and Discussion

3.1. Electrochemical measurements

The same tap water stored in a large tank has been used throughout this section. This water supplied by the city of Rennes is a soft tap water typically available in France. Its composition is given in Table I.

Table I. Composition of tap water supplied by the city of Rennes in France.

Standard tap water	maximum acceptable concentration
Cl 42 mg.l ⁻¹	-
Sulfate 20 mg.l ⁻¹	250 mg.l ⁻¹
Ca 37 mg.l ⁻¹	-
Na 9 mg.l ⁻¹	150 mg.l ⁻¹
Si 5 mg.l ⁻¹	-
Nitrate 33 mg.l ⁻¹	50 mg.l ⁻¹
P 50 µg.l ⁻¹	-
Cu 15 µg.l ⁻¹	1 µg.l ⁻¹
Fe < 5 µg.l ⁻¹	0.2 µg.l ⁻¹

In electrochemical reactions when the overvoltage is large enough, the total current density can be assumed to be either entirely cathodic or entirely anodic according to the respective ranges. Tafel law can then be applied and the corrosion potential as well as the corrosion current can be easily determined by the extrapolated Tafel straight line [31]. The experimental results do not obey Tafel law at all in the anodic regime. The representation is better in the cathodic regime. For the sake of comparing the inhibiting properties with numerical data, we have given the corrosion voltage and current by extrapolation of a pseudo-Tafel straight line in the cathodic part.

As for the polarization resistance, we have adopted the same empirical definition already used in the case of steel corrosion [32]. This parameter r_p is a measurement of the difficulty at which uniform corrosion will develop. The higher r_p is the lower risk of uniform corrosion. This resistance is determined from the polarization curve :

$$r_p = \Delta E / i$$

by choosing the voltage difference between the anodic and the cathodic branches for the given current density $i = 10^{-4} \text{ A.cm}^{-2}$.

The polarization curves of Al 6060 with respectively 0, 1 and 1.5% INIBAL are studied. The corrosion potential is shifted significantly by approximately 400 mV towards the more positive potentials. The corrosion current density is decreased and the polarization resistance is increased with the inhibitor. These data are given in Table II. In addition to these evidences, the effectiveness of the inhibitor can even more clearly be seen by the extended width of the passivation range.

Table II. Potential, current and resistance of corrosion of aluminium in some aqueous solutions at T = 293K

Nature of solution	Corrosion potential (mV)	Corrosion current ($\mu\text{A.cm}^{-2}$)	Polarisation resistance ($\Omega.\text{cm}^2$)
Plan water	-1250	10	6 100
1% inibal	-950	4.7	9 150
2% inibal	-900	3.2	13 600
20% inibagel	-950	3.4	14 400
30% inibagel	-850	2.1	14 400
Non-deaerated plan water	-1250	10	6 000
1g.l ⁻¹ NaNO ₃ (deaerated)	-1250	3.2	15 000
1g.l ⁻¹ NaNO ₃	-1250	3.4	14 600

The polarization curves have been measured separately with each of the individual components of the inhibitor, in order to identify the action mode of the complete formulation on the electrochemical corrosion. Little effect is observed with the organic inhibitors like benzotriazole, tolyltriazole, etc... The shift of the corrosion potential can be attributed to molybdate and nitrate whereas the spectacular broadening of the passivation range is mainly due to nitrate.

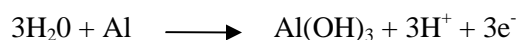
The overall same curve is observed as might have been expected on the electrochemical behavior of SANIBAGEL, which combines the antifreeze properties of monopropylene glycol to the inhibiting properties of INIBAL. The main difference is a further increase of the passivation range owing to an increase of the electrical resistance of the aluminium oxide layer.

3.1.1. Influence of dissolved oxygen

The presence of dissolved oxygen in the circulating water is a subject of controversy. In a system with metallic turbings, no leak and no outside expansion vessel, the air introduced at the first filling should be expected to disappear after a short period due to the decreased solubility of oxygen in hot water and also to the scavenging effect of the metallic parts, particularly with steel radiators and cast iron boilers. However,

one often observes in practice a number of possible sources of possible sources of continuous injection of oxygen: pump seal not perfectly airproof, expansion vessels with open surface or through the plastic tubings used in the heating floors [32].

We have checked the influence of dissolved oxygen by comparing the behavior of aluminium in water saturated with air at 293 K and in deaerated water, respectively. The deaeration was obtained through a preliminary treatment of the aqueous solution by bubbling of purified argon. The polarization curves are so close that one can conclude that aluminium is not sensitive on the presence of oxygen in the circulating water. The oxide film formed in water originates from the transformation of the hydroxide formed at the early stage from the reaction between aluminium and water :



The same comparison has been carried out in water added with a number of inhibitors.

Moreover, the polarization curves with NaNO_3 at the concentration of 1g.l^{-1} are found to coincide so closely that one can conclude to the absence of effect of dissolved oxygen in the presence of ions possessing oxidizing properties. More quantitatively, the experimental corrosion potential, current and polarization resistance given in Table III are confirming that aluminium is not sensitive to the presence of a small quantity of dissolved oxygen, as far as the electrochemical corrosion is concerned.

Table III. Allowable maxima (ASTM D-3306).

Metal	mg/sample	$\mu\text{g}/\text{cm}^2$
Copper	10	350
Solder	30	1 000
Brass	10	350
Steel	10	350
Cast iron	10	350
Aluminium	30	1 000

3.1.2. Influence of temperature

In the working conditions of a heating system, the temperature is cycled between different regimes. In order to closely simulate the corrosion conditions, the electrochemical tests have also been carried out at 60 and 90°C. We have first studied the influence of temperature with untreated water. The corrosion potential is seen to move towards more cathodic values. However, the opposite trend had been reported in a similar study with synthetic tap water [33]. We cannot explain this difference, though it must be pointed out that the materials tested were different: Al-6060 in the present study whereas Rother and Kuron [33] tested pure Al 99.8 H. More significant is the increase of both the cathodic and anodic currents from 20 to 60°C, which would lead to believe to endoenergetic reactions. However, when the temperature is further increased from 60 to 90°C, the current density remains at almost same value. In the former investigation of the temperature effect between 25 and 90°C, the current density was also found maximum at 70°C [33]. It is therefore interesting to note the further decrease of the electrochemical corrosion with temperature.

The influence of temperature with 2%, we can observe the displacement of the corrosion potential towards more noble values. Considering that the action of the inhibitor at 20°C consists in a shift of 400 mV towards noble potentials, the combined effects of temperature and corrosion inhibitor is a total noble shift of almost 1 000 mV. VUKASOVICH and SULLIVAN [34] had already measured that the separate addition of nitrate shifted the pitting potential nobly about 500 mV at the concentration of 2 g/l of ethylene-glycol at room temperature. Unfortunately, the situation is less favorable for the corrosion current which increases with temperature. The enhancement is maximum at 60°C. The comparison with the influence of temperature on

the corrosion of Al-6060 in water without inhibitor shows however that the inhibitor continues to give a satisfactory protection at high temperature in reducing both the cathodic and anodic currents.

3. 2. Gravimetric test ASTM-1384

We have measured the mass losses (in $\mu\text{g}\cdot\text{cm}^{-2}$) of the following metals and alloys: Cu, Brass (Cu: 63%, Zn: 37%, Solder (Pb: 67%, Sn: 33%), Cast iron, Steel, Aluminium after immersion for 14 days at the temperature of 88°C without aeration. The standard samples of Cu, brass and solder are electrically connected as are the steel, cast iron and aluminium samples. This arrangement follows the requirements of the test, originally designed for the antifreeze formulations used in the automobile industry (the temperature of 88°C being the nominal temperature at which the thermostat has to open up in the vehicle cooling system). The cleaning of the samples prior to the experiment as well as the removal of the corrosion products after the experiment strictly followed the NACE standard instructions TM – 10- 69. The allowable maximum for each metal is recalled on Table III as the loss per sample and per unit area.

A few results selected from a number of systematic measurements are given on Table IV as the mass losses in $\mu\text{g}\cdot\text{cm}^{-2}$. The numbers accompanied by a star indicate a mass gain in the few cases where strongly adherent corrosion products remained on the metals even after the cleaning and etching procedure. When the losses exceed 750 $\mu\text{g}\cdot\text{cm}^{-2}$, the mass loss is reported on top of the interrupted bars.

3.2.1. Influence of benzotriazole and tolyltriazole (derivatives)

The dispute about the effect of the triazoles on the metals other than copper was recalled in the introduction. The conditions of the multimetal system (e.g. steel radiators, aluminium boiler, copper pipes) are simulated by the simultaneous presence in the metals of the ASTM test. We have studied the influence of benzotriazole (500 $\text{mg}\cdot\text{l}^{-1}$) and tolyltriazole (500 $\text{mg}\cdot\text{l}^{-1}$) in aqueous solution of monoethylene glycol (33%). Triazoles decrease the weight losses not only of the copper alloys but also of all the metals (Table IV).

Table IV. Influence of benzotriazole and tolyltriazole (mass loss in $\mu\text{g}\cdot\text{cm}^{-2}$)

Metal	tap water	benzotriazole + ethylene glycol	tolyltriazole + ethylene glycol
Copper	106	45	68
Solder	811	242	470
Brass	98	38	15*
Steel	848	45	23
Cast iron	879	598	242
Aluminium	227	53	45

When copper is present in a system, an oxide film is formed at the surface. The copper oxide is slightly soluble in water and therefore, some copper ions appear in the circulating water. Those ions tend to deposit at some points of the other metals where they act as very efficient microcathodes. The results of Table IV clearly demonstrate the strong inhibition of aluminium, steel, solder and cast iron that is given by the triazoles when copper or copper alloys are present owing to the prevention of galvanostatic couples. The benzotriazole and derivatives have good protective effect on copper [35]. Casenave and coll [36] studied the inhibition of the aluminum corrosion in presence of benzotriazole (BTA). The polarization curves shows that the BTA is a very good cathodic inhibitor. According to these authors, the BTA is more efficient on the alloy of aluminum than on the pure aluminum. Zheludkevich and coll. [37b] confirmed the results of Casenave and coll. [36].

3.2.2. Influence of the glycol

The protection against corrosion of the aluminium heat exchangers used in the gas condensing boilers led to develop the inhibitor INIBAL and the inhibited antifreeze agents INIBAGEL and SANIBAGEL; one had to decide which same components should be used in addition to the glycol. The action of mono-ethylene glycol alone is represented on Table V compared with the results for a solution of 1% INIBAL and 33% INIBAGEL. The pH falls down from 7 to 4.4 after the test while the stabilized at 7.7 with INIBAL and 7.3 with INIBAGEL. The electrical conductivity also does not vary around a fixed value of 10^{-3} S.cm⁻¹. Both solutions maintain the weight losses below the allowable limits when one except the moderate exceeding loss of the cast iron. The Al-6060 test-pieces show an excellent protection against corrosion provided by the inhibitor as well as by the inhibited antifreeze. The samples are darkened by a passivating layer which is not removed by the nitric acid attack and a mass gain of a few milligrammes is consistently found. The chemical composition of the layer has been determined through the XPS analyses described in the next section.

3. 2. 3. Influence of the dicarboxylic acids

The results for two long chain dicarboxylic acids, namely adipic acid (HOOC (CH₂)₄ COOH) and sebacic (HOOC (CH₂)₈ COOH) are given on Table VI.

Table V. Influence of the glycol (mass loss in $\mu\text{g.cm}^{-2}$)

Metal	1% INIBAL	33% INIBAGEL	33% Ethylene glycol
Copper	114	23*	136
Solder	583	674	871
Brass	76	61	159
Steel	159	114	962
Cast iron	924	235	909
Aluminium	189	242	53

Table VI. Influence of the dicarboxylic acids (mass loss in $\mu\text{g.cm}^{-2}$)

Metal	2% INIBAL	1% INIBAL + adipic acid	1% INIBAL + sebacic acid
Copper	76	15	8
Solder	98*	288*	182*
Brass	23	76	45
Steel	68	76	61
Cast iron	773	727	705
Aluminium	273	674	606

These compounds like all the fatty acids have reported inhibiting properties [38, 39] particularly against the corrosion of aluminium [40]. An amount of 500 mg of adipic acid exactly neutralized with NaOH (270 mg) and of 680 mg of sebacic acid, also neutralized, have respectively been added in one liter of 1% INIBAL aqueous solutions. There is a small but marked beneficial effect on copper and solder. However, no improvement on the cast iron is observed unlike in a previous study [38] where disodium sebacate was mixed with benzotriazole. The aluminium mass loss is rather increased. We conclude that the ASTM-1384 test does not prove a significant improvement in the protection of a multimetal system given by the long chain dicarboxylic acids in the conditions of our basic formulation.

3.2.4. Influence of sodium benzoate

Sodium benzoate is one of the most used and at the same time most criticized inhibitor [30]. Table VII shows the mass losses in aqueous solutions at 1% INIBAL with and without a further addition of ammonium benzoate (4g.l^{-1}) or sodium benzoate (4g.l^{-1}). The graph also shows a comparative study of deionized and tap waters. The positive action of benzoate is clearly demonstrated, particularly on solder and cast iron. This well known inhibiting effect of benzoate is therefore confirmed, at least when the concentration and the pH are falling within a given range. However, it is also known that benzoate can present an adverse effect when the concentration becomes either beyond or below that range [30].

3.2.5. Influence of the counter-ion

Many inorganic inhibitors owe their properties to an inhibiting anion. The choice of the counter-cation is a compromise of several factors: behavior towards corrosion, solubility of the salt and cost. We have compared the mostly used cations, namely Na^+ and NH_4^+ . The results with benzoate are given in Table VII. No marked difference is observed. Na^+ has no reported influence towards corrosion of aluminium and its alloys in aqueous solution [41]. Sodium silicate and sodium borate are used extensively to protect metals including aluminium against corrosion. The NH_4^+ ion has no direct action either. However, some ammonium salts develop an acid hydrolysis, which can become detrimental when the buffering power is lost.

3. 3. XPS Surface analyses

In recent years, surface analytical instrumentation (XPS, AES, Rutherford Backscattering...) has been used to provide data which have proved essential in understanding the corrosion inhibition mechanisms. The systems which have been studied with those modern techniques and subsequently elucidated have recently been reviewed [42]. In the present work, we have used XPS and Auger Electron Spectroscopy to analyse the layer formed at the surface of the Al-6060 heat exchangers at the atomic level. The samples ($2\text{ cm} \times 1\text{ cm}$) are analysed after immersion for 14 days at 88°C (heat treatment of ASTM-D1384 test) after careful rinsing. Blank experiments have been carried out in deionized water and in the standard tap water. The XPS spectrums obtained are shown in Figure 1(a, b).

Table VII. Influence of benzoate (mass loss in $\mu\text{g.cm}^{-2}$)

Metal	Tap water + 1% INIBAL	Deionized water + 1% INIBAL	Deionized water + 1% INIBAL + ammonium benzoate	Deionized water + 1% INIBAL + sodium benzoate
Copper	106	76	61	68
Solder	530	780	53	38
Brass	76	68	45	45
Steel	152	227	152	91
Cast iron	917	871	644	706
Aluminium	189	38	30*	38*

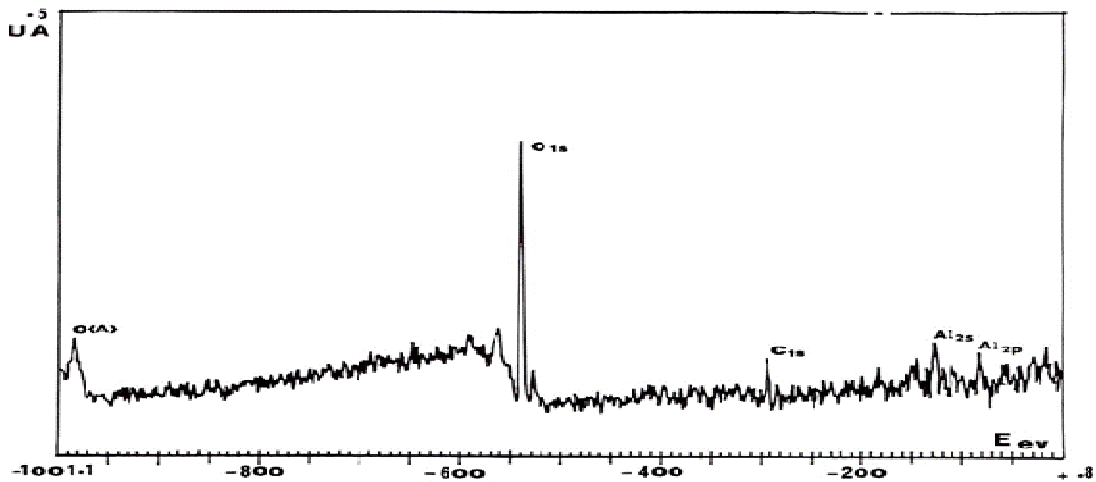


Figure 1(a). XPS spectrum of Al-6060 in deionized water.

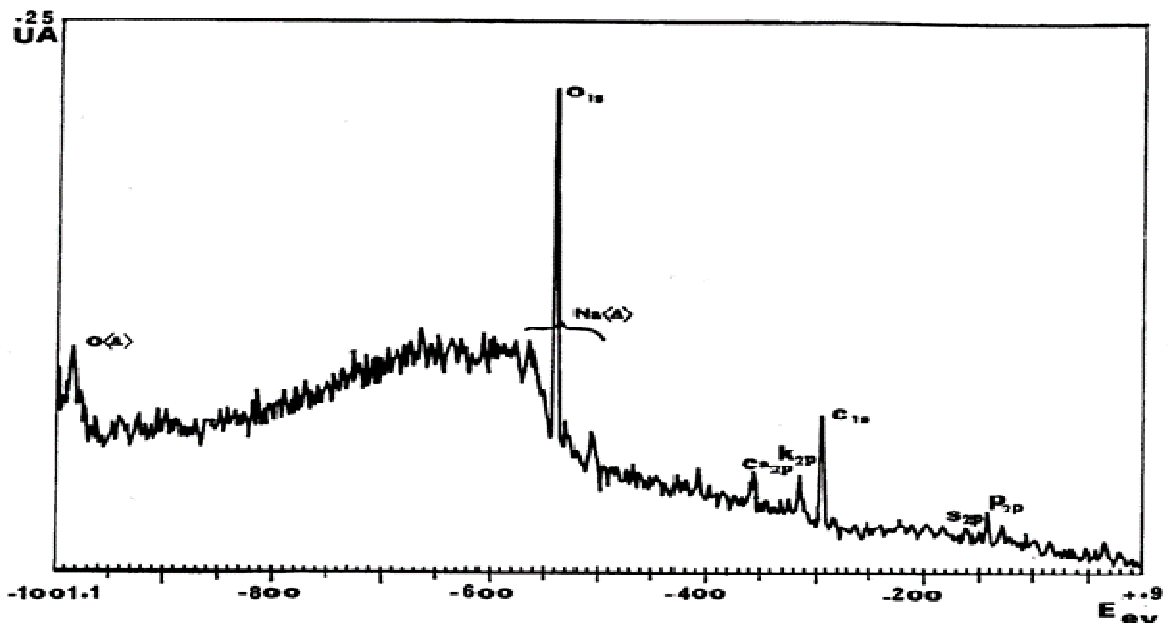


Figure 1(b). XPS spectrum of Al-6060 in tap water.

One notices the characteristic peaks of Oxygen, Calcium, Carbon, Phosphorus, Sulfur and Sodium. Simultaneously, the aluminium peak (prominent in deionized water) has practically vanished. The hyperfine structure of the peaks allows to conclude that the aluminium surface submitted to untreated tap water is covered by a layer of a minimum thickness of 15   formed by a mixture of pollutants (calcium, sodium, carbonate, phosphate, sulfate) present in water.

Particular attention has been paid to the role of benzotriazole, benzoate and molybdate on the formation of the passivating layer. A solution of Na_2MoO_4 in deionized water leads to Al, Mo and O peaks. Owing to the energy difference of the oxygen bonding which can be detected by XPS, the method separates the oxygens bound to Al in the Al oxide from those bound to Mo in MoO_4^{2-} . The coating layer contains only 4% Mo atoms, which shows that the absorption of molybdate is weak by itself in deionized water Figure 2(a). On the contrary, Figure 2b shows that when aluminium is submitted to Na_2MoO_4 dissolved in the standard tap

water, strong peaks of Mo and Ca appear at the expense of the Al peak. The numerical treatment of the peaks gives 11% Ca atoms and 18% Mo atoms.

The crystallographic examination of the CaMoO_4 layer reveals a rather amorphous state. The solubility limit being very small and the precipitation rate very fast, no crystalline structure can grow. The layer is therefore uniform throughout the system, which is an advantage over other film forming agents like phosphate, carbonate, sulfate and silicate. The later precipitates in localized points, forming crystalline seeds which then become bigger and bigger with the well-known adverse secondary effects. Even in the central heating systems which are in principle close circuits, the total amount of Ca^{2+} ions cannot be neglected. Almost inevitable further additions of fresh water let those crystalline deposits to again build up.

The detailed structure of the oxygen peak is given in Figure 3. A single peak is observed in water with no molybdate. When molybdate is used with deionized water, one observes a complex structure with aluminium and a small peak due to molybdate. When molybdate is added to tap water (containing $36 \text{ mg.l}^{-1} \text{ Ca}^{2+}$), one observes the major peak of molybdate with another structure for alumina.

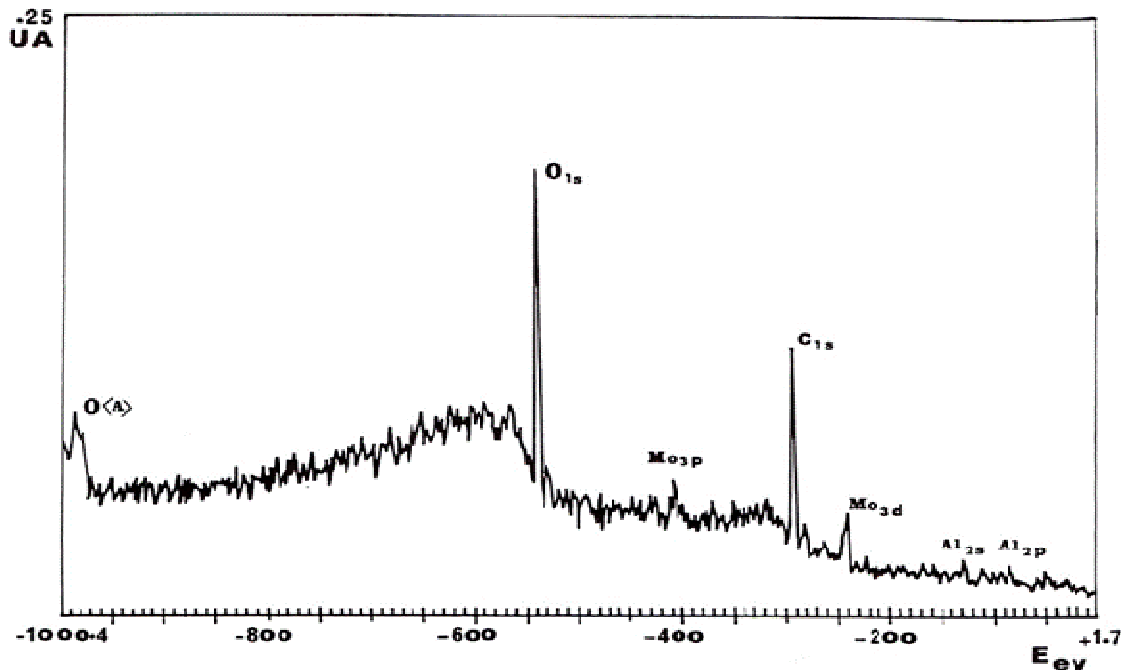


Figure 2(a). XPS spectrum of Al-6060 in a solution of Na_2MoO_4 in deionized water.

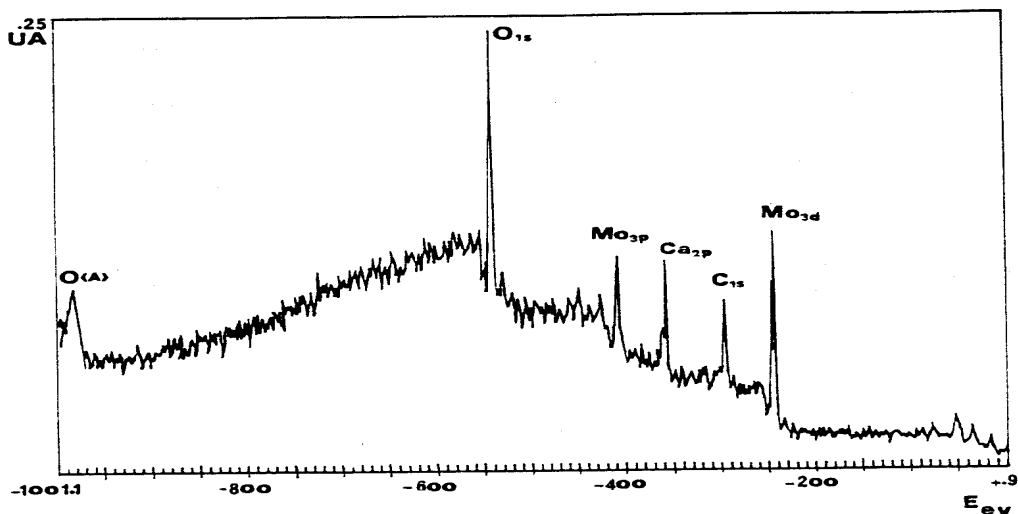


Figure 2(b). XPS spectrum of Al-6060 in a solution of Na_2MoO_4 in tap water.

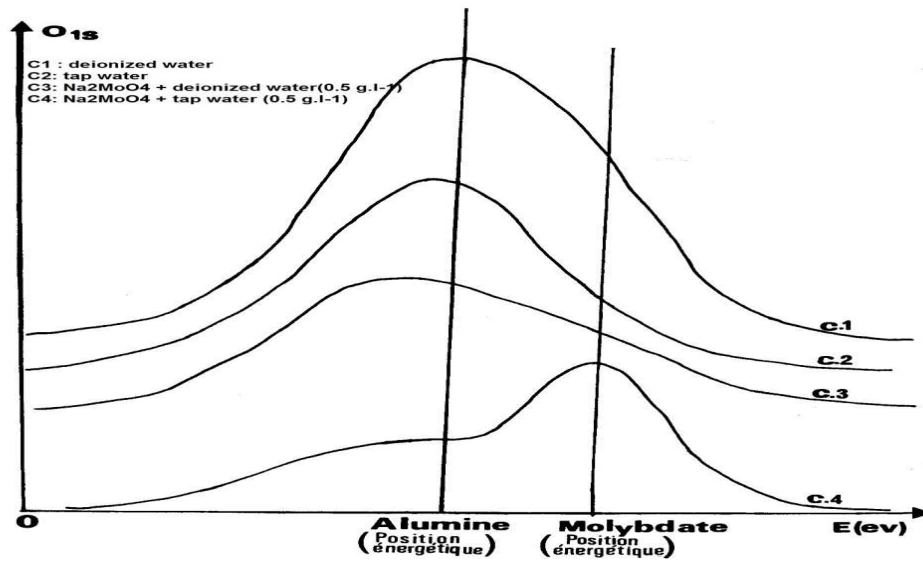


Figure 3. Detailed XPS peak of oxygen on Al-6060.

Absence of aluminium peaks shows that the molybdate ion does not give a chemically protective film on the aluminium surfaces. One obtains rather a physic-sorbed coating of CaMoO_4 which forms with Ca^{2+} ions of the tap water.

The chemical composition of the exchanger surface with the complete formulation of INIBAL at the concentration of 1% is given in Figure 4. One notices the simultaneous presence of Al and Mo. The depth analysis allowed with the argon sputtering shows that the Mo atoms are embedded inside a tight film of aluminium oxide which passivates the metal surface. The detailed analysis of the carbon peak (Figure 5) shows two contributions :

- carbon bonded to nitrogen atoms (originating from the tolyltriazole derivative)
- aliphatic or aromatic carbon probably due to an accidental contribution of the glassware grease.

A layer of 80 Å has been removed by sputtering in order to separate the polluting agents. The C peak comes down to 27 atom %, the O and the Al peaks strongly increase by the same proportion to reach respectively 53 and 19 atom %. Mo (0.3%) are still present while a tiny peak of Mg is emerging.

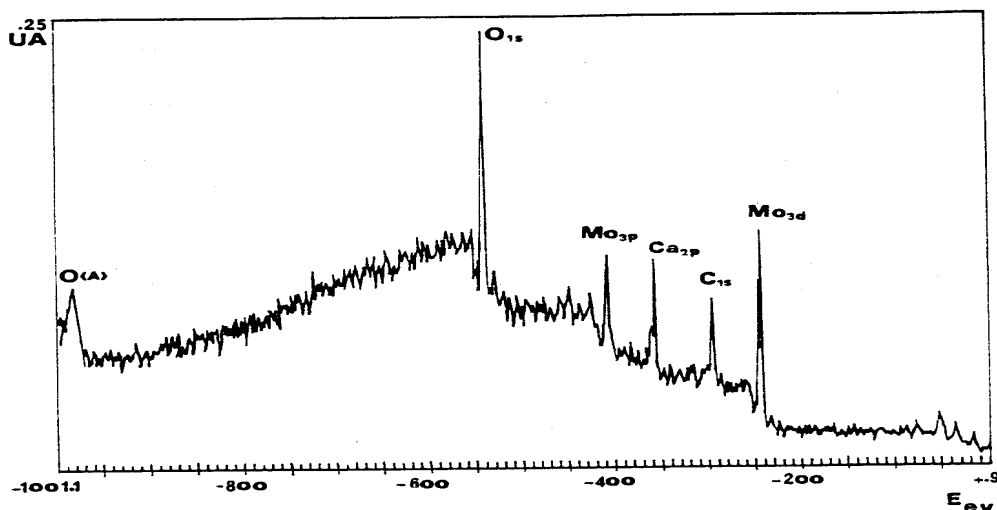


Figure 4. XPS spectrum of Al-6060 in a solution of 1% INIBAL in tap water

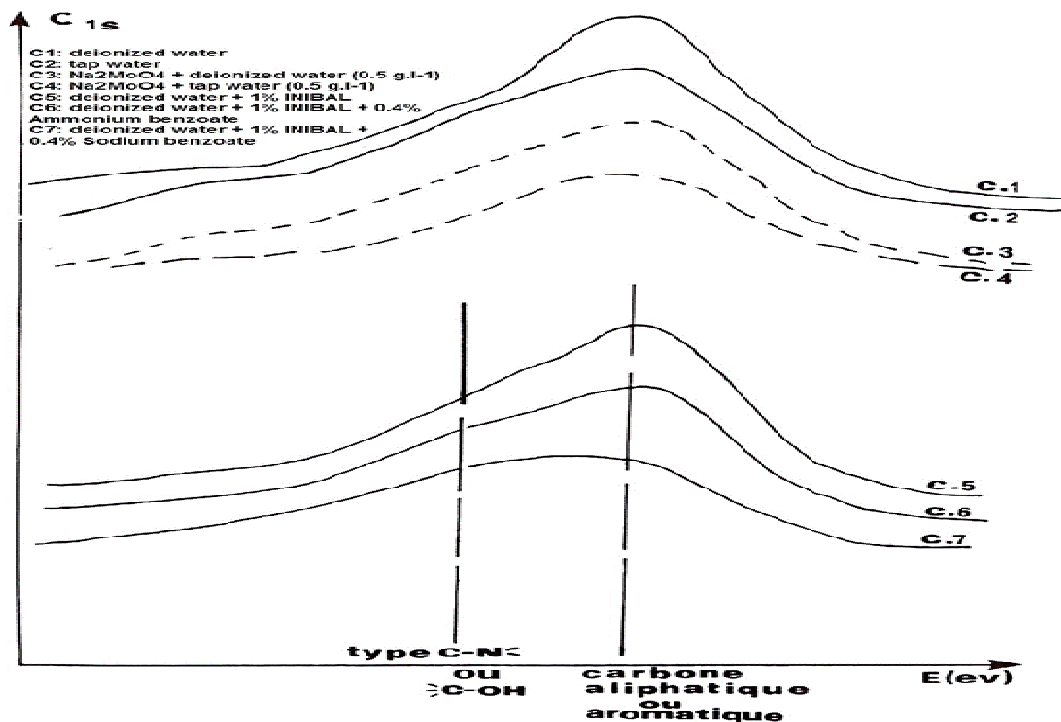


Figure 5. Detailed XPS peak of carbon on Al-6060. in seven experiences

One can conclude that the visible coating layer on the aluminium surface results from the passivating power of the inhibitor. It is a strongly adherent film formed in presence of nitrate and reinforced by the triazole and molybdate compounds.

3.4. Practical experimentations and inhibitor life time

A sample of the circulating water is regularly extracted from the sampling of 100 experimental houses heated with a gas condensing boiler GEMINOX treated with 1% INIBAL. In addition to the pH and electrical conductivity which are found very stable, one measures the concentration of the metallic ions (Aluminium, Copper, Iron) as well as the concentration of individual components of the inhibitor. An increasing concentration of metals, particularly Al, in the circulating water might be expected as a warning sign of failure. On the results measured after 12 months of normal utilization, one can note that some aluminium appears almost immediately in the treated water at a concentration which soon stabilizes around an average value of 0.6 mg.l^{-1} . Any value which would exceed 2 mg.l^{-1} would then indicate some alarming corrosion.

The measurements of the concentrations of the separate components of the inhibitor have proved to be extremely useful. The principle of this measure was to do the quantitative analysis of the monopropylene glycol and the benzotriazole by high resolution (300 MHz) NMR using acetone as internal calibration. This measure is effected quantitatively while adding in the withdrawals a known quantity of acetone while measuring the peaks integrated of the monopropylene glycol and the acetone on the spectrgrams obtained by the Nuclear Magnetic Resonance (Figure 6). A high accuracy is obtained even at a concentration of some ppm as seen in Figure 7. This confirms the XPS studies revealing the powerful adsorption of the triazoles

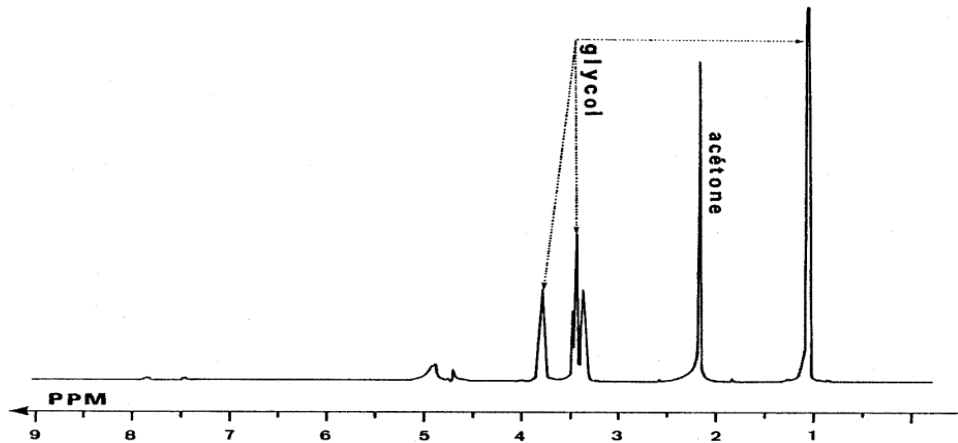


Figure 6. Measure of the concentration in inhibitor by high resolution NMR.

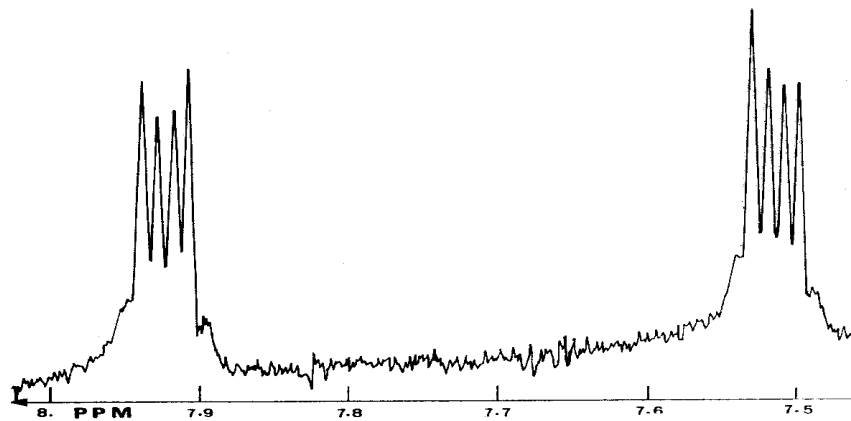


Figure 7. NMR spectrum of benzotriazole.

The conclusion of this field survey is that one must not underestimate the depletion of the corrosion inhibitors. This may become critical in the modern systems where the ratio of the water volume to the total metallic surface increases with the development of more and more efficient boilers and radiators and the subsequent tube diameter reduction.

A central heating system offers all the possible causes of corrosion : chemical corrosion due to permeation of oxygen, acid or alkaline corrosion in given concentration and pH ranges, electrochemical corrosion due to mixture of metals of different electrochemical potentials, bacterian corrosion (with anaerobic bacteria such as desulphovibrio) and cavitation erosion-corrosion. The common use is to take the tap water to fill the circuit. The tap water is submitted to a huge scatter in the concentration of Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , NO_3^- and other impurities, even inside the French territory. These very difference entail an increased complexity of the corrosion problems. In addition, the highly technological boilers and systems of the last generation also lead to enhanced possible corrosion: the thickness of the metallic walls of the heat exchangers has been thinned down, new materials like aluminium and plastic tubing are more and more involved, the speed of the circulating water has been increased with systematic use of pumps, the diameter of the pipes is reduced, as is the total volume of the circulating water.

The subsequent increased danger of corrosion has entailed an increasing demand of corrosion inhibitors. However, the existence of so many different commercial formulations shows that the ideal universal corrosion inhibitor protecting all metals from all sources of corrosion in all circumstances is still to be discovered. A major difficulty lies in the choice of the tests to evaluate the inhibiting power of any formulation. We have preferred to compromise the results obtained from independent testing methods: gravimetric, electrochemical, surface analysis and a field study.

Conclusion

The corrosion inhibitor INIBAL and inhibited antifreeze liquids INIBAGEL and SANIBAGEL have been formulated after different methods of testing. The first priority has been given to protection of the aluminium alloys used in central heating systems against electrochemical, chemical and flow-induced corrosion. Cavitation damage is caused by combined mechanical and chemical effects. It can provoke catastrophic failures. Therefore action against erosion-corrosion is essential. It is also a delicate problem as some components which are very efficient in some solutions can present catastrophic adverse effects in presence of other components like in the example of the combination phosphate + molybdate [34].

The second most important point is a required low toxicity in agreement with the French legislation for the single exchange central heating.

The next priority has been given to the protection of steel. The gravimetric tests as well as the electrochemical measurements (not reported here) show this to be reasonably well achieved, mainly due to anodic inhibiting properties.

In the meanwhile, copper and copper alloys are given an excellent protection. Through this was not the first goal, the strong protection of copper and brass can be considered as a valuable by-product. The only test about the behavior of the solder is the gravimetric one, which also shows a very positive action.

Last, the results with and without inhibitor also show a significant protection of cast iron as compared with untreated tap water, despite the slight departure from the ASTM-1384 allowable mass loss.

References

1. Proctor and Gamble Ltd., *Brit. Pat.* 652 (1947) 339.
2. Walker, R., *Corrosion*, 29 (1973) 290.
3. Cerisola, G., De Anna, P.L., Bassolli, M., Bonara, P.L. and Lorenzelli, V., *5th Eur. Symp. Corros. Inhibitors*, 4 (1980) 1011.
4. Brunoro, G., Trabanelli, G., Zucchi, F. and Monticelli, C., *Metall. Ital.*, 77 (1985) 691.
5. Bénérière, F. and Laouali, D., *7th European Symposium on Corrosion Inhibitors* (1990) 535.
6. Khedr, M.G.A. and Lashien, A.M.S., *J. Electrochem. Soc.*, 136 (1989) 968.
7. Prajati, S.N., Bhatt, I.M. and Soni, K.P., *Indian J. Technol.*, 14 (1976) 52.
8. Maeda, A., *Japan Pat.*, *J.P.* 52/29441 (1977).
9. Tanimoto, F., Kitano, H. and Aizawa, Y., *Japan Pat.*, *JP* 52/3537 (1977).
10. Minkin, V.V. and Balazin, S.A. *Khim. Neft. Mashinostr.*, 1, 26 (1978), and *Zashch. Met.*, 100 (1979).
11. Chiyoda, . K.K., *Japan Pat.* 57/152476 (1982).
12. Farr, J.P.G. and Saremi, M., *Surface Technology*, 19 (1983) 137.
13. Lamprey, H., *U.S. Pat.* 2,147 (1939) 409.
14. Roebuck, A.H. and Pritchett, T.R., *Corrosion Inhibitors for Aluminium*, *Mat. Pro.*, 5 (1966) 16.
15. Laouali, D. et Bénérière, F., *J. Soc. Ouest-Afr. Chim.* 014, (2002) 89-113.
16. Federal Hazardous Substances act, as amended, 16 CFR 1500.3 Subsection (c) (II) *U.S. Government Printing Office, Washington D.C.* (1974).
17. Moutarlier, V., Gigandet, M. P. Ricq, L. et Pagetti, J. : Electrochemical characterisation of anodic oxidation films formed in presence of corrosion inhibitors. *Applied Surface Science*, 183(1-2) (2001) 1–9.
18. Moutarlier, V., Gigandet, M. P., Pagetti, J. et Ricq, L. : Molybdate/sulfuric acid anodising of 2024-aluminium alloy : Influence of inhibitor concentration on film growth and on corrosion resistance, *Surf. Coat. Tech.*, 173(1) (2003) 87–95.
19. Moutarlier, V., Gigandet, M. P., Pagetti, J. et Normand, B. : Influence of oxalic acid addition to chromic acid on the anodising of Al 2024 alloy. *Surf. Coat. Tech.*, 182(1), (2004) 117–123.

- 20a. Moutarlier, V., Gigandet, M., Normand, B., Pagetti, J. : EIS characterisation of anodic films formed on 2024 aluminium alloy, in sulphuric acid containing molybdate or permanganate species. *Corros. Sci.*, 47 (2005) 937.
- 20b. Moutarlier, V., Gigandet, M., Pagetti, J. et Linget, S. : Influence of molybdate species added to sulphuric acid on composition and morphology of the anodic layers formed on 2024 aluminium alloy. *Thin Solid Films*, 483(2005) 197–204.
21. Bayers, A.I., *U.S. Pat.* 2, 153 (1939) 952.
22. Hatch, G.B., “Inhibition of cooling Water”, in “Corrosion Inhibitors”, *National Association of Corrosion Engineers, Nathan Ed., Houston (U.S.A.)* (1973).
23. Uhlig, H.H., Gilman, J., *Corrosion*, 20, (1964) 289.
24. Abd El Haleem, S.M., Killa, H.M., 5th *Europ. Symp, on Corrosion Inhibitors*, (1980) 725.
25. Duprat, M., Dabosi, F. Moran, F. and Rocher, S., 5th *Europ. Symp, on Corrosion Inhibitors*, (1980) 689.
26. Duprat, M., Dabosi, F., 5th *Europ. Symp, on Corrosion Inhibitors*, (1980) 675.
27. "Standard method for corrosion test for engine antifreezes", ASTM Designation : D 1384- 70, *The American Society for testing and Materials* (1959).
28. Laouali, D., *Thèse d'Université de Rennes 1*, (1989) p.120.
29. Haman, M., Pellerin, F., Guernet, M., Mahuzier, G., "*Méthodes spectrales et Analyse organique*" *Chimie analytique* (1997) p. 868.
30. Turgoose, S., 6th *Europ. Symp, on Corrosion Inhibitors*, 1041 (1985).
31. Lattes, A. De Savignac, A., Dupin, P., *Materials Chemistry* 6 (1981) 443.
32. Kruse, C. L., Neubert, M., *Sanitär-Heizungs-Technik* (1988) 5.
33. Rother, H.J., Kuron, D., 5th *Europ. Symp, on Corrosion Inhibitors*, (1980) 989.
34. Vukasovich, M.S., Sullivan, F.J., *National Association of Corrosion Engineers*, (1983) 25.
35. Zhang, D., Gao, L., Zhou, G., Inhibition of copper corrosion in aerated hydrochloric acid solution by heterocyclic compounds containing a mercapto group. *Corros. Sci.*, 46 (2004) 3031.
36. Casenave, C., Pebere, N., Dabosi, F. : An electrochemical impedance study of the corrosion inhibition of a 2024 aluminum alloy in neutral chloride solutions. *Materials Science Forum*, 192-194 (1995) 599–610.
- 37b. Zheludkevich, M., Yasakau, K., Poznyak, S., Ferreira, M. : Triazole and thiazole derivatives as corrosion inhibitors for AA2024 aluminium alloy. *Corros. Sci.*, 47(12) (2005) 3368–3383.
38. Pemberton, R.C., Mercer, A.D., Wright, E.J., Thomas, J.G.N., 6th *Europ. Symp. On Corrosion Inhibitors*, (1985) 1241.
39. Butler, G., Mercer, A.D., *Br. Corros. J.*, 12 (1977) 171.
40. Elna Co., *Jpn Kokai Tokkyo Koho J.P.* 58 (1984) 223-308.
41. Vargel, C., Le comportement de l'aluminium et de ses alliages“, *DUNOD ed, Paris* (1979).
42. Sastri, V.S., Packwood, R.H., Moore, V.E., Bednar, J., 6th *Europ. Symp. On Corrosion Inhibitors*, (1985) 741.

(2012) www.jmaterenvirosci.com