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(71) Demandeur/Applicant:
COMMONWEALTH SCIENTIFIC AND INDUSTRIAL
RESEARCH ORGANISATION, AU
(72) Inventeurs/Inventors:
WHITE, PAUL A., AU;
COLE, IVAN S., AU
(74) Agent: BERESKIN & PARR LLP/S.E.N.C.R.L.,S.R.L.

(54) Titre : PROCÉDES ANTICORROSION
(54) Title: METHODS FOR INHIBITING CORROSION

(57) **Abrégé/Abstract:**

The present disclosure is directed to the methods for identifying a combined corrosion inhibitor formulation comprising at least a first and second corrosion inhibitor formulation for inhibiting corrosion in various substrates, for example in metal substrates. The present disclosure is also directed to compositions for inhibiting corrosion comprising a combined corrosion inhibitor formulation each independently selected from organic heterocyclic compounds and metal salts, metal anions, metal complexes, or any combinations thereof selected from rare earth, alkali earth and transition metals.

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(71) Applicant: **COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION**
[AU/AU]; Clunies Ross St, Acton, Australian Capital Territory 2601 (AU).

(72) Inventors: **WHITE, Paul A**; C/- CSIRO, Clunies Ross St, Acton, Australian Capital Territory 2601 (AU). **COLE, Ivan S**; C/- CSIRO, Clunies Ross St, Acton, Australian Capital Territory 2601 (AU).

(74) Agent: **FB RICE PTY LTD**; Level 14, 90 Collins St, Melbourne, Victoria 3000 (AU).

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(54) Title: METHODS FOR INHIBITING CORROSION

(57) Abstract: The present disclosure is directed to the methods for identifying a combined corrosion inhibitor formulation comprising at least a first and second corrosion inhibitor formulation for inhibiting corrosion in various substrates, for example in metal substrates. The present disclosure is also directed to compositions for inhibiting corrosion comprising a combined corrosion inhibitor formulation each independently selected from organic heterocyclic compounds and metal salts, metal anions, metal complexes, or any combinations thereof selected from rare earth, alkali earth and transition metals.

WO 2018/064721 A1

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METHODS FOR INHIBITING CORROSION**Field**

The present disclosure relates to methods for identifying a combined corrosion inhibitor formulation comprising at least a first and second corrosion inhibitor formulation for inhibiting corrosion in various substrates, for example in metal substrates. The present disclosure also relates to compositions for inhibiting corrosion comprising a combined corrosion inhibitor formulation each independently selected from organic heterocyclic compounds and metal salts, metal anions, metal complexes, or any combinations thereof selected from rare earth, alkali earth and transition metals.

Background

Protection of substrates, such as metal substrates, against atmospheric corrosion presents a difficult challenge and has significant economic importance. A range of metal substrates requiring protection from corrosion typically include steel, magnesium metals, copper, brass, bronze, zinc metals and alloys used for protective coatings. The range of fields and applications of particular interest include organic coatings, flow systems, coolant systems, air-conditioning systems, shipping, marine, oil and gas, water and waste water treatment plants, pipelines and other applications where metal protection is required.

Corrosion inhibitors are substances that when added in small concentrations to specific environmental conditions have the ability to reduce the corrosion rate of metal exposed to that environment. Corrosion inhibitors can be classified based on the chemical nature of the substance, for example organic or inorganic inhibitors; or by their mechanism of action, for example anodic inhibitors, cathodic inhibitors or mixed inhibitors. As the name suggests, anodic inhibitors cause a large anodic shift of the corrosion potential resulting in metal passivation, while the cathodic inhibitors act by slowing down the cathodic reaction or precipitate on the cathodic sites to limit the diffusion of the reducing species. Mixed inhibitors, in most cases are film forming compounds, which reduce both the anodic and cathodic reactions.

Some examples of anodic inhibitors include chromates, nitrates, molybdates. Examples of cathodic inhibitors include sulphite and bisulphite ions. Examples of

5 mixed inhibitors include silicates and phosphates.

Pigment grade corrosion inhibitors used in organic primers are well known to require anionic species with inhibitor activity that have limited, but effective, solubility in water. For these reasons, chromate based corrosion inhibitor species have been preferred in both corrosion control technologies applied on steel for protection against atmospheric corrosion, for example provided in conversion coatings and high performance organic primers. The hexavalent chromate ion has proven to be an excellent corrosion inhibitor for many metals and alloy systems for almost a decade. However, the toxic and carcinogenic nature of the chromate ion has been understood for some time and there has been extensive research for almost 30 years for finding environmentally acceptable replacements.

It is generally known that if toxicity, efficiency, and price are considered, the number of inorganic corrosion inhibitor species available for chromate replacement is limited essentially to a few anionic species, including molybdates, phosphates, borates, silicates and cyanamides. As a consequence, all commercial non-chromate corrosion inhibitor pigments are molybdates, phosphates, borates, silicates or cyanamides, or combinations of these compounds. In comparison to chromates, inherent limitations of their corrosion preventing mechanism render the anionic species less effective inhibitors of corrosion, in general, and specifically of atmospheric corrosion of aluminium. Consequently, it appears that inorganic chemistry is unable to produce inhibitors of atmospheric corrosion, which could be comparably effective, non-toxic alternative of the hexavalent chromate.

In contrast, a large array of organic corrosion inhibitors have been more recently known and applied in various corrosion control technologies. Excessive solubility in water and/or volatility of most of the known organic inhibitors are limitations when used in conversion coating technologies and in organic coatings.

Considerable progress has been made with identifying alternative corrosion inhibitors and the salts of transition metal and rare earth metals offer possible alternatives for many applications, including deoxidising and pickling solutions, etchants, anodizing and conversion coatings, primer paints and sealants. Alkali metal salts of carboxylic acids such as cinnamates have also been found to effectively inhibit

5 the corrosion of mild steel.

Following the work of Mercer *et al* who demonstrated that the alkali metal salts of carboxylic acids such as cinnamates effectively inhibited the corrosion of mild steel, Forsyth *et al* (2002) hypothesised that the combination of the rare earth metal ions with an effective organic inhibitor could provide new compounds that suppress both anodic
10 and cathodic reactions (i.e. a mixed inhibitor), with a degree of synergy that would lead to vastly improved corrosion protection. This was confirmed by Behrouzvaziri *et al.*(2008) and Blin *et al.*(2007) who showed with electrochemical studies that lanthanum 4 hydroxy cinnamate provided excellent inhibition of corrosion in chloride solutions.

15 WO 2013/083293 describes a range of polymer coatings for steels substrates that act as the corrosion inhibitors and reduce the formation of blisters and filiform corrosion.

Organic compounds with aromatic character such as carbocyclic and heterocyclic aromatic structures have also been found to be effective inhibitors of
20 corrosion of steel and its alloys, and for example, can be provided with metal salts or in the form of a metal complex. For example, Blin *et al* (2004) relates to corrosion rate measurements based on weight loss experiments and linear polarization resistance techniques for evaluating the corrosion inhibiting complexes comprising a rare earth-based organic complex formed from a rare earth metal and an organic compound for
25 the corrosion protection of mild steel.

Several techniques can be used to evaluate the performance of corrosion inhibitors (V. S. Sastri, 2011). Some of these techniques include mass loss measurements, salt-spray (fog) test, electrochemical impedance spectroscopy, potentiodynamic polarisation and polarisation resistance. Many of these techniques are
30 either destructive, cannot be monitored as a function of time and do not provide tangible and easy to interpret results, whereas, the polarisation resistance technique is a non-destructive method that can determine very low corrosion rates accurately, quickly, and monitored as a function of time.

Most of the known alternative chromate based corrosion inhibitors suffer from
35 various problems including poor corrosion inhibiting activity or incompatibility with

5 various coating compositions.

There is a need for identifying alternative corrosion inhibitor compositions for the protection of substrates, for example on metal substrates such as steel, which are chromate-free corrosion inhibitor compositions.

Summary

10 Research was undertaken to identify new combined corrosion inhibitor formulations for protecting various substrates, such as metal substrates, from corrosion. It was identified that particular combinations of at least a first and a second corrosion inhibitor formulations could be used as improved corrosion inhibitor compositions. It was surprisingly found that a combination of at least a first and second corrosion
15 inhibitor formulation were advantageously useful as combined corrosion inhibitor formulations for inhibiting corrosion on a substrate that could also be further advantageously categorised as providing a polarisation value that was greater than the sum of the polarisation values for each of the individual corrosion inhibitors. Further advantages were identified from combined corrosion inhibitor formulation comprising
20 at least two corrosion inhibitors selected from metal salts, metal anions, metal complexes, or any combinations thereof, as promoting corrosion protection of various substrates. Advantageously, the combined corrosion inhibitor formulations comprising at least three corrosion inhibitors were found to further increase the corrosion protection of various substrates. The research also identified that combined corrosion
25 inhibitor formulations comprising at least four corrosion inhibitors increased the corrosion protection of various substrates even further.

In one aspect, there is provided a method of identifying a combined corrosion inhibitor formulation for inhibiting corrosion of a metal substrate, wherein the combined corrosion inhibitor formulation comprises at least a first corrosion inhibitor
30 formulation comprising at least one corrosion inhibitor and a second corrosion inhibitor formulation comprising at least one corrosion inhibitor that is different to a corrosion inhibitor in the first corrosion inhibitor formulation, the method comprising the steps of:

5 independently applying each of the first and second corrosion inhibitor formulations to the substrate and determining a polarisation resistance value for each of the first and second corrosion inhibitor formulations;

combining the first and second corrosion inhibitor formulations together to provide the combined corrosion inhibitor formulation;

10 applying the combined corrosion inhibitor formulation to the substrate and determining a polarisation resistance value for the combined corrosion inhibitor formulation, wherein, when said polarisation value for the combined corrosion inhibitor formulation is greater than the sum of the polarisation values for each of the first and second corrosion inhibitor formulation, said combined corrosion inhibitor formulation
15 is categorised as positive.

In an embodiment, there is provided a method of identifying a combined corrosion inhibitor formulation for inhibiting corrosion of a metal substrate, wherein the combined corrosion inhibitor formulation comprises at least a first corrosion inhibitor formulation comprising at least one corrosion inhibitor and a second corrosion
20 inhibitor formulation comprising at least one corrosion inhibitor that is different to a corrosion inhibitor in the first corrosion inhibitor formulation, the method comprising the steps of:

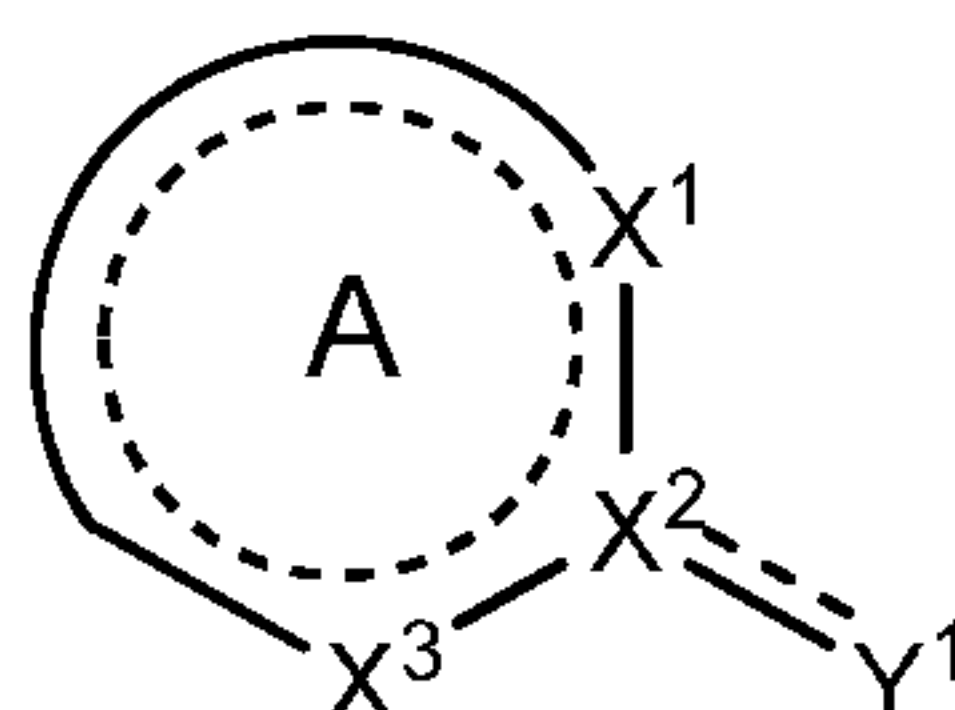
independently applying each of the first and second corrosion inhibitor formulations to the substrate and determining a polarisation resistance value for each of
25 the first and second corrosion inhibitor formulations;

combining the first and second corrosion inhibitor formulations together to provide the combined corrosion inhibitor formulation;

applying the combined corrosion inhibitor formulation to the substrate and determining a polarisation resistance value for the combined corrosion inhibitor
30 formulation, wherein, when said polarisation value for the combined corrosion inhibitor formulation is greater than the sum of the polarisation values for each of the first and second corrosion inhibitor formulation, said combined corrosion inhibitor formulation is categorised as positive;

wherein the corrosion inhibitors are each independently selected from the group
35 consisting of:

- 5 a metal salt, metal anion, metal complex, or any combination thereof, wherein the metal is selected from the group consisting of Zn, La, Pr, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Co, Cu, Y, Ca, Sr, Ba, Sc, Mo, V, W and Zr; and
 an organic heterocyclic compound according to Formula 1:



10

Formula 1

wherein

- A is a 5- or 6-membered aryl, heteroaryl or heterocyclic ring, which is optionally substituted with one or more substituents and optionally fused with one or more aryl or heteroaryl rings, wherein a dotted line represents one or more optional
 15 double bonds;

Y^1 is selected from S, SH, NH_2 or is absent, wherein the dotted line represents a double bond when Y^1 is S or is absent when Y^1 is SH or NH_2 ;

X^1 , X^2 , and X^3 are selected from N, NR^5 , O, S, CR^6 and CR^7R^8 ,

- R^5 is selected from hydrogen, amino, C_1 - C_{10} alkyl, C_2 - C_{10} alkenyl, C_2 - C_{10} alkynyl, aryl and heteroaryl, in which each amino, alkyl, alkenyl, alkynyl, aryl or heteroaryl
 20 group may be optionally substituted, and

- R^6 , R^7 and R^8 , are each independently selected from hydrogen, halogen, carboxyl, sulphide, thiol, amino, C_1 - C_{10} alkyl, C_2 - C_{10} alkenyl, C_2 - C_{10} alkynyl, aryl and heteroaryl, in which each amino, alkyl, alkenyl, alkynyl, aryl or heteroaryl group may
 25 be optionally substituted; and

wherein the combined corrosion inhibitor formulation comprises at least two corrosion inhibitors selected from metal salts, metal anions, metal complexes, or any combinations thereof.

- The method of identifying a combined corrosion inhibitor formulation for
 30 inhibiting corrosion of a metal substrate, wherein the combined corrosion inhibitor formulation comprises: (i) at least two metal salts and at least one organic heterocyclic compound of Formula 1 or (ii) at least one metal salt, at least one metal anion and at

- 5 least one organic heterocyclic compound of Formula 1 or (iii) at least two metal complexes, or (iv) at least one metal complex and at least one metal anion.

When the method of identifying the combined corrosion inhibitor formulation is according to (i), the at least two metal salts are selected from the group consisting of Pr^{3+} , Gd^{3+} , Ce^{3+} , Dy^{3+} , Sm^{3+} , Er^{3+} , Lu^{3+} , Zn^{2+} , Co^{2+} , Cu^{2+} , and the at least one organic
 10 heterocyclic compound of formula 1 is selected from the group consisting of 3-amino-1,2,4-triazole, benzimidazole, 1H-benzotriazole, 5-amino-2-mercapto-1,3,4-thiadiazole, 9H-purine-8-thiol, 1,2,4-triazole, 1,2,4-triazole-3-thiol, and 5-methyl-2-mercapto-1,3,4-thiadiazole.

When the method of identifying the combined corrosion inhibitor formulation is according to (ii), the at least one metal salt is selected from the group consisting of Pr^{3+} , Gd^{3+} , Ce^{3+} , Dy^{3+} , Sm^{3+} , Er^{3+} , Lu^{3+} , Zn^{2+} , Co^{2+} , Cu^{2+} , the at least one metal anion is selected from the group consisting of MoO_4^{2-} , VO_4^{3-} , ZrO_4^{2-} , WO_4^{2-} , and the at least one organic heterocyclic compound of Formula 1 is selected from the group consisting of 3-amino-1,2,4-triazole, benzimidazole, 1H-benzotriazole, 5-amino-2-mercapto-
 15 1,3,4-thiadiazole, 9H-purine-8-thiol, 1,2,4-triazole, 1,2,4-triazole-3-thiol, and 5-methyl-2-mercapto-1,3,4-thiadiazole.

When the method of identifying the combined corrosion inhibitor formulation is according to (iii), the at least two metal complexes are selected from the group consisting of zinc molybdate, erbium molybdate, lutetium molybdate, zinc vanadate, zinc benzotriazole, dysprosium benzotriazole, lutetium benzotriazole, gadolinium
 25 benzotriazole, gadolinium molybdate, praseodymium benzimidazole, lutetium benzimidazole, zinc benzimidazole.

When the method of identifying the combined corrosion inhibitor formulation is according to (iv), the at least one metal complex is selected from the group consisting
 30 of zinc molybdate, erbium molybdate, lutetium molybdate, zinc vanadate, zinc benzotriazole, dysprosium benzotriazole, lutetium benzotriazole, gadolinium benzotriazole, gadolinium molybdate, praseodymium benzimidazole, lutetium benzimidazole, zinc benzimidazole, and the at least one metal anion is selected from the group consisting of MoO_4^{2-} , VO_4^{3-} , ZrO_4^{2-} , WO_4^{2-} .

5 The method of identifying a combined corrosion inhibitor formulation for inhibiting corrosion of a metal substrate, wherein the combined corrosion inhibitor formulation may comprise at least four corrosion inhibitors comprising: (v) at least two corrosion inhibitors selected from metal salts and at least two corrosion inhibitors selected from organic heterocyclic compounds of Formula 1; or (vi) at least one metal salt corrosion inhibitor, at least one metal anion corrosion inhibitor, and at least two corrosion inhibitors selected from organic heterocyclic compounds of Formula 1; or (vii) at least three metal salts, metal anions, metal complexes, or any combinations thereof, and at least one corrosion inhibitor selected from an organic heterocyclic compound of Formula 1.

15 When the method of identifying the combined corrosion inhibitor formulation is according to (v) the at least two metal salts are selected from the group consisting of Pr^{3+} , Gd^{3+} , Ce^{3+} , Dy^{3+} , Sm^{3+} , Er^{3+} , Lu^{3+} , Zn^{2+} , Co^{2+} , Cu^{2+} , and the at least two organic heterocyclic compounds of Formula 1 are selected from the group consisting of 3-amino-1,2,4-triazole, benzimidazole, 1H-benzotriazole, 5-amino-2-mercapto-1,3,4-thiadiazole, 9H-purine-8-thiol, 1,2,4-triazole, 1,2,4-triazole-3-thiol, and 5-methyl-2-mercapto-1,3,4-thiadiazole.

25 When the method of identifying the combined corrosion inhibitor formulation is according to (vi) the at least one metal salt selected from the group consisting of Pr^{3+} , Gd^{3+} , Ce^{3+} , Dy^{3+} , Sm^{3+} , Er^{3+} , Lu^{3+} , Zn^{2+} , Co^{2+} , Cu^{2+} , the at least one metal anion selected from the group consisting of MoO_4^{2-} , VO_4^{3-} , ZrO_4^{2-} , WO_4^{2-} , and the at least two organic heterocyclic compounds of Formula 1 selected from the group consisting of 3-amino-1,2,4-triazole, benzimidazole, 1H-benzotriazole, 5-amino-2-mercapto-1,3,4-thiadiazole, 9H-purine-8-thiol, 1,2,4-triazole, 1,2,4-triazole-3-thiol, and 5-methyl-2-mercapto-1,3,4-thiadiazole.

30 When the method of identifying the combined corrosion inhibitor formulation is according to (vii) the at least three corrosion inhibitors are selected from metal salts, metal anions, metal complexes, or any combinations thereof, selected from the group consisting of Pr^{3+} , Gd^{3+} , Ce^{3+} , Dy^{3+} , Sm^{3+} , Er^{3+} , Lu^{3+} , Zn^{2+} , Co^{2+} , Cu^{2+} , MoO_4^{2-} , VO_4^{3-} , ZrO_4^{2-} , WO_4^{2-} , zinc molybdate, lutetium molybdate, zinc benzotriazole, lutetium benzotriazole, gadolinium benzotriazole, gadolinium molybdate, and at least one

5 organic heterocyclic compound of Formula 1 is selected from the group consisting of 3-amino-1,2,4-triazole, benzimidazole, 1H-benzotriazole, 5-amino-2-mercapto-1,3,4-thiadiazole.

The combining of the first and second corrosion inhibitor formulations together to provide the combined corrosion inhibitor formulation may be based on the first
10 corrosion inhibitor formulation providing either an immediate inhibitive response or a delayed inhibitive response and the second corrosion inhibitor formulation providing either an immediate inhibitive response or a delayed inhibitive response.

The combining of the first and second corrosion inhibitor formulations together to provide the combined corrosion inhibitor formulation may be based on the first
15 corrosion inhibitor formulation providing a delayed inhibitive response and the second corrosion inhibitor formulation providing an immediate inhibitive response.

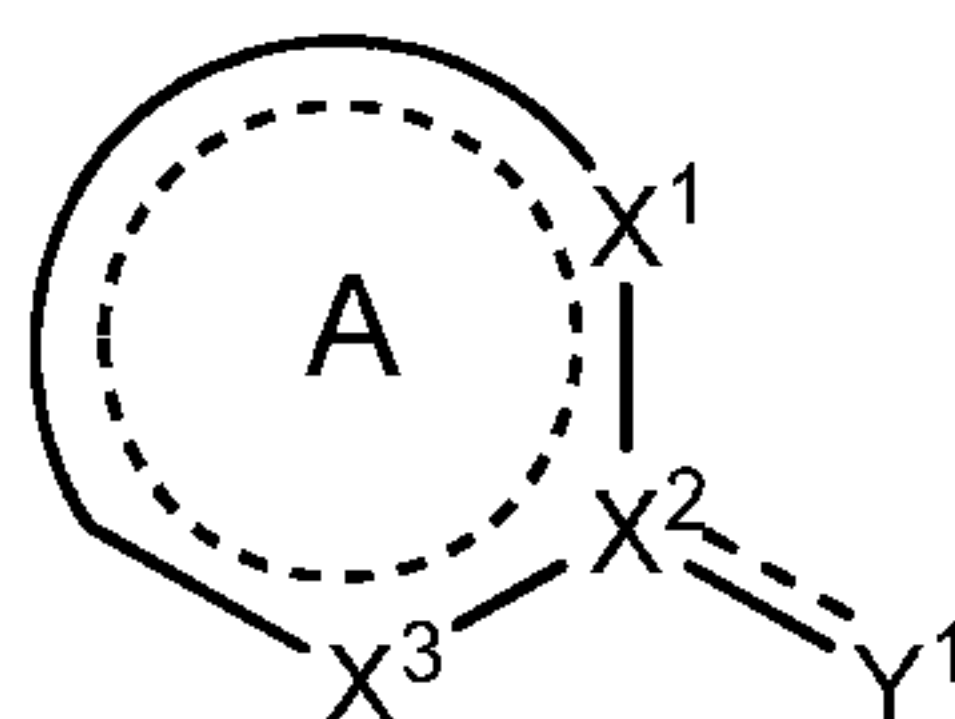
The immediate inhibitive response may be provided by an instantaneous corrosion inhibitor and a delayed inhibitive response may be provided by a film-forming inhibitor.

20 When the first corrosion inhibitor formulation comprises a corrosion inhibitor providing a delayed inhibitive response and the second corrosion inhibitor formulation comprises a corrosion inhibitor providing an immediate inhibitive response, the polarisation response for the combined corrosion inhibitor formulation polarisation resistance response may be a continuous inhibitive response.

25 The corrosion inhibitors may be each independently selected from the group consisting of:

a metal salt, metal anion, metal complex, or any combination thereof, wherein the metal is selected from the group consisting of Zn, La, Pr, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Co, Cu, Y, Ca, Sr, Ba, Sc, Mo, V, W and Zr; and

30 an organic heterocyclic compound according to Formula 1:



Formula 1

wherein

5 A is a 5- or 6-membered aryl, heteroaryl or heterocyclic ring, which is optionally substituted with one or more substituents and optionally fused with one or more aryl or heteroaryl rings, wherein a dotted line represents one or more optional double bonds;

Y^1 is selected from S, SH, NH_2 or is absent, wherein the dotted line represents a
10 double bond when Y^1 is S or is absent when Y^1 is SH or NH_2 ;

X^1 , X^2 , and X^3 are selected from N, NR^5 , O, S, CR^6 and CR^7R^8 ,

R^5 is selected from hydrogen, amino, C_1 - C_{10} alkyl, C_2 - C_{10} alkenyl, C_2 - C_{10} alkynyl, aryl and heteroaryl, in which each amino, alkyl, alkenyl, alkynyl, aryl or heteroaryl group may be optionally substituted, and

15 R^6 , R^7 and R^8 , are each independently selected from hydrogen, halogen, carboxyl, sulphide, thiol, amino, C_1 - C_{10} alkyl, C_2 - C_{10} alkenyl, C_2 - C_{10} alkynyl, aryl and heteroaryl, in which each amino, alkyl, alkenyl, alkynyl, aryl or heteroaryl group may be optionally substituted.

 For the organic heterocyclic compounds of Formula 1, R^6 , R^7 and R^8 , are each
20 independently selected from hydrogen, halogen, carboxyl, amino, C_1 - C_{10} alkyl, C_2 - C_{10} alkenyl, C_2 - C_{10} alkynyl, aryl and heteroaryl, in which each amino, alkyl, alkenyl, alkynyl, aryl or heteroaryl group may be optionally substituted.

 The metals may be selected from at least one of Zn, Mo, Sm, Dy, Tb, Pr, Er, Tm, Lu and Gd.

25 The substrate may be a metal substrate. It will be appreciated that the metal substrate can include any substrate material having at least a portion of its surface being metallic. The metal substrate may comprise any metal requiring protection from corrosion. The metal substrate may be of steel, zinc, magnesium, copper, brass and bronze. The metal substrate may be a steel substrate.

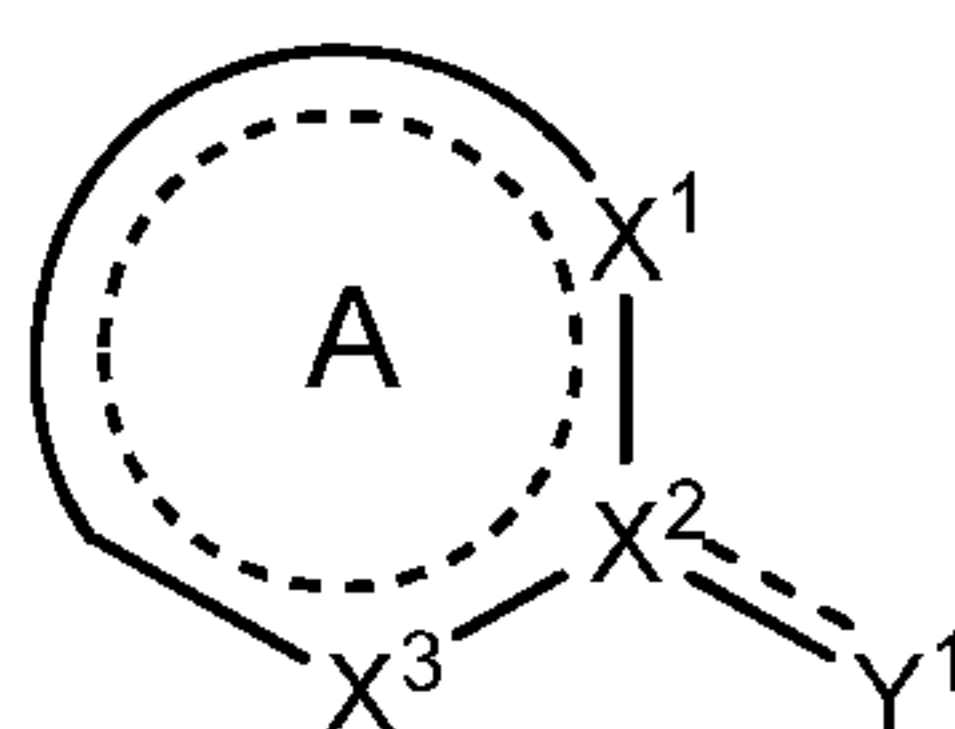
30 In another aspect there is provided a combined corrosion inhibitor formulation prepared according to the method described herein.

 In another aspect there is provided a combined corrosion inhibitor formulation for inhibiting corrosion of a metal substrate, wherein the combined corrosion inhibitor formulation comprises at least a first corrosion inhibitor formulation comprising at least
35 one corrosion inhibitor and a second corrosion inhibitor formulation comprising at least

5 one corrosion inhibitor that is different to a corrosion inhibitor in the first corrosion inhibitor formulation;

wherein the corrosion inhibitors are each independently selected from the group consisting of:

a metal salt, metal anion, metal complex, or any combination thereof, wherein
 10 the metal is selected from the group consisting of Zn, La, Pr, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Co, Cu, Y, Ca, Sr, Ba, Sc, Mo, V, W and Zr; and
 an organic heterocyclic compound according to Formula 1:



Formula 1

15 wherein

A is a 5- or 6-membered aryl, heteroaryl or heterocyclic ring, which is optionally substituted with one or more substituents and optionally fused with one or more aryl or heteroaryl rings, wherein a dotted line represents one or more optional double bonds;

20 Y^1 is selected from S, SH, NH_2 or is absent, wherein the dotted line represents a double bond when Y^1 is S or is absent when Y^1 is SH or NH_2 ;

X^1 , X^2 , and X^3 are selected from N, NR^5 , O, S, CR^6 and CR^7R^8 ,

R^5 is selected from hydrogen, amino, C_1 - C_{10} alkyl, C_2 - C_{10} alkenyl, C_2 - C_{10} alkynyl, aryl and heteroaryl, in which each amino, alkyl, alkenyl, alkynyl, aryl or heteroaryl
 25 group may be optionally substituted, and

R^6 , R^7 and R^8 , are each independently selected from hydrogen, halogen, carboxyl, sulphide, thiol, amino, C_1 - C_{10} alkyl, C_2 - C_{10} alkenyl, C_2 - C_{10} alkynyl, aryl and heteroaryl, in which each amino, alkyl, alkenyl, alkynyl, aryl or heteroaryl group may be optionally substituted; and

30 wherein the combined corrosion inhibitor formulation comprises: (i) at least two metal salts and at least one organic heterocyclic compound of Formula 1 or (ii) at least one metal salt, at least one metal anion and at least one organic heterocyclic compound of Formula 1 or (iii) at least two metal complexes, or (iv) at least one metal complex

- 5 and at least one metal anion; or (v) at least two corrosion inhibitors selected from metal salts and at least two corrosion inhibitors selected from organic heterocyclic compounds of Formula 1; or (vi) at least one metal salt corrosion inhibitor, at least one metal anion corrosion inhibitor, and at least two corrosion inhibitors selected from organic heterocyclic compounds of Formula 1; or (vii) at least three metal salts, metal
10 anions, metal complexes, or any combinations thereof, and at least one corrosion inhibitor selected from an organic heterocyclic compound of Formula 1.

When the combined corrosion inhibitor formulation is according to (i), the at least two metal salts are selected from the group consisting of Pr^{3+} , Gd^{3+} , Ce^{3+} , Dy^{3+} , Sm^{3+} , Er^{3+} , Lu^{3+} , Zn^{2+} , Co^{2+} , Cu^{2+} , and the at least one organic heterocyclic compound
15 of formula 1 is selected from the group consisting of 3-amino-1,2,4-triazole, benzimidazole, 1H-benzotriazole, 5-amino-2-mercapto-1,3,4-thiadiazole, 9H-purine-8-thiol, 1,2,4-triazole, 1,2,4-triazole-3-thiol, and 5-methyl-2-mercapto-1,3,4-thiadiazole.

When the combined corrosion inhibitor formulation is according to (ii), the at least one metal salt is selected from the group consisting of Pr^{3+} , Gd^{3+} , Ce^{3+} , Dy^{3+} , Sm^{3+} , Er^{3+} , Lu^{3+} , Zn^{2+} , Co^{2+} , Cu^{2+} , the at least one metal anion is selected from the
20 group consisting of MoO_4^{2-} , VO_4^{3-} , ZrO_4^{2-} , WO_4^{2-} , and the at least one organic heterocyclic compound of Formula 1 is selected from the group consisting of 3-amino-1,2,4-triazole, benzimidazole, 1H-benzotriazole, 5-amino-2-mercapto-1,3,4-thiadiazole, 9H-purine-8-thiol, 1,2,4-triazole, 1,2,4-triazole-3-thiol, and 5-methyl-2-mercapto-1,3,4-
25 thiadiazole.

When the combined corrosion inhibitor formulation is according to (iii), the at least two metal complexes are selected from the group consisting of zinc molybdate, erbium molybdate, lutetium molybdate, zinc vanadate, zinc benzotriazole, dysprosium benzotriazole, lutetium benzotriazole, gadolinium benzotriazole, gadolinium
30 molybdate, praseodymium benzimidazole, lutetium benzimidazole, zinc benzimidazole.

When the combined corrosion inhibitor formulation is according to (iv), the at least one metal complex is selected from the group consisting of zinc molybdate, erbium molybdate, lutetium molybdate, zinc vanadate, zinc benzotriazole, dysprosium benzotriazole, lutetium benzotriazole, gadolinium benzotriazole, gadolinium
35 molybdate, praseodymium benzimidazole, lutetium benzimidazole, zinc benzimidazole,

5 and the at least one metal anion is selected from the group consisting of MoO_4^{2-} , VO_4^{3-} , ZrO_4^{2-} , WO_4^{2-} .

When the combined corrosion inhibitor formulation is according to (v) the at least two metal salts are selected from the group consisting of Pr^{3+} , Gd^{3+} , Ce^{3+} , Dy^{3+} , Sm^{3+} , Er^{3+} , Lu^{3+} , Zn^{2+} , Co^{2+} , Cu^{2+} , and the at least two organic heterocyclic compounds
10 of Formula 1 are selected from the group consisting of 3-amino-1,2,4-triazole, benzimidazole, 1H-benzotriazole, 5-amino-2-mercapto-1,3,4-thiadiazole, 9H-purine-8-thiol, 1,2,4-triazole, 1,2,4-triazole-3-thiol, and 5-methyl-2-mercapto-1,3,4-thiadiazole.

When the combined corrosion inhibitor formulation is according to (vi) the at least one metal salt selected from the group consisting of Pr^{3+} , Gd^{3+} , Ce^{3+} , Dy^{3+} , Sm^{3+} ,
15 Er^{3+} , Lu^{3+} , Zn^{2+} , Co^{2+} , Cu^{2+} , the at least one metal anion selected from the group consisting of MoO_4^{2-} , VO_4^{3-} , ZrO_4^{2-} , WO_4^{2-} , and the at least two organic heterocyclic compounds of Formula 1 selected from the group consisting of 3-amino-1,2,4-triazole, benzimidazole, 1H-benzotriazole, 5-amino-2-mercapto-1,3,4-thiadiazole, 9H-purine-8-thiol, 1,2,4-triazole, 1,2,4-triazole-3-thiol, and 5-methyl-2-mercapto-1,3,4-thiadiazole.

20 When the combined corrosion inhibitor formulation is according to (vii) the at least three corrosion inhibitors are selected from metal salts, metal anions, metal complexes, or any combinations thereof, selected from the group consisting of Pr^{3+} , Gd^{3+} , Ce^{3+} , Dy^{3+} , Sm^{3+} , Er^{3+} , Lu^{3+} , Zn^{2+} , Co^{2+} , Cu^{2+} , MoO_4^{2-} , VO_4^{3-} , ZrO_4^{2-} , WO_4^{2-} , zinc molybdate, lutetium molybdate, zinc benzotriazole, lutetium benzotriazole,
25 gadolinium benzotriazole, gadolinium molybdate, and at least one organic heterocyclic compound of Formula 1 is selected from the group consisting of 3-amino-1,2,4-triazole, benzimidazole, 1H-benzotriazole, 5-amino-2-mercapto-1,3,4-thiadiazole.

It will be appreciated by persons skilled in the art that numerous variations and/or modifications may be made to the above-described embodiments, without
30 departing from the broad general scope of the present disclosure. The present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive.

Brief Description of the Figures

Some embodiments of the present disclosure are described and illustrated
35 herein, by way of example only, with reference to the accompanying Figures in which:

5 **Figure 1** is a graph showing polarisation resistance electrochemical experiments performed on mild steel for a selection of metal salt corrosion inhibitors and their combination.

Figure 2 is a graph showing polarisation resistance electrochemical experiments performed on mild steel for a selection of metal salt corrosion inhibitors
10 and their combination.

Figure 3 is a graph showing polarisation resistance electrochemical experiments performed on mild steel for a selection of metal salt corrosion inhibitors and their combination.

Figure 4 is a graph showing polarisation resistance electrochemical experiments performed on mild steel for a selection of corrosion inhibitors selected
15 from metal salts, organic heterocyclic compounds and their combination.

Figure 5 is a graph showing polarisation resistance electrochemical experiments performed on mild steel for 1:1:1 combined corrosion inhibitor formulations selected from a combination of metal salt, metal anion and organic
20 heterocyclic compounds.

Figure 6 is a graph showing polarisation resistance electrochemical experiments performed on mild steel for 1:1:1:1 combined corrosion inhibitor formulations selected from a combination of metal salt, metal anion and organic heterocyclic compounds.

25 **Description of Embodiments**

 The present disclosure describes the following various non-limiting examples, which relate to investigations undertaken to identify alternative chromate free corrosion inhibitors. It was surprisingly found that a combined corrosion inhibitor formulation comprising at least a first and second corrosion inhibitor formulation were
30 advantageously useful as corrosion inhibiting combinations for inhibiting corrosion on a substrate that could also be further advantageously categorised as providing a polarisation value that was greater than the sum of the polarisation values for each of the individual corrosion inhibitors. The combined corrosion inhibitor formulations comprising at least two corrosion inhibitors selected from metal salts, metal anions,
35 metal complexes, or any combinations thereof, of at least some embodiments or

5 examples as described herein provide an advantage of further promoting corrosion protection of various substrates. In some embodiments, the combined corrosion inhibitor formulations comprise at least three corrosion inhibitors. One advantage of the combined corrosion inhibitors comprising at least three corrosion inhibitors of the present disclosure, at least according to some embodiments or examples as described
10 herein, is that they can further enhance the corrosion inhibition on a substrate. In another embodiment, the combined corrosion inhibitor formulations may comprise at least four corrosion inhibitors. The combined corrosion inhibitors comprising at least four corrosion inhibitors of the present disclosure, at least according to some embodiments or examples as described herein, can advantageously increase the
15 corrosion protection of various substrates even further.

GENERAL TERMS

As used herein, the term “substrate” refers to any structure that may require protection from corrosion and that can be cleaned and/or protected and/or modified to provide unique properties. The substrate may comprise at least a portion of its surface
20 being metallic or being of any other material susceptible to corrosion. The substrate may be a metal substrate.

As used herein, the term “metal substrate” refers to a structure having at least a portion of its surface being metallic that can be cleaned and/or protected and/or modified to provide unique properties. A “metal substrate” is not limited to any
25 particular type of metallic surface, and in terms of applying a corrosion inhibiting coating, such metal substrates typically include zinc, magnesium, copper, brass, bronze, and steel, for example mild steel, carbon steel, stainless steel, high strength/low alloy steel, galvanised steel, or galfan steel.

As used herein, the term “protective composition” refers to any composition
30 suitable for use in providing some form of corrosion protection to a substrate. For example, a protective composition can include a powder coating composition for use in protecting steel from corrosion, or a film-forming organic polymer based composition for protecting steel from corrosion.

As used herein, the term “extender” or “extender pigment” when used without

5 qualification, refers to a type of pigment that is typically incorporated into a paint formulation to provide volume to the final resulting coating after paint curing, although it can be added for other reasons, such as to reduce cost. An extender can additionally or alternatively be an active component in making a total system more corrosion resistant. Extenders which add volume are often referred to as “fillers” or
10 “extenders/fillers.”

As used herein, the term “coating” refers to a polymeric material (organic or inorganic) that can be applied either as a liquid (e.g., paint) or solid (e.g., powder) to a substrate to form a polymeric film. Such polymeric materials include, but are not limited to, powder coatings, paints, sealants, conducting polymers, sol gels (e.g.
15 Boegel™ made by Boeing Co. having offices in Chicago, Ill.), silicates, silicones, zirconates, titanates, and the like. A “coating” is comprised of a complex mixture of binders, solvents, pigments and additives. Many coatings have one or more substances from each of the four categories. Coating properties, such as gloss and color, are related to the film surface, for example as a two-dimensional entity. However, the bulk
20 properties of a coating are related to its three-dimensional structure. Phase continuity is a volume concept, and the coating performance is dependent on the integrity of the binder phase.

As used herein, the term “film-forming organic polymer” or “film-forming polymeric material” refers to any polymeric material that can be used to make coatings,
25 including monomers, co-monomers, resins or polymers. The polymeric material can also be referred to as a “binder”, and can be either organic or inorganic. The organic polymeric material generally has a carbon backbone and the inorganic polymeric material generally has a silicone backbone. Organic binders are made up of organic monomers and oligomers from which the binders generally derive their names.
30 Examples of these would be acrylic, epoxy, urethane, melamine, and so forth. Binders include epoxy-based resin binders such as a water reducible epoxy-polyamide system (for organic polymeric materials) or non-epoxy-based resin binders such as urethanes, ureas, acrylates, alkyds, melamines, polyesters, vinyls, vinyl esters, silicones, siloxanes, silicates, sulfides, silicate polymers, epoxy novolacs, epoxy phenolics, drying oils,
35 hydrocarbon polymers, and the like.

5 As used herein, the term “weight percent (wt %)” when used without qualification, typically refers to the weight percent of a particular solid component, e.g., pigment, extender, etc., as compared with all solid components present, excluding polymeric resins. For example, if the only solid component present in the coating is a corrosion-inhibiting carbon pigment, the corrosion-inhibiting carbon pigment is
10 considered to have a wt % of 100.

 Throughout this specification the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated element, integer or step, or group of elements, integers or steps, but not the exclusion of any other element, integer or step, or group of elements, integers or steps. The various
15 embodiments disclosed and described in this specification can comprise, consist of, or consist essentially of the features and characteristics as variously described herein. The word “comprise”, “comprises”, or “comprising” includes those embodiments that “consist of” or “consist essentially of” the features and characteristics as variously described.

20 Any discussion of documents, acts, materials, devices, articles or the like which has been included in the present specification is solely for the purpose of providing a context for the present disclosure. It is not to be taken as an admission that any or all of these matters form part of the prior art base or were common general knowledge in the field relevant to the present disclosure as it existed before the priority date of each
25 claim of this application.

CHEMICAL TERMS

 As will be understood, an aromatic group means a cyclic group having $4m+2$ π electrons, where m is an integer equal to or greater than 1. As used herein, "aromatic" is used interchangeably with "aryl" to refer to an aromatic group, regardless of the
30 valency of aromatic group. Thus, aryl refers to monovalent aromatic groups, bivalent aromatic groups and higher multivalency aromatic groups.

 The term “joined” refers to a ring, moiety or group that is joined to at least one other ring, moiety or group by a single covalent bond.

 The term “fused” refers to one or more rings that share at least two common
35 ring atoms with one or more other rings.

5 A heteroaromatic group is an aromatic group or ring containing one or more heteroatoms, such as N, O, S, Se, Si or P. As used herein, "heteroaromatic" is used interchangeably with "heteroaryl", and a heteroaryl group refers to monovalent aromatic groups, bivalent aromatic groups and higher multivalency aromatic groups containing one or more heteroatoms.

The term "optionally substituted" means that a group is either substituted or unsubstituted, at any available position. Substitution can be with one or more groups selected from, e.g., alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aryl, heterocyclyl, heteroaryl, formyl, alkanoyl, cycloalkanoyl, aroyl, heteroaroyl, carboxyl, alkoxycarbonyl, cycloalkyloxycarbonyl, aryloxycarbonyl, heterocyclyloxycarbonyl, heteroaryloxycarbonyl, alkylaminocarbonyl, cycloalkylaminocarbonyl, arylaminocarbonyl, heterocyclylaminocarbonyl, heteroarylaminocarbonyl, cyano, alkoxy, cycloalkoxy, aryloxy, heterocyclyloxy, heteroaryloxy, alkanoate, cycloalkanoate, aryloate, heterocyclyloate, heteroaryloate, alkylcarbonylamino, cycloalkylcarbonylamino, arylcarbonylamino, heterocyclylcarbonylamino, heteroarylcarbonylamino, nitro, hydroxyl, halogen, haloalkyl, haloaryl, haloheterocyclyl, haloheteroaryl, haloalkoxy, silylalkyl, alkenylsilylalkyl, alkynylsilylalkyl, and amino. The optional substitution may be one or more groups selected from halogen, alkyl, formyl, and amino. The optional substituents may include salts of the groups, for example carboxylate salts. It will be appreciated that other groups not specifically described may also be used.

"Alkyl" whether used alone, or in compound words such as alkoxy, alkylthio, alkylamino, dialkylamino or haloalkyl, represents straight or branched chain hydrocarbons ranging in size from one to about 10 carbon atoms, or more. Thus alkyl moieties include, unless explicitly limited to smaller groups, moieties ranging in size, for example, from one to about 6 carbon atoms or greater, such as, methyl, ethyl, n-propyl, iso-propyl and/or butyl, pentyl, hexyl, and higher isomers, including, e.g., those straight or branched chain hydrocarbons ranging in size from about 6 to about 10 carbon atoms, or greater.

"Alkenyl" whether used alone, or in compound words such as alkenyloxy or
35 haloalkenyl, represents straight or branched chain hydrocarbons containing at least one

5 carbon-carbon double bond, including, unless explicitly limited to smaller groups, moieties ranging in size from two to about 6 carbon atoms or greater, such as, methylene, ethylene, 1-propenyl, 2-propenyl, and/or butenyl, pentenyl, hexenyl, and higher isomers, including, e.g., those straight or branched chain hydrocarbons ranging in size, for example, from about 6 to about 10 carbon atoms, or greater.

10 "Alkynyl" whether used alone, or in compound words such as alkynyloxy, represents straight or branched chain hydrocarbons containing at least one carbon-carbon triple bond, including, unless explicitly limited to smaller groups, moieties ranging in size from, e.g., two to about 6 carbon atoms or greater, such as, ethynyl, 1-propynyl, 2-propynyl, and/or butynyl, pentynyl, hexynyl, and higher isomers,
15 including, e.g., those straight or branched chain hydrocarbons ranging in size from, e.g., about 6 to about 10 carbon atoms, or greater.

"Cycloalkyl" represents a mono- or polycarbocyclic ring system of varying sizes, e.g., from about 3 to about 10 carbon atoms, e.g., cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl or cycloheptyl. The term cycloalkyloxy represents the same
20 groups linked through an oxygen atom such as cyclopentyloxy and cyclohexyloxy. The term cycloalkylthio represents the same groups linked through a sulfur atom such as cyclopentylthio and cyclohexylthio.

"Cycloalkenyl" represents a non-aromatic mono- or polycarbocyclic ring system, e.g., of about 3 to about 10 carbon atoms containing at least one carbon-carbon double
25 bond, e.g., cyclopentenyl, cyclohexenyl or cycloheptenyl. The term "cycloalkenyloxy" represents the same groups linked through an oxygen atom such as cyclopentyloxy and cyclohexenyloxy. The term "cycloalkenylthio" represents the same groups linked through a sulfur atom such as cyclopentenylthio and cyclohexenylthio.

The terms, "carbocyclic" and "carbocyclyl" represent a ring system wherein the
30 ring atoms are all carbon atoms, e.g., of about 3 to about 10 carbon atoms, and which may be aromatic, non-aromatic, saturated, or unsaturated, and may be substituted and/or carry fused rings. Examples of such groups include benzene, cyclopentyl, cyclohexyl, or fully or partially hydrogenated phenyl, naphthyl and fluorenyl.

"Aryl" whether used alone, or in compound words such as arylalkyl, aryloxy or
35 arylthio, represents: (i) an optionally substituted mono- or polycyclic aromatic

5 carbocyclic moiety, e.g., of about 6 to about 60 carbon atoms, such as phenyl, naphthyl or fluorenyl; or, (ii) an optionally substituted partially saturated polycyclic carbocyclic aromatic ring system in which an aryl and a cycloalkyl or cycloalkenyl group are fused together to form a cyclic structure such as a tetrahydronaphthyl, indenyl, indanyl or fluorene ring.

10 "Heterocyclyl" or "heterocyclic" whether used alone, or in compound words such as heterocyclyloxy represents: (i) an optionally substituted cycloalkyl or cycloalkenyl group, e.g., of about 3 to about 60 ring members, which may contain one or more heteroatoms such as nitrogen, oxygen, or sulfur (examples include pyrrolidinyl, morpholino, thiomorpholino, or fully or partially hydrogenated thienyl, 15 furyl, pyrrolyl, thiazolyl, oxazolyl, oxazinyl, thiazinyl, pyridyl and azepinyl); (ii) an optionally substituted partially saturated polycyclic ring system in which an aryl (or heteroaryl) ring and a heterocyclic group are fused together to form a cyclic structure (examples include chromanyl, dihydrobenzofuryl and indolinyl); or (iii) an optionally substituted fully or partially saturated polycyclic fused ring system that has one or more 20 bridges (examples include quinuclidinyl and dihydro-1,4-epoxynaphthyl).

"Heteroaryl" or "hetaryl" whether used alone, or in compound words such as heteroaryloxy represents: (i) an optionally substituted mono- or polycyclic aromatic organic moiety, e.g., of about 1 to about 10 ring members in which one or more of the ring members is/are element(s) other than carbon, for example nitrogen, oxygen, sulfur 25 or silicon; the heteroatom(s) interrupting a carbocyclic ring structure and having a sufficient number of delocalized pi electrons to provide aromatic character, provided that the rings do not contain adjacent oxygen and/or sulfur atoms. Typical 6-membered heteroaryl groups are pyrazinyl, pyridazinyl, pyrazolyl, pyridyl and pyrimidinyl. All regioisomers are contemplated, e.g., 2-pyridyl, 3-pyridyl and 4-pyridyl. Typical 5- 30 membered heteroaryl rings are furyl, imidazolyl, oxazolyl, isoxazolyl, isothiazolyl, oxadiazolyl, pyrrolyl, 1,3,4-thiadiazolyl, thiazolyl, thienyl, triazolyl, and silole. All regioisomers are contemplated, e.g., 2-thienyl and 3-thienyl. Bicyclic groups typically are benzo-fused ring systems derived from the heteroaryl groups named above, e.g., benzofuryl, benzimidazolyl, benzthiazolyl, indolyl, indolizinyl, isoquinolyl, 35 quinazolinyl, quinolyl and benzothienyl; or, (ii) an optionally substituted partially

5 saturated polycyclic heteroaryl ring system in which a heteroaryl and a cycloalkyl or cycloalkenyl group are fused together to form a cyclic structure such as a tetrahydroquinolyl or pyrindinyl ring.

"Formyl" represents a -CHO moiety.

10 "Alkanoyl" represents a -C(=O)-alkyl group in which the alkyl group is as defined supra. An alkanoyl group may range in size from about C₂-C₂₀. One example is acyl.

"Aroyl" represents a -C(=O)-aryl group in which the aryl group is as defined supra. An aroyl group may range in size from about C₇-C₂₀. Examples include benzoyl and 1-naphthoyl and 2-naphthoyl.

15 "Heterocycloyl" represents a -C(=O)-heterocyclyl group in which the heterocyclic group is as defined supra. An heterocycloyl may range in size from about C₄-C₂₀.

"Heteroaroyl" represents a -C(=O)-heteroaryl group in which the heteroaryl group is as defined supra. A heteroaroyl group may range in size from about C₆-C₂₀. An
20 example is pyridylcarbonyl.

"Carboxyl" represents a -CO₂H moiety.

"Oxycarbonyl" represents a carboxylic acid ester group -CO₂R which is linked to the rest of the molecule through a carbon atom.

"Alkoxycarbonyl" represents an -CO₂-alkyl group in which the alkyl group is as
25 defined supra. An alkoxycarbonyl group may range in size from about C₂-C₂₀. Examples include methoxycarbonyl and ethoxycarbonyl.

"Aryloxycarbonyl" represents an -CO₂-aryl group in which the aryl group is as defined supra. Examples include phenoxycarbonyl and naphthoxycarbonyl.

30 "Heterocyclyloxycarbonyl" represents a -CO₂-heterocyclyl group in which the heterocyclic group is as defined supra.

"Heteroaryloxycarbonyl" represents a -CO₂-heteroaryl group in which the heteroaryl group is as defined supra.

"Aminocarbonyl" represents a carboxylic acid amide group -C(=O)NHR or -C(=O)NR₂ which is linked to the rest of the molecule through a carbon atom.

5 "Alkylaminocarbonyl" represents a $-C(=O)NHR$ or $-C(=O)NR_2$ group in which R is an alkyl group as defined supra.

"Arylaminocarbonyl" represents a $-C(=O)NHR$ or $-C(=O)NR_2$ group in which R is an aryl group as defined supra.

10 "Heterocyclylaminocarbonyl" represents a $-C(=O)NHR$ or $-C(=O)NR_2$ group in which R is a heterocyclic group as defined supra. NR_2 may for example be a heterocyclic ring, which is optionally substituted.

"Heteroarylaminocarbonyl" represents a $-C(=O)NHR$ or $-C(=O)NR_2$ group in which R is a heteroaryl group as defined supra. NR_2 may for example be a heteroaryl ring, which is optionally substituted.

15 "Cyano" represents a $-CN$ moiety.

"Hydroxyl" represents a $-OH$ moiety.

"Alkoxy" represents an $-O$ -alkyl group in which the alkyl group is as defined supra. Examples include methoxy, ethoxy, n-propoxy, iso-propoxy, and the different butoxy, pentoxy, hexyloxy and higher isomers.

20 "Aryloxy" represents an $-O$ -aryl group in which the aryl group is as defined supra. Examples include, without limitation, phenoxy and naphthoxy.

"Alkenyloxy" represents an $-O$ -alkenyl group in which the alkenyl group is as defined supra. An example is allyloxy.

25 "Heterocyclyloxy" represents an $-O$ -heterocyclyl group in which the heterocyclic group is as defined supra.

"Heteroaryloxy" represents an $-O$ -heteroaryl group in which the heteroaryl group is as defined supra. An example is pyridyloxy.

"Alkanoate" represents an $-OC(=O)-R$ group in which R is an alkyl group as defined supra.

30 "Aryloate" represents a $-OC(=O)-R$ group in which R is an aryl group as defined supra.

"Heterocyclyloate" represents an $-OC(=O)-R$ group in which R is a heterocyclic group as defined supra.

35 "Heteroaryloate" represents an $-OC(=O)-R$ group in which R is a heteroaryl group as defined supra.

5 "Amino" represents an -NH₂ moiety.

"Alkylamino" represents an -NHR or -NR₂ group in which R is an alkyl group as defined supra. Examples include, without limitation, methylamino, ethylamino, n-propylamino, isopropylamino, and the different butylamino, pentylamino, hexylamino and higher isomers.

10 "Arylamino" represents an -NHR or -NR₂ group in which R is an aryl group as defined supra. An example is phenylamino.

"Heterocyclylamino" represents an -NHR or -NR₂ group in which R is a heterocyclic group as defined supra. NR₂ may for example be a heterocyclic ring, which is optionally substituted.

15 "Heteroaryl amino" represents a -NHR or -NR₂ group in which R is a heteroaryl group as defined supra. NR₂ may for example be a heteroaryl ring, which is optionally substituted.

"Carbonylamino" represents a carboxylic acid amide group -NHC(=O)R that is linked to the rest of the molecule through a nitrogen atom.

20 "Alkylcarbonylamino" represents a -NHC(=O)R group in which R is an alkyl group as defined supra.

"Arylcarbonylamino" represents an -NHC(=O)R group in which R is an aryl group as defined supra.

25 "Heterocyclylcarbonylamino" represents an -NHC(=O)R group in which R is a heterocyclic group as defined supra.

"Heteroarylcarbonylamino" represents an -NHC(=O)R group in which R is a heteroaryl group as defined supra.

"Nitro" represents a -NO₂ moiety.

"Aldehyde" represents a -C(=O)H group.

30 "Alkanal" represents an alkyl-(C=O)H group in which the alkyl group is as defined supra.

"Alkylsilyl" represents an alkyl group that is linked to the rest of the molecule through the silicon atom, which may be substituted with up to three independently selected alkyl groups in which each alkyl group is as defined supra.

5 “Alkenylsilyl” presents an alkenyl group that is linked to the rest of the molecule through the silicon atom, which may be substituted with up to three independently selected alkenyl groups in which each alkenyl group is as defined supra.

“Alkynylsilyl” presents an alkynyl group that is linked to the rest of the molecule through the silicon atom, which may be substituted with up to three
10 independently selected alkynyl groups in which each alkenyl group is as defined supra.

The term “halo” or “halogen” whether employed alone or in compound words such as haloalkyl, haloalkoxy or haloalkylsulfonyl, represents fluorine, chlorine, bromine or iodine. Further, when used in compound words such as haloalkyl, haloalkoxy or haloalkylsulfonyl, the alkyl may be partially halogenated or fully
15 substituted with halogen atoms which may be independently the same or different. Examples of haloalkyl include, without limitation, $-\text{CH}_2\text{CH}_2\text{F}$, $-\text{CF}_2\text{CF}_3$ and $-\text{CH}_2\text{CHFCl}$. Examples of haloalkoxy include, without limitation, $-\text{OCHF}_2$, $-\text{OCF}_3$, $-\text{OCH}_2\text{CCl}_3$, $-\text{OCH}_2\text{CF}_3$ and $-\text{OCH}_2\text{CH}_2\text{CF}_3$. Examples of haloalkylsulfonyl include, without limitation, $-\text{SO}_2\text{CF}_3$, $-\text{SO}_2\text{CCl}_3$, $-\text{SO}_2\text{CH}_2\text{CF}_3$ and $-\text{SO}_2\text{CF}_2\text{CF}_3$.

20 The terms “thiol”, “thio”, “mercapto” or “mercaptan” refer to any organosulphur group containing a sulphurhydryl moiety $-\text{SH}$, which includes a $\text{R}-\text{SH}$ group where R is a moiety containing a carbon atom for coordination to the $-\text{SH}$ moiety, for example an alkylsulphur group as defined supra. For example, the thiol or mercapto group may be a sulphurhydryl moiety $-\text{SH}$.

25 The terms “thione”, “thioketones” or “thiocarbonyls” refer to any organosulphur group containing a $-\text{C}=\text{S}$ moiety, which includes a $\text{R}-\text{C}=\text{S}$ group, for example where R is an alkyl group defined supra. For example, the thione group may be a $-\text{C}=\text{S}$ moiety.

The term “exocyclic” refers to an atom or group that is attached externally to a
30 cyclic ring system of a heteroaryl or heterocyclic compound, which contrasts with an “endocyclic” atom or group that is within the ring system such that the atoms form a part of the ring system of the heteroaryl or heterocyclic compound.

The compounds described herein may include salts, solvates, hydrates, isomers, tautomers, racemates, stereoisomers, enantiomers or diastereoisomers of those
35 compounds. For example salts may include sodium, potassium, calcium, nitrates,

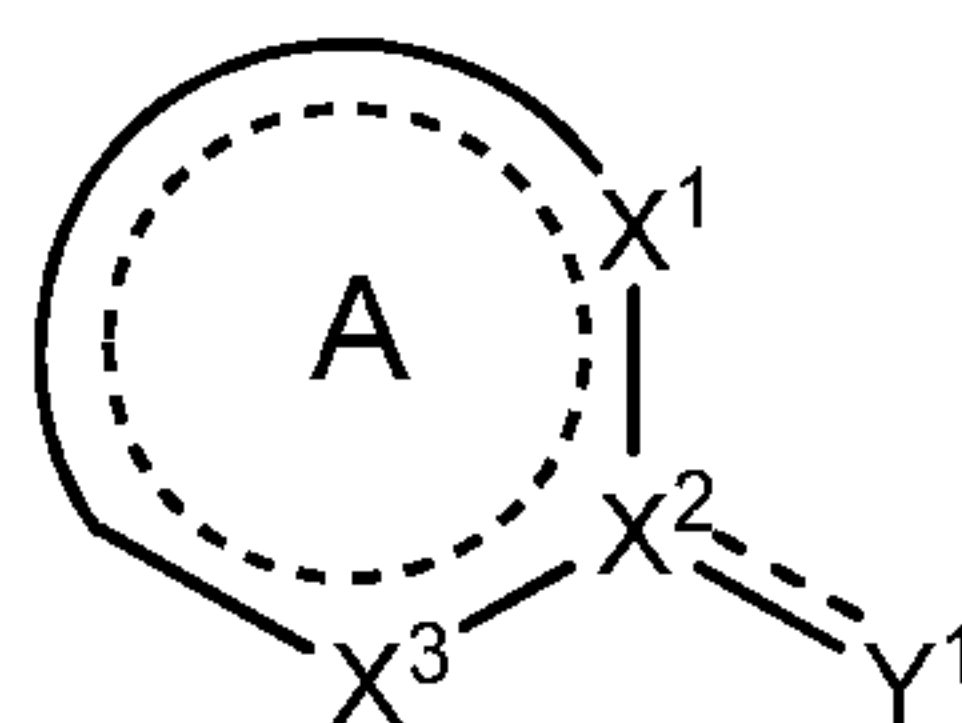
5 phosphates, sulphates, molybdates, and chlorides. In one embodiment the compounds include salts thereof selected from sodium salts.

ORGANIC HETEROCYCLIC COMPOUND

The corrosion inhibitors of the present disclosure may be selected from an organic heterocyclic compound. The organic heterocyclic compounds may be each
 10 optionally substituted and optionally fused with one or more substituents or groups. The organic heterocyclic compounds may be selected from an optionally substituted, optionally fused, heteroaryl or heterocyclic compound. The organic heterocyclic compound may include salts, for example, thiol sodium salt.

The one or more organic heterocyclic compounds may each be selected from an
 15 optionally substituted, optionally fused, 5 or 6-membered mono or bicyclic heteroaryl or heterocyclic compound.

The organic heterocyclic compound may be selected from a compound of Formula 1 or salt thereof:



Formula 1

20

wherein

A is a 5- or 6-membered aryl, heteroaryl or heterocyclic ring, which is optionally substituted with one or more substituents and optionally fused with one or more aryl or heteroaryl rings, wherein a dotted line represents one or more optional
 25 double bonds,

Y^1 is selected from S, SH, NH_2 or is absent, wherein the dotted line represents a double bond when Y^1 is S or is absent when Y^1 is SH or NH_2 ,

X^1 , X^2 , and X^3 are selected from N, NR^5 , O, S, CR^6 and CR^7R^8 ,

R^5 is selected from hydrogen, amino, C_1 - C_{10} alkyl, C_2 - C_{10} alkenyl, C_2 -
 30 C_{10} alkynyl, aryl and heteroaryl, in which each amino, alkyl, alkenyl, alkynyl, aryl or heteroaryl group may be optionally substituted, and

R^6 , R^7 and R^8 , are each independently selected from hydrogen, halogen,

5 carboxyl, sulphide, thiol, amino, C₁-C₁₀alkyl, C₂-C₁₀alkenyl, C₂-C₁₀alkynyl, aryl and heteroaryl, in which each amino, alkyl, alkenyl, alkynyl, aryl or heteroaryl group may be optionally substituted.

For the organic heterocyclic compounds of Formula 1, Y¹ may be absent. X¹ and X² may be selected from N, NH, and S. X¹ and X² may be selected from N and S.
 10 X¹ and X² may be selected from N and NH. X³ may be selected from N, NH, O, and S. X³ may be selected from N, NH, and S. X³ may be selected from N and NH. X¹, X² and X³ may be each independently selected from N, NH and S. X¹, X² and X³ may be each independently selected from N and NH. X¹ and X² may be each independently selected from N and NH. X¹ and X³ may be selected from N and NH, and X² may be selected
 15 from CR⁶ and CR⁷R⁸.

For the organic heterocyclic compounds of Formula 1, Y¹ may be absent. X¹ and X² may each be independently selected from N, NH, and S. X¹ may be further selected from N and S. X¹ may be further selected from N and NH. X² may be further selected from CR⁶ and CR⁷R⁸. X² may be further selected from N, NH, and S. X² may
 20 be further selected from N and NH. X¹ and X² each may be further independently selected from N and NH.

For the organic heterocyclic compounds of Formula 1, Y¹ may be SH. X¹ may be selected from N, NH, and S. X¹ may be selected from N and S. X¹ may be selected from N and NH. X³ may be selected from N, NH, O, and S. X³ may be selected from N,
 25 NH, and S. X³ may be selected from N and NH. X¹ and X³ may be each independently selected from N, NH and S. X¹ and X³ may be each independently selected from N and NH. X¹ may be selected from N and NH, and X³ may be selected from CR⁶ and CR⁷R⁸.

For the organic heterocyclic compounds of Formula 1, Y¹ may be SH, and X¹ and X² may each be independently selected from N, NH, and S. X¹ may be further
 30 selected from N and S. X¹ may be further selected from N and NH. X² may be further selected from CR⁶ and CR⁷R⁸. X² may be further selected from N, NH, and S. X² may be further selected from N and NH. X¹ and X² each may be further independently selected from N and NH.

For the organic heterocyclic compounds of Formula 1, Y¹ may be NH₂. X¹ may
 35 be selected from N, NH, and S. X¹ may be selected from N and S. X¹ may be selected

5 from N and NH. X^3 may be selected from N, NH, O, and S. X^3 may be selected from N, NH, and S. X^3 may be selected from N and NH. X^1 and X^3 may be each independently selected from N, NH and S. X^1 and X^3 may be each independently selected from N and NH. X^1 and X^3 may be selected from N and NH, and X^2 may be selected from CR^6 and CR^7R^8 .

10 For the organic heterocyclic compounds of Formula 1, Y^1 may be NH_2 , and X^1 and X^3 may each be independently selected from N, NH, and S. X^1 may be further selected from N and S. X^1 may be further selected from N and NH. X^2 may be further selected from CR^6 and CR^7R^8 . X^3 may be further selected from N, NH, and S. X^3 may be further selected from N and NH. X^1 and X^3 each may be further independently
15 selected from N and NH, and X^2 may be selected from CR^6 and CR^7R^8 .

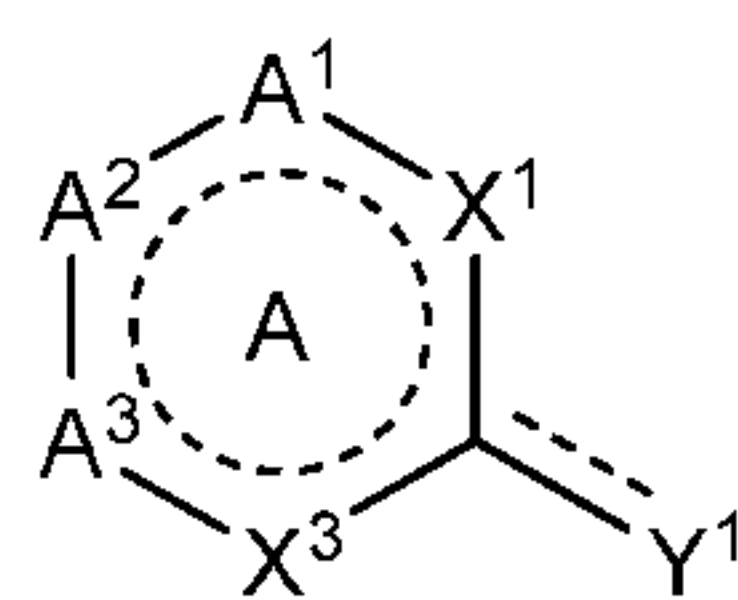
Optionally fused groups of ring A may be monocyclic or polycyclic. Optional fused groups of the A ring may be optionally substituted mono- or bicyclic aryl, heteroaryl or heterocyclic ring, for example where a compound of Formula 1 is a bicyclic compound. The monocyclic aryl groups may be an optionally substituted 6
20 membered ring, such as benzene. The polycyclic aryl groups may be two or more optionally substituted 6-member rings fused together, such as naphthalene, anthracene, pyrene, tetracene, and pentacene. The heteroaryl groups may be selected from 5-membered monocyclic rings, such as thiophene, furan, pyrrole, silole, imidazole, 1,3-thiazole, 1,3,4-oxadiazole, 1,3,4-thiadiazole, or 6 membered rings, such as pyridine and
25 triazine, wherein each ring may be optionally substituted.

Optional substituents of ring A ring may be selected from halogen, cyano, carboxy, amino, hydroxy, alkanolic acid, alkanoate salt, carbamoyl, C_1 - C_{10} alkyloxycarbonyl, C_1 - C_{10} alkyl, C_1 - C_{10} haloalkyl, C_1 - C_{10} alkylamino, C_3 - C_{10} cycloalkyl, C_2 - C_{10} alkenyl, C_3 - C_{10} cycloalkenyl, C_2 - C_{10} alkynyl, C_3 - C_{10} cycloalkynyl,
30 aryl and aryl C_1 - C_{10} alkyl, heteroaryl and heteroaryl C_1 - C_{10} alkyl, C_1 - C_{10} alkyloxy, C_3 - C_{10} cycloalkyloxy and wherein amino, alkanolic acid, alkanolic salt, alkyloxycarbonyl, alkyl, haloalkyl, alkylamino, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl, aryl, arylalkyl, heteroaryl, heteroarylalkyl, alkyloxy and cycloalkyloxy in each occurrence may be optionally substituted, for example further substituted with one or
35 more of halogen, hydroxyl, amino, nitro, carboxylic acid. The optional substitution may

5 be any one or more groups selected from halogen, alkyl, formyl, and amino. The optional substituents may include salts of the functional groups, for example carboxylate salts.

Ring A may be heterocyclic, for example an unsaturated heterocyclic compound. Ring A may be heteroaromatic or partially unsaturated. For example, ring A
 10 may contain one or more double bonds between ring atoms. Ring A may also contain one or more optional substituents and optional fused groups. Ring A may be a monocyclic 5 or 6 membered heteroaryl or heterocyclic ring. Ring A may be a bicyclic ring comprising two rings joined together that are each independently selected from 5 and 6 membered rings. Ring A may be a bicyclic ring comprising two rings fused
 15 together that are each independently selected from 5 and 6 membered rings. Ring A may be a bicyclic heteroaryl or heterocyclic ring containing a 5 membered heterocyclic ring fused to a 6 membered aryl, carbocyclic, heterocyclic or heteroaryl ring.

The organic heterocyclic compound may be selected from a compound of Formula 1(a) or salts thereof:



20

Formula 1(a)

wherein

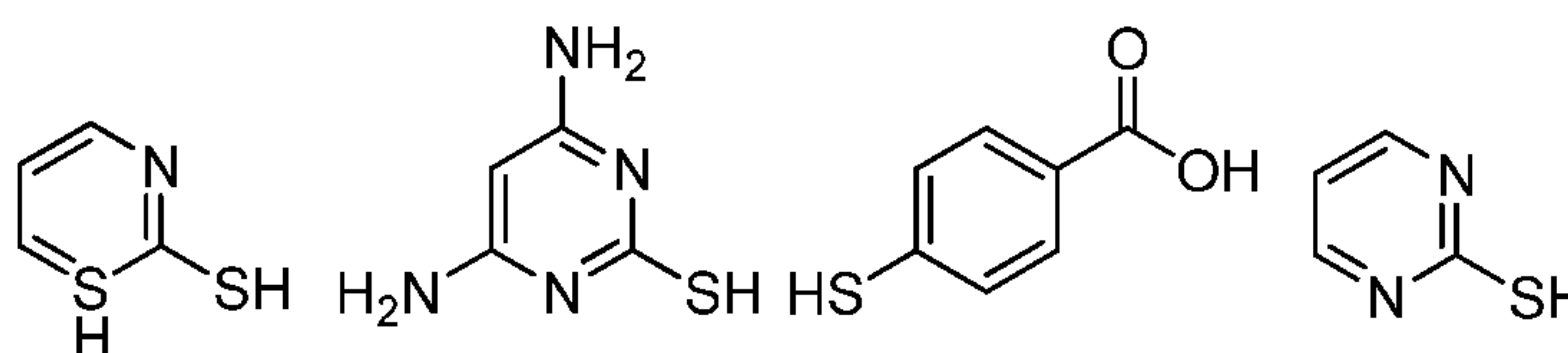
A, Y¹, X¹ and X³ are defined according to Formula 1 as described above;

A¹, A² and A³ are each independently selected from C=O, C=S, N, NR¹³, O, S,
 25 SO₂, CR¹⁴, CR¹⁵R¹⁶;

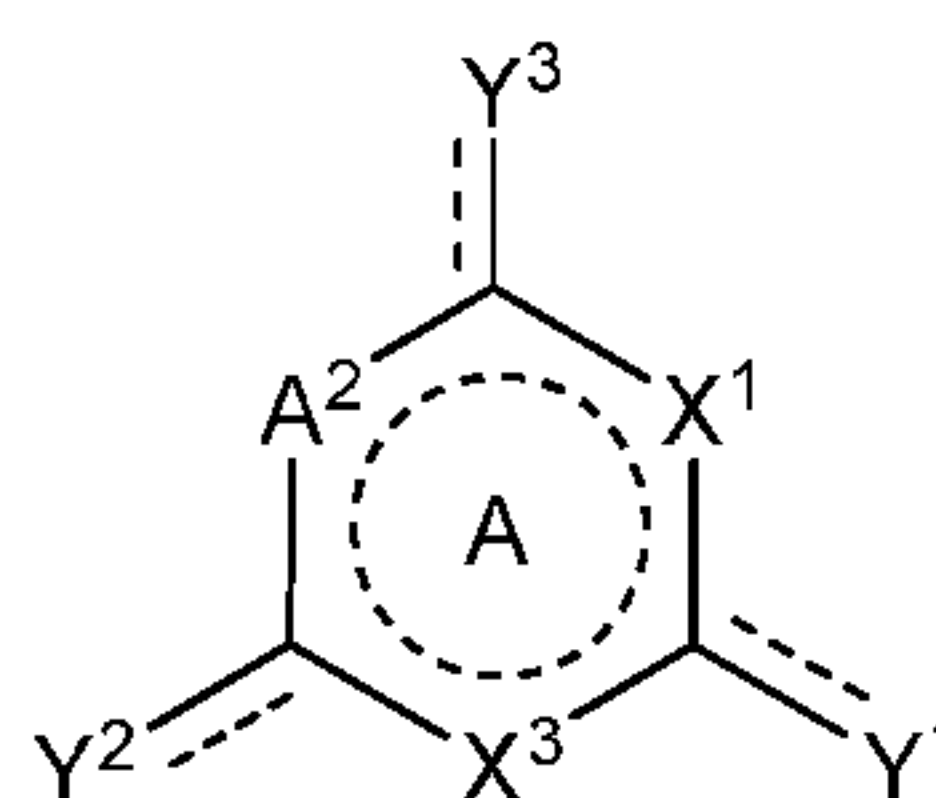
R¹³ is selected from hydrogen, amino, C₁-C₁₀alkyl, C₂-C₁₀alkenyl, C₂-C₁₀alkynyl, aryl and heteroaryl, in which each amino, alkyl, alkenyl, alkynyl, aryl or heteroaryl group may be optionally substituted; and

R¹⁴, R¹⁵ and R¹⁶, are each independently selected from hydrogen, halogen, thiol,
 30 amino, C₁-C₁₀alkyl, C₂-C₁₀alkenyl, C₂-C₁₀alkynyl, aryl and heteroaryl, in which each amino, alkyl, alkenyl, alkynyl, aryl or heteroaryl group may be optionally substituted, and optionally two of R¹³, R¹⁴, R¹⁵ and R¹⁶, join together to form an optionally substituted aryl or heteroaryl ring fused to the A ring.

5 In an embodiment, A^1 and A^3 are CR^{14} . In another embodiment, R^{14} is selected from amino and thiol. In another embodiment, A^1 and A^3 are each independently selected from C-SH and C-NH₂. In another embodiment, A^1 and A^3 are C-SH. In another embodiment, Y^1 is SH. In another embodiment, X^1 and X^2 are N. In another embodiment, A^2 is N. Some specific examples of compounds of Formula 1(a) are
 10 provided as follows:



The organic heterocyclic compound may be selected from a compound of Formula 1(a)(i) or salts thereof:



15

Formula 1(a)(i)

wherein

A is a 5- or 6-membered aryl, heteroaryl or heterocyclic ring, which is optionally substituted with one or more substituents and optionally fused with one or more aryl or heteroaryl rings, wherein a dotted line represents one or more optional
 20 double bonds;

A^2 , X^1 and X^3 are each independently selected from N, NH, O, and S;

Y^1 , Y^2 and Y^3 are each independently selected from NH₂, S or SH, wherein the dotted line represents a double bond when Y^1 is S or is absent when Y^1 is SH or NH₂;

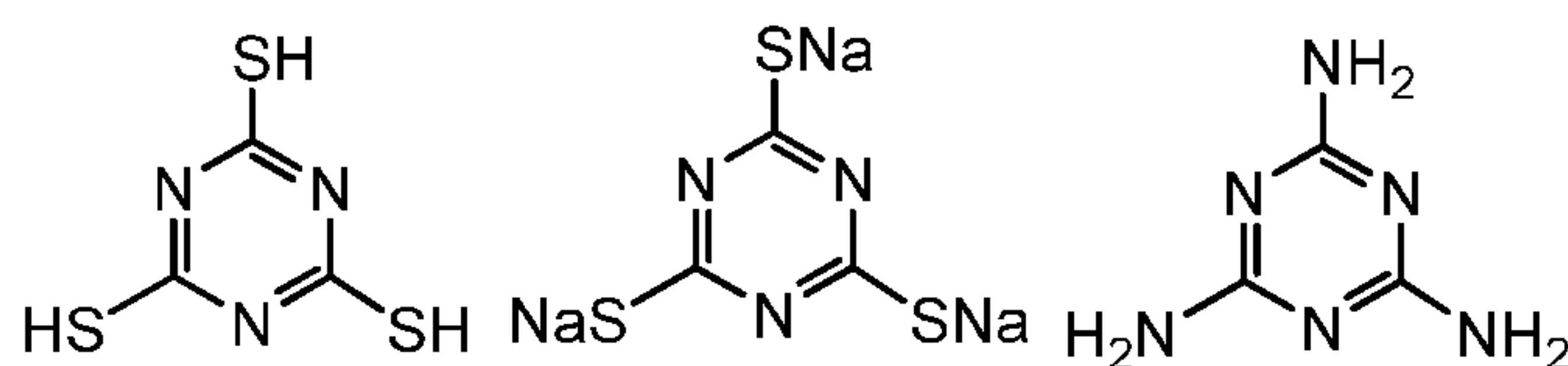
X^1 and X^2 are defined according to Formula 1 as described above;

25 A^1 , A^2 and A^3 are each independently selected from C=O, C=S, N, NR^{13} , O, S, SO₂, CR^{14} , $CR^{15}R^{16}$; and

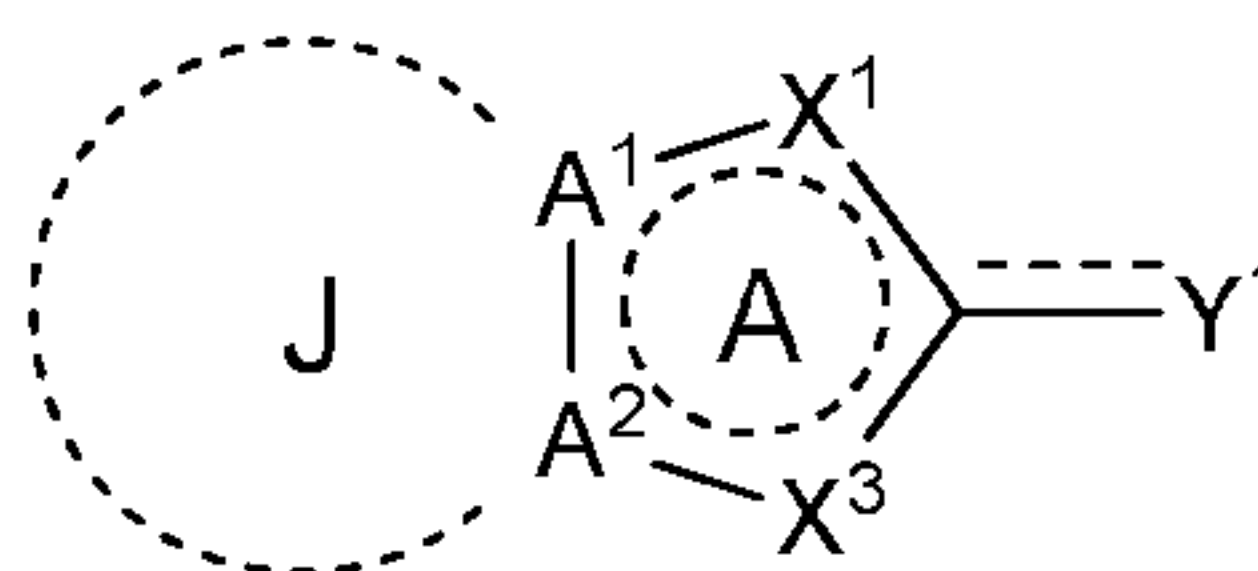
R^{14} , R^{15} and R^{16} are defined according to Formula 1a as described above.

In an embodiment, A^2 , X^1 and X^2 are N. In another embodiment, Y^1 , Y^2 and Y^3 are SH.

5 Some specific examples of compounds of Formula 1(a)(i) are provided as follows:



In one embodiment, the organic heterocyclic compound may be selected from a compound of Formula 1(b) or salt thereof:



Formula 1(b)

wherein

A ring is an optionally substituted 5-membered heterocyclic ring, wherein a dotted line represents one or more optional double bonds;

15 X^1 , X^3 and Y^1 are defined according to Formula 1 as described above;

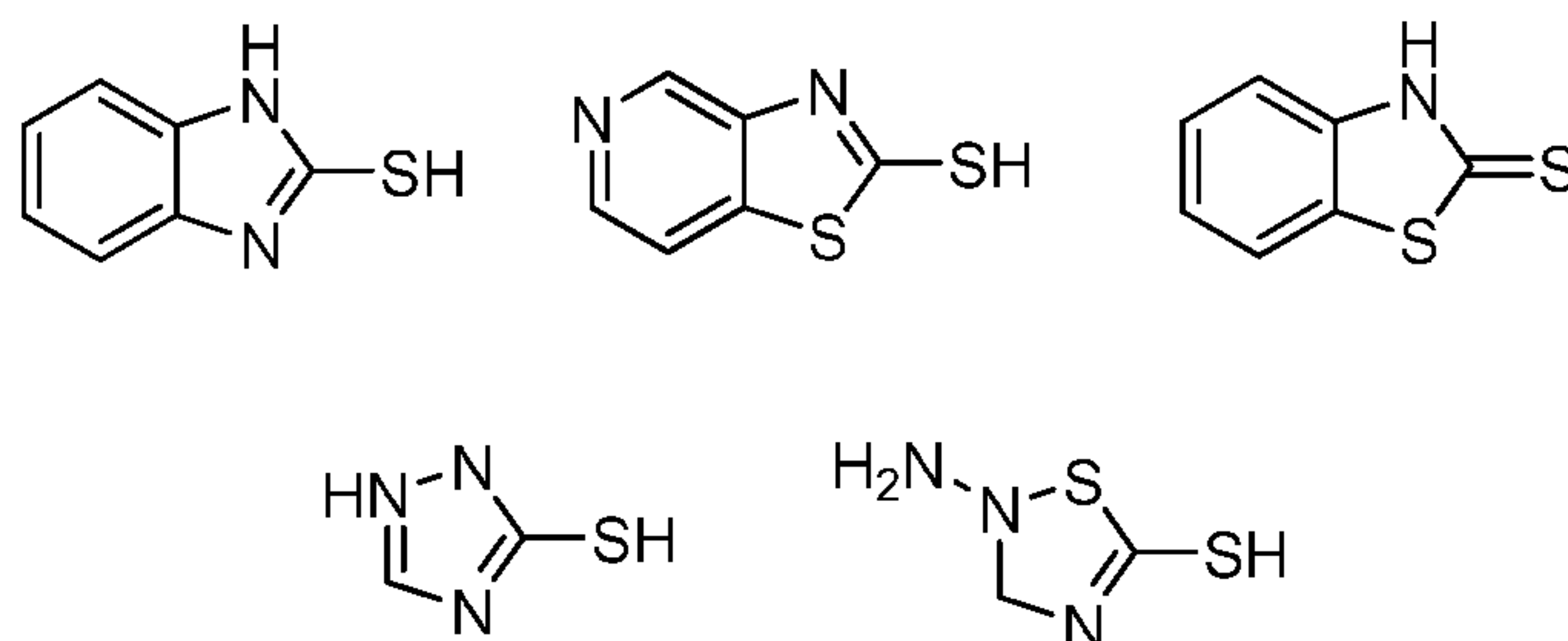
A^1 and A^2 are each independently selected from C=O, C=S, N, NR^{13} , O, S, SO_2 , CR^{14} and $CR^{15}R^{16}$; and are optionally joined together to form an optionally substituted aryl, heteroaryl or heterocyclic ring J that is fused to the A ring;

20 R^{13} is selected from hydrogen, amino, C_1 - C_{10} alkyl, C_2 - C_{10} alkenyl, C_2 - C_{10} alkynyl, aryl and heteroaryl, in which each amino, alkyl, alkenyl, alkynyl, aryl or heteroaryl group may be optionally substituted; and

R^{14} , R^{15} and R^{16} , are each independently selected from hydrogen, halogen, carboxyl, amino, C_1 - C_{10} alkyl, C_2 - C_{10} alkenyl, C_2 - C_{10} alkynyl, aryl and heteroaryl, in which each amino, alkyl, alkenyl, alkynyl, aryl or heteroaryl group may be optionally substituted, and optionally two of R^{13} , R^{14} , R^{15} and R^{16} , join together to form an optionally substituted aryl or heteroaryl ring fused to the A ring.

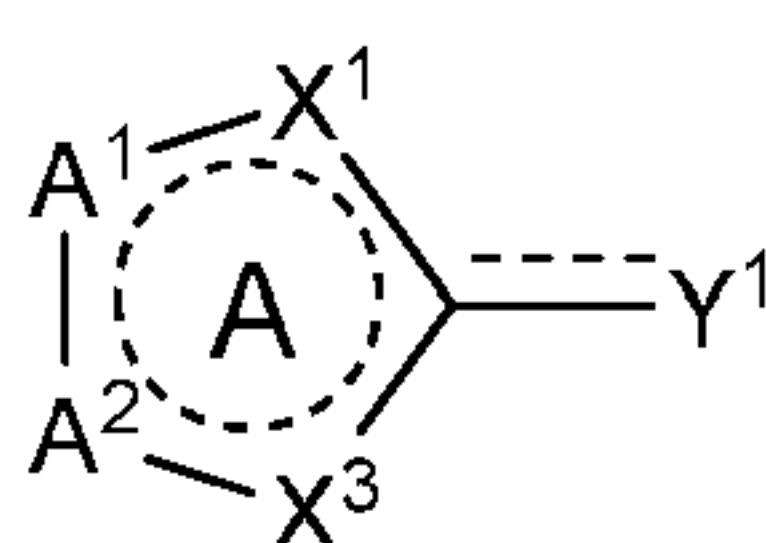
Some specific examples of compounds of Formula 1(b) are provided as follows:

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The at least one organic heterocyclic compound may be selected from a compound of Formula 1(b)(i) or salt thereof:



Formula 1(b)(i)

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wherein

A ring is an optionally substituted 5-membered heterocyclic ring, wherein a dotted line represents one or more optional double bonds;

X^1 , X^3 and Y^1 are defined according to Formula 1b as described above;

A^1 and A^2 are each independently selected from N, NR^{13} , O, S, CR^{14} and

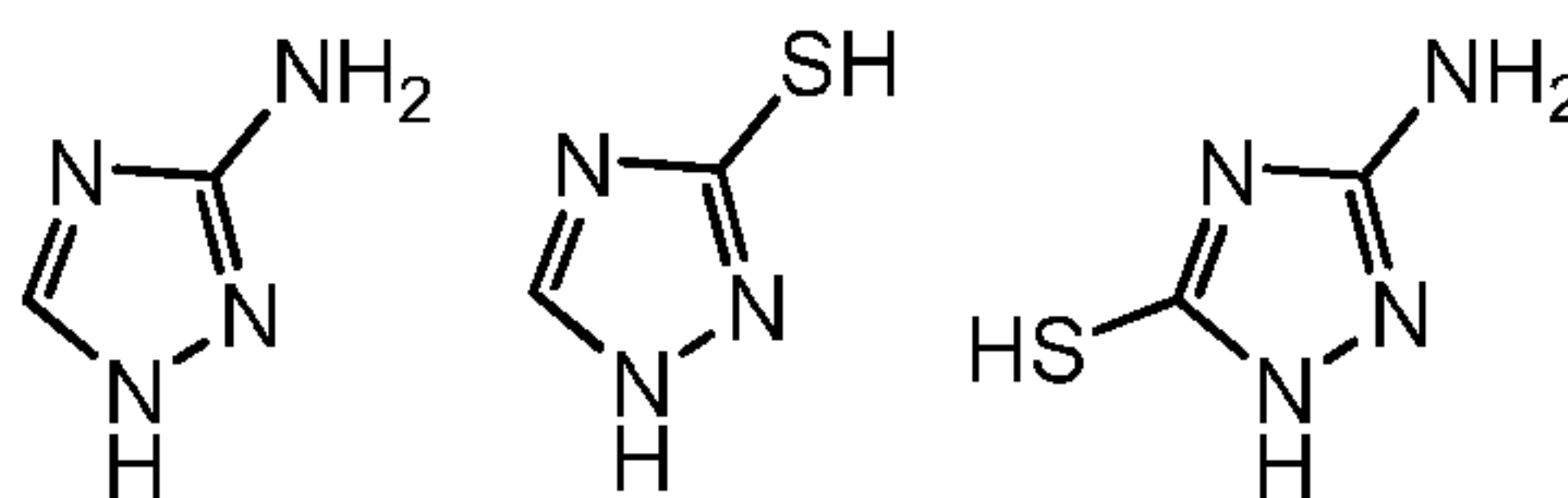
15 $CR^{15}R^{16}$;

R^{13} is selected from hydrogen, amino, C_1 - C_{10} alkyl, C_2 - C_{10} alkenyl, C_2 - C_{10} alkynyl, aryl and heteroaryl, in which each amino, alkyl, alkenyl, alkynyl, aryl or heteroaryl group may be optionally substituted; and

R^{14} , R^{15} and R^{16} are defined according to Formula 1b as described above..

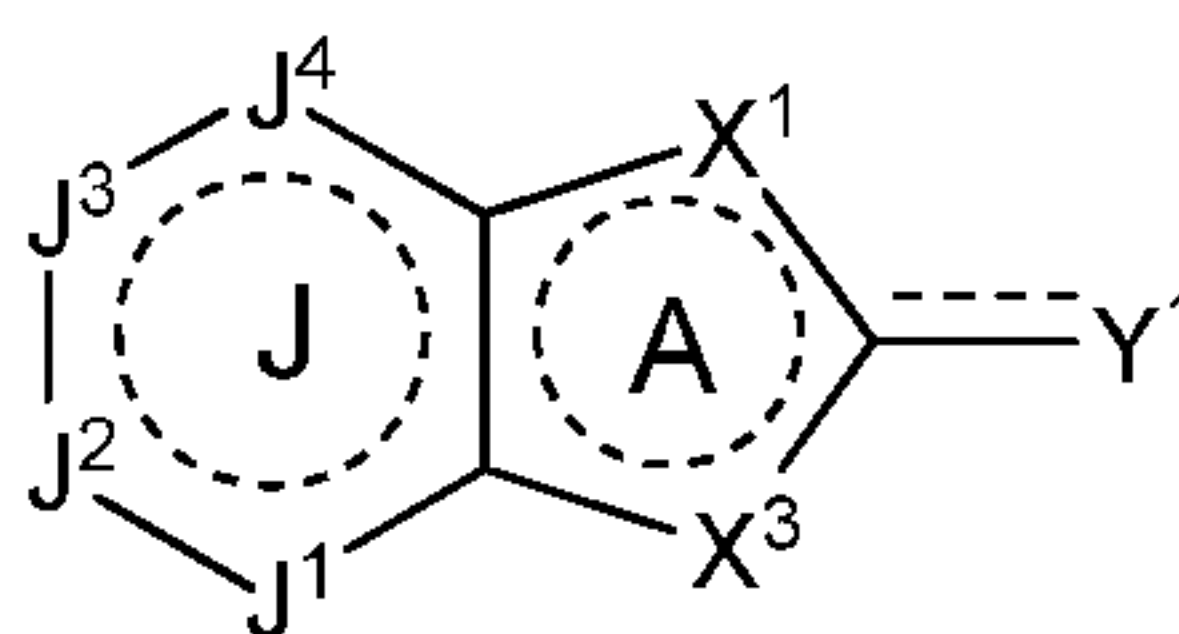
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Some specific examples of compounds of Formula 1(b)(i) are provided as follows:



The organic heterocyclic compound may be selected from a compound of Formula 1(b)(ii) or salt thereof:

32



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Formula 1(b)(ii)

wherein

A ring is an optionally substituted 5-membered heterocyclic ring and J ring is an optionally substituted 6-membered aryl or heterocyclic ring, wherein a dotted line represents one or more optional double bonds;

10

X^1 , X^3 and Y^1 are defined according to Formula 1a as described above;

J^1 , J^2 , J^3 and J^4 are each independently selected from N, NR^{13} , O, S, CR^{14} and $CR^{15}R^{16}$;

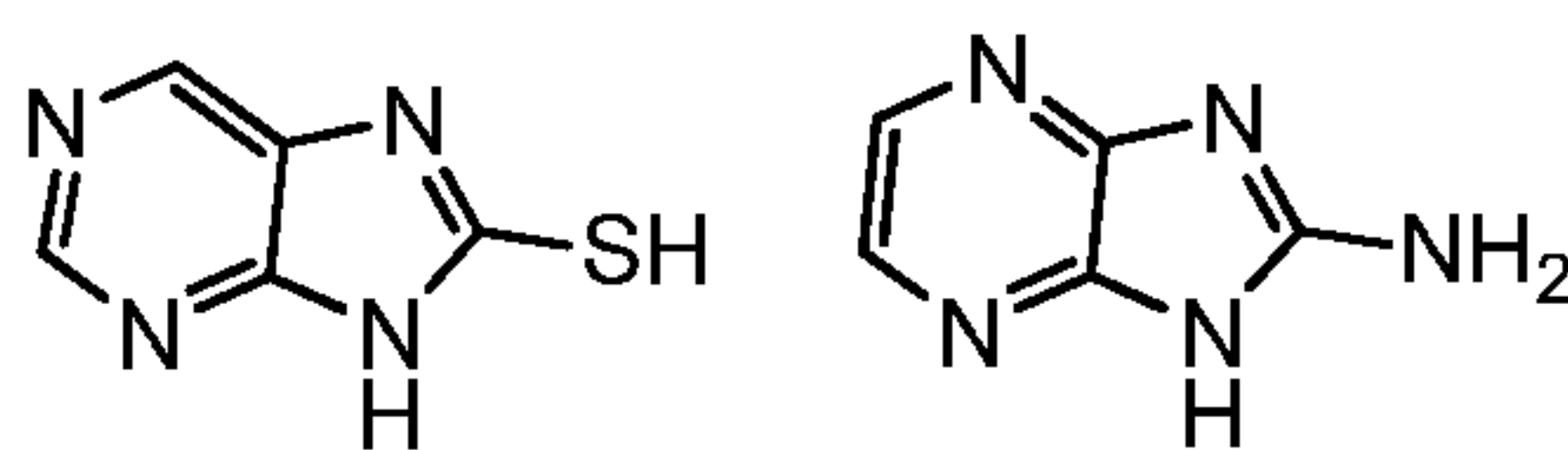
R^{13} is selected from hydrogen, amino, C_1 - C_{10} alkyl, C_2 - C_{10} alkenyl, C_2 - C_{10} alkynyl, aryl and heteroaryl, in which each amino, alkyl, alkenyl, alkynyl, aryl or heteroaryl group may be optionally substituted; and

15

R^{14} , R^{15} and R^{16} , are each independently selected from hydrogen, halogen, carboxyl, amino, C_1 - C_{10} alkyl, C_2 - C_{10} alkenyl, C_2 - C_{10} alkynyl, aryl and heteroaryl, in which each amino, alkyl, alkenyl, alkynyl, aryl or heteroaryl group may be optionally substituted.

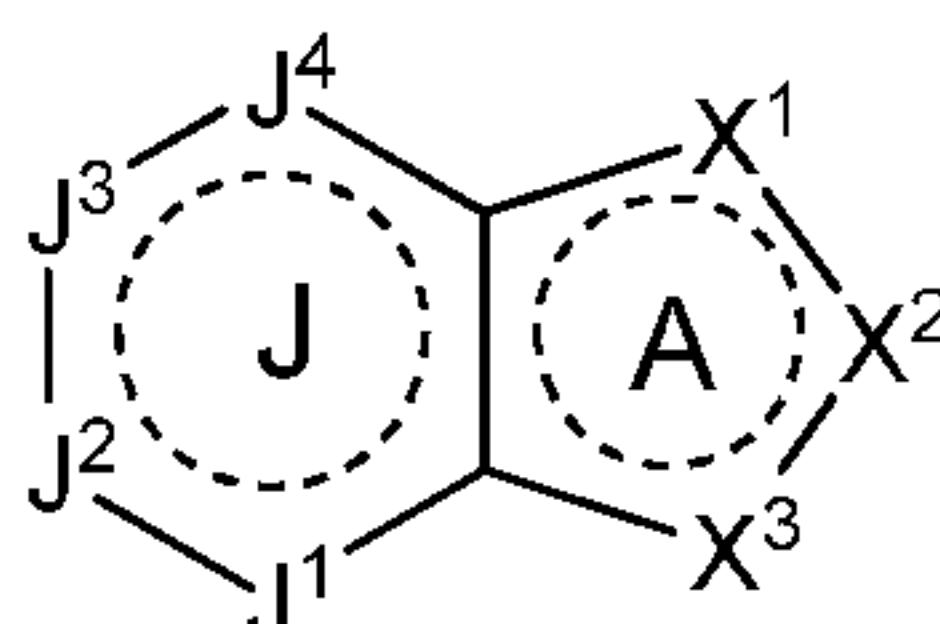
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Some specific examples of compounds of Formula 1(b)(ii) are provided as follows:



The organic heterocyclic compound may be selected from a compound of Formula 1(b)(iii) or salt thereof:

25



Formula 1(b)(iii)

5 wherein

A ring is an optionally substituted 5-membered heterocyclic ring and J ring is an optionally substituted 6-membered aryl or heterocyclic ring, wherein a dotted line represents one or more optional double bonds;

X^1 , X^2 , X^3 are defined according to Formula 1a as described above;

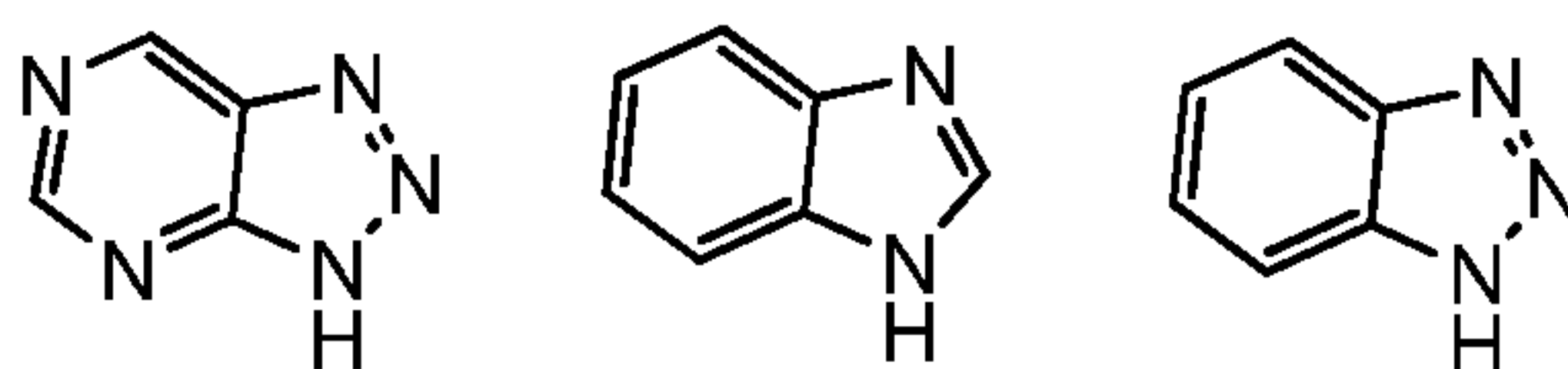
10 Y^1 is absent;

J^1 , J^2 , J^3 and J^4 are each independently selected from N, NR^{13} , O, S, CR^{14} and $CR^{15}R^{16}$;

R^{13} is selected from hydrogen, amino, C_1 - C_{10} alkyl, C_2 - C_{10} alkenyl, C_2 - C_{10} alkynyl, aryl and heteroaryl, in which each amino, alkyl, alkenyl, alkynyl, aryl or
15 heteroaryl group may be optionally substituted; and

R^{14} , R^{15} and R^{16} , are each independently selected from hydrogen, halogen, carboxyl, amino, C_1 - C_{10} alkyl, C_2 - C_{10} alkenyl, C_2 - C_{10} alkynyl, aryl and heteroaryl, in which each amino, alkyl, alkenyl, alkynyl, aryl or heteroaryl group may be optionally substituted.

20 Some specific examples of compounds of Formula 1(b)(iii) are provided as follows:

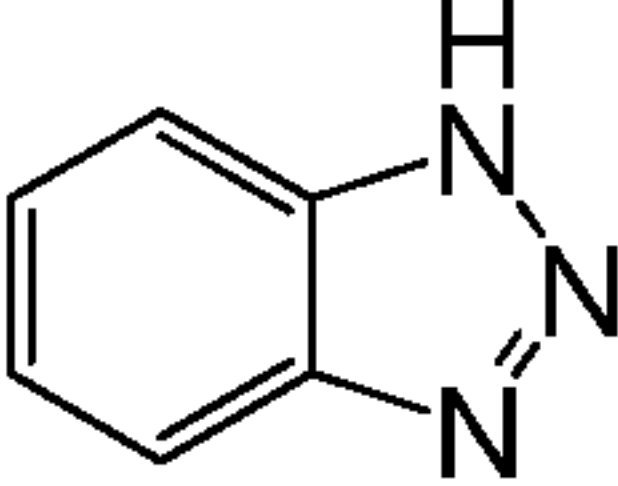
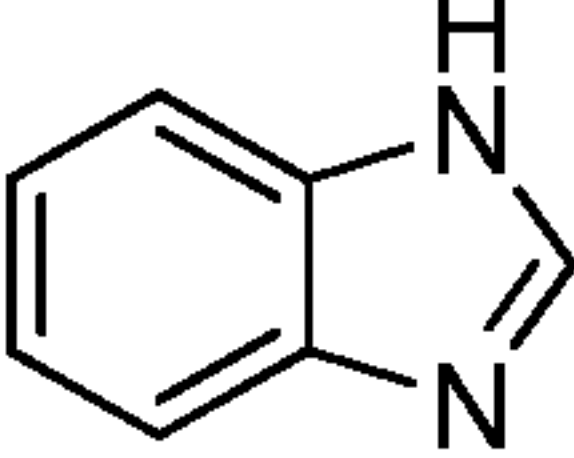
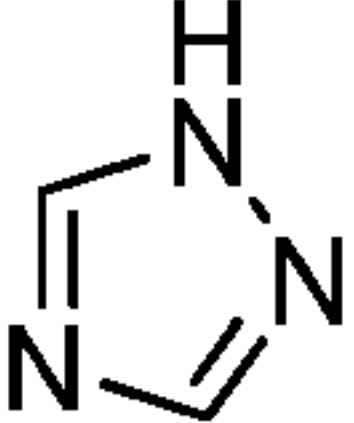
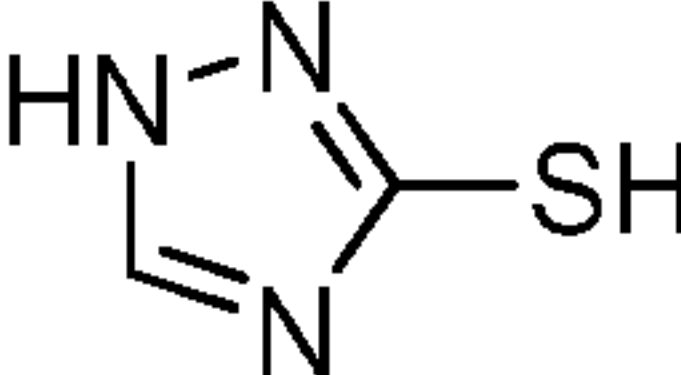
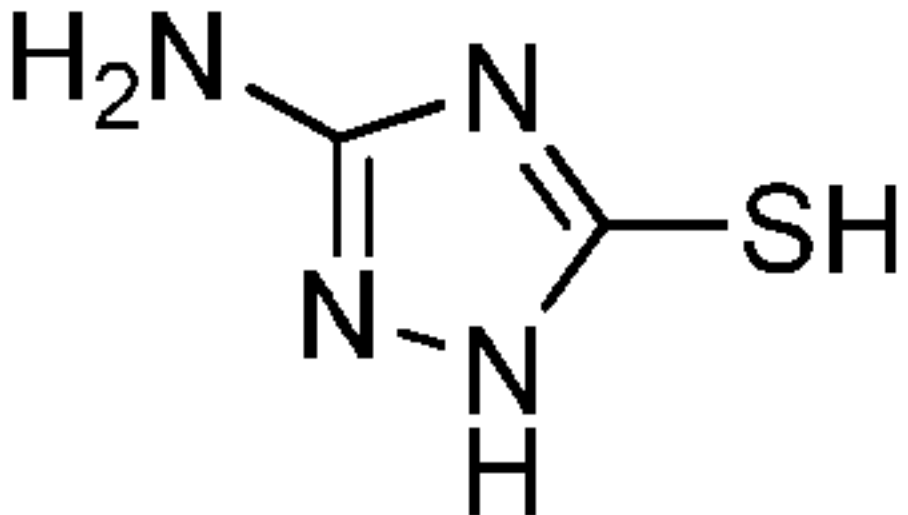
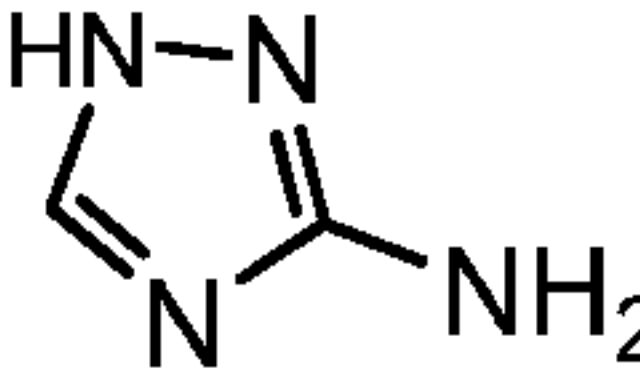
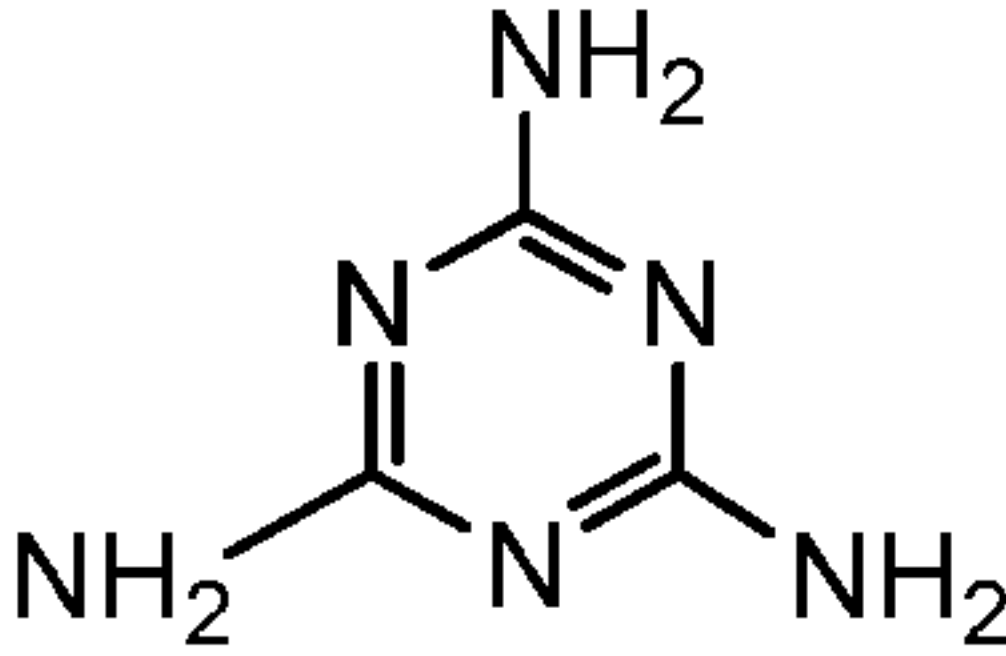
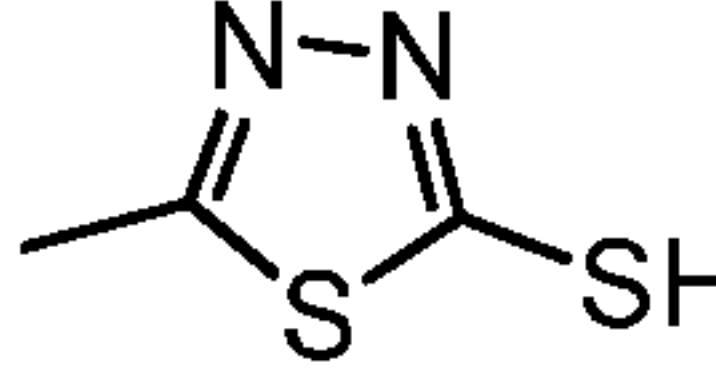
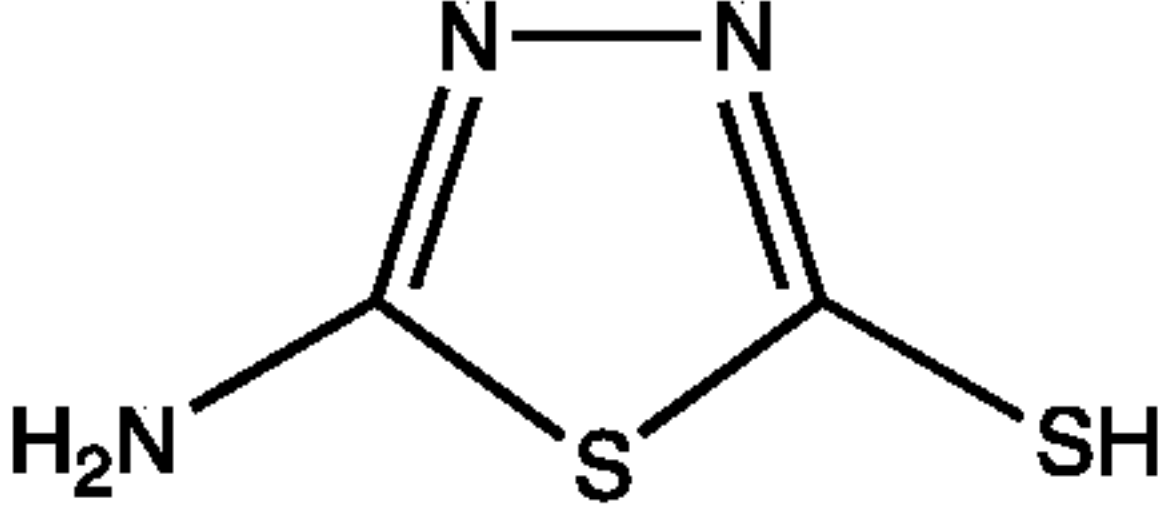
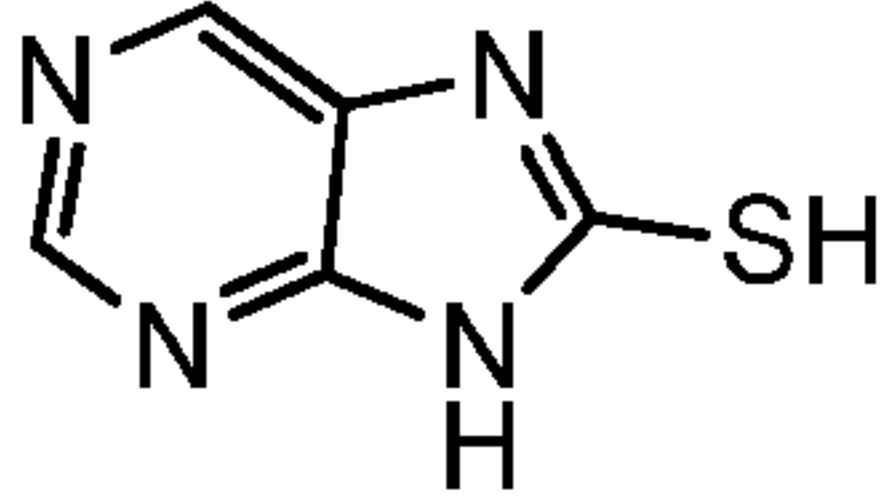


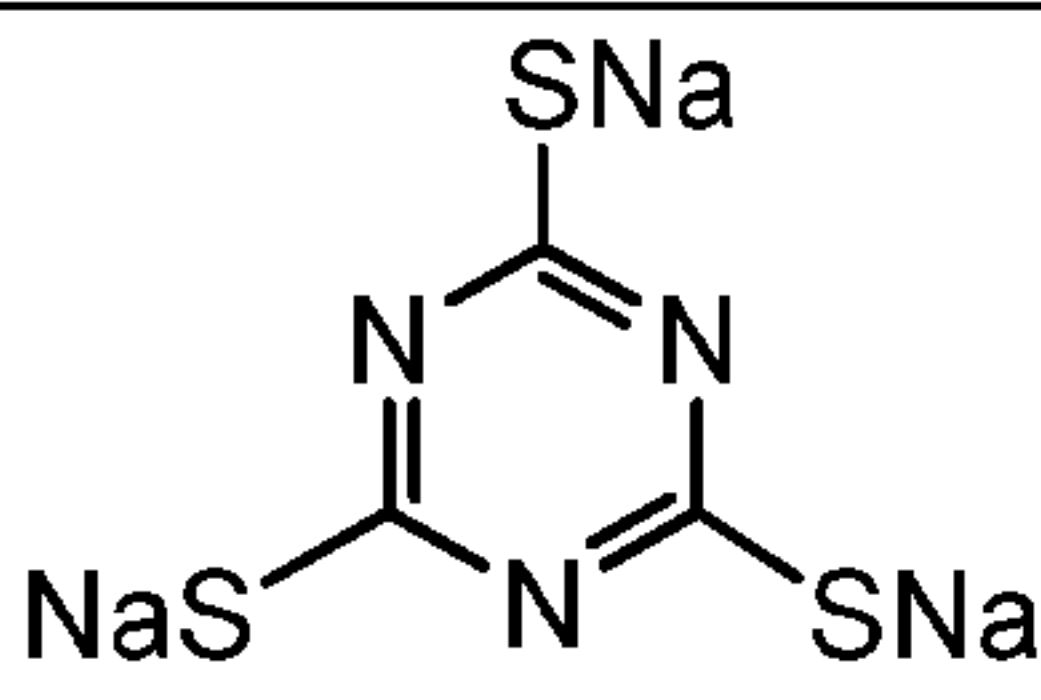
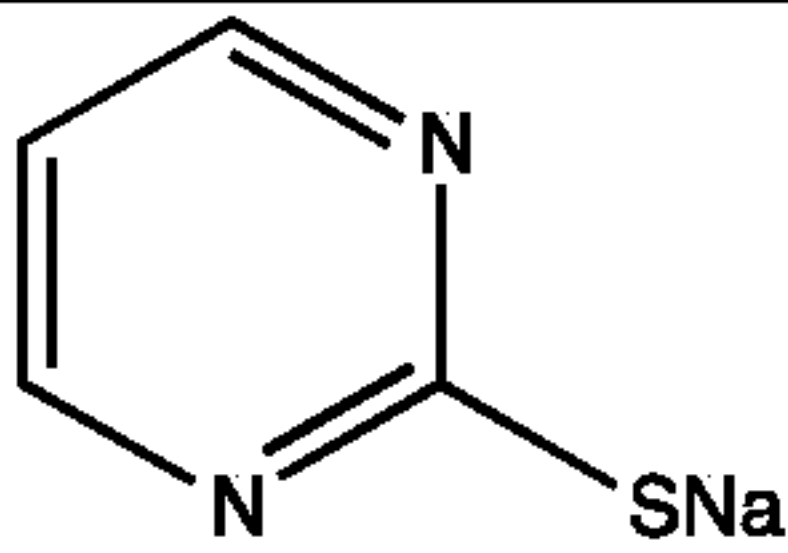
It will be appreciated that any of the embodiments or examples described above or herein for Formula 1 may also provide embodiments for any compounds of Formula
25 1(a), 1(a)(i), 1(b), 1(b)(i), 1(b)(ii) or 1(b)(iii).

The organic compounds may exist as one or more stereoisomers. The various stereoisomers can include enantiomers, diastereomers and geometric isomers. Those skilled in the art will appreciate that one stereoisomer may be more active than the other(s). In addition, the skilled person would know how to separate such
30 stereoisomers. Accordingly, the present disclosure comprises mixtures, individual stereoisomers, and optically active mixtures of the compounds described herein.

Some specific examples of heteroaryl and heterocyclic organic compounds of Formula 1 are shown in Table 1 as follows:

5 Table 1

Ref. No.	Chemical Name	Chemical Structure
1	1H-benzotriazole	
2	benzimidazole	
3	1,2,4-triazole	
4	1,2,4-triazole-3-thiol	
5	3-amino,5-mercapto-1,2,4-triazole	
6	3-amino-1,2,4-triazole	
7	1,3,5-triazine-2,4,6-triamine	
8	5-methyl-2-mercapto-1,3,4-thiadiazole	
9	5-amino-2-mercapto-1,3,4-thiadiazole	
10	9H-purine-8-thiol	

11	1,3,5-triazine-2,4,6-trithiol, trisodium salt	
12	2-mercaptopyrimidine, sodium salt	

5

METAL SALTS, METAL ANIONS AND METAL COMPLEXES

The corrosion inhibitors of the present disclosure may be selected from metal salts, metal anions, or in the form of a metal complex. The metals of the metal salts, metal anions and metal complexes may be selected from alkali earth metals, transition metals and rare earth metals, for example a group consisting of Zn, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Ce, Co, Y, Bi, Cd, Pb, Ag, Sb, Sn, Cu, Fe, Ni, Li, Ca, Sr, Mg, Zr, Nd, Ba, Mo, Sc, W, V, and any combinations thereof. The combined corrosion inhibitor formulations may comprise at least one metal salt, at least one metal anion, or at least one metal complex, wherein the metal is selected from the group consisting of Zn, La, Pr, Ce, Co, Cu, Y, Ca, Sr, Ba, Gd, Dy, Er, Tb, Mo, Sc, Sm, and Zr. The metals may be selected from at least one of Zn, Co, Cu, Mo, Ce, Gd, Dy, Er, Lu, Tb, Sm, and Pr. The metals may be selected from at least one of Zn, Co, Cu, Mo, Sm, Ce, Er, Lu, and Gd. The metals may be selected from Zn, Mo, Co, Cu W, V, Zr, Sm, Dy, Tb, Ce, Pr, Er, Tm, Lu and Gd. The metals may be selected from Zn, Mo, Co, Cu, W, V, Zr, Ce, Pr, Er, Lu, and Gd. The metals may be selected from Zn, Mo, Co, Cu, Ce, Gd, Er, Lu, W, and Zr. The metals may be selected from Zn, Co, Cu, Mo, Pr, Gd, Er and Lu. The metals may be selected from Zn, Mo, Pr, Ce, Gd, Er and Lu. The metals may be selected from at least one of Zn, Mo, and Gd. The metal may be Zn. The metal may be Mo. The metal may be Pr. The metal may be Gd. The metal may be Dy. The metal may be Sm. The metal may be Er. The metal may be Lu. The metal may be Co. The metal may be Cu. The metal may be Tb. The metal may be W. The metal may be V. The metal may be Zr. It will be appreciated that the metals may have different oxidation states. For example, the typical oxidation state for Zn is -2, +1

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5 and/or +2. The typical oxidation states for Pr are +2, +3, +4 and/or +5. The typical oxidation states for Ce are +2, +3 and +4. The typical oxidation states for Mo are -4, -2, -1, +1, +2, +3, +4, +5 and/or +6. The typical oxidation states for Gd are +1, +2, and/or +3. The typical oxidation states for Tb are +1, +2, +3 and/or +4. The typical oxidation states for Dy are +2, +3 and/or +4. The typical oxidation states for Er are +2 and/or +3.

10 It will be appreciated that various combinations and groups of the above mentioned metal salts, metal anions, metal complexes, may be used in the formulations of the present disclosure.

It will be appreciated that reference to metal salt in the combined corrosion inhibiting formulations described herein refers to a metal in the form of a metal salt comprising both anions and cations. For example a Cl anion is the counterion for a Zn metal cation. Some example counterions that may be used are NO_3^- , Cl^- , SO_4^{2-} , Na^+ .

15 For example, the metal salt may be selected from at least one of ZnCl_2 , CoCl_2 , CuCl_2 , CeCl_3 , ErCl_3 , LuCl_3 , PrCl_3 , SmCl_3 , GdCl_3 and DyCl_3 .

It will be appreciated that reference to metal anion in the combined corrosion inhibiting formulations described herein refers to a metal in the form of a metal anion. For example, the metal anion may be selected from at least one of MoO_4^{2-} , VO_4^{3-} , ZrO_4^{2-} , WO_4^{2-} . The metal anion may be MoO_4^{2-} . The metal anion may be VO_4^{3-} . The metal anion may be ZrO_4^{2-} . The metal anion may be WO_4^{2-} . Some example counterions that may be used are Na^+ , Zn^+ , NH_4^+ .

20

25 It will be appreciated that reference to metal complex in the combined corrosion inhibitor formulations described herein refers to a metal in the form of a metal complex. It will also be appreciated that reference to metal complex in the combined corrosion inhibitor formulations described herein may refer to a metal-organic complex. A metal complex may be formed when a combined corrosion inhibitor formulation comprises at least two corrosion inhibitors, and may for example comprise at least three or a least four corrosion inhibitors. For example, a metal complex may be formed from an organic heterocyclic compound of Formula 1 and a metal selected from the group consisting of Zn, La, Pr, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Co, Cu, Y, Ca, Sr, Ba, Sc, Mo, W, V and Zr. A further example, a metal complex may be formed when the corrosion inhibitors are selected from at least one metal salt and at

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- 5 least one organic heterocyclic compounds of Formula 1. A metal complex may be formed when the corrosion inhibitors are selected from at least one metal anion and at least one organic heterocyclic compounds of Formula 1. A metal complex may be formed when the corrosion inhibitors are selected from at least two metal salts and at least two organic heterocyclic compounds of Formula 1. A metal complex may be
- 10 formed when the corrosion inhibitors are selected from at least two metal anions and at least two organic heterocyclic compounds of Formula 1. The metal complex may form from the reaction of each of the at least two metal salts or metal anions with each of the at least two organic heterocyclic compounds of Formula 1. The combined corrosion inhibitor formulation may comprise at least two metal-organic complexes. A metal
- 15 complex may be formed when then the corrosion inhibitors are selected from at least one metal salt and at least one metal anion. For example, the metal complex may be zinc molybdate, praseodymium molybdate, cerium molybdate, erbium molybdate, lanthanum molybdate, gadolinium molybdate, lutetium molybdate, dysprosium molybdate, zinc vanadate, praseodymium vanadate, cerium vanadate, erbium vanadate,
- 20 lanthanum vanadate, gadolinium vanadate, lutetium vanadate, dysprosium vanadate, zinc zirconate, praseodymium zirconate, cerium zirconate, erbium zirconate, lanthanum zirconate, gadolinium zirconate, lutetium zirconate, dysprosium zirconate, zinc tungstate, praseodymium tungstate, cerium tungstate, erbium tungstate, lanthanum tungstate, gadolinium tungstate, lutetium tungstate, dysprosium tungstate,
- 25 praseodymium benzotriazole, zinc benzotriazole, cerium benzotriazole, erbium benzotriazole, lanthanum benzotriazole, gadolinium benzotriazole, dysprosium benzotriazole, lutetium benzotriazole, gadolinium molybdate, praseodymium benzimidazole, dysprosium benzimidazole, lutetium benzimidazole, zinc benzimidazole, cerium benzimidazole, erbium benzimidazole,
- 30 lanthanum benzimidazole, gadolinium benzimidazole.

SUBSTRATES FOR CORROSION PROTECTION

- Substrates that may be protected from corrosion by the corrosion inhibiting agents or compositions thereof as described herein may be metal substrates. It will be appreciated that the metal substrate can include any substrate material having at least a
- 35 portion of its surface being metallic, for example a portion of its external surface being

5 metallic. The metal substrate may comprise any metal requiring protection from corrosion. The metal substrate may comprise a metal or alloy selected from steel, copper, magnesium brass, bronze and zinc. The metal substrate may be steel, for example mild steel, carbon steel, stainless steel, high strength/low alloy steel, galvanised steel, Al-Zn coated steel, and weathering steel. For example the metal
10 substrate may be mild steel.

COMBINATIONS, COMPOSITIONS AND FORMULATIONS

The present disclosure also relates to compositions for inhibiting corrosion comprising at least a first and second corrosion inhibitor formulation for inhibiting corrosion of a substrate wherein the first corrosion inhibitor formulation comprises at
15 least one corrosion inhibitor and the second corrosion inhibitor formulation comprises at least one corrosion inhibitor that is different to the corrosion inhibitor of the first corrosion inhibitor formulation. The corrosion inhibitors are each independently selected from the group consisting of an organic heterocyclic compound of Formula 1 as described herein and a metal salt, metal anion, metal complex, or any combination
20 thereof, wherein the metal is selected from rare earth, alkali earth and transition metals, as described herein, or any embodiments thereof. It will be appreciated that reference to any combined corrosion inhibitor formulation in the composition described herein refers to the individual corrosion inhibitors themselves together in one composition and not reaction products thereof.

25 For example, the combined corrosion inhibitor formulation may comprise at least one organic heterocyclic compound of Formula 1 as described herein or any embodiments thereof and at least one metal salt, metal anion or metal complex, wherein the metal is selected from the group consisting of Zn, La, Pr, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Co, Cu, Y, Ca, Sr, Ba, Sc, Mo, W, V, and Zr. For example,
30 the metal may be any one of Zn, Mo, Gd, Dy, Er, Tb, and Pr; the metal may be Zn, Mo, and Gd; the metal may be Mo, W, V and Zr; the metal may be Zn, V, and Er; the metal may be Zn, V, and Lu; the metal may be Co, V, and Er; the metal may be Zn, W, and Er; the metal may be Zn, W, and Lu; the metal may be Co, Mo, and Er; the metal may be Co, Mo, Lu; the metal may be Cu, Mo, Er; the metal may be Cu, Mo, and Pr; the
35 metal may be Cu, Mo, and Lu; the metal may be Zn, Mo, and Er; the metal may be Zn,

5 Mo and Lu; the metal may be Zn, Mo and Pr; the metal may be Zn, Mo, and Gd; the metal may be Gd, Mo, and Er; the metal may be Gd, Mo, Lu; the metal may be Gd, Mo, Er; the metal may be Gd, Mo, and Pr; the metal may be Gd, Mo, and Lu; or the metal may be Zn, Mo, and Gd; the metal may be Zn; the metal may be Mo; the metal may be Gd; the metal may be Er; the metal may be Dy; the metal may be W; the metal
10 may be V; or the metal may be Zr.

The combined corrosion inhibitor formulation may comprise at least one organic heterocyclic compound of Formula 1(a)(i) or salt thereof, as described herein or any embodiments thereof and at least one metal salt, metal anion, or metal complex, wherein the metal is selected from the group consisting of Zn, Co, Cu, Mo, Gd, Dy, Er,
15 Tb, Sm, Lu, W, V, and Pr; the metal may be Mo, W, V and Zr; the metal may be Zn, V, and Er; the metal may be Zn, V, and Lu; the metal may be Co, V, and Er; the metal may be Zn, W, and Er; the metal may be Zn, W, and Lu; the metal may be Co, Mo, and Er; the metal may be Co, Mo, Lu; the metal may be Cu, Mo, Er; the metal may be Cu, Mo, and Pr; the metal may be Cu, Mo, and Lu; the metal may be Zn, Mo, and Er; the
20 metal may be Zn, Mo and Lu; the metal may be Zn, Mo and Pr; the metal may be Zn, Mo, and Gd; the metal may be Gd, Mo, and Er; the metal may be Gd, Mo, Lu; the metal may be Gd, Mo, Er; the metal may be Gd, Mo, and Pr; the metal may be Gd, Mo, and Lu; or the metal may be Zn, Mo, and Gd.

The combined corrosion inhibitor formulation may comprise at least one
25 organic heterocyclic compound of Formula 1(b) or salt thereof, as described herein or any embodiments thereof and at least one metal salt, metal anion, or metal complex, wherein the metal is selected from the group consisting of Zn, La, Pr, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Co, Cu, Y, Ca, Sr, Ba, Sc, Mo, V, W and Zr; the metal may be Mo, W, V and Zr; the metal may be Zn, V, and Er; the metal may be Zn, V, and Lu; the metal may be Co, V, and Er; the metal may be Zn, W, and Er; the metal
30 may be Zn, W, and Lu; the metal may be Co, Mo, and Er; the metal may be Co, Mo, Lu; the metal may be Cu, Mo, Er; the metal may be Cu, Mo, and Pr; the metal may be Cu, Mo, and Lu; the metal may be Zn, Mo, and Er; the metal may be Zn, Mo and Lu; the metal may be Zn, Mo and Pr; the metal may be Zn, Mo, and Gd; the metal may be
35 Gd, Mo, and Er; the metal may be Gd, Mo, Lu; the metal may be Gd, Mo, Er; the metal

5 may be Gd, Mo, and Pr; the metal may be Gd, Mo, and Lu; or the metal may be Zn, Mo, and Gd.

The combined corrosion inhibitor formulation may comprise at least one organic heterocyclic compound of Formula 1(b)(i) or salt thereof, as described herein or any embodiments thereof and at least one metal salt, metal anion, or metal complex,
10 wherein the metal is selected from the group consisting of Zn, Co, Cu, Mo, Gd, Dy, Er, Tb, Sm, Lu, W, V, and Pr; the metal may be Mo, W, V and Zr; the metal may be Zn, V, and Er; the metal may be Zn, V, and Lu; the metal may be Co, V, and Er; the metal may be Zn, W, and Er; the metal may be Zn, W, and Lu; the metal may be Co, Mo, and Er; the metal may be Co, Mo, Lu; the metal may be Cu, Mo, Er; the metal may be Cu,
15 Mo, and Pr; the metal may be Cu, Mo, and Lu; the metal may be Zn, Mo, and Er; the metal may be Zn, Mo and Lu; the metal may be Zn, Mo and Pr; the metal may be Zn, Mo, and Gd; the metal may be Gd, Mo, and Er; the metal may be Gd, Mo, Lu; the metal may be Gd, Mo, Er; the metal may be Gd, Mo, and Pr; the metal may be Gd, Mo, and Lu; or the metal may be Zn, Mo, and Gd.

20 The combined corrosion inhibitor formulation may comprise at least one organic heterocyclic compound of Formula 1(b)(ii) or salt thereof, as described herein or any embodiments thereof and at least one metal salt, metal anion, or metal complex, wherein the metal is selected from the group consisting of Zn, Co, Cu, Mo, Gd, Dy, Er, Tb, Sm, Lu, W, V, and Pr; the metal may be Mo, W, V and Zr; the metal may be Zn, V,
25 and Er; the metal may be Zn, V, and Lu; the metal may be Co, V, and Er; the metal may be Zn, W, and Er; the metal may be Zn, W, and Lu; the metal may be Co, Mo, and Er; the metal may be Co, Mo, Lu; the metal may be Cu, Mo, Er; the metal may be Cu, Mo, and Pr; the metal may be Cu, Mo, and Lu; the metal may be Zn, Mo, and Er; the metal may be Zn, Mo and Lu; the metal may be Zn, Mo and Pr; the metal may be Zn,
30 Mo, and Gd; the metal may be Gd, Mo, and Er; the metal may be Gd, Mo, Lu; the metal may be Gd, Mo, Er; the metal may be Gd, Mo, and Pr; the metal may be Gd, Mo, and Lu; or the metal may be Zn, Mo, and Gd.

The combined corrosion inhibitor formulation may comprise at least one organic heterocyclic compound of Formula 1(b)(iii) or salt thereof, as described herein
35 or any embodiments thereof and at least one metal salt, metal anion, or metal complex,

5 wherein the metal is selected from the group consisting of Zn, Co, Cu, Mo, Gd, Dy, Er, Tb, Sm, Lu, W, V and Pr; the metal may be Mo, W, V and Zr; the metal may be Zn, V, and Er; the metal may be Zn, V, and Lu; the metal may be Co, V, and Er; the metal may be Zn, W, and Er; the metal may be Zn, W, and Lu; the metal may be Co, Mo, and Er; the metal may be Co, Mo, Lu; the metal may be Cu, Mo, Er; the metal may be Cu, Mo, and Pr; the metal may be Cu, Mo, and Lu; the metal may be Zn, Mo, and Er; the metal may be Zn, Mo and Lu; the metal may be Zn, Mo and Pr; the metal may be Zn, Mo, and Gd; the metal may be Gd, Mo, and Er; the metal may be Gd, Mo, Lu; the metal may be Gd, Mo, Er; the metal may be Gd, Mo, and Pr; the metal may be Gd, Mo, and Lu; or the metal may be Zn, Mo, and Gd.

15 The combined corrosion inhibitor formulation may comprise at least one organic heterocyclic compound of Formula 1(a)(i) or salt thereof, as described herein or any embodiments thereof and at least one metal salt, metal anion, or metal complex, wherein the metal is selected from the group consisting of Zn, Co, Cu, Gd, Er, Lu, Mo, W, V and Zr.

20 The combined corrosion inhibitor formulation may comprise at least one organic heterocyclic compound of Formula 1(b) or salt thereof, as described herein or any embodiments thereof and at least one metal salt, metal anion, or metal complex, wherein the metal is selected from the group consisting of Zn, Co, Cu, Gd, Er, Lu, Mo, W, V and Zr.

25 The combined corrosion inhibitor formulation may comprise at least one organic heterocyclic compound of Formula 1(b)(i) or salt thereof, as described herein or any embodiments thereof and at least one metal salt, metal anion, or metal complex, wherein the metal is selected from the group consisting of Zn, Co, Cu, Gd, Er, Lu, Mo, W, V and Zr.

30 The combined corrosion inhibitor formulation may comprise at least one organic heterocyclic compound of Formula 1(b)(ii) or salt thereof, as described herein or any embodiments thereof and at least one metal salt, metal anion, or metal complex, wherein the metal is selected from the group consisting of Zn, Co, Cu, Gd, Er, Lu, Mo, W, V and Zr.

35 The combined corrosion inhibitor formulation may comprise at least one

- 5 organic heterocyclic compound of Formula 1(b)(iii) or salt thereof, as described herein or any embodiments thereof and at least one metal salt, metal anion, or metal complex, wherein the metal is selected from the group consisting of Zn, Co, Cu, Gd, Er, Lu, Mo, W, V and Zr.

The combined corrosion inhibitor formulation may comprise at least two
10 organic heterocyclic compound of Formula 1(a) or salt thereof, as described herein or any embodiments thereof.

The combined corrosion inhibitor formulation may comprise at least two organic heterocyclic compound of Formula 1(a)(i) or salt thereof, as described herein or any embodiments thereof.

15 The combined corrosion inhibitor formulation may comprise at least two organic heterocyclic compound of Formula 1(b) or salt thereof, as described herein or any embodiments thereof.

The combined corrosion inhibitor formulation may comprise at least two organic heterocyclic compound of Formula 1(b)(i) or salt thereof, as described herein
20 or any embodiments thereof.

The combined corrosion inhibitor formulation may comprise at least two organic heterocyclic compound of Formula 1(b)(ii) or salt thereof, as described herein or any embodiments thereof.

The combined corrosion inhibitor formulation may comprise at least two
25 organic heterocyclic compound of Formula 1(b)(iii) or salt thereof, as described herein or any embodiments thereof.

The combined corrosion inhibitor formulation may comprise at least three organic heterocyclic compound of Formula 1(a) or salt thereof, as described herein or any embodiments thereof.

30 The combined corrosion inhibitor formulation may comprise at least three organic heterocyclic compound of Formula 1(a)(i) or salt thereof, as described herein or any embodiments thereof.

The combined corrosion inhibitor formulation may comprise at least three organic heterocyclic compound of Formula 1(b) or salt thereof, as described herein or
35 any embodiments thereof.

5 The combined corrosion inhibitor formulation may comprise at least three organic heterocyclic compound of Formula 1(b)(i) or salt thereof, as described herein or any embodiments thereof.

 The combined corrosion inhibitor formulation may comprise at least three organic heterocyclic compound of Formula 1(b)(ii) or salt thereof, as described herein
10 or any embodiments thereof.

 The combined corrosion inhibitor formulation may comprise at least three organic heterocyclic compound of Formula 1(b)(iii) or salt thereof, as described herein or any embodiments thereof.

 The combined corrosion inhibitor formulation may comprise at least four
15 organic heterocyclic compound of Formula 1(a) or salt thereof, as described herein or any embodiments thereof.

 The combined corrosion inhibitor formulation may comprise at least four organic heterocyclic compound of Formula 1(a)(i) or salt thereof, as described herein or any embodiments thereof.

20 The combined corrosion inhibitor formulation may comprise at least four organic heterocyclic compound of Formula 1(b) or salt thereof, as described herein or any embodiments thereof.

 The combined corrosion inhibitor formulation may comprise at least four organic heterocyclic compound of Formula 1(b)(i) or salt thereof, as described herein
25 or any embodiments thereof.

 The combined corrosion inhibitor formulation may comprise at least four organic heterocyclic compound of Formula 1(b)(ii) or salt thereof, as described herein or any embodiments thereof.

 The combined corrosion inhibitor formulation may comprise at least four
30 organic heterocyclic compound of Formula 1(b)(iii) or salt thereof, as described herein or any embodiments thereof.

 The combined corrosion inhibitor formulation may comprise at least one organic heterocyclic compound of Formula 1(a) or salt thereof, as described herein or any embodiments thereof and at least one organic heterocyclic compound of Formula
35 1(a)(i) or salt thereof, as described herein or any embodiments thereof.

5 The combined corrosion inhibitor formulation may comprise at least one organic heterocyclic compound of Formula 1(a) or salt thereof, as described herein or any embodiments thereof and at least one organic heterocyclic compound of Formula 1(b) or salt thereof, as described herein or any embodiments thereof.

 The combined corrosion inhibitor formulation may comprise at least one
10 organic heterocyclic compound of Formula 1(a) or salt thereof, as described herein or any embodiments thereof and at least one organic heterocyclic compound of Formula 1(b)(i) or salt thereof, as described herein or any embodiments thereof.

 The combined corrosion inhibitor formulation may comprise at least one organic heterocyclic compound of Formula 1(a) or salt thereof, as described herein or
15 any embodiments thereof and at least one organic heterocyclic compound of Formula 1(b)(ii) or salt thereof, as described herein or any embodiments thereof.

 The combined corrosion inhibitor formulation may comprise at least one organic heterocyclic compound of Formula 1(a) or salt thereof, as described herein or any embodiments thereof and at least one organic heterocyclic compound of Formula
20 1(b)(iii) or salt thereof, as described herein or any embodiments thereof.

 The combined corrosion inhibitor formulation may comprise at least one organic heterocyclic compound of Formula 1(a)(i) or salt thereof, as described herein or any embodiments thereof and at least one organic heterocyclic compound of Formula 1(a)(i) or salt thereof, as described herein or any embodiments thereof.

25 The combined corrosion inhibitor formulation may comprise at least one organic heterocyclic compound of Formula 1(a)(i) or salt thereof, as described herein or any embodiments thereof and at least one organic heterocyclic compound of Formula 1(b) or salt thereof, as described herein or any embodiments thereof.

 The combined corrosion inhibitor formulation may comprise at least one
30 organic heterocyclic compound of Formula 1(a)(i) or salt thereof, as described herein or any embodiments thereof and at least one organic heterocyclic compound of Formula 1(b)(i) or salt thereof, as described herein or any embodiments thereof.

 The combined corrosion inhibitor formulation may comprise at least one organic heterocyclic compound of Formula 1(a)(i) or salt thereof, as described herein or
35 any embodiments thereof and at least one organic heterocyclic compound of Formula

5 1(b)(ii) or salt thereof, as described herein or any embodiments thereof.

The combined corrosion inhibitor formulation may comprise at least one organic heterocyclic compound of Formula 1(a)(i) or salt thereof, as described herein or any embodiments thereof and at least one organic heterocyclic compound of Formula 1(b)(iii) or salt thereof, as described herein or any embodiments thereof.

10 The combined corrosion inhibitor formulation may comprise at least one organic heterocyclic compound of Formula 1(b) or salt thereof, as described herein or any embodiments thereof and at least one organic heterocyclic compound of Formula 1(b) or salt thereof, as described herein or any embodiments thereof.

The combined corrosion inhibitor formulation may comprise at least one
15 organic heterocyclic compound of Formula 1(b) or salt thereof, as described herein or any embodiments thereof and at least one organic heterocyclic compound of Formula 1(b)(i) or salt thereof, as described herein or any embodiments thereof.

The combined corrosion inhibitor formulation may comprise at least one organic heterocyclic compound of Formula 1(b) or salt thereof, as described herein or
20 any embodiments thereof and at least one organic heterocyclic compound of Formula 1(b)(ii) or salt thereof, as described herein or any embodiments thereof.

The combined corrosion inhibitor formulation may comprise at least one organic heterocyclic compound of Formula 1(b) or salt thereof, as described herein or any embodiments thereof and at least one organic heterocyclic compound of Formula
25 1(b)(iii) or salt thereof, as described herein or any embodiments thereof.

The combined corrosion inhibitor formulation may comprise at least one organic heterocyclic compound of Formula 1(b)(i) or salt thereof, as described herein or any embodiments thereof and at least one organic heterocyclic compound of Formula 1(b)(i) or salt thereof, as described herein or any embodiments thereof.

30 The combined corrosion inhibitor formulation may comprise at least one organic heterocyclic compound of Formula 1(b)(i) or salt thereof, as described herein or any embodiments thereof and at least one organic heterocyclic compound of Formula 1(b)(ii) or salt thereof, as described herein or any embodiments thereof.

The combined corrosion inhibitor formulation may comprise at least one
35 organic heterocyclic compound of Formula 1(b)(i) or salt thereof, as described herein

5 or any embodiments thereof and at least one organic heterocyclic compound of Formula 1(b)(iii) or salt thereof, as described herein or any embodiments thereof.

The combined corrosion inhibitor formulation may comprise at least one organic heterocyclic compound of Formula 1(b)(ii) or salt thereof, as described herein or any embodiments thereof and at least one organic heterocyclic compound of
10 Formula 1(b)(ii) or salt thereof, as described herein or any embodiments thereof.

The combined corrosion inhibitor formulation may comprise at least one organic heterocyclic compound of Formula 1(b)(ii) or salt thereof, as described herein or any embodiments thereof and at least one organic heterocyclic compound of Formula 1(b)(iii) or salt thereof, as described herein or any embodiments thereof.

15 The combined corrosion inhibitor formulation may comprise at least one organic heterocyclic compound of Formula 1(b)(iii) or salt thereof, as described herein or any embodiments thereof and at least one organic heterocyclic compound of Formula 1(b)(iii) or salt thereof, as described herein or any embodiments thereof.

The combined corrosion inhibitor formulation may comprise at least two metal
20 salts, metal anions, metal complexes, or any combination thereof, wherein the metal is selected from the group consisting of Zn, La, Pr, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Co, Cu, Y, Ca, Sr, Ba, Sc, Mo, W, V, and Zr. For example, the metal may be any one of Zn, Mo, Gd, Dy, Er, Tb, and Pr; the metal may be Zn, Co, Cu, Gd, Er, Lu, Mo, W, V and Zr; the metal may be Zn, Co, Cu, Gd, Er, Lu, Mo and W; the metal
25 may be Zn, Co, Cu, Gd, Er, Lu, Mo and V; the metal may be Zn, Co, Cu, Gd, Er, Lu, Mo and Zr; the metal may be Zn, Gd, Er, Lu, W and V; the metal may be Zn, Gd, Er, Lu, W and Zr; the metal may be Zn, Gd, Er, Lu, V and Zr; the metal may be Zn, Co, Cu, Mo, Gd, Er and Lu; the metal may be Zn, Mo, and Gd; the metal may be Zn and Mo; the metal may be Mo and Gd; the metal may be Gd and Dy; the metal may be Mo
30 and Sm; or the metal may be Dy and Zn.

The combined corrosion inhibitor formulation may comprise at least three metal salts, metal anions, metal complexes or any combination thereof, wherein the metal is selected from the group consisting of Zn, La, Pr, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Co, Cu, Y, Ca, Sr, Ba, Sc, Mo, V, W and Zr. For example, the metal may
35 be any one of Zn, Mo, Gd, Dy, Er, Tb, and Pr; the metal may be Zn, Co, Cu, Gd, Er,

5 Lu, Mo, W, V and Zr; the metal may be Zn, Co, Cu, Gd, Er, Lu, Mo and W; the metal may be Zn, Co, Cu, Gd, Er, Lu, Mo and V; the metal may be Zn, Co, Cu, Gd, Er, Lu, Mo and Zr; the metal may be Zn, Gd, Er, Lu, W and V; the metal may be Zn, Gd, Er, Lu, W and Zr; the metal may be Zn, Gd, Er, Lu, V and Zr; the metal may be Zn, Co, Cu, Mo, Gd, Er and Lu; the metal may be Zn, Mo, and Gd; the metal may be Zn, Dy
10 and Mo; the metal may be Mo, Dy and Gd; the metal may be Gd, Er, and Zn; or the metal may be Dy, Er and Gd.

The combined corrosion inhibitor formulation may comprise at least four metal salts, metal anions, metal complexes, or any combination thereof, wherein the metal is selected from the group consisting of Zn, La, Pr, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er,
15 Tm, Yb, Lu, Co, Cu, Y, Ca, Sr, Ba, Sc, Mo, and Zr. For example, the metal may be any one of Zn, Mo, Gd, Dy, Er, Tb, and Pr; the metal may be Zn, Co, Cu, Gd, Er, Lu, Mo, W, V and Zr; the metal may be Zn, Co, Cu, Gd, Er, Lu, Mo and W; the metal may be Zn, Co, Cu, Gd, Er, Lu, Mo and V; the metal may be Zn, Co, Cu, Gd, Er, Lu, Mo and Zr; the metal may be Zn, Gd, Er, Lu, W and V; the metal may be Zn, Gd, Er, Lu, W
20 and Zr; the metal may be Zn, Gd, Er, Lu, V and Zr; the metal may be Zn, Co, Cu, Mo, Gd, Er and Lu; the metal may be Zn, Mo, Dy and Gd; the metal may be Zn, Dy, Er and Mo; the metal may be Mo, Dy, Tb and Gd; the metal may be Gd, Er, Tb, and Zn; or the metal may be Tb, Dy, Er and Gd.

The combined corrosion inhibitor formulation may comprise at least one
25 organic heterocyclic compound of Formula 1(a) or salt thereof, as described herein or any embodiments thereof and at least one metal salt, metal anion, metal complex, or any combination thereof, wherein the metal is selected from the group consisting of Zn, La, Pr, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Co, Cu, Y, Ca, Sr, Ba, Sc, Mo, V, W and Zr; the metal may be Zn, Co, Cu, Gd, Er, Lu, Mo, W, V and Zr; the
30 metal may be Zn, Co, Cu, Gd, Er, Lu, Mo and W; the metal may be Zn, Co, Cu, Gd, Er, Lu, Mo and V; the metal may be Zn, Co, Cu, Gd, Er, Lu, Mo and Zr; the metal may be Zn, Gd, Er, Lu, W and V; the metal may be Zn, Gd, Er, Lu, W and Zr; or the metal may be Zn, Gd, Er, Lu, V and Zr; or the metal may be Zn, Co, Cu, Mo, Gd, Er and Lu.

The combined corrosion inhibitor formulation may comprise at least one
35 organic heterocyclic compound of Formula 1 or salt thereof, as described herein or any

5 embodiments thereof and at least one metal salt, metal anion, metal complex, or any
combination thereof, wherein the metal is selected from the group consisting of Zn, La,
Pr, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Co, Cu, Y, Ca, Sr, Ba, Sc, Mo, V,
W and Zr. For example the at least one metal salt, metal anion, metal complex, or any
combination thereof may be Zn, Co, Cu, Mo, Sm, Dy, Tb, Pr, Er, Tm, Lu and Gd; Zn,
10 Co, Cu, Mo, Pr, Er and Gd; or Zn, Mo, and Gd; the metal may be Zn, Co, Cu, Gd, Er,
Lu, Mo, W, V and Zr; the metal may be Zn, Co, Cu, Gd, Er, Lu, Mo and W; the metal
may be Zn, Co, Cu, Gd, Er, Lu, Mo and V; the metal may be Zn, Co, Cu, Gd, Er, Lu,
Mo and Zr; the metal may be Zn, Gd, Er, Lu, W and V; the metal may be Zn, Gd, Er,
Lu, W and Zr; or the metal may be Zn, Gd, Er, Lu, V and Zr; or the metal may be Zn,
15 Co, Cu, Mo, Gd, Er and Lu.

 The combined corrosion inhibitor formulation may comprise at least one
organic heterocyclic compound of Formula 1 or salt thereof, as described herein or any
embodiments thereof and at least two metal salts, metal anions, metal complexes, or
any combination thereof, wherein the metal is selected from the group consisting of Zn,
20 La, Pr, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Co, Cu, Y, Ca, Sr, Ba, Sc,
Mo, V, W and Zr. For example the at least two metal salts, metal anions, metal
complexes, or any combination thereof may be Zn, Co, Cu, Mo, Sm, Dy, Tb, Pr, Er,
Tm, Lu and Gd; or Zn, Mo, Pr, Er and Gd; or Zn, Mo, and Gd; the metal may be Zn,
Co, Cu, Gd, Er, Lu, Mo, W, V and Zr; the metal may be Zn, Co, Cu, Gd, Er, Lu, Mo
25 and W; the metal may be Zn, Co, Cu, Gd, Er, Lu, Mo and V; the metal may be Zn, Co,
Cu, Gd, Er, Lu, Mo and Zr; the metal may be Zn, Gd, Er, Lu, W and V; the metal may
be Zn, Gd, Er, Lu, W and Zr; the metal may be Zn, Gd, Er, Lu, V and Zr; or the metal
may be Zn, Co, Cu, Mo, Gd, Er and Lu.

 The combined corrosion inhibitor formulation may comprise at least one
30 organic heterocyclic compound of Formula 1 or salt thereof, as described herein or any
embodiments thereof and at least three metal salts, metal anions, metal complexes, or
any combination thereof, wherein the metal is selected from the group consisting of Zn,
La, Pr, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Co, Cu, Y, Ca, Sr, Ba, Sc,
Mo, V, W and Zr. For example the at least three metal salts, metal anions, metal
35 complexes, or any combination thereof may be Co, Cu, Zn, Mo, Sm, Dy, Tb, Pr, Er,

5 Tm, Lu, V, W and Gd; or Co, Cu, Zn, Mo, Pr, Er and Gd; the metal may be Co, Cu, Zn, Gd, Er, Lu, Mo, W, V and Zr; the metal may be Co, Cu, Zn, Gd, Er, Lu, Mo and W; the metal may be Co, Cu, Zn, Gd, Er, Lu, Mo and V; the metal may be Co, Cu, Zn, Gd, Er, Lu, Mo and Zr; the metal may be Co, Cu, Zn, Gd, Er, Lu, W and V; the metal may be Co, Cu, Zn, Gd, Er, Lu, W and Zr; the metal may be Co, Cu, Zn, Gd, Er, Lu, V and Zr; or Co, Cu, Zn, Mo, Er, Lu and Gd.

It will be appreciated that any of the embodiments or examples described above or herein for Formula 1 may also provide embodiments for any compounds of Formula 1(a), 1(a)(i), 1(b), 1(b)(i), 1(b)(ii) or 1(b)(iii).

The combined corrosion inhibitor formulation may comprise at least one
 15 organic heterocyclic compound of Formula 1 or salt thereof, as described herein or any embodiments thereof and at least one metal salt, metal anion, metal complex, or any combination thereof, wherein the metal is selected from the group consisting Zn, Co, Cu, Mo, Pr, Gd, Er, Lu, W, V and Zr. For example the at least one metal salt, metal anion, metal complex, or any combination thereof may be Mo, Co, Cu, W, V, Gd, Er, Lu and Zr; the metal may be Zn, Co, Cu, Mo, Gd, Er and Lu; the metal may be Mo; the metal may be V; the metal may be Zr; the metal may be Er; the metal may be Lu; the metal may be Co; the metal may be Cu; the metal may be Gd; or the metal may be W.

The combined corrosion inhibitor formulation may comprise at least one
 25 organic heterocyclic compound of Formula 1 or salt thereof, as described herein or any embodiments thereof and at least two metal salts, metal anions, metal complexes, or any combination thereof, wherein the metal is selected from the group consisting of Zn, Co, Cu, Mo, W, V, Pr, Gd, Er, Lu, and Zr. For example the at least two metal salts, metal anions, metal complexes, or any combination thereof may be Mo, W, V, Gd, Er, Lu, and Zr; the metal may be Mo, Gd, Er, Lu and W; the metal may be Mo, Gd, Er, Lu, and V; the metal may be Mo, Gd, Er, Lu, Pr, and Zr; the metal may be W, Gd, Er, Lu, Pr, and V; the metal may be W, Gd, Er, Lu, Pr, and Zr; the metal may be V, Gd, Er, Lu, Pr, and Zr; or the metal may be Zn, Co, Cu, Mo, Gd, Er and Lu.

The combined corrosion inhibitor formulation may comprise at least one
 35 organic heterocyclic compound of Formula 1 or salt thereof, as described herein or any embodiments thereof and at least three metal salts, wherein the metal is selected from

5 the group consisting of Zn, Co, Cu, Mo, W, V, Gd, Er, Lu, Pr and Zr. For example the at least three metal salts, metal anions, metal complexes, or any combination thereof may be Zn, Mo, W, Gd, Er, Lu, Pr, V and Zr; the metal may be Zn, Mo, V, Gd, Er, Lu, Pr, and W; the metal may be Zn, Mo, W, Gd, Er, Lu, Pr, and Zr; the metal may be Zn, Gd, Er, Lu, V, W, Pr and Zr; or the metal may be Zn, Co, Cu, Mo, Zr, Pr, Lu, Gd, Er
10 and V; or Zn, Co, Cu, Mo, Gd, Er and Lu.

It will be appreciated that any of the embodiments or examples described above or herein for Formula 1 may also provide embodiments for any compounds of Formula 1(a), 1(a)(i), 1(b), 1(b)(i), 1(b)(ii) or 1(b)(iii).

The combined corrosion inhibitor formulation may comprise at least two
15 organic heterocyclic compound of Formula 1 or salt thereof, as described herein or any embodiments thereof and at least two metal salts, metal anions, metal complexes, or any combination thereof, wherein the metal is selected from the group consisting of Zn, La, Pr, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Co, Y, Ca, Sr, Ba, Sc, Mo, W, V and Zr. For example the at least two metal salts, metal anions, metal complexes,
20 or any combination thereof may be Zn, Co, Cu, Mo, Sm, Dy, Tb, Pr, Er, Tm, Lu and Gd; or Zn, Co, Cu, Mo, Pr, Er, Lu, and Gd; or Zn, Mo, Er, Lu and Gd; or Zn, Co, Cu, Mo, Gd, Er and Lu.

A further advantage can be provided when the combined corrosion inhibitor formulations comprise at least three corrosion inhibitors as described herein or any
25 embodiments thereof. For example, the combined corrosion the combined corrosion inhibitor formulation may comprise, for example (i) at least two metal salts and at least one organic heterocyclic compound of Formula 1 or (ii) at least one metal salt, at least one metal anion and at least one organic heterocyclic compound of Formula 1 or (iii) at least two metal complexes, or (iv) at least one metal complex and at least one metal
30 anion.

The combined corrosion inhibitor formulation may be according to (i), and the at least two metal salts may be selected from the group consisting of Pr^{3+} , Gd^{3+} , Ce^{3+} , Dy^{3+} , Sm^{3+} , Er^{3+} , Lu^{3+} , Zn^{2+} , Co^{2+} , Cu^{2+} , and the at least one organic heterocyclic compound of formula 1 may be selected from the group consisting of 3-amino-1,2,4-
35 triazole, benzimidazole, 1H-benzotriazole, 5-amino-2-mercapto-1,3,4-thiadiazole, 9H-

5 purine-8-thiol, 1,2,4-triazole, 1,2,4-triazole-3-thiol, and 5-methyl-2-mercapto-1,3,4-thiadiazole. The at least two metal salts may be Pr^{3+} , Gd^{3+} , Ce^{3+} , Er^{3+} , Lu^{3+} , Zn^{2+} , Co^{2+} , and the at least one organic heterocyclic compound of Formula 1 may be 3-amino-1,2,4-triazole, benzimidazole, 1H-benzotriazole, 5-amino-2-mercapto-1,3,4-thiadiazole.

The combined corrosion inhibitor formulation may be according to (ii), and the
 10 at least one metal salt may be selected from the group consisting of Pr^{3+} , Gd^{3+} , Ce^{3+} , Dy^{3+} , Sm^{3+} , Er^{3+} , Lu^{3+} , Zn^{2+} , Co^{2+} , Cu^{2+} , the at least one metal anion may be selected from the group consisting of MoO_4^{2-} , VO_4^{3-} , ZrO_4^{2-} , WO_4^{2-} , and the at least one organic heterocyclic compound of Formula 1 may be selected from the group consisting of 3-amino-1,2,4-triazole, benzimidazole, 1H-benzotriazole, 5-amino-2-mercapto-1,3,4-
 15 thiadiazole, 9H-purine-8-thiol, 1,2,4-triazole, 1,2,4-triazole-3-thiol, and 5-methyl-2-mercapto-1,3,4-thiadiazole. The at least one metal salt may be Pr^{3+} , Gd^{3+} , Ce^{3+} , Er^{3+} , Lu^{3+} , Zn^{2+} , Co^{2+} , the at least one metal anion may be MoO_4^{2-} , VO_4^{3-} , WO_4^{2-} , and the at least one organic heterocyclic compound of Formula 1 may be 3-amino-1,2,4-triazole, benzimidazole, 1H-benzotriazole, 5-amino-2-mercapto-1,3,4-thiadiazole.

20 The combined corrosion inhibitor formulation may be according to (iii), and the at least two metal complexes may be selected from the group consisting of zinc molybdate, erbium molybdate, lutetium molybdate, zinc vanadate, zinc benzotriazole, dysprosium benzotriazole, lutetium benzotriazole, gadolinium benzotriazole, gadolinium molybdate, praseodymium benzimidazole, lutetium benzimidazole, zinc
 25 benzimidazole. The at least two metal complexes may be zinc molybdate, lutetium molybdate, zinc benzotriazole, lutetium benzotriazole, gadolinium benzotriazole, gadolinium molybdate.

The combined corrosion inhibitor formulation may be according to (iv), and the at least one metal complex may be selected from the group consisting of zinc
 30 molybdate, erbium molybdate, lutetium molybdate, zinc vanadate, zinc benzotriazole, dysprosium benzotriazole, lutetium benzotriazole, gadolinium benzotriazole, gadolinium molybdate, praseodymium benzimidazole, lutetium benzimidazole, zinc benzimidazole, and the at least one metal anion may be selected from the group consisting of MoO_4^{2-} , VO_4^{3-} , ZrO_4^{2-} , WO_4^{2-} . The at least one metal complex may be
 35 zinc molybdate, lutetium molybdate, zinc benzotriazole, lutetium benzotriazole,

5 gadolinium benzotriazole, gadolinium molybdate, and the at least one metal anion may be MoO_4^{2-} , VO_4^{3-} , ZrO_4^{2-} .

A further advantage can be provided when the combined corrosion inhibitor formulations comprise at least four corrosion inhibitors as described herein or any embodiments thereof. For example, the combined corrosion inhibitor formulation may
 10 comprise at least four corrosion inhibitors comprising, for example (v) at least two metal salts and at least two organic heterocyclic compounds of Formula 1; or (vi) at least one metal salt, at least one metal anion, and at least two organic heterocyclic compounds of Formula 1; or (vii) at least three corrosion inhibitors selected from metal salts, metal anions, metal complexes, or any combinations thereof, and at least one
 15 organic heterocyclic compound of Formula 1.

The combined corrosion inhibitor formulation may be according to (v), and the at least two metal salts may be selected from the group consisting of Pr^{3+} , Gd^{3+} , Ce^{3+} , Dy^{3+} , Sm^{3+} , Er^{3+} , Lu^{3+} , Zn^{2+} , Co^{2+} , Cu^{2+} , and the at least two organic heterocyclic compounds of Formula 1 may be selected from the group consisting of 3-amino-1,2,4-triazole, benzimidazole, 1H-benzotriazole, 5-amino-2-mercapto-1,3,4-thiadiazole, 9H-purine-8-thiol, 1,2,4-triazole, 1,2,4-triazole-3-thiol, and 5-methyl-2-mercapto-1,3,4-thiadiazole. The at least two metal salts may be Pr^{3+} , Gd^{3+} , Ce^{3+} , Er^{3+} , Lu^{3+} , Zn^{2+} , Co^{2+} , and the at least two organic heterocyclic compounds may be 3-amino-1,2,4-triazole, benzimidazole, 1H-benzotriazole, 5-amino-2-mercapto-1,3,4-thiadiazole.
 20

The combined corrosion inhibitor formulation may be according to (vi), and the at least one metal salt may be selected from the group consisting of Pr^{3+} , Gd^{3+} , Ce^{3+} , Dy^{3+} , Sm^{3+} , Er^{3+} , Lu^{3+} , Zn^{2+} , Co^{2+} , Cu^{2+} , and the at least one metal anion may be selected from the group consisting of MoO_4^{2-} , VO_4^{3-} , ZrO_4^{2-} , WO_4^{2-} , and the at least two organic heterocyclic compounds of Formula 1 may be selected from the group
 30 consisting of 3-amino-1,2,4-triazole, benzimidazole, 1H-benzotriazole, 5-amino-2-mercapto-1,3,4-thiadiazole, 9H-purine-8-thiol, 1,2,4-triazole, 1,2,4-triazole-3-thiol, and 5-methyl-2-mercapto-1,3,4-thiadiazole. The at least one metal salt may be Pr^{3+} , Gd^{3+} , Ce^{3+} , Er^{3+} , Lu^{3+} , Zn^{2+} , Co^{2+} , the at least one metal anion may be MoO_4^{2-} , VO_4^{3-} , ZrO_4^{2-} , and the at least two organic heterocyclic compounds of Formula 1 may be 3-amino-
 35 1,2,4-triazole, benzimidazole, 1H-benzotriazole, 5-amino-2-mercapto-1,3,4-thiadiazole.

5 The combined corrosion inhibitor formulation may be according to (vii), and the at least three corrosion inhibitors selected from metal salts, metal anions, metal complexes, or any combinations thereof, may be selected from the group consisting of Pr^{3+} , Gd^{3+} , Ce^{3+} , Dy^{3+} , Sm^{3+} , Er^{3+} , Lu^{3+} , Zn^{2+} , Co^{2+} , Cu^{2+} , MoO_4^{2-} , VO_4^{3-} , ZrO_4^{2-} , WO_4^{2-} , zinc molybdate, lutetium molybdate, zinc benzotriazole, lutetium benzotriazole, 10 gadolinium benzotriazole, gadolinium molybdate, and the at least one organic heterocyclic compound of Formula 1 may be selected from the group consisting of 3-amino-1,2,4-triazole, benzimidazole, 1H-benzotriazole, 5-amino-2-mercapto-1,3,4-thiadiazole. The at least three corrosion inhibitors selected from metal salts, metal anions, metal complexes, or any combinations thereof, may be Pr^{3+} , Gd^{3+} , Ce^{3+} , Er^{3+} , 15 Lu^{3+} , Zn^{2+} , MoO_4^{2-} , WO_4^{2-} , lutetium molybdate, zinc benzotriazole, and the at least one organic heterocyclic compound of Formula 1 may be 3-amino-1,2,4-triazole, benzimidazole, 1H-benzotriazole.

It will be appreciated that any of the embodiments or examples described above or herein for Formula 1 may also provide embodiments for any compounds of Formula 20 1(a), 1(a)(i), 1(b), 1(b)(i), 1(b)(ii) or 1(b)(iii).

The corrosion inhibitor compositions are suitable for use and application to various substrates, such as metal substrates, and for example can be provided for use in coolant systems, air-conditioning systems, water and waste water treatment plants, and pipelines. The compositions may be used dissolved in a fluid, such as water. For 25 example the composition may be dissolved in fluid coolant systems or cooling towers.

The corrosion inhibitor compositions are suitable for use and application to various substrates, such as metal substrates, and for example can be provided as coating compositions. The compositions may include one or more other additives or corrosion inhibiting agents suitable for particular use with a type of substrate.

30 The corrosion inhibiting compositions may be a film forming formulation. For example the combined corrosion inhibitor formulations may form a thin film on a substrate. The film may be in the form of a layer or coating. The film forming formulation may form a thin film on a substrate where the inhibitors chemically adsorb on the surface of the substrate and form a protective thin film with inhibitor effect or by 35 combination between inhibitor ions and substrate surface. A key advantage of a thin

5 film on a substrate is that the film may provide a layer or coating over a substrate that may effectively prevent corrosion of the substrate. A further advantage of the thin film may be that the thin film provides good surface coverage of the substrate. A further example of the thin film may be that the inhibitors may be electrochemically attracted to the electrochemically active sites of the metal substrate, thereby preventing corrosion
10 at either the anodic or cathodic sites, or both the anodic and cathodic sites.

The film may comprise at least one organic heterocyclic compound of Formula 1 as described herein or any embodiments thereof and at least one metal salt, metal anion, metal complex, or any combination thereof, wherein the metal is selected from the group consisting of Zn, La, Pr, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu,
15 Co, Cu, Y, Ca, Sr, Ba, Sc, Mo, V, W and Zr. For example, the metal may be any one of Zn, Co, Cu, Mo, Gd, Dy, Er, Lu, Tb, and Pr; the metal may be Co, Cu, Zn, Mo, Er, Lu, and Gd; the metal may be Zn; the metal may be Co; the metal may be Cu; the metal may be Mo; the metal may be Gd; the metal may be Er, the metal may be Lu; or the metal may be Dy.

20 It will be appreciated that any of the embodiments or examples described above or herein for Formula 1 may also provide embodiments for any compounds of Formula 1(a), 1(a)(i), 1(b), 1(b)(i), 1(b)(ii) or 1(b)(iii).

The present disclosure also relates to determining film thickness of a thin film following application of a combined corrosion inhibitor formulation, as described
25 herein or any embodiments thereof, on a metal substrate.

The thickness of the thin film may be identified using a focused ion beam (FIB) scanning electron microscope (SEM) technique. For example, by aligning the SEM and FIB at a reference point the thin film on the metal substrate may be inspected and a certain area of interest determined. Software patterns may be used to control where and
30 how the ion beam is scanning on the metal substrate and therefore where the thin film is being removed. The milled area of the metal substrate may be imaged in real time by the electron beam while the milling is in progress.

The thin film may have a thickness of from about 5 nm to about 1500 nm, from about 10 nm to about 1400 nm, from about 20 nm to about 1300 nm, from about 30 nm,
35 to about 1200 nm, from about 40 nm to about 1100 nm, from about 50 nm to about

5 1000 nm, from about 60 nm to about 900 nm, 70 nm to about 800 nm, from about 80
nm to about 700 nm, from about 90 nm to about 600 nm, from about 100 nm to about
500 nm, from about 150 nm to about 400 nm, from about 200 nm to about 350 nm. The
film may have a thickness less than about 1500 nm, less than about 1400 nm, less than
about 1300 nm, less than about 1200 nm, less than about 1100 nm, less than about 1000
10 nm, less than about 900 nm, less than about 800 nm, less than about 700 nm, less than
about 600 nm, less than about 500 nm, less than about 400 nm, less than about 350 nm.

The corrosion inhibiting composition can be a coating composition comprising
a film-forming organic polymer. The coating composition may be a paint composition.
The coating composition may comprise one or more resins, for example epoxy based
15 resins. The coating composition may be a paint composition, for example an epoxy
resin based paint composition.

The coating composition may be a powder coating composition, for example a
powder coating composition suitable for use in powder coating of various metal
substrates including steel, copper, zinc, or magnesium as described herein. For
20 example, the metal substrate may be mild steel.

The coating composition may be a spray composition.

The coating compositions can be applied to a substrate, in either a wet or "not
fully cured" condition that dries or cures over time, that is, solvent evaporates. The
coatings can dry or cure either naturally or by accelerated means, for example an
25 ultraviolet light cured system to form a film or "cured" paint. The coatings can also be
applied in a semi or fully cured state, such as an adhesive.

The corrosion inhibiting composition can also be an encapsulated corrosion
inhibiting composition. The encapsulated corrosion inhibiting composition may
comprise at least two corrosion inhibitors as described herein, or any embodiments
30 thereof. For example, the encapsulated corrosion inhibitor compositions may comprise
at least one polymeric film; at least one metal salt, metal anion, metal complex, or any
combination thereof, wherein the metal is selected from the group consisting of Zn, La,
Pr, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Co, Y, Ca, Sr, Ba, Sc, Mo, V, W
and Zr; and at least one organic heterocyclic compound of Formula 1 as described
35 herein or any embodiments thereof. The polymeric film may include a predetermined

5 thickness and permeability to permit controlled diffusion of the particle ions upon interaction with water.

The corrosion inhibiting composition may be a corrosion inhibiting kit. The corrosion inhibiting kit may comprise two or more components and for example include instructions that the compounds are mixed prior to application onto a metal
10 substrate. For example a first component may be at least one organic heterocyclic compound of Formula 1 as described herein and at least one metal salt, metal anion, metal complex, or any combination thereof, wherein the metal is selected from rare earth, alkali earth and transition metals, as described herein, or any embodiments thereof; and a second component may be a coating composition, for example a paint
15 composition. The paint composition may be an epoxy based paint composition. A third component may be an additive, for example a hardener for the resin or any additive described herein.

The compositions may include a list of ingredients, and/or components, and can also include a list of instructions for preparing and mixing together the ingredients,
20 and/or components to make a coating composition.

It will be appreciated that the compositions can include one or more additives, such as pigments, fillers and extenders. Examples of suitable additives with which the corrosion inhibitors described herein can be combined include, for example, binders, solvents, pigments (including soluble or non-soluble extenders, fillers, corrosion-
25 inhibiting pigments, and the like), solvents, additives (e.g., curing agents, surfactants, dyes, amino acids and the like), and so forth. Note that some additives can also properly be considered a pigment and vice versa (e.g., matting agents). More specifically, these "additives" include, but are not limited to, glycine, arginine, methionine, and derivatives of amino acids, such as methionine sulfoxide, methyl
30 sulfoxide, and iodides/iodates, gelatin and gelatin derivatives, such as animal and fish gelatins, linear and cyclic dextrans, including alpha and beta cyclodextrin, triflic acid, triflates, acetates, talc, kaolin, organic-based ionic exchange resins, such as organic-based cationic and anionic exchange resins, organic-based ionic exchange resins, such as organic-based cationic and anionic exchange resins, organic-based ionic exchange
35 resins that have been pre-exchanged or reacted with the salts, oxides, and/or mixed

- 5 oxides of rare earth material, and metal sulfates, such as sulfates of rare earth materials, magnesium sulfate, calcium sulfate (anhydrous and hydrated forms), strontium sulfate, barium sulfate, and the like, and combinations thereof.

It will be appreciated that the compositions may comprise, or consist of any one or more of the components or additives described herein.

- 10 The compositions may also include other additives such as rheology modifiers, fillers, tougheners, thermal or UV stabilizers, fire retardants, lubricants, surface active agents. The additive(s) are usually present in an amount of less than about 10% based on the total weight of the activation treatment or the combination of solvent(s), agent(s) and additive(s). Examples include:
- 15 (a) rheology modifiers such as hydroxypropyl methyl cellulose (e.g. Methocel 311, Dow), modified urea (e.g. Byk 411, 410) and polyhydroxycarboxylic acid amides (e.g. Byk 405);
- (b) film formers such as esters of dicarboxylic acid (e.g. Lusolvan FBH, BASF) and glycol ethers (e.g. Dowanol, Dow);
- 20 (c) wetting agents such as fluorochemical surfactants (e.g. 3M Fluorad) and polyether modified poly-dimethyl-siloxane (e.g. Byk 307, 333);
- (d) surfactants such as fatty acid derivatives (e.g. Bermadol SPS 2543, Akzo) and quaternary ammonium salts;
- (e) dispersants such as non-ionic surfactants based on primary alcohols (e.g. 25 Merpel 4481, Dupont) and alkylphenol-formaldehyde-bisulfide condensates (e.g. Clariant 1494);
- (f) anti-foaming agents;
- (g) anti-corrosion reagents such as phosphate esters (e.g. ADD APT, Anticor C6), alkylammonium salt of (2-benzothiazolythio) succinic acid (e.g. Irgacor 153 30 CIBA) and triazine dithiols;
- (h) stabilizers such as benzimidazole derivatives (e.g. Bayer, Preventol BCM, biocidal film protection);
- (i) leveling agents such as fluorocarbon-modified polymers (e.g. EFKA 3777);
- (j) pigments or dyes such as fluorescents (Royale Pigment and chemicals);
- 35 (k) organic and inorganic dyes such as fluorescein; and
- (l) Lewis acids such as lithium chloride, zinc chloride, strontium chloride, calcium chloride and aluminium chloride.

- 5 (m) Suitable flame retardants which retard flame propagation, heat release and/or smoke generation which may be added singularly or optionally include:
- Phosphorus derivatives such as molecules containing phosphate, polyphosphate, phosphites, phosphazine and phosphine functional groups, for example, melamine phosphate, dimelamine phosphate, melamine
 - 10 polyphosphate, ammonia phosphate, ammonia polyphosphate, pentaerythritol phosphate, melamine phosphite and triphenyl phosphine.
 - Nitrogen containing derivatives such as melamine, melamine cyanurate, melamine phthalate, melamine phthalimide, melam, melem, melon, melam cyanurate, melem cyanurate, melon cyanurate, hexamethylene tetraamine,
 - 15 imidazole, adenine, guanine, cytosine and thymine.
 - Molecules containing borate functional groups such as ammonia borate and zinc borate.
 - Molecules containing two or more alcohol groups such as pentaerythritol, polyethylene alcohol, polyglycols and carbohydrates, for
 - 20 example, glucose, sucrose and starch.
 - Molecules which endothermically release non-combustible decomposition gases, such as, metal hydroxides, for example, magnesium hydroxide and aluminum hydroxide.
 - Expandable graphite.

25 *METHOD OF IDENTIFYING CORROSION INHIBITOR COMBINATIONS*

The present disclosure also relates to a method of identifying a combined corrosion inhibitor formulation comprising at least a first and second corrosion inhibitor formulation for inhibiting corrosion. The first corrosion inhibitor formulation comprises at least one corrosion inhibitor and the second corrosion inhibitor

30 formulation comprises at least one corrosion inhibitor that is different to the corrosion inhibitor of the first corrosion inhibitor formulation. The corrosion inhibitors are as described herein or any embodiments thereof.

The main goal in the method is to identify corrosion rate of a combination of at least three corrosion inhibitors each independently selected from the group comprising

35 an organic heterocyclic compound of Formula 1 as described herein and a metal salt, metal anion, metal complex, or any combination thereof, wherein the metal is selected

5 from rare earth, alkali earth and transition metals, as described herein, or any
embodiments thereof, using a polarization resistance technique.

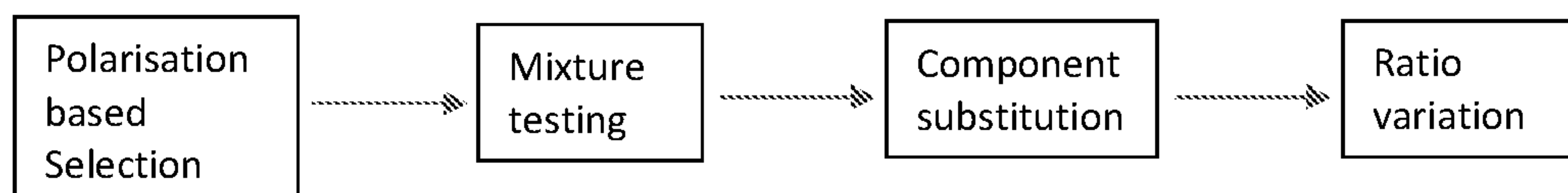
The polarization resistance technique provides the following advantages: (1) it
is rapid, for example it increases the number of experiments per unit time, (2) it is
relatively simple and low cost, (3) the corrosion rate can be obtained directly from
10 readings of the applied polarizing current, (4) non-destructive of the substrate, and can
monitor corrosion inhibitor performance over time.

The polarisation resistance of a corrosion inhibitor may take place in a sodium
chloride (NaCl) solution and at room temperature for 168 hours using the polarisation
resistance electrochemical test. The substrate may be a metal substrate steel, such as
15 mild steel. The NaCl solutions may be prepared at a concentration from about 10^{-1} to
about 10^{-6} M. The combined corrosion inhibitor formulation may be prepared at a total
concentration of about 10^{-3} M.

The polarisation resistance test allows for corrosion analysis of the corrosion
inhibitors and corrosion inhibitor combinations. The method of identifying corrosion
20 rate of the corrosion inhibitor combinations is important for this technique because of
the need to categorise the polarisation resistance value. For example, when the
polarisation value for the combination of corrosion inhibitors is greater than the sum of
the polarisation values for each of the individual corrosion inhibitors, the combination
is categorised as positive. Whereas, when the polarisation value for the combination of
25 corrosion inhibitors is less than or equal to the sum of the polarisation values for each
of individual corrosion inhibitors, the combination is categorised as negative.

A polarisation resistance value that is categorised as positive may also referred
to as a synergistic result. A polarisation resistance value that is categorised as negative
may also be referred to as an antagonistic result.

30 The process used to identify a combined corrosion inhibitor formulation is
shown schematically below.



5 The polarisation based selection may include conducting various polarisation resistance tests on each individual corrosion inhibitor solution and analysing the response. The response obtained for each corrosion inhibitor solution may indicate whether a particular corrosion inhibitor is a film-forming inhibitor or an instantaneous inhibitor. Additionally, a corrosion inhibitor identified as a film-forming inhibitor may
10 be classified as having a delayed inhibitive response. And an instantaneous inhibitor may be classified as having an immediate inhibitive response. The polarisation based selection may provide a database of each individual corrosion inhibitor being classified as having a delayed inhibitive response, an immediate inhibitor response, or an undefined inhibitive response.

15 For example, polarisation resistance is typically presented in ohms (Ω). The ohms value may be dependent on the exposed surface area of the metal substrate. For example, reducing the surface area of the metal substrate below $\pi \text{ cm}^2$ may provide polarisation resistance values of about 100,000 Ω . For example, for a $\pi \text{ cm}^2$ mild steel substrate a polarisation value of about 500 to about 1,000 Ω may be classified as a poor
20 corrosion inhibitor. For example, for a $\pi \text{ cm}^2$ mild steel substrate a polarisation value of about 1,000 to about 5,000 Ω may be classified as a good corrosion inhibitor. For example, for a $\pi \text{ cm}^2$ mild steel substrate a polarisation value of greater than about 5,000 Ω may be classified as an excellent corrosion inhibitor.

25 It will be appreciated that these polarization resistance values may change with different metal substrates. It will also be appreciated that the polarization resistance value is the sum of all the corrosion events occurring simultaneously on the metal substrate.

30 For example, the polarisation resistance value for an immediate inhibitive response may be provided in a range of about 200 Ω to about 10,000 Ω within a time period of 1 minute to 90 hours, about 250 Ω to about 9,000 Ω within a time period of 1 minute to 85 hours, about 300 Ω to about 8,000 Ω within a time period of 1 minute to 80 hours, about 350 Ω to about 7,000 Ω within a time period of 1 minute to 75 hours, about 400 Ω to about 6,000 Ω within a time period of 1 minute to 70 hours, about 450 Ω to about 5,000 Ω within a time period of 1 minute to 65 hours, and about 500 Ω to
35 about 4,000 Ω within a time period of 1 minute to 60 hours. For example the

5 polarisation resistance value for a delayed inhibitive response may be provided in a range of about 200 Ω to about 10,000 Ω within a time period of 1 minute to 480 hours, about 250 Ω to about 9,000 Ω within a time period of 1 minute to 432 hours, about 300 Ω to about 8,000 Ω within a time period of 1 minute to 336 hours, about 350 Ω to about 7,000 Ω within a time period of 1 minute to 240 hours, about 400 Ω to about 6,000 Ω within a time period of 1 minute to 216 hours, about 450 Ω to about 5,000 Ω within a time period of 1 minute to 192 hours, and about 500 Ω to about 4,000 Ω within a time period of 1 minute to 168 hours. For example, the polarisation resistance value for an undefined inhibitive response may fall in between any one of the polarisation resistance values described above.

15 The mixture or combination testing provides a combined corrosion inhibitor formulation by combining the first and second corrosion inhibitor formulations together. For example, the combined corrosion inhibitor formulation may include selecting at least two corrosion inhibitors from either classification as described above. The combined corrosion inhibitor formulation may include selecting at least three corrosion inhibitors from either classification as described above. The combined corrosion inhibitor formulation may include selecting at least four corrosion inhibitors from either classification as described above. The polarisation resistance value for the combined corrosion inhibitor formulation may be greater than, less than, or equal to the sum of the polarisation value for each of the individual corrosion inhibitors. For example, if the polarisation value for the combined corrosion inhibitor formulation is greater than the sum of the polarisation values for each of the individual corrosion inhibitors, the combined corrosion inhibitor formulation is categorised as positive. For example, if the polarisation value for the combined corrosion inhibitor formulation is less than or equal to the sum of the polarisation values for each of the individual corrosion inhibitors, the combination is categorised as negative.

30 A combined corrosion inhibitor formulation comprising at least a first and second corrosion inhibitor formulation, wherein the first corrosion inhibitor formulation comprises a corrosion inhibitor classified as having a delayed inhibitive response and the second corrosion inhibitor formulation comprising a corrosion inhibitor classified as having an immediate inhibitive response may provide a

5 polarisation resistance value that is consistent with an enhanced continuous inhibitive response. An enhanced continuous inhibitive response may be a polarisation resistance value that is greater than the sum of the polarisation values for each of the individual corrosion inhibitors, and categorised as positive. For example, if the combined corrosion inhibitor formulation comprised a first corrosion inhibitor formulation
 10 comprising at least one corrosion inhibitor having a delayed inhibitive response and the second corrosion inhibitor formulation comprising at least one corrosion inhibitor having an immediate inhibitive response may provide a polarisation resistance value that is positive and consistent with an enhanced continuous inhibitive response.

For example the polarisation resistance value for a combined corrosion inhibitor
 15 having an enhanced continuous inhibitive response may be provided in a range of about 200 Ω to about 17,000 Ω within a time period of 1 minute to 720 hours, about 250 Ω to about 16,000 Ω within a time period of 1 minute to 672 hours, about 300 Ω to about 15,000 Ω within a time period of 1 minute to 576 hours, about 400 Ω to about 14,000 Ω within a time period of 1 minute to 504 hours, about 500 Ω to about 13,000 Ω within
 20 a time period of 1 minute to 432 hours, about 600 Ω to about 12,000 Ω within a time period of 1 minute to 360 hours, about 700 Ω to about 11,000 Ω within a time period of 1 minute to 312 hours, about 800 Ω to about 10,000 Ω within a time period of 1 minute to 264 hours, about 900 Ω to about 9,000 Ω within a time period of 1 minute to 216 hours, and about 1,000 Ω to about 8,000 Ω within a time period of 1 minute to 168
 25 hours.

Component substitution may include substitution with any one or more corrosion inhibitors from a first combined corrosion inhibitor formulation to provide a second combined corrosion inhibitor formulation. If the polarisation value for the second combined corrosion inhibitor formulation is greater than the sum of the
 30 polarisation values for the first combined corrosion inhibitor formulation, the second combined corrosion inhibitor formulation is categorised as positive. If the polarisation value for the second combined corrosion inhibitor formulation is less than or equal to the sum of the polarisation values for first combined corrosion inhibitor formulation, the second combined corrosion inhibitor formulation is categorised as negative.

5 Ratio variation may include variation of the ratio of individual corrosion inhibitors in a combined corrosion inhibitor formulation. For example, if the polarisation value for a 1:1:1:1 combined corrosion inhibitor formulation is less than or equal to the sum of the polarisation values for each of the individual corrosion inhibitor formulations, the 1:1:1:1 combined corrosion inhibitor formulation may be varied to
10 provide a combination having a ratio of, for example, 1:2:1:1.

EXAMPLES

In order that the present disclosure may be more clearly understood, embodiments of the disclosure are described in further detail below by reference to the following non-limiting experimental materials, methodologies, and examples.

15 **General procedure for the polarisation resistance electrochemical tests**

The combined corrosion inhibitor formulation comprises at least a first corrosion inhibitor formulation and a second corrosion inhibitor formulation wherein the first corrosion inhibitor formulation comprises at least one corrosion inhibitor, as described herein, or any embodiments thereof, and the second corrosion inhibitor
20 formulation comprises at least one corrosion inhibitor, as described herein, or any embodiments thereof, that is different to that of the first corrosion inhibitor. The first corrosion inhibitor formulation was prepared by dissolving at least one corrosion inhibitor into a solution of 0.1 M NaCl in deionised water. The second corrosion inhibitor formulation was prepared by dissolving at least one corrosion inhibitor into a
25 solution of 0.1 M NaCl in deionised water. The combined corrosion inhibitor formulation was prepared by adding the first corrosion inhibitor formulation and second corrosion inhibitor formulation together to provide combined corrosion inhibitor formulation having a total concentration of about 10^{-3} M.

The metal substrate (3 cm x 3 cm surface area) was abraded to a shiny surface
30 using coarse grade 120 grit SiC paper followed by less coarse 180 grit SiC paper. Metal substrates, for example mild steel, were rinsed with deionised water and air dried. A platinum coated mesh and saturated calomel electrode (SCE) constituted the counter and reference electrodes respectively to be coupled with the working electrode to form a standard 3-electrode cell. Each corrosion inhibitor formulation was left at an open

5 circuit potential (OCP) period of 5 minutes prior to starting the polarisation scan. Linear polarization was measured over a potential range of ± 10 mV vs. OCP at a scan rate of 0.167 mV/s every hour for 168 hours. Values of polarization resistance, R_p , were deduced from the slope of fitted current density vs. potential lines. The tests were performed in 180 ml solutions open to air for 168 hours. The polarisation experiments
10 were performed using a 16 channel Biologic VMP3 (variable multichannel potentiostat) with the EC-lab software v10.4.

Example 1

Na_2MoO_4 was prepared and analysed according to the general process described
15 above. GdCl_3 was prepared and analysed according to the general process described above. A 1:1 combination of Na_2MoO_4 and GdCl_3 was prepared and analysed according to the general process described above. The metal substrate was mild steel and prepared as described above. Figure 1 shows that the combination provides an unexpected synergistic result over the individual corrosion inhibitors. The polarisation
20 resistance value for Na_2MoO_4 is classified as having an immediate inhibitive response and the polarisation resistance value GdCl_3 is classified as having a delayed inhibitive response. The polarisation resistance value for the 1:1 combination of Na_2MoO_4 and GdCl_2 is categorized as positive and classified as having an enhanced continuous inhibitive response.

25

Example 2

Na_2MoO_4 was prepared and analysed according to the general process described above. SmCl_3 was prepared and analysed according to the general process described above. A 1:1 combination of Na_2MoO_4 and SmCl_3 was prepared and analysed
30 according to the general process described above. The metal substrate was mild steel and prepared as described above. Figure 2 shows that the combination provides an unexpected antagonistic result over the individual corrosion inhibitors. The polarisation resistance value for Na_2MoO_4 is classified as having an immediate inhibitive response and the polarisation resistance value SmCl_3 is classified as having an delayed inhibitive

- 5 response. The polarisation resistance value for the 1:1 combination of Na_2MoO_4 and SmCl_3 is categorized as negative.

Example 3

- Na_2MoO_4 was prepared and analysed according to the general process described above. ZnCl_2 was prepared and analysed according to the general process described above. A 1:1 combination of Na_2MoO_4 and ZnCl_2 was prepared and analysed according to the general process described above. The metal substrate was mild steel and prepared as described above. Figure 3 shows that the combination provides an unexpected antagonistic result over the individual corrosion inhibitors. The polarisation resistance value for Na_2MoO_4 is classified as having an immediate inhibitive response and the polarisation resistance value ZnCl_2 is classified as having a delayed inhibitive response. The polarisation resistance value for the 1:1 combination of Na_2MoO_4 and ZnCl_2 is categorized as negative.

20 *Example 4*

- ZnCl_2 was prepared and analysed according to the general process described above. PrCl_3 was prepared and analysed according to the general process described above. Benzotriazole was prepared and analysed according to the general process described above. A 1:1 combination of ZnCl_2 and PrCl_3 was prepared and analysed according to the general process described above. A 1:1:1 combination of ZnCl_2 and PrCl_3 and benzotriazole was prepared and analysed according to the general process described above. The metal substrate was mild steel and prepared as described above. Figure 4 shows that the 1:1 combination provides an unexpected synergistic result over the individual corrosion inhibitors. Figure 4 also shows that the 1:1:1 combination provides an unexpected enhanced synergistic result over the 1:1 combination and over the individual corrosion inhibitors. The polarisation resistance value for the 1:1:1 combination of ZnCl_2 , PrCl_3 and benzotriazole is categorized as positive and classified as having an enhanced continuous inhibitive response.

5 *Example 5*

A 1:1:1 combination of CoCl_2 , PrCl_3 and Na_2MoO_4 was prepared and analysed according to the general process described above. A 1:1:1 combination of LuCl_3 , 1H-benzotriazole and Na_2MoO_4 was prepared and analysed according to the general process described above. A 1:1:1 combination of CoCl_2 , PrCl_3 , 1H-benzotriazole was
10 prepared and analysed according to the general process described above. A 1:1:1 combination of GdCl_3 , 1H-benzotriazole and Na_2MoO_4 was prepared and analysed according to the general process described above. A 1:1:1 combination of ZnCl_2 , NdCl_3 and Na_2MoO_4 was prepared and analysed according to the general process described above. A 1:1:1 combination of ZnCl_2 , CeCl_3 and Na_2MoO_4 was prepared and analysed
15 according to the general process described above. The metal substrate was mild steel and prepared as described above. The six combinations prepared and analysed above were analysed by component substitution.

Figure 5 shows that the 1:1:1 combination of LuCl_3 , 1H-benzotriazole and Na_2MoO_4 provides an unexpected enhanced synergistic result over the 1:1:1
20 combination of GdCl_3 , 1H-benzotriazole and Na_2MoO_4 when LuCl_3 is substituted for GdCl_3 .

Figure 5 also shows that the 1:1:1 combination of ZnCl_2 , CeCl_3 and Na_2MoO_4 provides an unexpected enhanced synergistic result over the 1:1:1 combination of ZnCl_2 , NdCl_3 and Na_2MoO_4 when NdCl_3 is substituted for CeCl_3 . The polarisation
25 resistance value for the 1:1:1 combination of ZnCl_2 , CeCl_3 and Na_2MoO_4 is categorized as positive and classified as having an enhanced continuous inhibitive response.

Example 6

A 1:1:1:1 combination of ZnCl_2 , GdCl_3 , Na_2WO_4 and 1H-benzotriazole was
30 prepared and analysed according to the general process described above. A 1:1:1:1 combination of ZnCl_2 , GdCl_3 , Na_2MoO_4 and 1,3,5-triazine-2,4,6-triamine was prepared and analysed according to the general process described above. A 1:1:1:1 combination of ZnCl_2 , PrCl_3 , Na_2MoO_4 and benzimidazole was prepared and analysed according to the general process described above. A 1:1:1:1 combination of ZnCl_2 , LuCl_3 , Na_2WO_4
35 and 1H-benzotriazole was prepared and analysed according to the general process

5 described above. The metal substrate was mild steel and prepared as described above. The four combinations prepared and analysed above were analysed by component substitution. Figure 6 shows that the substitution of a GdCl_3 for PrCl_3 and 1,3,5-triazine-2,4,6-triamine for benzimidazole giving a 1:1:1:1 combination of ZnCl_2 , PrCl_3 , Na_2MoO_4 and benzimidazole provides a polarisation resistance value that is
10 categorized as positive and classified as having an enhanced continuous inhibitive response.

Figure 6 also shows that the combination of a 1:1:1:1 combination of ZnCl_2 , LuCl_3 , Na_2WO_4 and 1H-benzotriazole provides an unexpected synergistic result compared to the combination of ZnCl_2 , GdCl_3 , Na_2WO_4 and 1H-benzotriazole. The
15 substitution of a GdCl_3 for LuCl_3 giving a 1:1:1:1 combination of ZnCl_2 , LuCl_3 , Na_2WO_4 and 1H-benzotriazole provides a polarisation resistance value that is categorized as positive and classified as having an enhanced continuous inhibitive response.

CLAIMS:

1. A method of identifying a combined corrosion inhibitor formulation for inhibiting corrosion of a metal substrate, wherein the combined corrosion inhibitor formulation comprises at least a first corrosion inhibitor formulation comprising at least one corrosion inhibitor and a second corrosion inhibitor formulation comprising at least one corrosion inhibitor that is different to a corrosion inhibitor in the first corrosion inhibitor formulation, the method comprising the steps of:

independently applying each of the first and second corrosion inhibitor formulations to the substrate and determining a polarisation resistance value for each of the first and second corrosion inhibitor formulations;

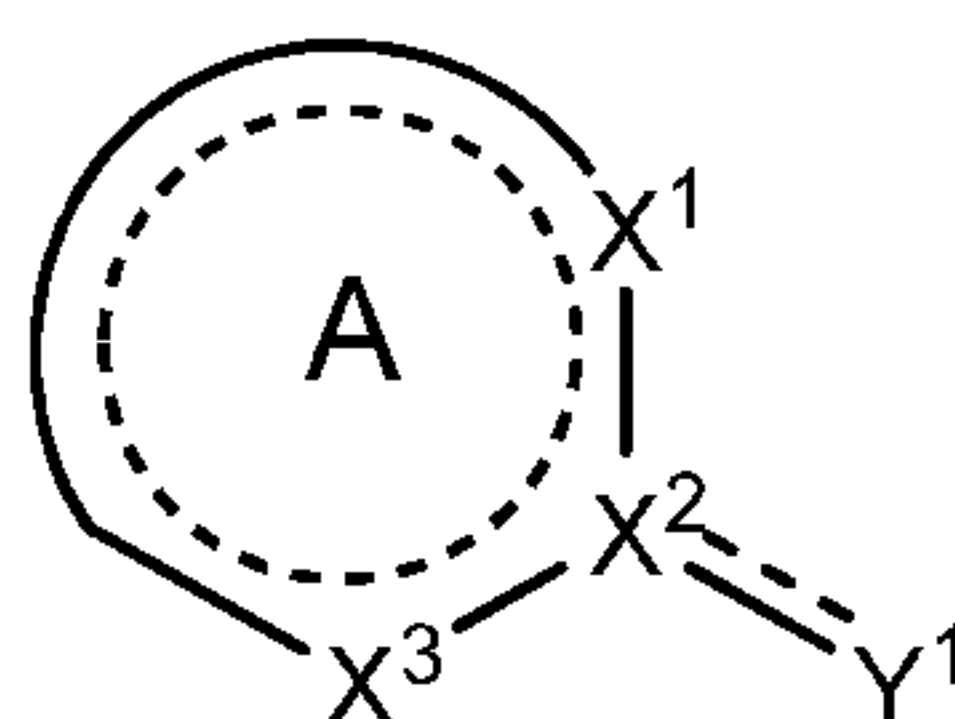
combining the first and second corrosion inhibitor formulations together to provide the combined corrosion inhibitor formulation;

applying the combined corrosion inhibitor formulation to the substrate and determining a polarisation resistance value for the combined corrosion inhibitor formulation, wherein, when said polarisation value for the combined corrosion inhibitor formulation is greater than the sum of the polarisation values for each of the first and second corrosion inhibitor formulation, said combined corrosion inhibitor formulation is categorised as positive;

wherein the corrosion inhibitors are each independently selected from the group consisting of:

a metal salt, metal anion, metal complex, or any combination thereof, wherein the metal is selected from the group consisting of Zn, La, Pr, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Co, Cu, Y, Ca, Sr, Ba, Sc, Mo, W, V and Zr; and

an organic heterocyclic compound according to Formula 1:



Formula 1

wherein

A is a 5- or 6-membered aryl, heteroaryl or heterocyclic ring, which is optionally substituted with one or more substituents and optionally fused with one or more aryl or heteroaryl rings, wherein a dotted line represents one or more optional double bonds;

Y^1 is selected from S, SH, NH_2 or is absent, wherein the dotted line represents a double bond when Y^1 is S or is absent when Y^1 is SH or NH_2 ;

X^1 , X^2 , and X^3 are selected from N, NR^5 , O, S, CR^6 and CR^7R^8 ,

R^5 is selected from hydrogen, amino, C_1 - C_{10} alkyl, C_2 - C_{10} alkenyl, C_2 - C_{10} alkynyl, aryl and heteroaryl, in which each amino, alkyl, alkenyl, alkynyl, aryl or heteroaryl group may be optionally substituted, and

R^6 , R^7 and R^8 , are each independently selected from hydrogen, halogen, carboxyl, sulphide, thiol, amino, C_1 - C_{10} alkyl, C_2 - C_{10} alkenyl, C_2 - C_{10} alkynyl, aryl and heteroaryl, in which each amino, alkyl, alkenyl, alkynyl, aryl or heteroaryl group may be optionally substituted; and

wherein the combined corrosion inhibitor formulation comprises at least two corrosion inhibitors selected from metal salts, metal anions metal complexes, or any combinations thereof.

2. The method of claim 1, wherein the combined corrosion inhibitor formulation comprises:

- (i) at least two metal salts and at least one organic heterocyclic compound of Formula 1, or
- (ii) at least one metal salt, at least one metal anion and at least one organic heterocyclic compound of Formula 1, or
- (iii) at least two metal complexes, or
- (iv) at least one metal complex and at least one metal anion.

3. The method of claim 2, wherein the combined corrosion inhibitor formulation is according to (i), and the at least two metal salts are selected from the group consisting of Pr^{3+} , Gd^{3+} , Ce^{3+} , Dy^{3+} , Sm^{3+} , Er^{3+} , Lu^{3+} , Zn^{2+} , Co^{2+} , Cu^{2+} , and the at least one organic heterocyclic compound of Formula 1 is selected from the group consisting of 3-amino-1,2,4-triazole, benzimidazole, 1H-benzotriazole, 5-amino-2-mercapto-1,3,4-

thiadiazole, 9H-purine-8-thiol, 1,2,4-triazole, 1,2,4-triazole-3-thiol, and 5-methyl-2-mercapto-1,3,4-thiadiazole.

4. The method of claim 2, wherein the combined corrosion inhibitor formulation is according to (ii), and the at least one metal salt is selected from the group consisting of Pr^{3+} , Gd^{3+} , Ce^{3+} , Dy^{3+} , Sm^{3+} , Er^{3+} , Lu^{3+} , Zn^{2+} , Co^{2+} , Cu^{2+} , the at least one metal anion is selected from the group consisting of MoO_4^{2-} , VO_4^{3-} , ZrO_4^{2-} , WO_4^{2-} , and the at least one organic heterocyclic compound of Formula 1 is selected from the group consisting of 3-amino-1,2,4-triazole, benzimidazole, 1H-benzotriazole, 5-amino-2-mercapto-1,3,4-thiadiazole, 9H-purine-8-thiol, 1,2,4-triazole, 1,2,4-triazole-3-thiol, and 5-methyl-2-mercapto-1,3,4-thiadiazole.

5. The method of claim 2, wherein the combined corrosion inhibitor formulation is according to (iii), and the at least two metal complexes are selected from the group consisting of zinc molybdate, erbium molybdate, lutetium molybdate, zinc vanadate, zinc benzotriazole, dysprosium benzotriazole, lutetium benzotriazole, gadolinium benzotriazole, gadolinium molybdate, praseodymium benzimidazole, lutetium benzimidazole, zinc benzimidazole, praseodymium molybdate, dysprosium molybdate, erbium benzotriazole, praseodymium benzimidazole, dysprosium benzimidazole, erbium benzimidazole, zinc tungstate, zinc vanadate, praseodymium vanadate, dysprosium vanadate, erbium vanadate, praseodymium tungstate, dysprosium tungstate, erbium tungstate.

6. The method of claim 2, wherein the combined corrosion inhibitor formulation is according to (iv), and the at least one metal complex is selected from the group consisting of zinc molybdate, erbium molybdate, lutetium molybdate, zinc vanadate, zinc benzotriazole, dysprosium benzotriazole, lutetium benzotriazole, gadolinium benzotriazole, gadolinium molybdate, praseodymium benzimidazole, lutetium benzimidazole, zinc benzimidazole, praseodymium molybdate, dysprosium molybdate, erbium benzotriazole, praseodymium benzimidazole, dysprosium benzimidazole, erbium benzimidazole, zinc tungstate, zinc vanadate, praseodymium vanadate, dysprosium vanadate, erbium vanadate, praseodymium tungstate, dysprosium tungstate,

erbium tungstate, and the at least one metal anion is selected from the group consisting of MoO_4^{2-} , VO_4^{3-} , ZrO_4^{2-} , WO_4^{2-} .

7. The method of any one of claims 1 to 6, wherein, when the first corrosion inhibitor formulation comprises at least one corrosion inhibitor providing a delayed inhibitive response and the second corrosion inhibitor formulation comprises at least one corrosion inhibitor providing an immediate inhibitive response, the polarisation response for the combined corrosion inhibitor formulation polarisation resistance response is a continuous inhibitive response.

8. The method of any one of claims 1 to 7, wherein the steps further comprise a component substitution step.

9. The method of any one of claims 1 to 8, wherein the steps further comprise a ratio variation step.

10. The method of any one of claims 1 to 9, wherein ring A is selected from an optionally substituted monocyclic 5 or 6 membered heteroaryl or heterocyclic ring or an optionally substituted bicyclic heteroaryl or heterocyclic ring, wherein the bicyclic ring has two rings independently selected from 5 and 6 membered rings.

11. The method of any one of claims 1 to 10, wherein the metal is selected from at least one of Zn, Co, Cu, Mo, W, V, Zr, Sm, Dy, Tb, Pr, Er, Tm, Lu and Gd.

12. The method of any one of claims 1 to 11, wherein the metal is selected from at least one of Zn, Co, Cu, Mo, W, V, Zr, Pr, Er, Lu, and Gd.

13. The method of any one of claims 1 to 11, wherein the metal is selected from at least one of Pr^{3+} , Gd^{3+} , Ce^{3+} , Dy^{3+} , Sm^{3+} , Er^{3+} , Lu^{3+} , Zn^{2+} , Co^{2+} , Cu^{2+} , and wherein the metal is in the form of a chloride, nitrate, sulphate salts or other soluble salts.

14. The method of any one of claims 1 to 13, wherein the metal anion is selected from at least one of MoO_4^{2-} , VO_4^{3-} , ZrO_4^{2-} , and WO_4^{2-} .

15. The method of any one of claims 1 to 14, wherein the metal complex is selected from at least one of zinc molybdate, erbium molybdate, lutetium molybdate, zinc vanadate, zinc benzotriazole, dysprosium benzotriazole, lutetium benzotriazole, gadolinium benzotriazole, gadolinium molybdate, praseodymium benzimidazole, lutetium benzimidazole, zinc benzimidazole, praseodymium molybdate, dysprosium molybdate, erbium benzotriazole, praseodymium benzimidazole, dysprosium benzimidazole, erbium benzimidazole, zinc tungstate, zinc vanadate, praseodymium vanadate, dysprosium vanadate, erbium vanadate, praseodymium tungstate, dysprosium tungstate, erbium tungstate.

16. The method of any one of claims 1 to 15, wherein the organic heterocyclic compound of Formula 1 is selected from at least one of 3-amino-1,2,4-triazole, benzimidazole, 1H-benzotriazole, 5-amino-2-mercapto-1,3,4-thiadiazole, 9H-purine-8-thiol, 1,2,4-triazole, 1,2,4-triazole-3-thiol, and 5-methyl-2-mercapto-1,3,4-thiadiazole.

17. The method of any one of claims 1 to 16, wherein the substrate is selected from the group consisting of steel, zinc, magnesium, copper, brass, and bronze.

18. The method of claim 17, wherein the substrate is steel.

19. The method of any one of claims 1 to 18, wherein the combined corrosion inhibitor formulation comprises at least four corrosion inhibitors comprising:

- (v) at least two metal salts and at least two organic heterocyclic compounds of Formula 1; or
- (vi) at least one metal salt, at least one metal anion, and at least two organic heterocyclic compounds of Formula 1; or
- (vii) at least three corrosion inhibitors selected from metal salts, metal anions, metal complexes, or any combinations thereof, and at least one organic heterocyclic compound of Formula 1.

20. The method of claim 19, wherein the combined corrosion inhibitor formulation is according to (v) and the at least two metal salts are selected from the group consisting of Pr^{3+} , Gd^{3+} , Ce^{3+} , Dy^{3+} , Sm^{3+} , Er^{3+} , Lu^{3+} , Zn^{2+} , Co^{2+} , Cu^{2+} , and the at least two organic heterocyclic compounds of Formula 1 selected from the group consisting

of 3-amino-1,2,4-triazole, benzimidazole, 1H-benzotriazole, 5-amino-2-mercapto-1,3,4-thiadiazole, 9H-purine-8-thiol, 1,2,4-triazole, 1,2,4-triazole-3-thiol, and 5-methyl-2-mercapto-1,3,4-thiadiazole.

21. The method of claim 19, wherein the combined corrosion inhibitor formulation is according to (vi) and the at least one metal salt selected from the group consisting of Pr^{3+} , Gd^{3+} , Ce^{3+} , Dy^{3+} , Sm^{3+} , Er^{3+} , Lu^{3+} , Zn^{2+} , Co^{2+} , Cu^{2+} , the at least one metal anion selected from the group consisting of MoO_4^{2-} , VO_4^{3-} , ZrO_4^{2-} , WO_4^{2-} , and the at least two organic heterocyclic compounds of Formula 1 are selected from the group consisting of 3-amino-1,2,4-triazole, benzimidazole, 1H-benzotriazole, 5-amino-2-mercapto-1,3,4-thiadiazole, 9H-purine-8-thiol, 1,2,4-triazole, 1,2,4-triazole-3-thiol, and 5-methyl-2-mercapto-1,3,4-thiadiazole.

22. The method of claim 19, wherein the combined corrosion inhibitor formulation is according to (vii) and the at least three corrosion inhibitors selected from metal salts, metal anions, metal complexes, or any combinations thereof, are selected from the group consisting of Pr^{3+} , Gd^{3+} , Ce^{3+} , Dy^{3+} , Sm^{3+} , Er^{3+} , Lu^{3+} , Zn^{2+} , Co^{2+} , Cu^{2+} , MoO_4^{2-} , VO_4^{3-} , ZrO_4^{2-} , WO_4^{2-} , zinc molybdate, lutetium molybdate, zinc benzotriazole, lutetium benzotriazole, gadolinium benzimidazole, gadolinium molybdate, praseodymium molybdate, dysprosium molybdate, erbium benzotriazole, praseodymium benzimidazole, dysprosium benzimidazole, erbium benzimidazole, zinc tungstate, zinc vanadate, praseodymium vanadate, dysprosium vanadate, erbium vanadate, praseodymium tungstate, dysprosium tungstate, erbium tungstate, and the at least one organic heterocyclic compound of Formula 1 selected from the group consisting of 3-amino-1,2,4-triazole, benzimidazole, 1H-benzotriazole, 5-amino-2-mercapto-1,3,4-thiadiazole.

23. The method according to any one of claims 1 to 22, wherein the combined corrosion inhibitor formulation is a film forming formulation.

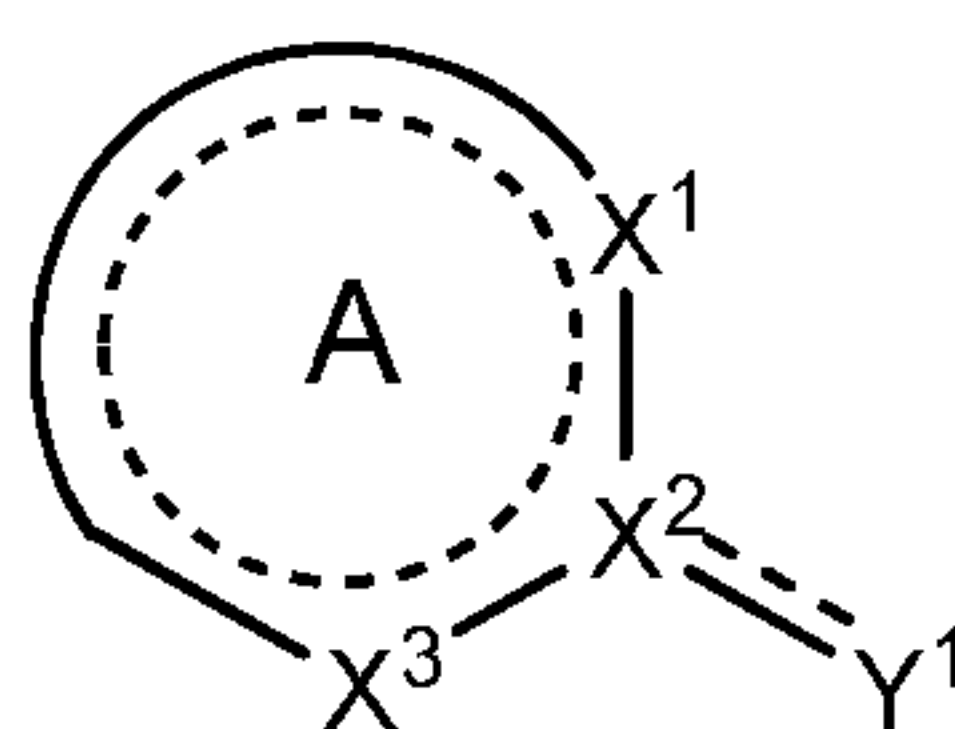
24. A combined corrosion inhibitor formulation as defined according to any one of claims 1 to 23.

25. A combined corrosion inhibitor formulation for inhibiting corrosion of a metal substrate, wherein the combined corrosion inhibitor formulation comprises at least a first corrosion inhibitor formulation comprising at least one corrosion inhibitor and a second corrosion inhibitor formulation comprising at least one corrosion inhibitor that is different to a corrosion inhibitor in the first corrosion inhibitor formulation;

wherein the corrosion inhibitors are each independently selected from the group consisting of:

a metal salt, metal anion, metal complex, or any combination thereof, wherein the metal is selected from the group consisting of Zn, La, Pr, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Co, Cu, Y, Ca, Sr, Ba, Sc, Mo, W, V, and Zr; and

an organic heterocyclic compound according to Formula 1:



Formula 1

wherein

A is a 5- or 6-membered aryl, heteroaryl or heterocyclic ring, which is optionally substituted with one or more substituents and optionally fused with one or more aryl or heteroaryl rings, wherein a dotted line represents one or more optional double bonds;

Y¹ is selected from S, SH, NH₂ or is absent, wherein the dotted line represents a double bond when Y¹ is S or is absent when Y¹ is SH or NH₂;

X¹, X², and X³ are selected from N, NR⁵, O, S, CR⁶ and CR⁷R⁸,

R⁵ is selected from hydrogen, amino, C₁-C₁₀alkyl, C₂-C₁₀alkenyl, C₂-C₁₀alkynyl, aryl and heteroaryl, in which each amino, alkyl, alkenyl, alkynyl, aryl or heteroaryl group may be optionally substituted, and

R⁶, R⁷ and R⁸, are each independently selected from hydrogen, halogen, carboxyl, sulphide, thiol, amino, C₁-C₁₀alkyl, C₂-C₁₀alkenyl, C₂-C₁₀alkynyl, aryl and heteroaryl, in which each amino, alkyl, alkenyl, alkynyl, aryl or heteroaryl group may be optionally substituted; and

wherein the combined corrosion inhibitor formulation comprises:

- (i) at least two metal salts and at least one organic heterocyclic compound of Formula 1, or
- (ii) at least one metal salt, at least one metal anion and at least one organic heterocyclic compound of Formula 1, or
- (iii) at least two metal complexes, or
- (iv) at least one metal complex and at least one metal anion, or
- (v) at least two metal salts and at least two organic heterocyclic compounds of Formula 1, or
- (vi) at least one metal salt, at least one metal anion, and at least two organic heterocyclic compounds of Formula 1, or
- (vii) at least three corrosion inhibitors selected from metal salts, metal anions, metal complexes, or any combinations thereof, and at least one organic heterocyclic compound of Formula 1.

26. The combined corrosion inhibitor formulation of claim 25, wherein the combined corrosion inhibitor formulation is according to (i), and the at least two metal salts are selected from the group consisting of Pr^{3+} , Gd^{3+} , Ce^{3+} , Dy^{3+} , Sm^{3+} , Er^{3+} , Lu^{3+} , Zn^{2+} , Co^{2+} , Cu^{2+} , and the at least one organic heterocyclic compound of formula 1 is selected from the group consisting of 3-amino-1,2,4-triazole, benzimidazole, 1H-benzotriazole, 5-amino-2-mercapto-1,3,4-thiadiazole, 9H-purine-8-thiol, 1,2,4-triazole, 1,2,4-triazole-3-thiol, and 5-methyl-2-mercapto-1,3,4-thiadiazole.

27. The combined corrosion inhibitor formulation of claim 25, wherein the combined corrosion inhibitor formulation is according to (ii), and the at least one metal salt is selected from the group consisting of Pr^{3+} , Gd^{3+} , Ce^{3+} , Dy^{3+} , Sm^{3+} , Er^{3+} , Lu^{3+} , Zn^{2+} , Co^{2+} , Cu^{2+} , the at least one metal anion is selected from the group consisting of MoO_4^{2-} , VO_4^{3-} , ZrO_4^{2-} , WO_4^{2-} , and the at least one organic heterocyclic compound of Formula 1 is selected from the group consisting of 3-amino-1,2,4-triazole, benzimidazole, 1H-benzotriazole, 5-amino-2-mercapto-1,3,4-thiadiazole, 9H-purine-8-thiol, 1,2,4-triazole, 1,2,4-triazole-3-thiol, and 5-methyl-2-mercapto-1,3,4-thiadiazole.

28. The combined corrosion inhibitor formulation of claim 25, wherein the combined corrosion inhibitor formulation is according to (iii), and the at least two metal complexes are selected from the group consisting of zinc molybdate, erbium molybdate, lutetium molybdate, zinc vanadate, zinc benzotriazole, dysprosium benzotriazole, lutetium benzotriazole, gadolinium benzotriazole, gadolinium molybdate, praseodymium benzimidazole, lutetium benzimidazole, zinc benzimidazole, praseodymium molybdate, dysprosium molybdate, erbium benzotriazole, praseodymium benzimidazole, dysprosium benzimidazole, erbium benzimidazole, zinc tungstate, zinc vanadate, praseodymium vanadate, dysprosium vanadate, erbium vanadate, praseodymium tungstate, dysprosium tungstate, erbium tungstate.

29. The combined corrosion inhibitor formulation of claim 25, wherein the combined corrosion inhibitor formulation is according to (iv), and the at least one metal complex is selected from the group consisting of zinc molybdate, erbium molybdate, lutetium molybdate, zinc vanadate, zinc benzotriazole, dysprosium benzotriazole, lutetium benzotriazole, gadolinium benzotriazole, gadolinium molybdate, praseodymium benzimidazole, lutetium benzimidazole, zinc benzimidazole, praseodymium molybdate, dysprosium molybdate, erbium benzotriazole, praseodymium benzimidazole, dysprosium benzimidazole, erbium benzimidazole, zinc tungstate, zinc vanadate, praseodymium vanadate, dysprosium vanadate, erbium vanadate, praseodymium tungstate, dysprosium tungstate, erbium tungstate, and the at least one metal anion is selected from the group consisting of MoO_4^{2-} , VO_4^{3-} , ZrO_4^{2-} , WO_4^{2-} .

30. The combined corrosion inhibitor formulation of claim 25, wherein the combined corrosion inhibitor formulation is according to (v) and the at least two metal salts are selected from the group consisting of Pr^{3+} , Gd^{3+} , Ce^{3+} , Dy^{3+} , Sm^{3+} , Er^{3+} , Lu^{3+} , Zn^{2+} , Co^{2+} , Cu^{2+} , and the at least two organic heterocyclic compounds of Formula 1 are selected from the group consisting of 3-amino-1,2,4-triazole, benzimidazole, 1H-benzotriazole, 5-amino-2-mercapto-1,3,4-thiadiazole, 9H-purine-8-thiol, 1,2,4-triazole, 1,2,4-triazole-3-thiol, and 5-methyl-2-mercapto-1,3,4-thiadiazole.

31. The combined corrosion inhibitor formulation of claim 25, wherein the combined corrosion inhibitor formulation is according to (vi) and the at least one metal salt selected from the group consisting of Pr^{3+} , Gd^{3+} , Ce^{3+} , Dy^{3+} , Sm^{3+} , Er^{3+} , Lu^{3+} , Zn^{2+} , Co^{2+} , Cu^{2+} , the at least one metal anion selected from the group consisting of MoO_4^{2-} , VO_4^{3-} , ZrO_4^{2-} , WO_4^{2-} , and the at least two organic heterocyclic compounds of Formula 1 selected from the group consisting of 3-amino-1,2,4-triazole, benzimidazole, 1H-benzotriazole, 5-amino-2-mercapto-1,3,4-thiadiazole, 9H-purine-8-thiol, 1,2,4-triazole, 1,2,4-triazole-3-thiol, and 5-methyl-2-mercapto-1,3,4-thiadiazole.

32. The combined corrosion inhibitor formulation of claim 25, wherein the combined corrosion inhibitor formulation is according to (vii) and the at least three corrosion inhibitors are selected from metal salts, metal anions, metal complexes, or any combinations thereof, selected from the group consisting of Pr^{3+} , Gd^{3+} , Ce^{3+} , Dy^{3+} , Sm^{3+} , Er^{3+} , Lu^{3+} , Zn^{2+} , Co^{2+} , Cu^{2+} , MoO_4^{2-} , VO_4^{3-} , ZrO_4^{2-} , WO_4^{2-} , zinc molybdate, lutetium molybdate, zinc benzotriazole, lutetium benzotriazole, gadolinium benzotriazole, gadolinium molybdate, praseodymium molybdate, dysprosium molybdate, erbium benzotriazole, praseodymium benzimidazole, dysprosium benzimidazole, erbium benzimidazole, zinc tungstate, zinc vanadate, praseodymium vanadate, dysprosium vanadate, erbium vanadate, praseodymium tungstate, dysprosium tungstate, erbium tungstate, and at least one organic heterocyclic compound of Formula 1 is selected from the group consisting of 3-amino-1,2,4-triazole, benzimidazole, 1H-benzotriazole, 5-amino-2-mercapto-1,3,4-thiadiazole.

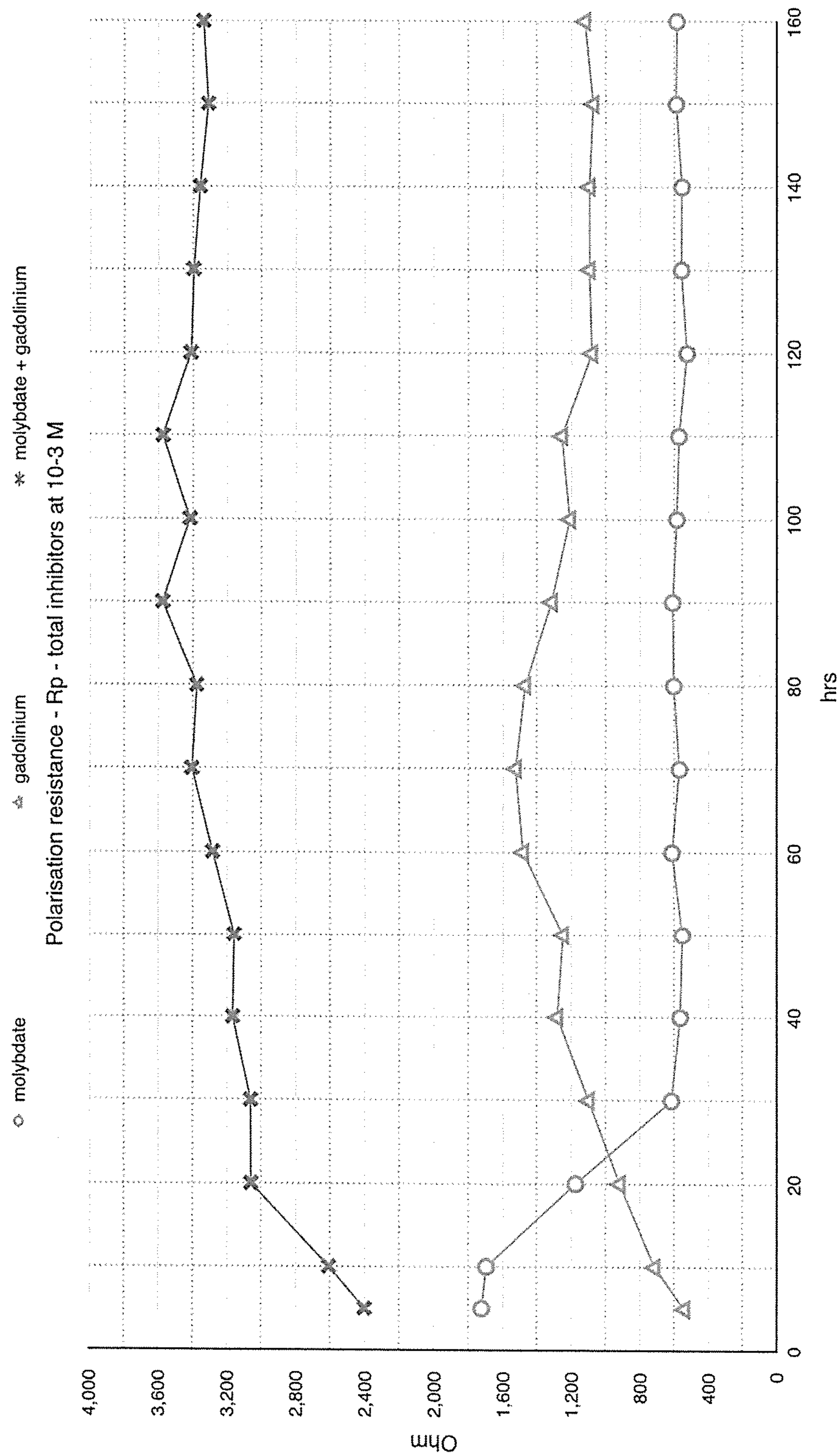


Figure 1

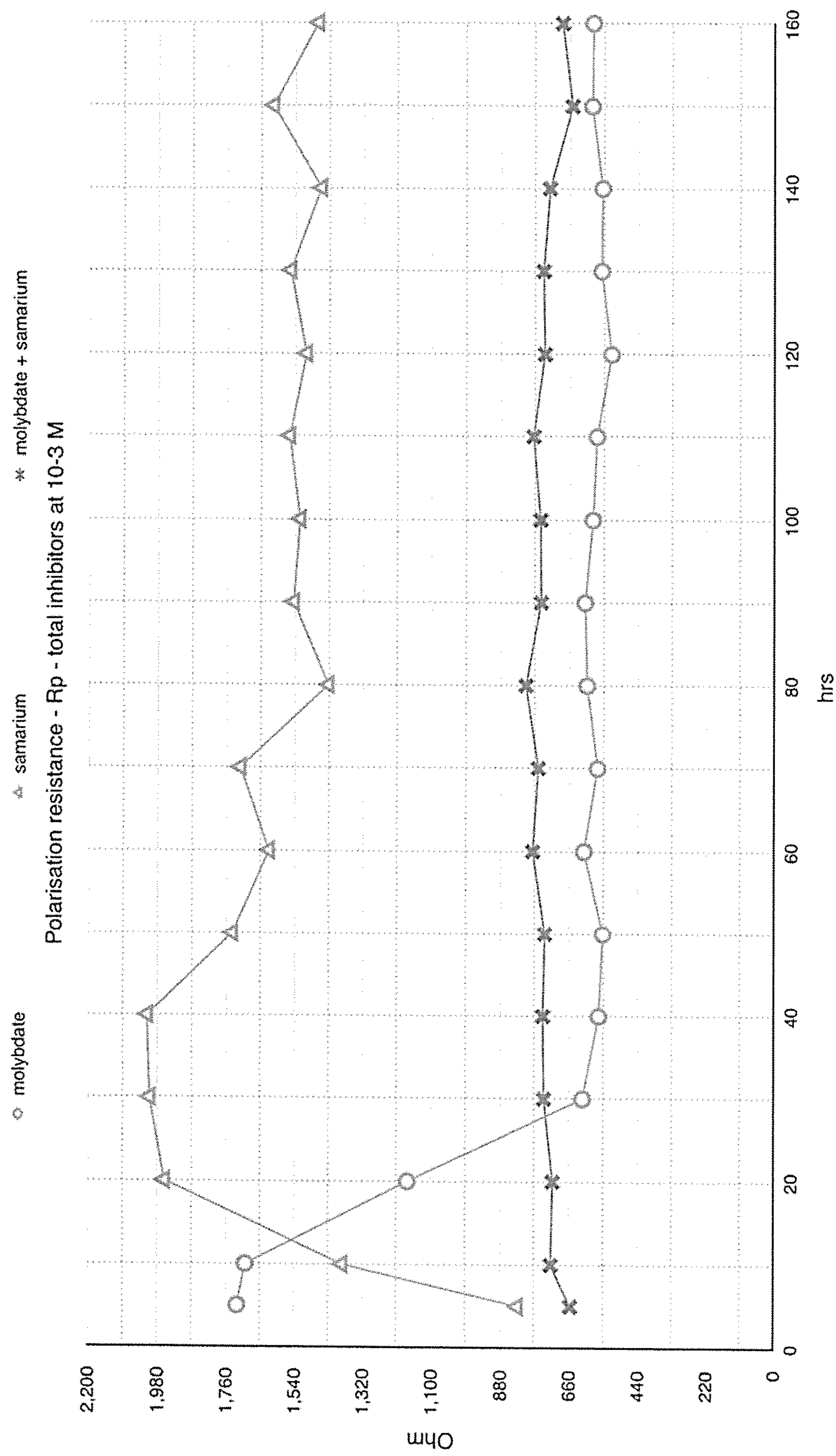


Figure 2

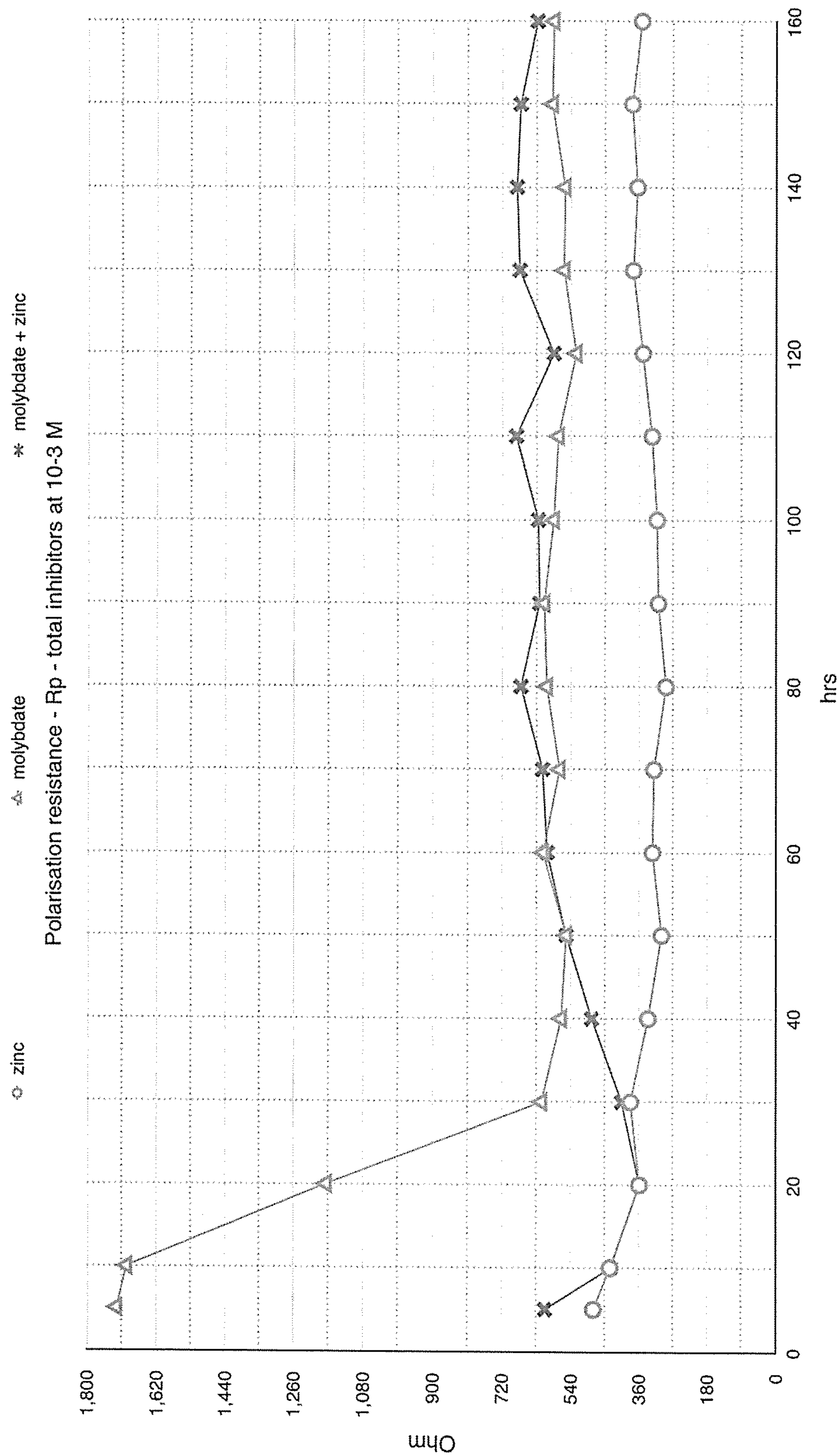


Figure 3

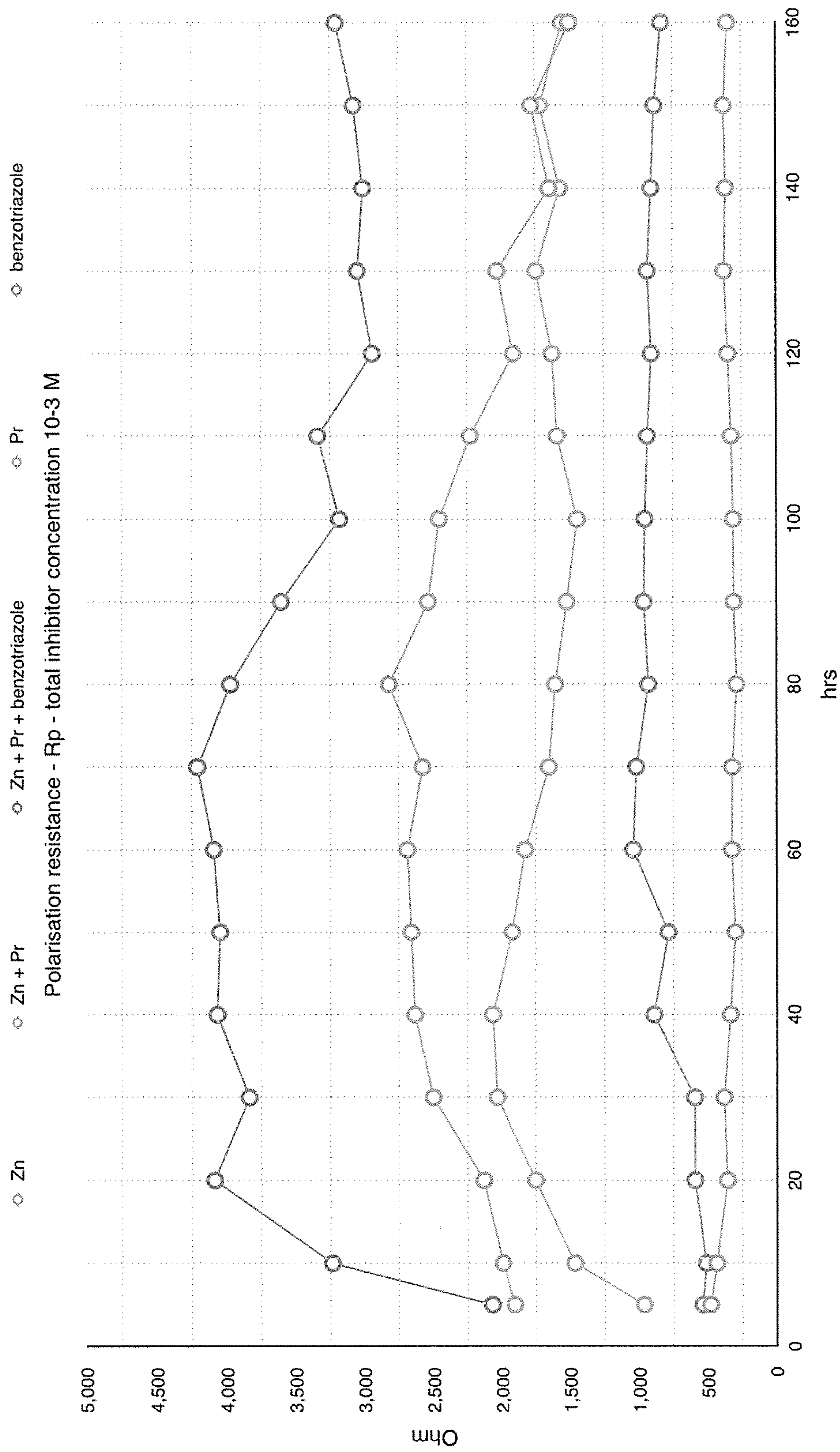


Figure 4

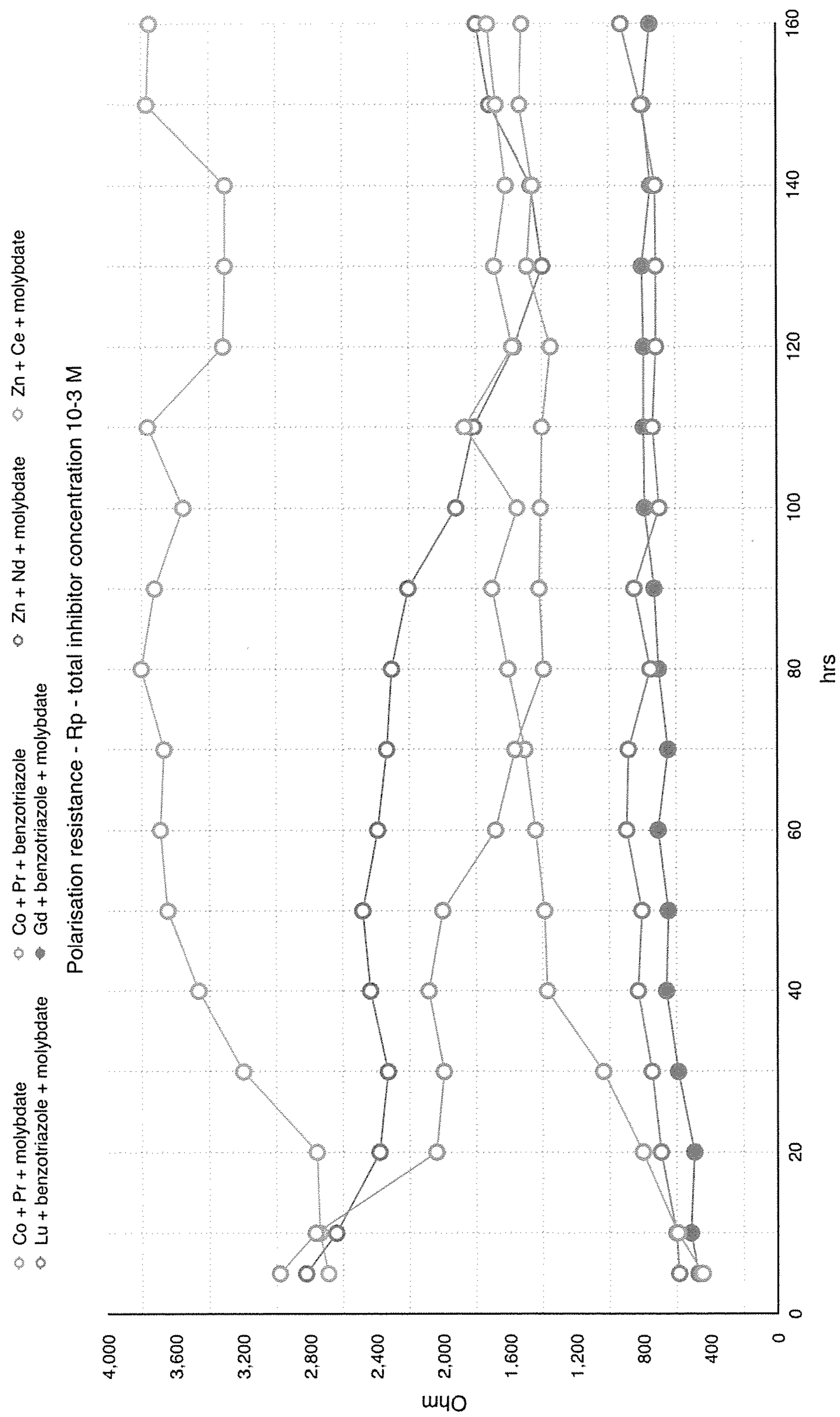


Figure 5

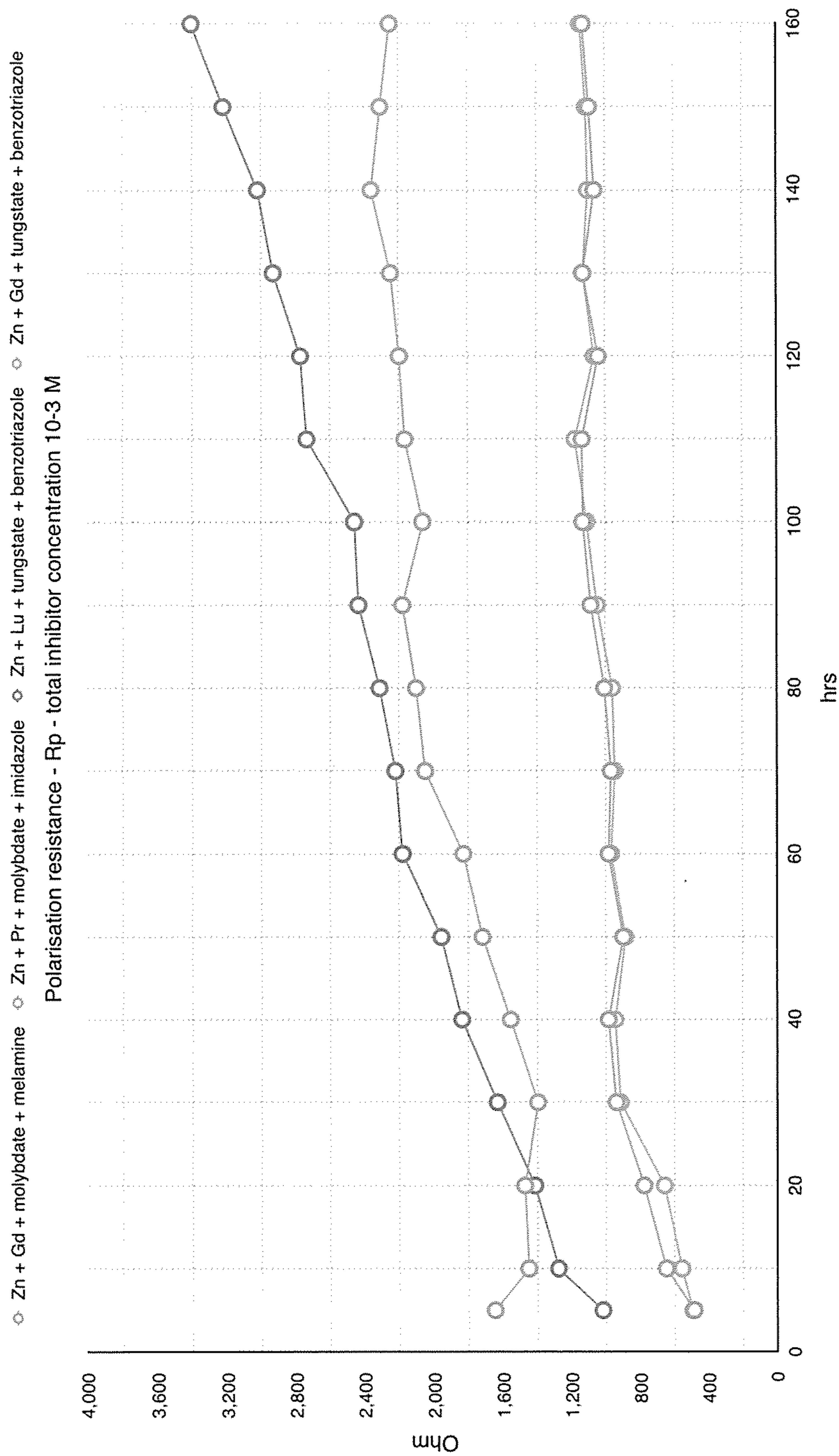


Figure 6