New Journal of Chemistry

Electronic Supporting Information

Towards Materials Discovery: Assays for Screening and Study of Chemical Interactions of Novel Corrosion Inhibitors in Solution and Coatings

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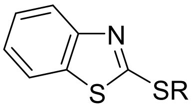
1. Materials

2-Mercaptobenzothiazole **7a** was purchased from Sigma-Aldrich and the methylation was achieved following a literature method[1] to access 2-(methylthio)-benzo[*d*]thiazole **7b** (**Figure S1**).



7a R = H
7b R = CH_3

Figure S1. Chemical structures of compound **7a** and **7b** used in cyclic voltammetry studies.

2. Computational Modelling and Materials Characterisation

Quantum chemistry calculations have been carried using density functional theory (DFT) as implemented in Gaussian 09 suite of programs.[2] Full geometry optimisations were undertaken using the B3LYP exchange-correlation functional.[3] The geometry of the gas phase target compounds was optimised at the B3LYP spin-restricted level of theory using the LAN2DZ basis set for chromium and strontium, and 6- 31+G(d) basis set for all other atoms. Vibrational frequency calculations were performed to verify that the optimised geometries corresponded to minima on the potential energy surface. Single point energy calculations and population analysis were then conducted employing the optimised geometries using the LAN2DZ basis set for chromium and strontium and a larger 6-311+G(d,p) basis set for all other atoms. The calculated energies of the frontier molecular orbitals (MOs), the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are shown in the **Figure S2** below.

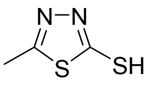
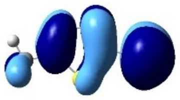
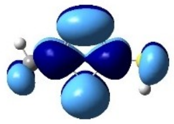
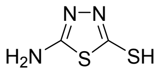
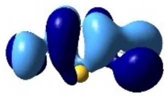
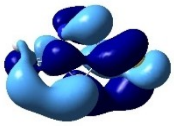
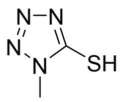
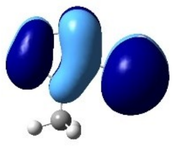
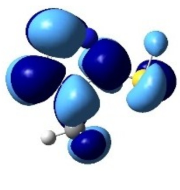
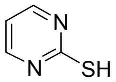
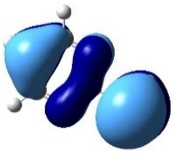
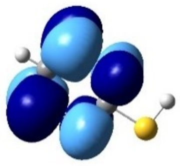
Entry	HOMO orbital	LOMO orbital
 **1**		
 **2**		
 **3**		
 **4**		

Figure S2. Contour plots of HOMO and LUMO orbitals of compounds **1-4**.

Cyclic voltammetry (CV) was undertaken on a Biologic VMP3 potentiostat interfaced to a PC running Echem for Windows. Measurements were run in nitrogen-purged dimethylformamide (DMF) with tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) (0.1 M) as the supporting electrolyte. Electrochemical grade Bu_4NPF_6 was purchased from Sigma-Aldrich, recrystallised twice from absolute ethanol/acetone and stored in a desiccator before use. The voltammograms were recorded using a standard 3 electrode configuration at room temperature with a glassy carbon (2 mm diameter) as the working electrode, platinum (10 mm square) as the counter electrode and silver wire pseudo-reference electrode internally calibrated with ferrocene/ferrocenium (Fc/Fc$^+$) couple. The sample concentration was 1 mM. Voltammograms were recorded between 1200 and -2700 mV vs Fc/Fc$^+$ at different scan rates (20–1000 mV/s) where a 30 second open-circuit voltage (OCV) was used prior to running the CV. CV data collected for the organic compounds are summarised in the table below.

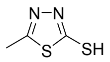
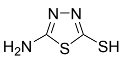
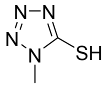
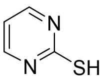
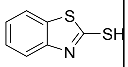
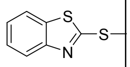
Entry	 **1**	 **2**	 **3**	 **4**	 **7a**	 **7a**
HOMO$_{(exp)}$ (eV) by CV	-6.18	-5.81	-5.98	-5.84	-6.06	-6.25
Oxidation onset by CV (V)	1.38	1.01	1.18	1.04	1.26	1.45

Table S1. Computational and CV data for compounds **1-4**, $SrCrO_4$ **5a**, $(Bu_4N)_2CrO_4$ **5b**, K_2CrO_4 **5c, 7a**, and **7b**. Where possible the HOMO and LUMO levels of the compounds were estimated from the onset oxidation potential using CV data, where the following equations were used, $E_{HOMO} = -[E_{ox} + 4.80]$ and $E_{LUMO} = -[4.80 - E_{red}]$, respectively. All potentials were referenced to the $E_{1/2}$ of the ferrocene/ferrocenium couple at 0.624 V vs NHE.[4]

3. HTP Optical Solution Assay for Materials Discovery on AA2024-T3

AA2024 sheets (100 mm x 75 mm) were abraded with very fine grade 3M Scotch-Brite CF-SR abrasive hand pad (A-VFN purple grade, containing alumina,) under running water, washed with deionised water (DI) and dried prior to use.

All samples were compared with positive controls (deionized H_2O, K_2CrO_4, and $K_2Cr_2O_7$) and a negative control (0.1M NaCl) at an initial pH 5.8. The DI water control was the only sample on the plate that did not contain 0.1M NaCl. Corrosion inhibitor molecules **1**, **2**, **3** and **4**, together with controls were tested at concentrations of 1×10^{-3} M and 1×10^{-4} M with pH 5.8 in the HTP optical well assay (**Figure S3**) and then further refined at 3×10^{-4} M and 5×10^{-4} M as shown in **Table S2**.

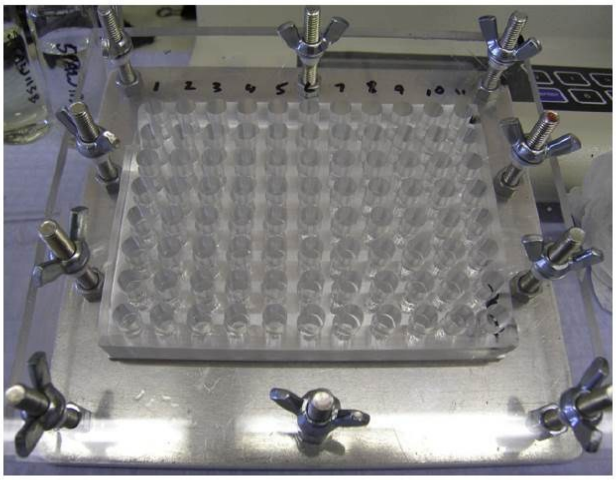
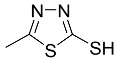
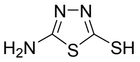
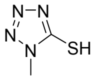
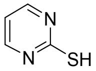


Figure S3. Experimental setup of the HTP optical well assay used in preliminary test of potential new inhibitors. Up to 88 wells can be used to evaluate different compounds, different concentrations, mixtures of compounds or multiples of the same compound. An 8 × 11 grid of 6 mm diameter holes in 10 mm thick polycarbonate is clamped to a 10 mm thick block of PDMS rubber containing the same pattern of holes above an abraded plate of AA2024-T3 above a 5 mm thick metal baseplate. (Used by permission from White et al.[5]) chromate and dichromate solutions were also used and repeat experiments were performed as needed.

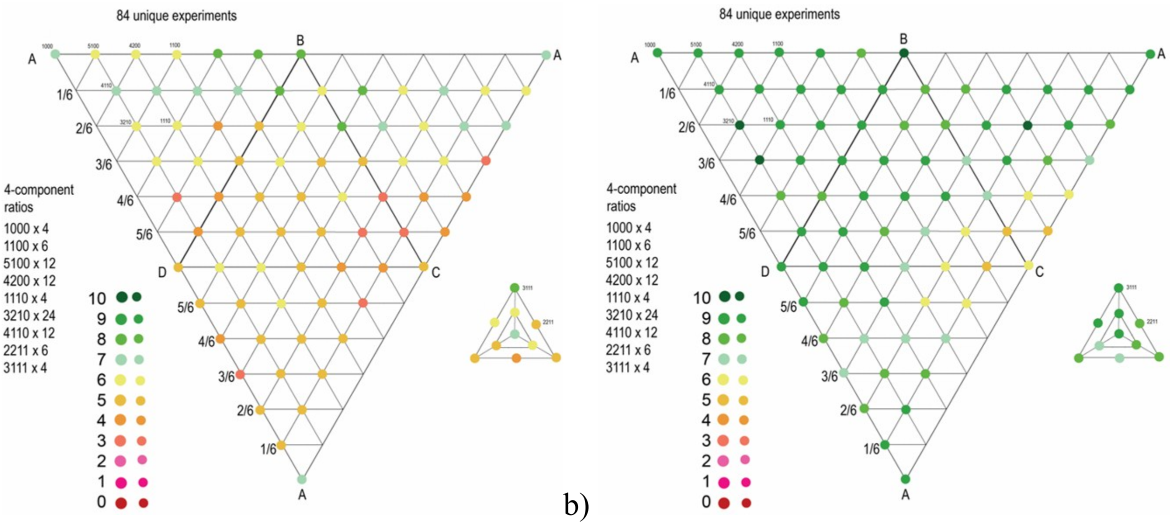
To evaluate the interactions of the four inhibitors in which unary, binary, ternary and quaternary mixtures in 1/6 increments was designed (84 unique solutions), together with 4 controls to fit on a single plate of 88 wells. Each of the 200 µL solutions were stored in a 96 well microplate and mixed by an 8-channel pipettor prior to transfer to the wells plate.

Table S3. HTP optical assay data for organic compounds **1-4**, chromates **5b-c** and dichromate **6** controls. The higher the rank number in the table refers to a greater corrosion inhibition, where K_2CrO_4 **5c** and $K_2Cr_2O_7$ **6** both have exceptionally high corrosion inhibition under these conditions (Note where a rank of 10 shows high corrosion inhibition and 0 is very poor inhibition).

Compound No.	Optical Rank (2×10^{-4} M)	Optical Rank (5×10^{-4} M)
 **1**	7	9
 **2**	9	10
 **3**	4	6
 **4**	6	9
$(Bu_4N)_2CrO_4$ **5b**	8	9
K_2CrO_4 **5c**	9	10
$K_2Cr_2O_7$ **6**	10	10
NaCl	0	0

The solutions were in contact with the metal surface for 24 hours. The wells were rinsed with DI water, the assembly disassembled, the plate rinsed again and dried in a desiccator.

After the AA2024-T3 plate was analysed, the results were colour coded on a scale from 10 (green, lowest corrosion) to 0 (red, most corrosion) and plotted on a quaternary map (**Figure S4**). Controls on the plate typically supply the extremes of the scale. **Figure S4** shows the experimental design of solutions prepared in which all solutions were at a specific concentration whether the solution was unary, binary, ternary or quaternary. In the diagram the three corners labelled as A fold up and out of the page and meet at a point to form the tetrahedron. The unary solutions are at the apices of the tetrahedron with corners labelled as A, B, C and D representing the solutions 1, 2, 3 and 4 respectively. The binary mixtures are along the vertices linking the four apices. Ternary mixtures are on the tetrahedron faces bound by the 4 triangles ABC, ABD, ACD and BCD. Quaternary mixtures are on the smaller tetrahedron which is offset from the centre of the BCD triangle but above the plane of the page.



a) b)

Figure S4a. 2 x 10^{-4} M at pH 5.8 and **Figure S4b.** 5 x 10^{-4} M at pH 5.8. Quaternary map diagram of the pure material and combinations used, the colour coded ranking scale and results obtained.

4. HTP Electrochemical Evaluation of Chromate Controls and Organic Compounds.

Figure S5. Image of current CSIRO HTP electrochemical assay used to evaluate single compounds and mixed inhibition compound systems for corrosion inhibition activity.

This set-up allows 16 simultaneous electrochemical experiments to be performed generating Polarisation Resistance (Rp, Ω, 7 days) and Tafel data (E_{corr}, $i_{corr,}$ 30 min, 24 h, 0.1 M NaCl). Solutions containing the potential inhibitor materials are of 180 mL volume. The latter electrochemical technique is used to determine % inhibition efficiency (%IE) data following a literature method[6] calculated from the equation used below.

$$\text{Inhibition Efficiency (IE\%)} = \frac{(i^{o}_{\text{coor}} - i^{i}_{\text{coor}})}{i^{o}_{\text{coor}}} \times 100$$

Where;

1) i^{o}_{corr} is the corrosion current in the absence of inhibitor
2) i^{i}_{corr} is the corrosion current in the presence of inhibitor

Table S4. HTP electrochemical evaluation of chromate and dichromate controls and novel compounds.

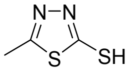
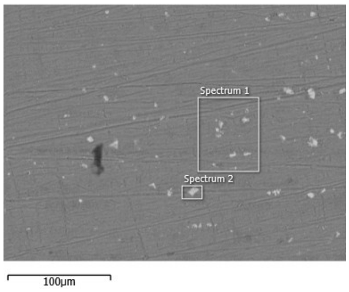
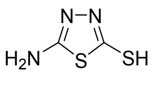
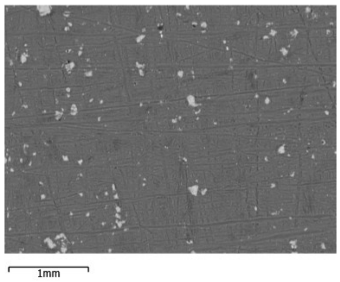
Solution number	**Optical rank (5 x 10^{-4} M)**	***i$_{corr}$* value (1 x 10^{-3} M)**	**%IE value (1 x 10^{-3} M)**	**R$_P$ values from Tafel (1 x 10^{-3} M)**	**R$_p$ Values from LPR (1 x 10^{-3} M)**
1	9	0.49	95	139684	266955
2	10	0.36	97	80103	253270
3	6	2.31	78	12530	37343
4	9	0.50	95	57201	249347
$(Bu_4N)_2CrO_4$ **5b**	9	0.23	97	92570	11901
K_2CrO_4 **5c**	10	0.04	100	857908	144291
$K_2Cr_2O_7$ **6**	10	0.05	100	536234	96903

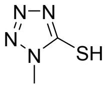
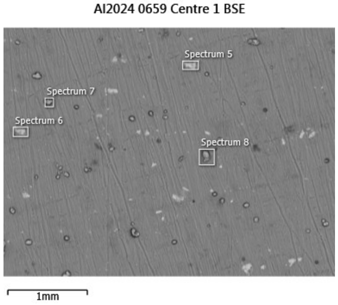
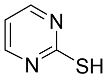
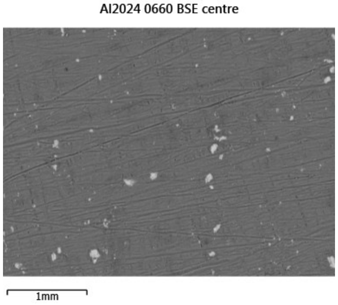
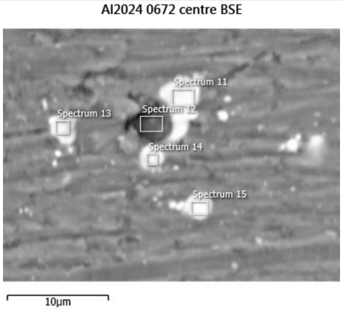
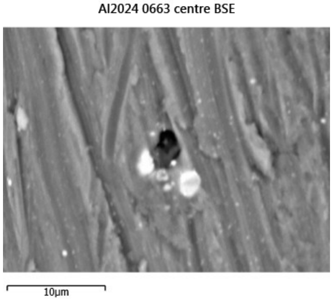
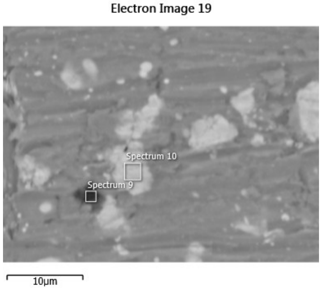
Notes: All solution where adjusted to an initial pH ~5.8. Data points are an average of two or more per experiments. Optical data values are an average of several data points (i.e. 2 or more). Electrochemical data are an average of 2 or more data points. Only one value for LPR.

5. Characterisation of Materials on the AA2024-T3 Surface

A Hitachi TM3030 Plus tabletop SE microscope with attached EDX was used. Samples examined in the SEM were imaged in the secondary electron (SE) and back-scattered electron (BSE) modes. Further, selected areas of the samples were mapped and analysed using the EDX. Samples were prepared by exposing the pre-cleaned metal surface to the inhibitor at 1 ×10^{-3} M at pH 5.8 in 0.1 M NaCl solution during a 24 h polarization resistance experiment at 25°C. The metal was left at open-circuit potential (OCP) except when a -10mV to +10 mV perturbation at 0.167 mV/s was applied for 2 minutes every hour.

Table S5. Showing characterisation data for the exposure of different compounds and chromate materials under 0.1 NaCl solution on AA2024 surface.

Compound Structure	**Comments about samples on left**	**SEM image**	**EDX**
No inhibitor, NaCl solution only			
 **1**	Very little corrosion seen. Couple of spots visible	Al2024 0657 area 1 BSE  	No sulfur seen
 **2**	No corrosion seen.	Al2024 0658 centre BSE  	No sulfur seen

 **3**	Visible corrosion.		Sulfur around trenched inter-metallics together with some Cl
 **4**	Very little corrosion seen.		Some small amounts of sulfur seen
$(Bu_4N)_2CrO_4$ **5b**	Very little corrosion seen.		Cr seen near inter-metallic hole
K_2CrO_4 **5c**	Very little corrosion seen. Couple of spots visible.		Cr seen near inter-metallic hole
$K_2Cr_2O_7$ **6**	Very little corrosion seen.		Cr seen near inter-metallic hole

6. FASTER Evaluation of Chromium-based Controls and Organic Compounds on AA2024-T3

AA2024-T3 sheets (31.5 mm x 31.5 mm) were abraded with very fine grade 3M Scotch-Brite CF-SR abrasive hand pad (A-VFN purple grade, containing alumina), washed with deionised water (DI) and dried prior to loading into sample holders. The total testing volume in each electrochemical was 4 mL. Electrochemical measurements were performed in a robotic electrochemical testing system equipped with a Biologic SP-150 potentiostat. Stock solutions were prepared at a fixed concentration of 1 x 10^{-3}M corrosion inhibitor and pH 5.8 in an aqueous 0.1M NaCl, which were dispensed into the testing wells. This was followed by sample exposure for a minimum of 24 hours period in the inhibitor/salt testing solution. Following this equilibration period, chromate controls, and organic compounds were assessed using the following electrochemical testing procedure: OCV for 30 mins, followed by a polarization scan -200 to 200 mV from OCV, at a scan rate of 10 mV/min. The testing configuration was as follows: SCE-RE contained inside a double junction tube, Pt-CE, Al 2024-WE. The resulting Tafel plot data was processed by curve fitting algorithms in Biologic EC-Lab (Ver. 11.25) to determine the i_{corr}, which was used directly to calculate the %IE (average triplicate data points).

7. Corrosion Testing Facilities: On-site and Outdoor Environmental Testing

In addition to the NSS test according to ASTM B117[7] ("Standard practice for operating salt spray (fog) apparatus") as described previously (shown in **Figure S6)** that enables us to test commercial and R&D samples. We also have other outdoor testing facilities that enable evaluation of coatings under environmental conditions (**Figures S7** and **S8**). New materials and coatings showing enhanced corrosion inhibition performance would be evaluated in these outdoor settings against commercial benchmark materials.

CSIRO has 3 outdoor corrosion sites in Victoria. In Flinders in southern Victorian on the coast of Bass Strait we have two sites. One located at the Flinders Navy Base on a cliff overlooking Bass Strait and is in a Marine environment, the other is to the north of Flinders approximately 1 km from the coast at the Flinders Water Board site, which is a milder coastal site. The third corrosion site is located at the CSIRO's Clayton site in metropolitan Melbourne and is a mild urban site. All three sites have both a sheltered and an open exposure rack. These sites allow us to expose samples at different corrosivity levels and different levels of marine influence to study how different protective systems respond to the real world environment.

Figure S6. The Neutral Salt Spray Chambers located and used at CSIRO Clayton for tests.

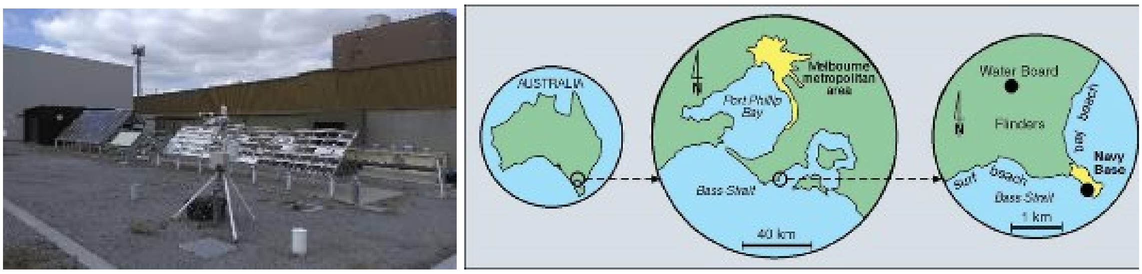


Figure S7. CSIRO Clayton (urban site) for environmental testing and map showing our marine sites.

Figure S8. Flinders Navy Base (marine) and Flinders Water Board (coastal) for field environmental testing.

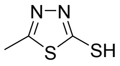
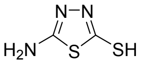
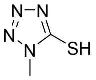
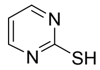
8. Preparation of PU Coatings Containing Inhibitor Materials by Weight Loading

Polyurethane samples containing different inhibitors used for neutral salt spray and electrochemical analysis (EIS and LRP) were both prepared the same way and at the same time for consistency. The AA2024-T3 plate was abraded with Scotchbrite VFA (purple) under running water, rinsed with deionized water, air dried and stored at 40˚C until use.

Coating preparation – 10 weight % in PU

Commercially available polyurethane (2.7g) PU (Cabots Cabothane Clear oil based polyurethane) was mixed in a planetary mixer with *n*-butyl acetate (BA) (0.5g). The inhibitor (0.3g, 10wt% of material) was partially pre-ground with a glass Muller and ground glass slab before the liquid was added and ground together until a suspension with a smooth consistency was obtained. The suspension was transferred onto a pre-prepared aluminium plate (255 x 75 mm) and a coating obtained from an auto film applicator (Sheen Instruments 1137) with the bar set at minimum speed (50 mm/s). The coatings were air dried for an hour and then dried at 40˚C overnight. The coated samples were further heated at 70˚C overnight in an oven and then guillotined into 3 samples of 75 mm square which were used for both NSS and leaching/scribing electrochemistry tests. The dry film thickness of the coatings was measured using a Positector 200 series ultrasonic coating thickness gauge to be 25 ± 5 µm.

Table S6. 10% Weight of Material in PU Coating for Neutral Salt Spray Evaluation.

Material	 **1**	 **2**	 **3**	 **4**	$SrCrO_4$ **5a**	$(Bu_4N)_2CrO_4$ **5b**
Molecular Weight	132.20	133.19	116.14	112.15	203.61	372.46
Amount used	10 wt% (0.3 g)	10 wt% (0.3 g)	10 wt% (0.3 g)	10 wt% (0.3 g)	10 wt% (0.3 g)	10 wt% (0.3 g)
No. of moles	2.269×10^{-3}	2.252×10^{-3}	2.583×10^{-3}	2.583×10^{-3}	1.473×10^{-3}	8.055×10^{-4}
Ratio comparison relative to $SrCrO_4$	1.54 equiv excess	1.53 equiv excess	1.75 equiv excess	1.82 equiv excess	1 equiv excess	0.55 equiv shortage
PU used	2.7 g	2.7 g	2.7 g	2.7 g	2.7 g	2.7 g

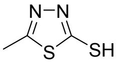
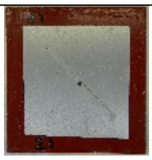
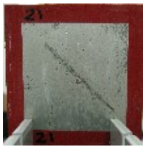
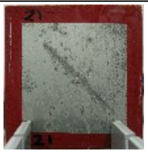
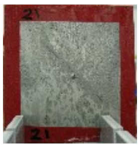
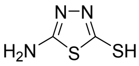
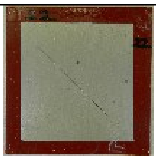
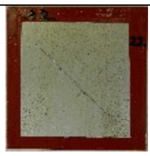
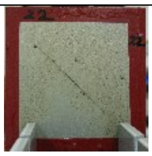
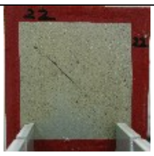
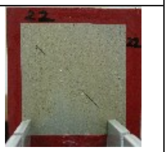
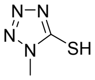
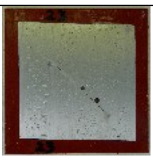
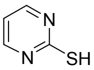
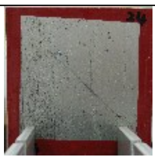
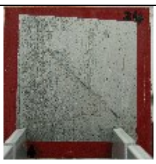
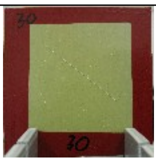
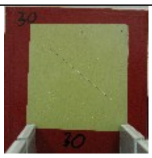
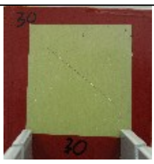
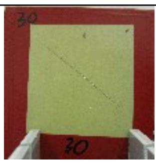
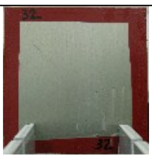
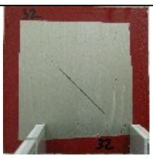
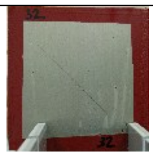
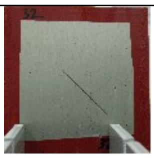
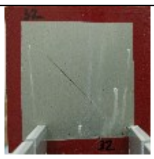
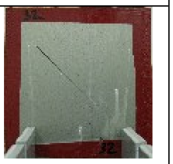
Coating Scribe Method

The PU/inhibitor coatings were cut under the surface of a salt solution using a 60° angled scribe tool to generate a scribe 48 mm long with an exposed metal surface area of 2 (4.8d/sin30) cm^2 where d is the cut surface width. On two samples d was measured as 120 μm giving a surface area of 1.152 cm^2 and a depth of 103 μm per scribe. The as-cut scribe was not exposed to air, but only the salt solution during this process. These samples were then used directly in the neutral salt spray and electrochemical tests.

9. Neutral Salt Spray Testing for 10% Weight Loading of Inhibitor Materials into PU Coatings

NSS test according to ASTM B117[7] ("Standard practice for operating salt spray (fog) apparatus") was performed in a Vötsch Salt Spray Chamber to provide a corrosion evaluation of the coatings. The edges of the samples were sealed with paint type "323 Red" from Atotech Australia, Dandenong South Victoria. The samples were placed in the salt spray chamber at approximately 35° from the vertical. The spray solution consisted of 5% NaCl in de-ionised water, pH adjusted so the collected spray was at a pH between 6.5 and 7 and chamber maintained at 35°C. At various time intervals samples were removed from the chamber and photographs taken. Duplicate samples were prepared.

Figure S9. Neutral Salt Spray Chamber evaluation of 10% wt of material in PU coating

Inhibitor	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6
 **1**						
 **2**						
 **3**						
 **4**						
$SrCrO_4$ **5a**						
$(NBu_4)_2CrO_4$ **5b**						

10. Preparation of PU Films with Different $SrCrO_4$ Loadings

Polyurethane samples containing different weight % loading of $SrCrO_4$ inhibitors used for neutral salt spray and electrochemical analysis (EIS and LPR) were both prepared the same way and at the same time for consistency. The AA2024-T3 plate was abraded with Scotchbrite VFA (purple) under running water, rinsed with deionized water, air dried and stored at 40˚C until use.

Coating preparation – 10 weight % in PU

Commercially available polyurethane (2.7g) PU (Cabots Cabothane Clear oil based polyurethane) was mixed in a planetary mixer with *n*-butyl acetate (BA) (0.5g). The inhibitor (0.3g, 10wt% of material) was partially pre-ground with a glass Muller and ground glass slab before the liquid was added and ground together until a smooth consistency suspension was obtained. The suspension was transferred onto a pre-prepared aluminium plate (255 x 75 mm) and a coating obtained from an auto film applicator (Sheen Instruments 1137) with the bar at minimum speed (50 mm/s). The coatings were air dried for an hour and then dried at 40˚C overnight. The coated samples were then heated at 70˚C overnight in an oven and then guillotined into 3 samples of 75 mm square which were used for both NSS and leaching/scribing electrochemistry tests. The dry film thickness of the coatings was measured using a Positector 200 series ultrasonic coating thickness gauge to be 25 ± 5 µm.

Table S7. Coatings with different Strontium Chromate weight content in Polyurethane.

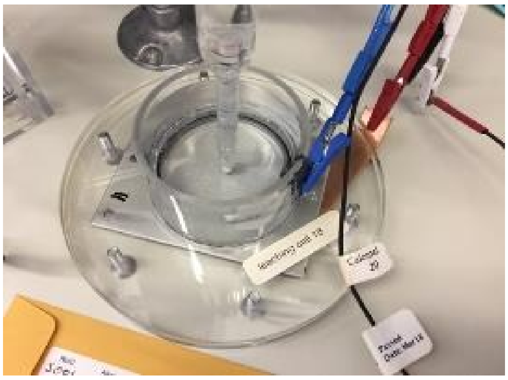
Material	**Control**	**$SrCrO_4$**			
		1 wt%	**2 wt%**	**5 wt%**	**10 wt%**
Amount used (mg)	None	27.2	55	141	300
Mole equiv. (mol)	-	1.336×10^{-4}	2.701×10^{-4}	6.925×10^{-4}	1.473×10^{-3}
PU used	2.7 g	2.7 g	2.7	2.7	2.7 g
Total Mass	2.7 g	2.73 g	2.76 g	2.84 g	3.00 g

11. Evaluation of Scribed Weight % of SrCrO$_4$ in PU Coating; Comparing Film Quality by Electrochemical Methods

Electrochemical Impedance Spectroscopy (EIS) spectra were recorded at the open circuit potential (OCP) using a Biologic VMP3 16 channel potentiostat utilising an EIS card. The EIS measurements were performed over a frequency range from 10^6 Hz to 0.15 Hz applying a 20 mV sinusoidal amplitude and performing 100 measurements with a logarithmic spacing between the start and finish frequencies. Ten measurements were made per frequency.

Coated 75 mm square plates were clamped to an open perspex cylindrical cell with an O-ring diameter of 6 cm. A thin copper tab was clamped to the bottom of the bare Al plate to provide conductivity to the coated Al working electrode (**Figure S7**). A mixed-metal oxide coated expanded titanium mesh (AMAC Corrosion, Kilsyth, Victoria, Australia) was used as counter electrode and a calomel electrode inside a double junction tube filled with saturated KCl used as reference. A solution of 0.1 M NaCl (100 mL, pH 5.8) was added to the cylinder and the electrochemical tests conducted with a repeating EIS, LPR and OCP cycle. Each cycle took approximately 30 mins and 144 cycle repeats took around 72 hours per experiment. The intact coated plates went through one EIS/LPR cycle and then the coating was scribed under the surface of a salt solution using a 60° angled scribe tool to generate two scribes 48mm long with an exposed metal surface area of [2(4.8d/sin30)] cm^2 where d is the cut surface width. On two samples d was measured as 120 µm giving a total exposed surface area of 2.304 cm^2 at a depth of 103 µm. The as-cut scribe was not exposed to air, but only to the salt solution during this process. The samples were then subjected to the further LPR electrochemical cycling.

Figure S10. Electrochemical cell for testing scribed coatings.



12. Comparison of Varying Weight % of $SrCrO_4$ and 10 wt% of Materials in PU Coating by Solution Based Linear Polariszation Resistance

Linear Polarization Resistance (LPR) spectra were recorded at the open circuit potential (OCP) using a Biologic VMP3 16 channel potentiostat as described previously, using a solution of 0.1 M NaCl (100 mL, pH 5.8) and ambient temperature. The samples were polarised using a sweep rate of 0.167 mV/s over a range of -10 mV to +10 mV versus the OCP.

13. References

1. Xie, J.-G.; Quan, J.; Li, S.-B.; Zheng, Y.; Zhu, L.-M., SH-Methylation of SH-Containing Heterocycles with Dimethyl Carbonate via Phase-Transfer Catalytic Reaction. *Synth. Commun.* **2011,** *41* (6), 871-878.
2. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V. C.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O. A., A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision D.01, Gaussian, Inc.: Wallingford CT.,* , **2013**.
3. Becke, A. D., Density-functional Thermochemistry. III. The Role of Exact exchange. *J. Chem. Phys.* **1993,** *98* (7), 5648-5652.
4. Pavlishchuk, V. V.; Addison, A. W., Conversion Constants for Redox Potentials Measured Versus Different Reference Electrodes in Acetonitrile Solutions at 25°C. *Inorg. Chim. Acta* **2000,** *298*, 97-102.
5. White, P. A.; Smith, G. B.; Harvey, T. G.; Corrigan, P. A.; Glenn, M. A.; Lau, D.; Hardin, S. G.; Mardel, J.; Markley, T. A.; Muster, T. H.; Sherman, N.; Garcia, S. J.; Mol, J. M. C.; Hughes, A. E., A New High-throughput Method for Corrosion Testing. *Corros. Sci.* **2012,** *58*, 327-331.
6. Muster, T. H.; Sullivan, H.; Lau, D.; Alexander, D. L. J.; Sherman, N.; Garcia, S. J.; Harvey, T. G.; Markley, T. A.; Hughes, A. E.; Corrigan, P. A.; Glenn, A. M.; White, P. A.; Hardin, S. G.; Mardel, J.; Mol, J. M. C., A Combinatorial Matrix of Rare Earth Chloride Mixtures as Corrosion Inhibitors of AA2024-T3: Optimisation Using Potentiodynamic Polarisation and EIS. *Electrochim. Acta* **2012,** *67*, 95-103.
7. Baboian, R.; Dean Jr., S. W.; Hack, H. P.; Hibner, E. L.; Scully, J. R., *Corrosion Tests and Standards: Application and Interpretation - Second Edition*. ASTM International: West Conshoshocken, PA, USA, **2005**.