Application Report

Corrosion prevention

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Author:	Dr. Christopher Rulison
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Drop Shape Analyzer – DSA100   Force Tensiometer – K100

Method:	
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Choosing a Corrosion Prevention Compound Surface Science Helping to Preserve Aeronautical Equipment

Abstract

Corrosion prevention compounds (commonly referred to as CPC's) are low viscosity, oily liquids commonly sprayed onto metal structures to slow corrosion. They are designed to prevent water, and therefore the reactions which it facilitates, from getting to metal surfaces in large quantities. CPC's have a variety of chemistries, and on boldly exposed and freshly produced surfaces they are largely effective.

However, the ability of CPC's to penetrate into secluded regions of complex structures varies fairly substantially from supplier to supplier and compound to compound. One of the largest areas of concern is "lap" joints. As the name implies, these are joints are formed by overlapping metal, such that there is effectively a capillary between two pieces of metal. Several such joints exist on a standard airplane body, and we have had several customers come to us to investigate the abilities of CPC's to penetrate these joints in particular.

The most demanding situation for a CPC is when the joint is already formed and somewhat corroded, and the application of the CPC is intended to prevent further corrosion (rather than to prevent corrosion all together on a "fresh off the production line" sample). A government contractor came to us with this problem recently and wanted to know what we could tell them about CPC choice for pre-corroded aluminum lap joints. We took the following approach.

Experimental section

Samples of a separated lap joint with minor corrosion inside the joint were tested for surface energy and surface polarity (fraction of the overall surface energy which is made up of polar component). This was done according to the Fowkes method. Fowkes theory is described in detail in technical note TN306e on our website (information database), if you need details. Diiodomethane and water where used as probe liquids and were found to have average contact angles of 56.5° and 67.8° respectively on exposed surfaces from the partially corroded aluminum lap joint. These angles are as opposed to average angles of 63.9° for diiodomethane and 80.5° for water on the customer's freshly formed and pre-treated aluminum stock. All reported angles were measured by the sessile drop method on a Krüss Drop Shape Analyzer – DSA100.

Applying Fowkes theory to these angles gives us the following data – which tells us that we are certainly not dealing with the same surface for partially corroded aluminum versus fresh aluminum.

Surface	Overall Surface Energy (mJ/m²)	Polar Component (mJ/m²)	Dispersive Component (mJ/m²)	Surface Polarity (%)
Corroded Aluminum from Joint	40.77	10.18	30.59	24.98
Fresh Aluminum Stock	35.26	4.04	31.22	11.47

Just due to the corrosion that has taken place (and these samples did, by no means, represent what most people would call a heavily corroded joint – rather they were just slightly discolored and had signs of only modest change) the surface energy of the aluminum increased more than 5 mJ/m² and the surface polarity more than doubled.

To see the problem this poses for CPC treatment one only needs to study the surface properties of the CPC candidates which our customer provided us for analysis. We'll call them samples A through E.

We measured the surface tensions of these samples by the Wilhelmy plate method using a Krüss Force Tensiometer – K100, and also measured their contact angles on poly(tetrafluoroethylene) PTFE on the same DSA100 used to characterize the aluminum samples. The following average surface tension and contact angle values were obtained.

CPC Type	Surface Tension (mN/m)	Contact Angle Against PTFE (degrees)
A	24.35	52.2
B	25.34	56.9
C	25.84	59.4
D	26.02	60.2
E	27.39	65.2

Of course, the reason to do this type of analysis is so that the PTFE contact angle data can be used along with Fowkes theory to separate the overall surface tension of each CPC into polar and dispersive components and % surface polarity. Technical note #TN306e, referenced earlier, also describes this part of Fowkes theory as applied to liquids. Using the above data, and the Fowkes theory, the following surface tension components were calculated for the various CPC's.

CPC	Overall Surface Tension (mN/m)	Polar Component (mN/m)	Dispersive Component (mN/m)	Surface Polarity (%)
A	24.35	2.93	21.42	12.02
B	25.34	3.90	21.44	15.39
C	25.84	4.72	21.12	18.27
D	26.02	4.95	21.07	19.01
E	27.39	6.39	21.00	23.34

You will note that the surface tension values in the data set only vary over a range of about 3 mN/m. However, the fractional surface polarity values vary by more than 11%. All of the CPC's show much lower surface tensions than the surface energy of the corroded aluminum from the joint – so one would think the wetting would be very favorable if the joint was dry and exposed. Also, some of the higher surface polarity CPC's have surface polarities approaching that of the corroded aluminum. So, initially at least, it would appear we could easily pick the most compatible CPC for the corroded aluminum surface from this list. It would be CPC E, since CPC E has the highest surface polarity and, thereby, the most compatible surface polarity to the corroded aluminum).

However, when we consider that the goal is to find the best CPC for potentially moist lap joints, the choice proves not to be so easy. When the surface is wet you are trying to replace a water/aluminum interface with two interfaces within the joint: a CPC/aluminum interface and a CPC/water interface. The free energy for such a transition is:

Free Energy for CPC to Displace Water =

$$\gamma_{CPC/Aluminum} + \gamma_{CPC/Water} - \gamma_{Water/Aluminum}$$

where γ = interfacial tension.

Interfacial tensions between the corroded aluminum and the CPC's, as well as for corroded aluminum and water, must be calculated based on the known properties of water (46.4 mN/m polar component and 26.4 mN/m dispersive component) and the properties of the

aluminums and CPC's as given above. There is no direct way to measure the interfacial tension at a liquid/solid interface. The calculations can be made using Good's equation – also described in technical note #TN306e, referenced above.

CPC/Water interfacial tensions can be measured directly, since both are liquids. And, they were measured for this work using the pendant drop method on the same Krüss Drop Shape Analyzer – DSA100 used to characterize the CPC's themselves and the aluminum surfaces. The following results were obtained.

	Calculated IFT Corroded Aluminum (mN/m)	Calculated IFT Fresh Aluminum (mN/m)	Measured IFT with Water (mN/m)
CPC – A	3.00	1.01	13.34
CPC – B	2.29	0.92	12.14
CPC – C	1.91	1.01	9.36
CPC – D	1.82	1.04	11.29
CPC – E	1.34	1.28	11.38
Water	13.27	23.26	-----

From these data the following free energies for water displacement by the CPC's can be calculated:

Free Energies for Water Displacement by CPC's		
	Free Energy for Water Displacement on Corroded Aluminum (mJ/m^2)	Free Energy for Water Displacement on Fresh Aluminum (mJ/m^2)
CPC – A	3.07	-8.91
CPC – B	1.16	-10.20
CPC – C	-2.00	-12.89
CPC – D	-0.16	-10.93
CPC – E	-0.55	-10.60

Here we give data for both the corroded aluminum and a fresh aluminum for comparison. Given that negative free energies for water displacement are favorable, you will quickly note that water displacement by each of the CPC's is favorable if the surface is fresh aluminum. However, with the corroded aluminum, water displacement is unfavorable for two of CPC's (A and B). For those CPC's which are predicted to support water displacement (show negative free energies of displacement) the prediction is that C will displace water better than E, and that displacement favorability for D is likely to be intermediate.
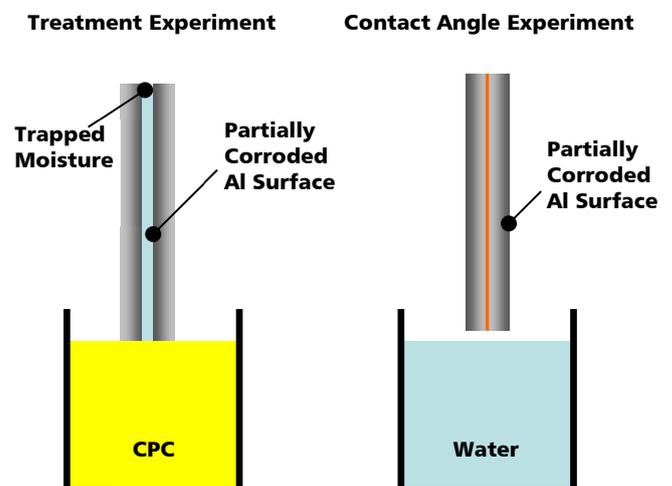
As to the cause for these trends – for the most part the interfacial tensions for the CPC's on the aluminums are rather low. This is to be expected, because it is well known that the CPC's are very effective in treating the

surface of even corroded aluminum in the absence of moisture. The interfacial tensions for the CPC's are what is high, and what drives some of the free energies to be higher than is desirable.

There is, however, some trade-off to be had with CPC's regarding interfacial tension. The interfacial tension with water cannot be made too low or else it will be easy for water to displace the CPC once it is in place. In other words, the CPC will wash off, and/or, the CPC film will emulsify water – thus bringing water closer to the surface. On the other hand, as we see here, if the interfacial tension is too high then the free energy for water displacement is high. We don't necessary understand those limits currently and the degradation of a CPC coating over time after treatment may be the subject of a future paper.

For now, we continue to focus on the ability of CPC's to displace water and penetrate lap joints, To that end, we designed one more experiment which attempts to directly confirm the impressions which the free energy of water displacement data above give us.

The experiment was conducted as follows. We took corroded aluminum pieces from the customer's separated lap joints (having dimensions of 2 cm x 10 cm), wet them with water by dipping, and combined them in pairs corroded-face to corroded-face, thus creating controllably moistened lap joints. The pieces were held together with binder clamps (four used to hold together each two piece sample). They were then brought down so that one of the 2 cm edges of the sample just touched the surface of a beaker of CPC, as shown below. Each sample (model lap joint) was allowed to sit touching the CPC surface for a period of 6 hours. It was then removed, separated into two individual aluminum pieces again, allowed to dry, and recombined backwards, with the two corroded surfaces exposed. Adhesive was used to firmly combine the samples this time – creating a dual sided sample having two main surfaces which were previously the "lap joint" interiors.

Treatment Experiment

Trapped Moisture
Partially Corroded Al Surface
CPC

Contact Angle Experiment

Partially Corroded Al Surface
Water

These dual sided surfaces were then tested for water contact angle as a function of dipping distance experiments, using the Wilhelmy technique on a Krüss Force Tensiometer – K100.

Our reason for designing such an experiment was that we knew that the contact angle for water on the non-CPC treated corroded surface was, on average, 67.8°. This is a result from the prior surface energy work. We also had measured the following average contact angles for the corroded surface when treated directly with each of the CPC's.

	Average Contact Angle for Water on Corroded Aluminum Directly Treated with each CPC (degrees)
CPC – A	104.5
CPC – B	102.0
CPC – C	100.1
CPC – D	102.4
CPC – E	100.6

Therefore, it stands to reason that we could measure the extent of penetration of each CPC into our moist lap joint after the fact with a contact angle as a function of position experiment as described above. The contact angle for water on the surface should be higher than 67.8° for the amount of distance that the CPC is able to penetrate.

The actual results for these experiments are shown in the graph below.

Contact Angle on Dried Pre-Corroded and then CPC Treated Model Lap Joint
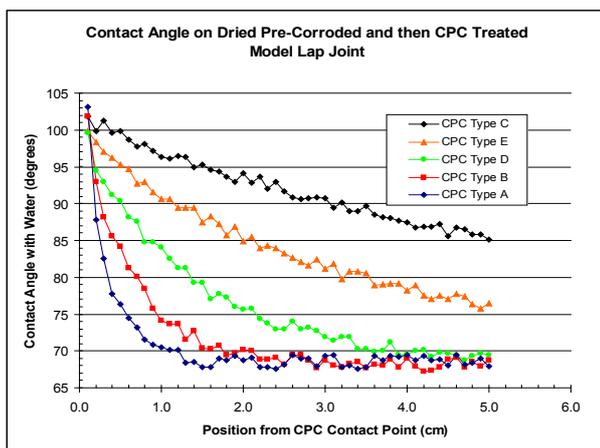
The contact angle as a function of position data from our model lap joint work do show a definite corollary trend with the previously reported free energy for water displacement data.

CPC's A and B, for which the free energies for water displacement are unfavorable (3.07 mJ/m^2 for A and 1.16 mJ/m^2 for B, respectively) show no more than, at most, 1.2 cm and 1.8 cm of lap joint CPC penetration respectively. It is important to note these are distances for any CPC penetration, and that the contact angle data strongly suggest that the level of CPC treatment drops off dramatically as a function of penetration distance. For CPC D, which has only a slightly favorable free energy for water displacement (-0.16 mJ/m^2) the contact angle data suggest some CPC penetration as far as 3.8 cm into the joint. And, for CPC C (-2.00 mJ/m^2) and to a lesser extent CPC E (-0.55 mJ/m^2) the CPC penetration extends, at some level, even beyond the 5.0 cm dipping distance over which we ran the contact angle experiments.

Conclusions

For this customer, the data clearly suggest that CPC C is the best choice for a corrosion prevention compound for their application.

However, the work also serves to clearly highlight the issues with the use of corrosion prevention compounds on partially corroded and potentially moist aluminum surfaces versus fresh aluminum surfaces. CPC's with higher surface polarities and lower interfacial tensions with water are identified as being more favorable candidates for use on partially corroded surfaces, particularly when they may be responsible for also displacing moisture from those surfaces. It remains uncertain however, what lower limit for water/CPC interfacial tension might be favorable if improvements in CPC's were to focus on lowering CPC/water interfacial tension. This may well depend on the mechanism used to lower that interfacial tension, and whether or not it affects the propensity of the CPC to be removed by moisture after deposition – which would need to be explored with an entirely different set of experiments.

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