Reprinted From: PRODUCTS FINISHING Magazine

Sailors assigned to the Saberhawks of Helicopter Maritime Strike Squadron 77 perform maintenance on the propellers of an MH-60R Sea Hawk helicopter. *(U.S. Navy photo by Mass Communication Specialist 3rd Class Travis K.*

Hex Chromium-Free Sealants for Defense and Aerospace

Results of second phase of research conducted by top defense contractors.

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Polysulfide sealants containing soluble hexavalent chromium compounds are used in aerospace and defense manufacturing to fill gaps and recesses in an attempt to prevent corrosion of the base metal.

However, regulatory mandates have accelerated a global effort to replace hex chrome-containing materials because of their toxicity. In 2011, the Defense Federal Acquisition Regulation Supplement mandated that no U.S. Department of Defense contracts can include a specification that results in a deliverable containing more than 0.1 percent hex chrome in any homogeneous material where acceptable substitutes are available.

It also prohibits the use or removal of hex chrome-containing materials during subsequent phases of the deliverable, unless an exception or approval applies. Sealant applications that contain hex chrome are not an exception.

Collaborative Project

To address the challenges of adopting hex chrome-free alternatives, TURI, the Toxics Use Reduction Institute at the University of Massachusetts Lowell, reached out to companies in the aerospace and defense industry that were interested in participating in a collaborative project.

In 2012, a Hexavalent Chromium-Free Sealant Evaluation Team was established with representatives from TURI, Lockheed Martin, Raytheon, Northrop Grumman, Bombardier, NASA, Naval Air Systems Command, Air Force Research Laboratory and Army Aviation and Missile Command (AMCOM). This article presents the results of the second phase of research conducted by the evaluation team.

Sealants industry spec test procedures don't currently provide sufficient and differentiable criteria for evaluating chromate and non-chromated materials in field applications where corrosion is expected to occur as a result of the environment. Therefore, for Phase II, the evaluation team developed a single test vehicle configuration to evaluate the following sealant applications: wet installation of fasteners, sealing over the head of a fastener, sealing of faying surfaces and butt joint sealing.

The testing was modeled after MIL-PRF-81733, but was modified to better distinguish between sealants (given the limited time frame available to conduct the test) by inducing failures (through preconditioning and scribing). Industry certified sealants were selected for Phase II, and only their corrosion-inhibiting capabilities were evaluated.

Thirty test vehicles were assembled to provide an experiment that included five replicates for each of the six types of sealants included in the evaluation, with each test vehicle receiving only one type of sealant. The six sealants selected for this evaluation are shown in Table 1.

The PS-870 sealant contains a hex chrome corrosion inhibitor and served as the control for the evaluation. Four sealants with non-hex chrome corrosion inhibitors were chosen: AC-735, PR-1775, PR-2870, and CS 5500N CI; and the PR-1440 sealant, which doesn't contain any corrosion inhibitor, served as the negative control.

Figure 1: Assembled test vehicle, top, bottom and side views.

Test Vehicles

The test vehicles used consisted of three aluminum plates with a series of eight matching holes through which eight threaded fasteners were inserted and held in place by eight nuts. The $^{1}/_{4}$-inch fasteners used had flat, countersunk heads and were made of stainless steel alloy UNS S66286 (A286). The aluminum plates used were made of UNS A97075 (7075) alloy, with dimensions of 0.25 inches thick, 2 inches wide, and 4.5 inches long.

This Phase II testing began in July 2013. The aluminum plates, procured by TURI, were sent to NASA for hole machining, then delivered to the Northrop Grumman facility in Linthicum, Maryland, where Iridite 14-2 conversion coating was applied to 30 test vehicles in accordance with their standard operating procedures in compliance with MIL-DTL-5541. The vehicles were then sent to Raytheon Missile Systems in Tucson, Arizona, for assembly. The completely assembled, painted and scribed test vehicle is shown in Figure 1.

To stress the sealant joints, the test vehicles were mechanically and thermally preconditioned at the NAVAIR facility in Patuxent River, Maryland. The preconditioning was conducted according to MIL-PRF-81733D Section 4.8.9.3.1 Cyclic Loading for Class 1 materials.

After preconditioning, 24 vehicles (four test vehicles for each of the six sealant types) were sent to Lockheed Martin Aeronautics at their Fort Worth, Texas, facility for accelerated corrosion testing where they were exposed to sulfur dioxide (SO_2) salt fog for 1,000 hours per ASTM G85 Annex 4. This test consisted of spraying neutral pH salt fog with the introduction of SO_2 gas directly into the chamber for one hour of a six-hour cycle. The pH of the salt fog was kept in the range of 2.5-3.2. The remaining six test vehicles were sent to the NASA Beachside Atmospheric Test Facility located at Kennedy Space Center for beachfront testing.

Results

It's important to note that each of the sealant products in this study have been individually qualified to their respective specifications. The test results and conclusions of this study are based solely on the specific, yet limited testing effort of corrosion resistance to environmental conditions in simulated field applications where damage is expected. The results are not

Table 1: Six Sealants Included in the Evaluation

Vendor	Vendor PN	Specification	Purpose	Chemical Class	Corrosion Inhibitor
PPG Aerospace	PS-870	MIL-PRF-81733 Type II Class 1 Grade A	Baseline/ Control	Polysulfide	Hexavalent Chromium
3M	AC-735	MIL-PRF-81733 Type II Class 1 Grade B and AMS 3265 Class B	Alternative Sealant	Polysulfide	Zinc Phosphate
PPG Aerospace	PR-1775	AMS 3265 Class B	Alternative Sealant	Polysulfide	Multiple Materials
PPG Aerospace	PR-2870 (RW-6040-71)	MIL-PRF-81733 Type II Class 2 Grade B	Alternative Sealant	Polythioether	Proprietary
Flame Master	CS 5500N CI	Not yet qualified	Alternative Sealant	Polysulfide	Molybdates
PPG Aerospace	PR-1440	AMS-S-8802 Type 2 Class B	Negative Control	Polysulfide	None

intended to be an endorsement or disapproval of the various sealant. For the purposes of this research, we considered the results to be statistically significant if the Confidence Level was at least 90 percent, with a corresponding alpha risk of 10 percent. If the results for any area of inspection did not meet this requirement, they were not included in this article.

After the accelerated salt fog test was completed, the 24 test vehicles were disassembled, then inspected for corrosion in the three major areas that were protected by sealant: faying surface and butt joint areas; fastener hole areas, including both the countersink and hole barrel areas (See Figure 2); and the exterior surface—ring areas around the fastener holes that were covered with sealant. For the top plate this ring area was approximately 0.1 inches wide, and for the bottom plate this was approximately 0.25 inches wide.

Because of the large amount of surface area that each sealant had to protect, the butt joint and faying surface category was regarded as the primary performance indicator of the overall sealant corrosion inhibition.

Corrosion Ratings

Ratings for the amount of corrosion in each area of interest were recorded as a percentage of corrosion observed for each area examined. Corrosion was only recorded if there was deterioration of the metal (pitting). A rating of 0 percent would reflect that no corrosion was present and a rating of 100 percent would indicate complete corrosion of that area. For each type of sealant, the four test vehicles were averaged together to provide a single corrosion rating.

According to Table 2 information, for the combined faying surface and butt joint areas, the percent corrosion values per sealant type varied from 1.6 percent to 5.7 percent. The percent corrosion for PR-1440 (5.7 percent), the negative control, was higher than AC-735 (1.6 percent), and was found to be statistically significant. Even though PR-1440 had a higher percentage of corrosion as compared with the other sealants, there was no statistical difference found for the percent corrosion levels between it and the CS 5500N CI, PR-1775, PS- 870 and PR-2870 sealants. Also, despite AC-735 having a lower percentage of corrosion compared with the other sealants, there was no statistical difference found for the percent corrosion levels between it and the CS 5500N CI, PR-1775, PS- 870 and PR-2870 sealants.

For the fastener holes with sealant overcoat and no scribes, the percent corrosion values per sealant type varied from 0.1 percent to 4.3 percent, as shown in Table 3. The percent corrosion for CS 5500N CI was higher than the corrosion levels for the PS-870, AC-735, PR-1775, PR-1440 and PR-2870 sealants, and was found to be statistically significant. There was no statistical difference found for the percent corrosion values between the AC-735, PR-1440, PR-1775, PS-870, and PR-2870 sealants. For the fastener areas with 1) sealant overcoat and scribes, and 2) no sealant overcoat and no scribe, there was no statistical significance found between sealant performance.

The fastener hole areas for all 24 test vehicles with sealant overcoat and no scribes (1 percent) had lower corrosion levels than fastener holes with either: 1) sealant overcoat and scribes (10.8 percent) or 2) no sealant overcoat (7.7 percent). This difference was found to be statistically significant.

For the ring around all fastener hole areas, the percent corrosion values per sealant type varied from 1.9 to 14.4 percent as shown in Table 4. The percent corrosion for PR-1440 and CS 5500N CI was higher than the PS-870, AC-735, PR-1775, and PR-2870 sealants, and was found to be statistically significant. There was no statistical difference found for the percent corrosion between the AC-735, PR-1775, PS-870, and PR-2870 sealants. Similar results were

Table 2: Corrosion Inspection Results by Sealant Product for Faying Surface and Butt Joint

Surface Area	PS-870	AC-735	PR-1775	PR-2870	CS 5500N CI	PR-1440	All Six Sealants	Four Cr-Free Sealants with CI
Combined Faying Surface & Butt Joint Areas	3.0%	1.6%	2.7%	3.1%	3.3%	5.7%	3.2%	2.7%

Table 3: Corrosion Inspection Results by Sealant Product for Fastener Hole Area

Surface Area	PS-870	AC-735	PR-1775	PR-2870	CS 5500N CI	PR-1440	All Six Sealants	Four Cr-Free Sealants with CI
Fastener Hole Area (Holes with Sealant Overcoat and No Scribes)	0.2%	0.1%	0.1%	0.1%	4.3%	1.1%	1.0%	1.2%
Fastener Hole Area (Holes with Sealant Overcoat and Scribes)	10.2%	12.8%	9.8%	15.9%	8.5%	7.8%	10.8%	11.8%
Fastener Hole Area (Holes with No Sealant Overcoat and No Scribes)	2.3%	8.9%	3.5%	8.5%	7.7%	15.1%	7.7%	7.2%

Table 4: Corrosion Inspection Results by Sealant Product for Ring Around Fastener Area

Surface Area	PS-870	AC-735	PR-1775	PR-2870	CS 5500N CI	PR-1440	All Six Sealants	Four Cr-Free Sealants with CI
Ring around fastener hole areas with sealant overcoat and no scribes	0.1%	0%	0%	0.3%	2.6%	3.4%	1.1%	0.7%
Ring around fastener hole areas with sealant overcoat and scribes	2.4%	3.5%	5.4%	5.6%	5.4%	14%	6.0%	5.0%
Ring around fastener hole areas with no sealant overcoat and no scribes	9.6%	2.5%	5.4%	9.2%	39%	33%	16.3%	14.1%
Ring areas around all fastener holes	3.3%	1.9%	3.4%	4.5%	12.8%	14.4%	6.7%	5.7%

obtained when examining just the ring around fastener hole areas with no sealant overcoat and no scribes.

Statistical Significance

There was no statistical significance found for the ring area around fastener holes with sealant and no scribes. For ring areas around fastener holes with sealant and scribes, the PS-870 had less corrosion than the PR-1440, otherwise there was no statistical significance found.

The primer and top coat on the surface of the test vehicles assembled with CS 5500N CI and PR-1440 sealant blistered badly during the salt fog exposure for unknown reasons, affecting these results. Future testing is being designed to further examine this phenomenon.

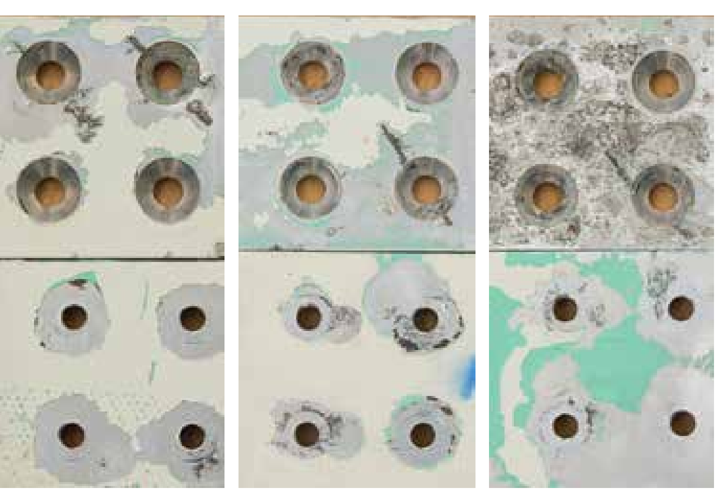

Figure 2: Examples of corrosion in countersunk hole for baseline, hex chrome-free sealant and negative control after sealant removal.

For the ring around fastener hole area of all 24 test vehicles, the fastener holes with a sealant overcoat with scribes (6 percent) and without scribes (1.1 percent) provided better corrosion protection than fastener holes with no sealant overcoat (16.3 percent). This difference was found to be statistically significant.

In conclusion, for all areas of interest, several alternative sealants containing non-hex chrome corrosion inhibitors (AC-735, PR-1775 and PR-2870) generally provided comparable corrosion prevention performance to the hex chrome control sealant, PS-870. The CS5500N CI non-hex chrome corrosion inhibiting sealant performed well in most of the areas of interest, and may have performed comparable with the other corrosion inhibiting chrome-free sealants, if not for the blistering on the surface areas of the test vehicles which could have caused a higher percentage of corrosion in those areas. The PR-1440 sealant with no corrosion inhibitor had a generally higher percentage of corrosion across all areas of interest and also blistered on the surface areas.

Please visit pfonline.com for a complete version of this research, as well as all reference notes.

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