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Evaluation for Alternatives to Hexavalent Chromium Sealants

Polysulfide sealants containing soluble hexavalent chromium compounds are currently being used in a variety of applications in aerospace/defense manufacturing. The applications mostly involve the filling of gaps and recesses to prevent water intrusion and collection in an attempt to prevent corrosion of the base metal. These sealants are most commonly used on aluminum assemblies and are often over coated with a variety of common coating systems with hexavalent chromium-based corrosion inhibitors. Hexavalent chromium compounds are of concern because they are carcinogens, mutagens, developmental toxicants, and have high acute toxicity. Workplace exposure to hexavalent chromium may cause health impacts, such as lung cancer and respiratory tract damage in workers who breathe airborne hexavalent chromium, and skin damage from dermal exposure (OSHA, 2009).

Regulatory and market drivers are motivating a global effort in the aerospace/defense industry to replace hexavalent chromium-containing materials with hexavalent chromium-free alternatives for various applications. For example, the Occupational Safety and Health Administration (OSHA) implemented new Hexavalent Chromium Standards for general industry in 2006 (29 CFR 1910.1026) where the average worker exposure to hexavalent chromium over the course of an 8-hour work shift was reduced to 5 ug/m3 (OSHA, 2009). The Defense Federal Acquisition Regulation Supplement (DFARS) was issued on May 5, 2011 (76 FR 22569), "Minimizing the Use of Materials Containing Hexavalent Chromium." It states that no Department of Defense contract (for programs prior to Milestone A) may include a specification or standard that results in a deliverable containing more than 0.1% hexavalent chromium in any homogeneous material *where acceptable substitutes are available*, or requires use or removal during subsequent phases of the deliverable, unless an exception or approval applies. There are several exceptions to the DFARS rule, such as conversion coatings and hard chrome plating (DFARS 2011). However, the DFARS rule applies to sealant and primer applications that contain hexavalent chromium.

Despite the known hazards and restrictions, hexavalent chromium materials continue to be used in the aerospace/defense industry, due to technical performance and economic challenges of transitioning to hexavalent chromium-free alternatives. The principal technical performance challenge is that the long-term, corrosion-inhibiting properties of the hexavalent chromium-free alternatives are not

VENDOR	VENDOR PN	SPECIFICATION	CHEMISTRY	CORROSION INHIBITOR
PPG Aerospace	PS-870	MIL-PRF-81733D Type II Class 1 Grade A	Polysulfide	Hexavalent chromium
3M	AC-735	MIL-PRF-81733D Type II Class 1 Grade B and AMS 3265 Class B	Polysulfide	Zinc phosphate
PPG Aerospace	PR-1775	AMS 3265 Class B	Polysulfide	Ammonium phosphite
PPG Aerospace	PR-2001	AMS 3277 Type II, Class B	Polythioether	None

Table 1: Sealants Included in the Design of Experiments

VENDOR	MODEL	PRIMER/ TOPCOAT	SPECIFICATION	HEXAVALENT CHROMIUM CONTAINING
Akzo Nobel Aerospace Coatings	10P20-13 High solids epoxy primer + EC-213 HS epoxy primer cure solution	Primer	MIL SPEC PRF 23377, Type 1, Class C	Yes
Deft Inc.	44GN098 1GK base and catalyst	Primer	MIL SPEC PRF 85582, Type 1, Class N	No
PRC-Desoto of PPG Aerospace	CA8211, 8211F37886MPY22K	Topcoat	MIL SPEC PRF 85285, Type 1	No

Table 2: Primers and Topcoat Included in the Design of Experiments

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considered as effective as the hexavalent chromium-containing materials. The costs and resources required for investigating and evaluating the various hexavalent chromium free materials and manufacturing processes may be prohibitive for an individual company to undertake alone. To that end, the Toxics Use Reduction Institute (TURI) at the University of Massachusetts Lowell reached out to companies in the defense/aerospace industry to collaborate in addressing the challenges of adopting hexavalent chromium-free alternatives. There was considerable interest in collaboration, and consequently a Hexavalent Chromium-Free Sealant Evaluation Team was established with representatives from TURI, Lockheed Martin, Raytheon, Northrop Grumman, NASA, NAVAIR, AFRL, and AMCOM G4.
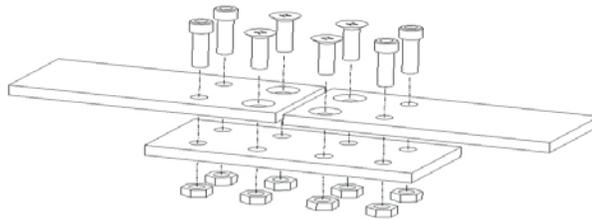
Figure 1: Test vehicle design.

For the past year, the Evaluation Team has collaborated to jointly conduct research, testing, and analysis for using hexavalent chromium-free sealants, with various hexavalent chromium-containing and hexavalent chromium-free conversion coatings and primer materials for aluminum assemblies. The objectives of this collaborative effort were as follows:

- Evaluation of existing alternatives to metal finishing applications in the aerospace/defense industry that use hexavalent chromium sealants.
- Selection of appropriate testing and evaluation criteria to evaluate the corrosion resistance of sealant materials in various applications.
- Generation of screening level data to either: 1) justify the use of DFARS-compliant alternatives; 2) support a request for a DFARs exemption on an application by application basis; or 3) provide information to make decisions regarding further testing requirements for DFARS compliance.

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- Development of a working relationship with research participants as a basis for continued collaborative research for addressing the use of hazardous substances.

Test Vehicle Design. Currently established industry specification test procedures for sealants do not provide sufficient and differentiable criteria for evaluating chromate and non-chromated materials in field applications where damage is expected to occur. Therefore, the team developed the necessary test vehicle configuration to evaluate the following five sealant applications simultaneously with induced damage in a corrosive environment: 1) wet installation of fasteners; 2) sealing over the head of a fastener; 3) butt joint sealing; 4) sealing of faying surfaces; and 5) the application of sealant to exposed material surface.

The test vehicle used for this evaluation consisted of three aluminum plates with a series of eight matching holes through which eight threaded fasteners were inserted and then held in place by eight nuts. The ¼-inch fasteners used were made of stainless steel alloy UNS S66286 (A286). This alloy created a galvanic mismatch with the aluminum plates, and is commonly used by the participating companies because of its relatively high ductility at below-zero temperatures, high strength, and non-magnetic properties. Four of the fasteners included in the test vehicle have flat heads (countersunk into the aluminum plate), and four of the fasteners have socket heads.

The test vehicles were 0.25-inch-thick aluminum plates using alloys UNS A96061 (6061) and UNS A97075 (7075). These alloys were selected because they were common alloys used by the members of the Evaluation Team. The aluminum plates are 2 inches wide and 4.5 inches long. The test vehicle design is shown in Figure 1.

Figure 2. Assembled test vehicle #46 – bottom and top views.

Design of Experiments. A total of 48 test vehicles were assembled to provide a design of experiment that included the following materials: two types of aluminum alloys, four types of sealants, two types of primers, two types of conversion coatings, and one type of topcoat. The hexavalent chromium-containing materials were selected because they were commonly used by members of the Evaluation Team and intended as a baseline for comparison. The hexavalent chromium-free materials were selected because they had relatively similar performance characteristics to the hexavalent chromium-containing materials. The design of experiments included the four types of sealants shown in Table 1.

The design of experiments included two types of primers and one type of topcoat as shown in Table 2.

The design of experiments included the following two conversion coatings to improve the adhesive bonding and anti-corrosion properties of the aluminum test panels:

- Iridite 14-2 as a baseline control conversion coating containing hexavalent chromium.
- Metalast TCP-HF HPA 100 hexavalent chromium-free conversion coatings containing trivalent chromium.

Research Approach. During September 2012, the Metalast conversion coating was applied to 20 test vehi-

cles at the Metalast facility in Minden, Nev., and the Iridite conversion coating was applied to 28 test vehicles at the Northrop Grumman facility in Linthicum, Md.

Each test vehicle had only one type of sealant applied. During October 2012, the test vehicles were assembled over a three-week period at the Raytheon facility in Tucson, Ariz., using the following method:

1. <u>Butt Joint Scribe:</u> Scribes were generated by an "Erichsen Scratch Stylus Acc to Sikkens Model 463" with a 1mm-wide carbon tip. Scribed an "X" on the top side of the bottom plate.
2. <u>Faying Surface:</u> Applied a smooth even coat of sealant (0.005 inches) to both sides of the mating panels using an orange stick or glass rod. Five-mil bond wires were used to control the thickness.
3. <u>Threaded Fasteners:</u> Fasteners were used as received from the supplier and not cleaned. Evenly coated all eight fasteners with sealant using orange stick or gloved finger. Inserted fasteners into the freshly mated panels. Installed nuts and torqued to 40 in-lbs.
4. <u>Butt Joint:</u> Applied sealing compound to the butt joint to completely fill the gap using an orange stick or glass rod.
5. <u>Clean:</u> Wiped excess sealant from the entire test vehicle prior to proceeding.

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6. <u>Fastener Heads:</u> Used an orange stick or glass rod to apply sealant to completely cover over and around two of each type of fastener head, as well as the corresponding nuts on each test vehicle.
7. <u>Flat Plate Surface:</u> Applied a strip of sealant on the back side approximately 0.005 inches x 0.25 inches. Two strips of tape (approximately 0.005 inches thick) were attached and the sealant was applied in between and then smoothed with a squeegee. The tape was then removed.
8. <u>Curing:</u> Cured the assembly for 48 hours at ambient laboratory temperature with the relative humidity between 35 and 48%.
9. <u>Prime and Paint:</u> Applied primers and topcoat to the test vehicles according to manufacturer instructions.
10. <u>Additional Scribes:</u> Scribed through the primer/topcoat at edge of test vehicle in four locations. Scribed through the primer/topcoat and the sealant along the length of the strip of sealant on the back side of the plate. In addition, scribes were applied to four fastener heads (two flush heads and two protruding heads) and two nuts on each test vehicle.

The completely assembled, painted, and scribed test vehicle is shown in Figure 2.

To stress the sealant joints, the test vehicles were then mechanically and thermally preconditioned at the NAV-AIR facility in Patuxent River, Md. The preconditioning was executed according to MIL-PRF-81733D Section 4.8.9.3.1 Cyclic Loading for Class 1 materials. The purpose of this testing was to simulate a very severe operating environment of especially harsh aerospace/defense applications. The preconditioning consisted of cyclic loading between 0 and 5,000 pounds for 250 cycles. The test vehicles were subjected to 250 cycles at a temperature of -65°F after a 30-minute soak at the same temperature with no load.

Accelerated corrosion testing was conducted on 44 test vehicles by Lockheed Martin Aeronautics at their Fort Worth, Texas, facility. The test vehicles were exposed to sulfur dioxide (SO_2) salt fog for 1008 hours (6 weeks) per ASTM G85 Annex 4. This test consisted of spraying salt fog with introduction of SO_2 gas directly into the chamber periodically. Two types of inspections — non-destructive and destructive — were performed on the test vehicles during the accelerated corrosion testing.

Long-term corrosion testing is being conducted for four test vehicles at the NASA Beachside Atmospheric Test Facility located at Kennedy Space Center, Fla. The beachfront laboratory is used to conduct real-time corrosion experiments. It provides remote monitoring of surrounding weather conditions, including wind speed and direction, and rainfall. The beachfront testing is occurring over a 12-month duration between November 2012 and November 2013. The results of this testing will be presented elsewhere.

Non-destructive Inspection Results.
Non-destructive inspections were used to examine the type and degree of corrosion on the test vehicles and were performed on all of the test vehicles at the following intervals of exposure to the salt fog: 336 hours (two weeks), 672 hours (four weeks), and 1008 hours (6 weeks). Non-destructive inspection of the test vehicles provided valuable information regarding the outside appearance of the test vehicles. However, the destructive inspection provided better insight for the corrosion inhibiting properties of the sealants.

Destructive Visual Inspection Results.
The test vehicles were dismantled to conduct the destructive inspection so that the amount of corrosion could be recorded. Destructive inspections occurred for four test vehicles after two weeks, for another four test vehicles after four weeks, and for the remaining 36 test vehicles at the end of the six weeks of testing. The test vehicles were dismantled by removing the fasteners, separating the plates of the test vehicles, as well as using toluene to strip the sealant and corrosion by-products to reveal the inner surfaces that were protected by sealant.
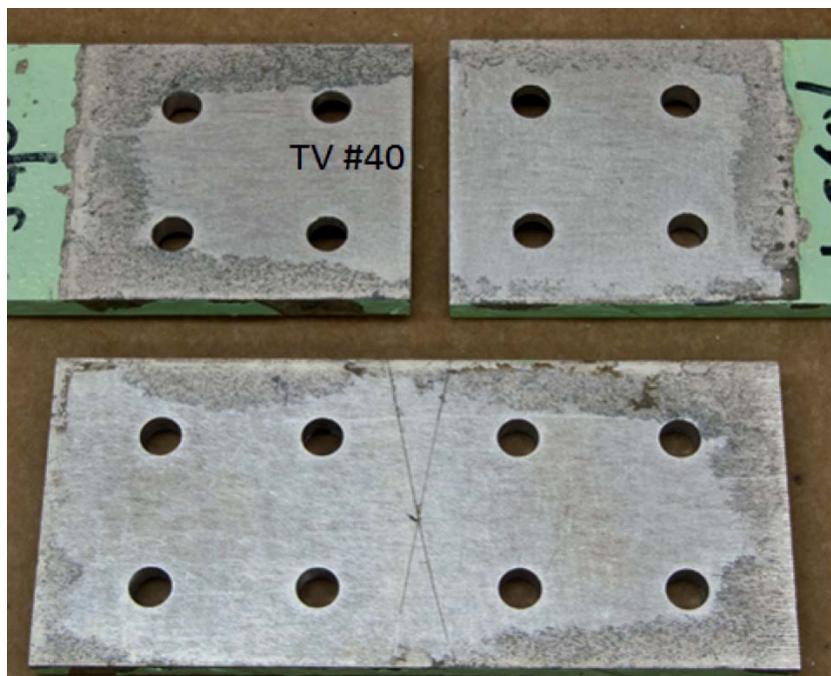

Figure 3: Corrosion on the faying surface of test vehicle #40.

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Figure 3 shows the corrosion on the faying surface of Test Vehicle #40 after 336 hours of salt fog exposure.

The test vehicles were divided into three categories: 1) 6061 aluminum alloy with hex-chrome free (HCF) primer; 2) 7075 aluminum alloy with HCF primer; and 3) 7075 aluminum alloy with hex-chrome (HC) primer. Within the three categories of test vehicles, there were two areas of interest: 1) butt joint and faying surface related areas and 2) fastener countersunk related areas, which created a total of six groups to analyze each sealant/conversion coating combination. Because of the large amount of surface area that each sealant had to protect for the butt joints and faying surfaces category, it was regarded as the primary performance indicator of sealant corrosion inhibition.

Table 3 presents the destructive inspection results for test vehicles that completed 1008 hours (six weeks) of SO_2 salt fog exposure. Ratings for the amount of corrosion in each area of interest were recorded as a percentage of corrosion for each area examined. Corrosion was only recorded if there was deterioration of the metal (pitting). A rating of 0% would reflect that no corrosion was present, and a rating of 100 % would indiate complete corrosion of that area of interest. For each sealant/conversion coating combination, there were two test vehicles that were averaged together to provide a single corrosion rating.

CONCLUSIONS

This study was not performed to any military or industry standard specification. The Evaluation Team developed this screening level test approach specifically for differentiating between hexavalent chromium-containing and hexavalent chromium-free sealants in field applications subject to a corrosive environment where damage can be expected. The testing was modeled after MIL-STD-81733, but was modified to better evaluate the performance differences between hexavalent chromium-containing and hexavalent chromium-free sealants, by inducing failures in the limited timeframe available to conduct the test. The testing included a large number of variables, a limited number of test vehicles, and no replicates. Consequently, there is not enough data to derive statistically significant results for the many variables. The results and conclusions of this study are based on the conditions of this limited testing effort and are not intended to be an endorsement or disapproval of the various products included in the test.

The following paragraphs summarize findings from this test effort:

Butt Joints and Faying Surfaces. When tested with an Iridite 14-2 hexavalent chromium-containing conversion coating, regardless of primer type or alloy type, the corrosion-inhibiting performance of the AC-735

BUTT JOINTS AND FAYING SURFACES (TVS 1-14)		
6061 with HCF Primer		
Sealant	Surf. Prep.	Average Corrosion
PS-870	Iridite	0.5%
PR-1775	Iridite	0.8%
PR-1775	Metalast	1.0%
AC-735	Iridite	1.0%
PR-2001	Iridite	2.7%
AC-735	Metalast	3.7%
PR-2001	Metalast	12%

BUTT JOINTS AND FAYING SURFACES (TVS 15-28)		
7075 with HCF Primer		
Sealant	Surf. Prep.	Average Corrosion
AC-735	Iridite	1.8%
PR-1775	Iridite	2.0%
PS-870	Iridite	2.2%
PR-2001	Iridite	4.2%
PR-1775	Metalast	29%
PR-2001	Metalast	63%
AC-735	Metalast	75%

BUTT JOINTS AND FAYING SURFACES (TVS 29-36)		
7075 with HC Primer		
Sealant	Surf. Prep.	Average Corrosion
AC-735	Iridite	1.5%
PR-1775	Iridite	2.0%
PS-870	Iridite	2.8%
PR-2001	Iridite	3.3%

COUNTERSINK AREAS (TVS 1-14)		
6061 with HCF Primer		
Sealant	Surf. Prep.	Average Corrosion
PR-2001	Metalast	0.8%
PR-2001	Iridite	1.0%
PR-1775	Metalast	1.1%
PR-1775	Iridite	1.4%
PS-870	Iridite	1.4%
AC-735	Iridite	2%
AC-735	Metalast	2%

COUNTERSINK AREAS (TVS 15-28)		
7075 with HCF Primer		
Sealant	Surf. Prep.	Average Corrosion
PR-1775	Iridite	31%
PR-1775	Metalast	48%
PS-870	Iridite	48%
PR-2001	Metalast	58%
PR-2001	Iridite	58%
AC-735	Iridite	68%
AC-735	Metalast	86%

COUNTERSINK AREAS (TVS 29-36)		
7075 with HC Primer		
Sealant	Surf. Prep.	Average Corrosion
PR-1775	Iridite	22%
PS-870	Iridite	48%
PR-2001	Iridite	62%
AC-735	Iridite	78%

Table 3. Destructive inspection results.

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and PR-1775 hexavalent chromium-free sealants was comparable to the PS-870 hexavalent chromium containing sealant.

Countersink Areas. When tested with an Iridite 14-2 hexavalent chromium-containing conversion coating, regardless of primer type or alloy type, the corrosion-inhibiting performance of the PR-1775 hexavalent chromium-free sealant was comparable or better to the PS-870 hexavalent chromium-containing sealant. For the countersink areas, there was high variability in the corrosion results. Although the fasteners were mated with nuts, the holes were not threaded. This situation, coupled with the severe preconditioning, may have led to variable water intrusion and subsequent corrosion.

Comparison of Aluminum Alloys. The 6061 aluminum alloy consistently exhibited better corrosion resistance compared to 7075 when similar conversion coatings and sealants were used. This difference in corrosion resistance was especially evident in the countersink areas of the test vehicles and was an expected result of the inherent corrosion resistance in the specific alloy.

Comparison of Conversion Coatings. The Iridite 14-2 conversion coating provided the best performing corrosion resistance result for the 6061 butt joint/faying surfaces, the 7075 butt joint/faying surfaces, and the 7075 countersink areas. Metalast TCP conversion coating provided the best performing corrosion resistance result for the 6061 countersink areas.

Comparison of Secondary Finishes. For similar sealant and conversion coating combinations on 6061 aluminum alloy test vehicles, no major difference was observed in corrosion resistance of sealant protected areas

for primer-only or primer and top-coated test vehicles. However, on 7075 aluminum alloy test vehicles, in general, a primer and topcoat provided more corrosion resistance for sealant protected areas than a primer-only finish.

No difference in corrosion resistance of sealant protected areas was observed for 7075 test vehicles with hex-chrome-free, primer-only or hex-chrome, primer-only secondary finishes.

Alloy 6061 with Hex-Chrome-Free Primer. For corrosion resistance in the butt joints and faying surfaces, PS-870 sealant with Iridite conversion coating, PR-1775 sealant with Iridite conversion coating, PR-1775 sealant with Metalast conversion coating, and AC-735 sealant with Iridite conversion coating provided the best performing results. For corrosion resistance in the countersink areas, PR-2001 sealant with Metalast conversion coating, PR-2001 sealant with Iridite conversion coating, and PR-1775 sealant with Metalast conversion coating provided the best results.

Alloy 7075 with Hex-Chrome-Free Primer. For corrosion resistance in the butt joints and faying surfaces, AC-735 sealant with Iridite conversion coating, PR-1775 sealant with Iridite conversion coating, and PS-870 sealant with Iridite conversion coating provided the best performing results.

For corrosion resistance in the countersink areas, PR-1775 sealant with Iridite conversion coating provided the best result.

Alloy 7075 with Hex-Chrome Primer. For corrosion resistance in the butt joints and faying surfaces, all sealant and conversion coating combinations performed relatively similar to each other.

For corrosion resistance in the countersink areas, PR-1775 sealant with Iridite conversion coating provided the best result. The results of the countersink area ratings for this group of test vehicles are similar to

the results of the 7075 test vehicles with hex-chrome-free primer. (Lockheed Martin, 2013.)

Next Steps. The Evaluation Team will complete the long-term corrosion testing and will then document the detailed results of the research — including the long-term corrosion testing results, in a future Toxics Use Reduction Institute technical paper.

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Diane Kleinschmidt, from the U.S. Navy, for test vehicle preconditioning and for technical input, and Kurt Kessel, from NASA, for beachfront testing of the test vehicles and for technical input.

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of Sn-Ni alloy deposited from diphosphate bath. Such electrochemical behavior is not typical to its cast analogue with the same chemical and phase composition, as shown in Figure 8(b).

To study the reasons of a discrepancy in corrosion behavior between the cast and electroplated alloys containing 69-70 at.% of Sn, some part of which is present in a tin phase, we examined the surface microstructure after anodic polarization of samples in sulfuric acid. From Figure 9(a) and Figure 9(b) it can be seen that the dissolving of tin breaks the surface layer of the cast alloy. On the reason of tin matrix destruction the crystals of intermetallic compounds are easily dropped out from the alloy. As a result, the deeper layers are opened and tin oxidation is continued that explains the anodic dissolution, as shown in Figure 8(b).

Tin-nickel alloy electroplated from diphosphate bath has a fine-grained and densely packed microstructure which does not change after anodic polarization, as it follows from Figure 9(c) and Figure 9(d). This fact confirms that high corrosion resistance of Sn-Ni alloy electroplated from diphosphate bath is due to its fine-grained and densely packed microstructure. To that end, the destruction of the alloy matrix during anodic polarization in the acid medium does not proceed. The obtained results show that electroplated Sn-Ni alloys containing 53-69 at.% of tin have dense and fine grained microstructure. This feature of their structure, together with the stability of intermetallic compounds, provides high corrosion resistance in sulfuric acid medium.

CONCLUSION

Electrochemical reduction of Sn-Ni alloys from chloride-fluorite and diphosphate baths has been studied. The effect of depolarization of both nickel and tin reduction for Sn-Ni alloys formation has been revealed.

It has been determined that Sn-Ni alloy electroplated from chloride-fluorite bath contains metastable phase of the intermetallic compound NiSn. This phase composition differs from that of its cast analogue. The Sn-Ni alloy electroplated from diphosphate bath contains stable phases of Sn, Ni_3Sn_2 and Ni_3Sn_4. This composition coincides fully with the composition of its cast analogue.

It has been shown that Sn-Ni alloy electroplated from chloride-fluorite bath and the Sn-Ni cast alloy of the same chemical composition do not dissolve during anodic polarization in sulfuric acid medium. It is due to high corrosion stability of NiSn, Ni_3Sn_2, Ni_3Sn_4 intermetallic compounds. Cast Sn-Ni alloy containing 53 at.% of tin dissolves easily due to anodic oxidation of tin phase, while Sn-Ni alloy electroplated from diphosphate bath does not dissolve in sulfuric acid medium, due to its dense, fine-grained microstructure.

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