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In-Situ Laser Conversion of Hexavalent Chromium into Non-Toxic Material

1. Background:

In 2012, General Lasertronics Corporation (Lasertronics) conducted an analysis of changes in the valence state of chromium under transient, high-temperature conditions generated during laser ablation. The purpose of the analysis was to evaluate the potential effectiveness of a laser-based coating removal process for *in-situ chemical conversion of hexavalent chromium to trivalent chromium* while operating on aircraft, vehicles, or related components during overhaul or inspection activities. Results of the analysis indicate that appropriate laser process parameters can efficiently produce this conversion in chromium valence state while removing chromate-containing coatings from substrate materials. The primary application contemplated in this analysis is the simultaneous removal of zinc chromate ($ZnCrO_4$) primer from airframe surfaces and components, and chemical conversion of toxic hexavalent chromium to benign trivalent chromium.

2. Process Description:

The laser ablation generates this beneficial conversion of hexavalent chromium to the non-toxic trivalent state by producing certain specific thermo-mechanical conditions on the surface of the chromate coating. These conditions require accurately pulsed laser operation with specific "irradiance" (power per unit area) values. Correct laser conditions produce an extremely rapid, high-temperature transient in the laser-illuminated spot on the target surface.

During this high-temperature transient, the coating material in the laser-illuminated spot reaches a temperature of approximately 3000°F in less than one-millionth of a second. The result is photoablation, or vaporization, of a small volume of coating, in this case zinc chromate primer, by the laser pulse. This photoablation event produces a vapor-phase mass flux of dissociated coating material that expands away from the laser-illuminated spot at sonic velocity.

The high transient temperatures also cause the reactant species in the chromate coating to react with the ambient oxygen present at the coating surface. The result is conversion of hexavalent chromium to the trivalent state, well within the duration of the individual laser pulses.

Lasertronics' closed-loop control and automated scan enable controlled and repeatable laser processing of airframe surfaces, with no risk of damage to the substrate.

3. Test Results:

Lasertronics recently completed a demonstration test of its FAA-endorsed airframe stripping process on a B727 aircraft that had been converted for cargo service. Pursuant to an FAA Airworthiness Directive (AD) directing airframe inspections, Lasertronics was invited to laser-

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strip paint and primer on selected areas of the airframe, including lap and butt joints in the fuselage pressure-boundary material. The primer in this aircraft's paint system was known to contain zinc chromate.

A certified industrial hygiene firm monitored air quality during the laser stripping operation. In addition to a "field blank" (control sample), air samples were taken from multiple locations near the technicians operating the laser, and from the exhaust duct of the waste effluent capture system. These air samples were then subjected to standard laboratory analysis, with particular attention to presence of hexavalent chromium. The instrumentation used to test for hexavalent chromium had a (lower) limit of detection (LOD) of 0.06 micrograms (μg). Each of the five air samples was collected during 187 minutes of laser airframe stripping. *Subsequent laboratory analysis of all five air samples and the control sample detected no hexavalent chromium at or above this LOD in any sample.*

The volume of these air samples averaged approximately 580 liters. When normalized to the 0.06 μg lower-bound instrument detection limit for hexavalent chromium, the minimum volumetric concentrations of hexavalent chromium required for detection in the air samples are 0.101 – 0.104 $\mu\text{g}/\text{m}^3$. The OSHA "Action Level" (2.5 $\mu\text{g}/\text{m}^3$) and "Permissible Exposure Limit" (5.0 $\mu\text{g}/\text{m}^3$) are approximately 24 and 49 times higher, respectively, than the lower-bound hexavalent chromium detection limits in these samples.

It is particularly noteworthy that the air sample collected at the waste effluent exhaust duct contained no detectable hexavalent chromium. The filtration system incorporates a HEPA filter rated at 99.95% extraction efficiency for particulates 0.1 microns (μm) or larger in size. The photoablation process generates vapor-phase aerosols with a distribution of effluent particle sizes that potentially would not be completely captured by the HEPA filter. Nonetheless, *no hexavalent chromium was detected in the air sample collected at the exhaust duct of the effluent waste filtration module.*

Although further tests are in order, these test data clearly indicate that the Lasertronics laser system can strip zinc chromate primer from airframe surfaces under real-world conditions with no measureable hexavalent chromium in either the proximate workplace or the vacuum exhaust mass flow from the process.

4. Conclusions:

- The Lasertronics coating removal process, operating within appropriate process parameters, converts hexavalent chromium to a trivalent state.
- Laboratory testing of multiple air samples collected during this three-hour test detected no hexavalent chromium.
- Likewise, no hexavalent chromium was detected in the exhaust duct of the laser effluent filtration unit.
- These results strongly suggest that the hexavalent chromium in the zinc chromate primer was chemically converted to trivalent chromium during laser photoablation.
- These preliminary results invite more thorough technical analysis by a qualified third-party research organization.
- Lasertronics' photoablation technology could impact waste management practices of hexavalent chromium across a broad spectrum of maintenance, refurbishment, and disposal programs.

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