



Trivalent Yellow Chromate New Discoveries & an Answer
to Plating Surface Finishing October 2007 article on the
Diphenylcarbazine Controversy

Presented by

Eric Olander - President

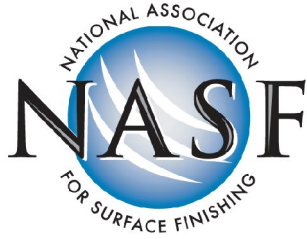
Electrochemical Products Inc.

June 17, 2008

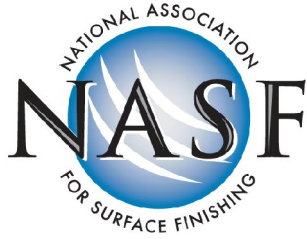
Indiana Convention Center

June 16-18, 2008

Indianapolis, IN

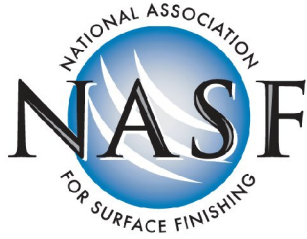


- Last Year discussed Yellow Trivalent Chromates
 - Corrosion Protection
 - UV Protection

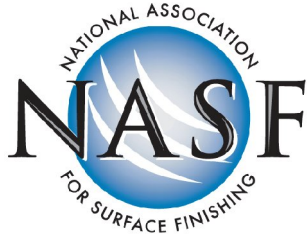


- Trivalent Yellow Update
 - New Color that has less green
 - Longer Corrosion Protection
 - QUV Results

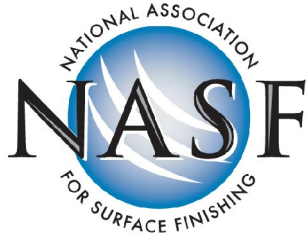
- Diphenylcarbazine Indicator – Potential solution to October 2007 Plating & Surface Finishing Challenge (Tom Rochester)



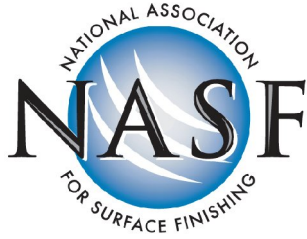
- Diphenylcarbazine Controversy
 - Tom Rochester discovered using the drop test found out that you can achieve a (+) test on trivalent chrome after ASTM B-117 salt spray corrosion starts.
 - Why is that happening?
 - NaCl forming Cl_2 (Chlorine) an oxidizer to make this happen
 - Zn corrosion mechanism



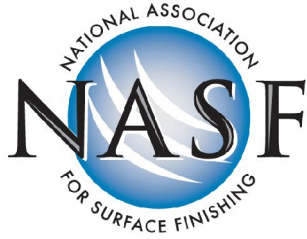
- **ISO 3613:2000 (E) Chromate Conversion coatings**
 - Test Method involves different test methods for zinc, cadmium, aluminum-zinc alloys and zinc-aluminum alloys



- **ISO 3613:2000 (E)**
Section 5.2
- One drop of diphenylcarbazine to the chromated zinc surface



- **ISO 3613:2000 (E)**
Section 5.5
- Test for the presence of hexavalent chromium in both colorless and colored coating. This method uses 1-5 drops of diphenylcarbazide.



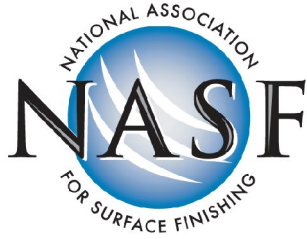
➤ **ISO 3613:2000 (E)**
Section 5.6

- Determination of hexavalent chromium content of colored chromate coating. This test method uses a spectrophotometer to measure the concentration of hexavalent chrome.

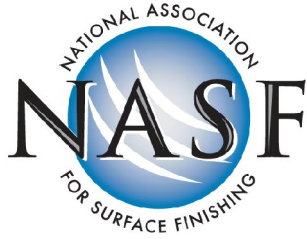


➤ **ISO 3613:2000 (E)**
Section 5.7

- This is the same as Section 5.6 test method, but an ICP is used to determine total chrome concentration.



- **Results using test method Section 5.5 & 5.6.**
 - Section 5.5 used 1-5 drops of (3.3 Test Solution C), 0.4 grams diphenylcarbazide, 20 ml. acetone and 20 ml. ethanol.



- After dissolution, add 20 mls. of 75% orthophosphoric acid solution and 20 mls. of DI water. Shelf life of material is 8 hours.



Failure Analysis' Materials Testing' Product Evaluation

MARK KULAS
ELECTROCHEMICAL PRODUCTS INC
17000 W. LINCOLN AVENUE
NEW BERLIN WI 531512781

3200 S. 166th Street
New Berlin, Wisconsin 53151-4141 USA
Telephone: (262) 782-6344
Toll Free: (800) 726-6385
Telefax: (262) 782-3653
E-Mail: stork.technimet@stork.com
Website: www.storktechnimet.com

Report No.	0710-21770	Your Ref	10605
Date	12/18/2007	Received	10/29/2007
Subject	Hexavalent Chromium Analysis of Exposure Samples		

Chemical Analysis Results

Sample 10	Conditions of Exposure	Hexavalent Chromium
Collection sample from chamber prior to exposure	N/A	Negative
Process D Blue	(1)	Negative
Process B Yellow	(1)	Negative
Process C Yellow	(1)	Negative
Process A Yellow	(1)	Negative
Process D Blue	(2)	Negative
Process B Yellow	(2)	Negative
Process C Yellow	(2)	Negative
Process A Yellow	(2)	Negative
Process D Blue	(3)	Negative
Process B Yellow	(3)	Negative
Process C Yellow	(3)	Negative
Process A Yellow	(3)	Negative
Collection sample from chamber after exposure	N/A	Negative
Process D Blue	(4)	Negative
Process B Yellow	(4)	Negative
Process C Yellow	(4)	Negative
Process A Yellow	(4)	Negative

Analysis completed using Ultraviolet-Visible Spectroscopy of extraction solution.
A negative result indicates <0.005 weight percent hexavalent chromium.

- (1) sample panels tested as received.
- (2) sample panels tested at first sign of white corrosion after exposure to salt spray per ASTM B117.
- (3) sample panels tested after considerable white corrosion as per EPI discretion after exposure to salt spray per ASTM B117.
- (4) sample panels tested after 523 hours exposure to the humidity chamber per ASTM 02247.

It is our policy to retain components and sample remnants for a minimum of 30 days from the report date, after which time they may be discarded. The data herein represents only the item(s) tested. This report shall not be reproduced, except in full, without prior permission of Stork Technimet, Inc.

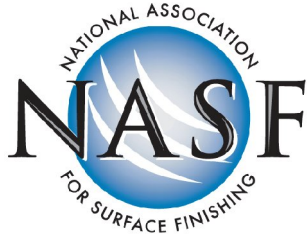
Electronic Original

Matthew K. Giesler

Signed: Matthew K. Giesler
Analytical Laboratory Manager

ISO/IEC 17025 nso 9002 Compliant!
Chemical 0098-01
Mechanical 0098-02

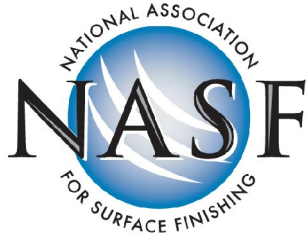
Stork Technimet, Inc. is an operating unit of Stork Materials Technology BV, Amsterdam, The Netherlands, which is a member of the Stork group.



➤ **Test Method**

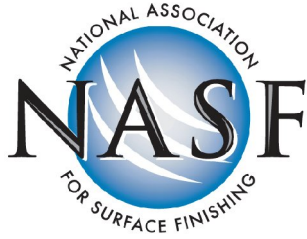
- Dedicated salt spray chamber (no other parts) for ASTM B-117
- Check salt spray solution prior to test < 0.1 ppm total chrome
- Check salt spray solution after < 0.1 ppm total chrome

Conclusion: No chrome dissolved into salt solution



➤ Humidity Test Results

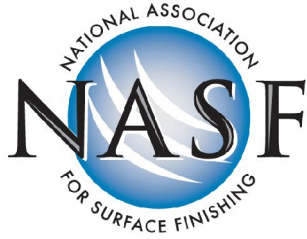
- Last year someone reported that a trivalent chrome zinc surface in humidity will convert to Cr^{+6}



➤ **Humidity Test ASTM-2247**

- Ran until we got the start of white corrosion
- Use ISO 3613:2000 (E) Section 5.6 spectrophotometer. Results negative.

Conclusion: Humidity test does not cause the trivalent to go to hexavalent.

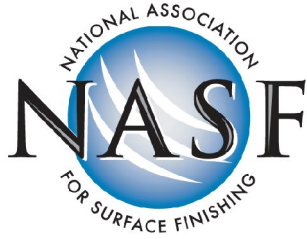


➤ **Salt Spraying Tips**

- 1). Do not put in hexavalent parts.
- 2). Dedicate a chamber for trivalent chromate parts.
- 3). Cooling water leaks.
- 4). Outside lab – find out what else is in the chamber.

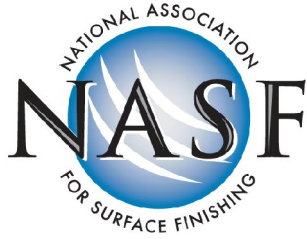


- **EPA Test Method 7196A for Hexavalent (Colorimetric)**
 - **Interfering Substances Section 3.0**
 - A). Hexavalent molybdenum
 - B). Mercury Salts
 - Up to 200 mg/liter of molybdenum and mercury

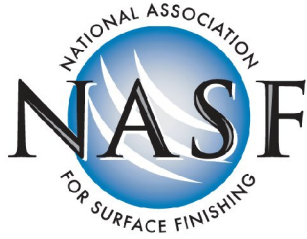


➤ **EPA Test Method 7196A**

- A). Vanadium interferes strongly, but concentrations up to 10 times that of chromium will not cause trouble.

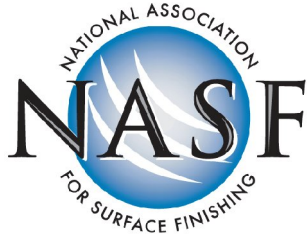


- **EPA Test Method 7196A**
 - Iron in concentrations greater than 1 mg/liter may produce a yellow color.

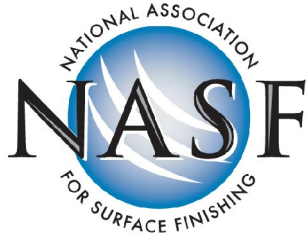


➤ Drop test questions

- 1). Diphenylcarbazide test for liquids not dry surfaces.
- 2). Resulting pH of the surface.
- 3). Zinc deposit contaminations of iron and others.
- 4). Other interferences that have not been discovered yet.

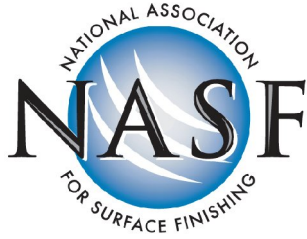


- **Spectrophotometer Method**
 - Excellent results that are repeatable.
 - Drop test result may lack accuracy.



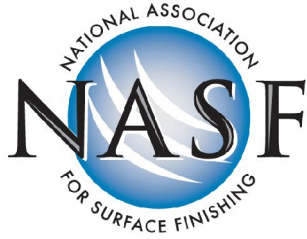
➤ **Trivalent Yellow Update**

- A new color that is yellow with a red hue.
- Found out about 50% of the users want a yellow-red hue.
- Chloride zinc with hexavalent yellow chrome has a yellow-red to green hue depending how the part is turned into the light.
- QUV/UV resistance of trivalent yellow processes.



➤ **Trivalent Yellow Update**

- Last year Process A & B were discussed in Cleveland
- New, Process “C” we will call it.
 - 1). Color again more to that yellow-green hue
 - 2). Corrosion protection improved upon from Process “A” & “B”



➤ **Trivalent Yellow Update**

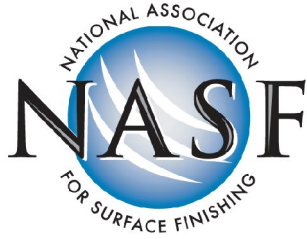
➤ **Corrosion Test Results**

- 300 hours to the first sign of white rust
 - 600 hours to 5% white rust
 - 800-900 hours to red rust
- * 0.3 mls. of acid chloride zinc used in testing.



➤ **Trivalent Yellow Update**

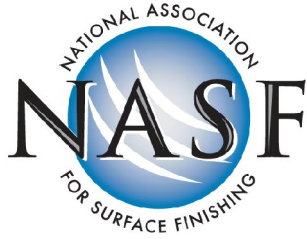
- Process "C" produces 5% white corrosion results that last 3 to 4 times longer than Process A & B.
- This corrosion result matches results with zinc alloy plating.
- Result is zinc plater can now achieve zinc alloy results without the expense and hassle of zinc alloy plating.



➤ **Trivalent Yellow Update**

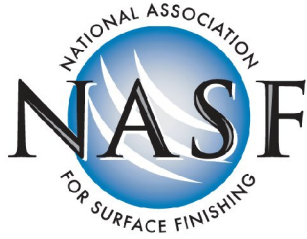
➤ **Process “C” Processing Procedure**

- 1). Zinc plating to 0.003” with acid chloride, alkaline non-cyanide and cyanide zinc
- 2). Cold water rinse
- 3). 0.5 – 1.0% sulfuric acid dip
- 4). Cold water rinse
- 5). Process “C” per parameters
- 6). Cold water rinse
- 7). Hot air dry - 150°F, spin dry or bake for hydrogen embrittlement

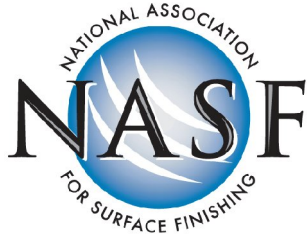


- **Trivalent Yellow Update**
 - **Solution Make-Up and Operating Parameters**

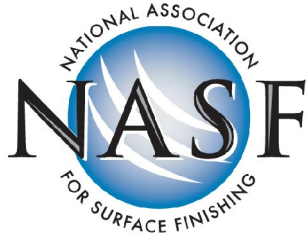
	<u>Range</u>	<u>Optimum</u>
Process "C" Part A	1 - 6%	3.0 %
Process "C" Part B	1 - 3%	2.0 %
Temperature	85 - 135°F	120°F (54°C)
pH	1.65 - 2.0	1.8
Time	30 – 120 seconds	90 seconds
Agitation	Air Agitation	



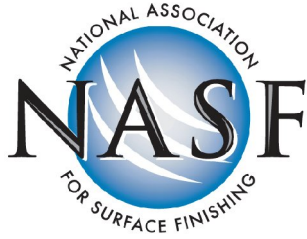
- **Trivalent Yellow Update**
 - **Operating Parameters**
 - Lower pH with 10% nitric solution
 - Raise pH with ammonium hydroxide
 - Initial bath make up needs to have pH raised to 1.8
 - Use a pH meter that is calibrated at 1.68



- **Trivalent Yellow Update**
 - **Scratch Resistance Test Method**
 - Yellow Trivalent, zinc plated Q-Panel edges taped
 - Using X-Acto knife, cut X across the zinc plate
 - Put panel in salt spray chamber
 - Looking for creeping corrosion where the X is cut into the surface

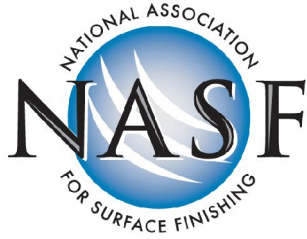


- **Trivalent Yellow Update**
 - **Scratch Resistance Corrosion Results**
 - Process A & B for 24-48 hours to first signs of white creeping corrosion
 - New Process C – achieve 200 hours
 - Why is this happening?



➤ **Trivalent Yellow Update**

- This is not a thick film trivalent chromate
- This is not self-healing like hexavalent chromate
- One theory is a synergistic affect of chemistries resulting in a new technology.
- One beta site using cyanide zinc barrel application 120+ hours



➤ **Trivalent Yellow Update**

- 1). Outstanding salt spray
300 hours to first sign of white rust
600 hours to 5% white rust
800 hours to red rust
- 2). Single dip process
- 3). Can be baked without losing corrosion resistance
- 4). Scratch resistance (white creeping corrosion)
- 5). New cheaper alternate process to zinc alloy plating