The 48th William Blum Lecture
Presented at NASF SUR/FIN 2010
in Grand Rapids, Michigan
June 14, 2010

Decorative Electroplating: Theory to Explain Rapid Corrosion Due to Calcium Chloride 'Russian Mud'

by
Dr. Donald Snyder
Recipient of the 2009 William Blum
NASF Scientific Achievement Award

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Editor's Note: The following summary article of the 48th William Blum Lecture, presented at SUR/FIN 2010 in Grand Rapids, Michigan on June 14, 2010, was taken from a summary article of the conference, published in *Plating & Surface Finishing*. The Powerpoint presentation used in Dr. Snyder's lecture follows this summary.

SUMMARY

A long-standing tradition dating to the selection of Dr. William Blum as the first recipient of the AESF Scientific Achievement Award in the 1950s, the 2009 NASF Scientific Achievement Award winner, Dr. Donald Snyder, of Atotech USA (Rock Hill, SC) was present to deliver the 2010 William Blum Lecture. His entire career has concentrated on decorative automotive finishes, focusing on trivalent chromium plating and corrosion studies. His talk covered a rather interesting problem in some serious corrosion failures in decorative chromium plated automotive hardware.

One would think that over 50-60 years, we would have seen everything when it came to corrosion performance of these parts. But no, there was one more, perhaps unseen until the Cold War had ended, when "the Russian mud problem" came to light. The increasing numbers of automobiles in Russia after the Cold War made a serious problem more visible and prevalent. Catastrophic failures of copper-nickel-chromium plated layers exhibited large-scale attack of the entire coating, resulting in direct attack of the substrate, with no classic corrosion-delaying side trips into the bright / semi-bright nickel underlayers. Dr. Snyder led us through the studies that had been undertaken, which found the culprit to be the heavy use of calcium chloride in wintertime on Russian roads, in contrast to the sodium chloride used in our road salt. Calcium chloride becomes a literal poultice when mixed with the mud surface that is common on many highways, and is a disastrous combination on decorative chromium coating systems. Even in long-established technology, there remains nothing new under the sun.

ATOTECH

Decorative Electroplating

Theory to explain rapid corrosion due to calcium chloride

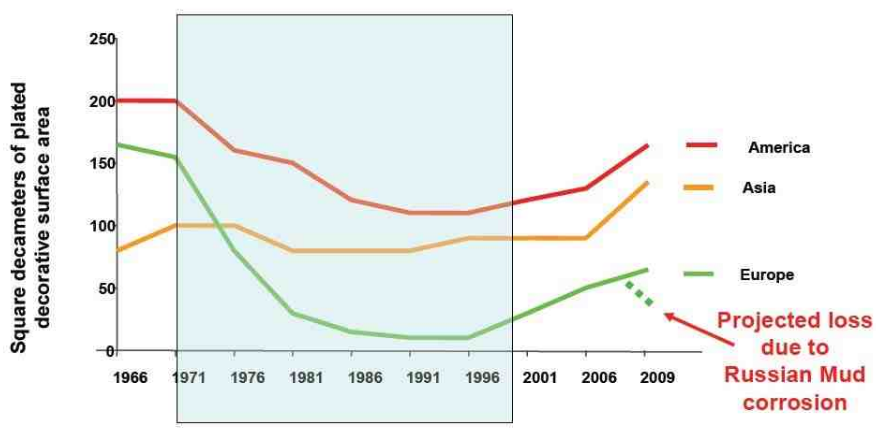
"Russian Mud"

1

TOTAL

Bright-Chromium Plated Surface per Passenger Car

Since the late 90s, there has been a world wide increase in the <u>average surface area</u> of decorative chromium plated parts used on passenger cars



Automotive / Truck industry is the largest single user of decorative parts

The decorative plating industry would not want anything to reduce this trend

Investigated Warranty Returns – Unconventional Corrosion

Moscow winter of 2006 – 2007

The form / appearance of the corrosion was more of a concern than the number of warranty returns for most automotive companies

The Winter of 2006 – 2007 Threatened to Alter The Increased use of Decorative Parts

Over the years, with the increased personal income in Russia, some auto companies have increased their marketing of luxury cars (lot of bright plated trim) in Russia – mainly in Moscow.

- The winter of 2006 – 2007 in Europe was exceptionally cold and a large amount of calcium chloride was used on Moscow streets (and others) to remove the snow and ice

- Unsightly corrosion of the chromium surface was observed on chromium plated parts that were less than one winter old

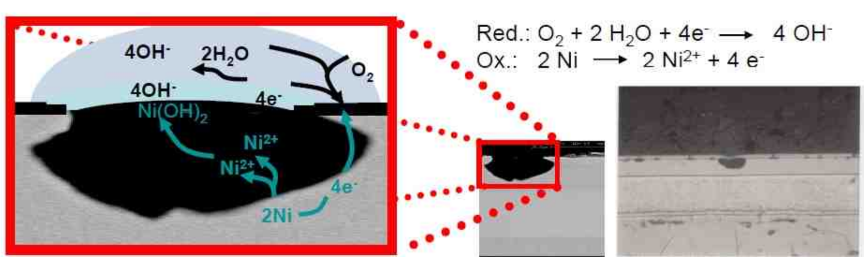
- Calcium chloride is used because …
  - more efficient than sodium chloride at lower temperatures
  - can be applied prior to the storm
  - used to reduce dusting on dirt / gravel roads (major concern in the USA)

Review of Conventional Corrosion of Copper / Nickel / Chromium Plated Parts

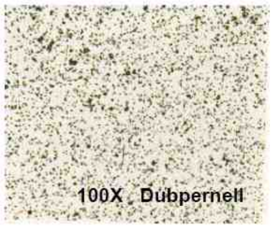
Requirements for Conventional Corrosion

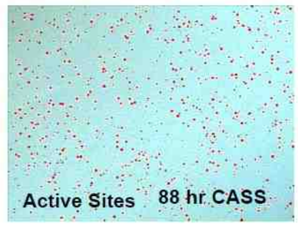
- Wet corrosion can be considered the reverse of plating – requiring …
  - Cathode
    - O_2 / $H_2O \longrightarrow$ OH on chromium deposit
  - Anode
    - Bright nickel deposit
  - Conductive electrolyte – transport electrons
    - Water with conducting ions such as chloride
  - Ability for ions to move
    - Migration of nickel ions through a liquid

Red.: $O_2 + 2\,H_2O + 4e^- \longrightarrow 4\,OH^-$
Ox.: $2\,Ni \longrightarrow 2\,Ni^{2+} + 4\,e^-$

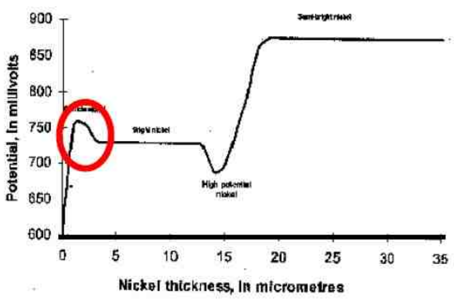


Corrosion of Micro-discontinuous Chromium
Micro-Porous Chromium

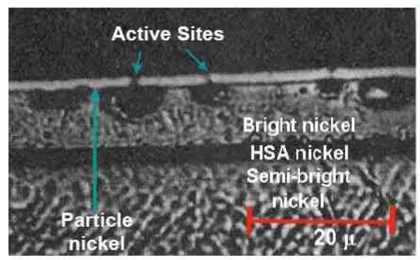




Appearance of Active Sites not objectionable – reflectivity maintained

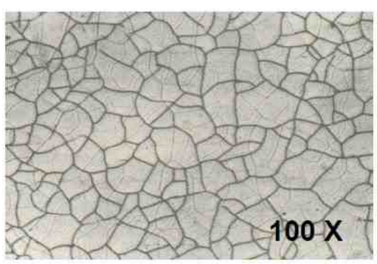


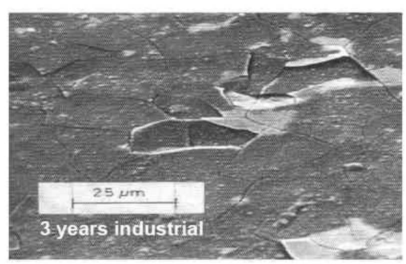
Classical corrosion of nickel/chromium

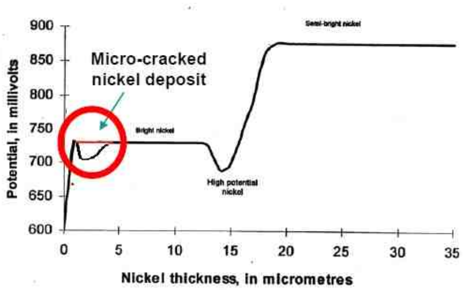


The substrate is protected while maintaining the reflectivity of the surface

Corrosion of Micro-discontinuous Chromium
Micro-Cracked Chromium







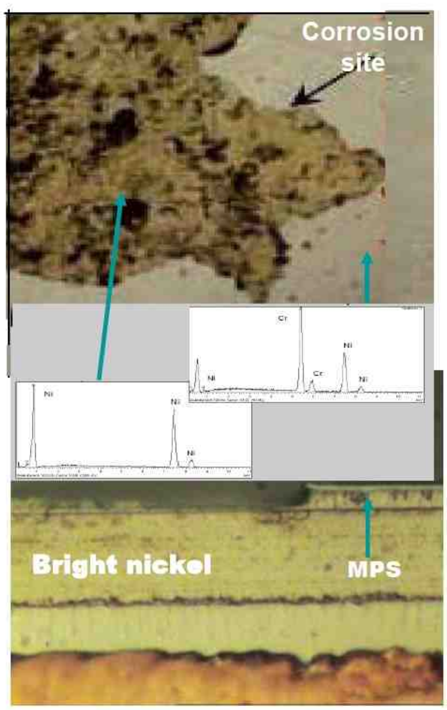
Undercutting of the chromium occurs due to "active" highly stressed micro-cracked nickel layer

Reflectivity is reduced

Moscow vehicle with corrosion in less than one year

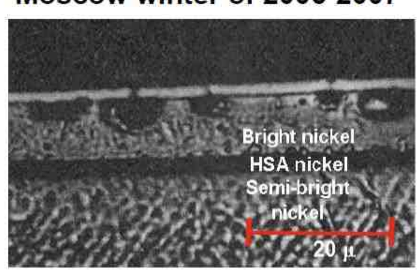
“Russian Mud”

Background



Warranty Return

Moscow winter of 2006-2007



Response from the automotive companies

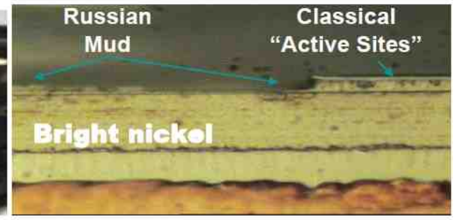
- Nissan evaluated many different deposits and test procedures
  - Developed an accelerated corrosion test to evaluate deposits
  - Determined that at least one trivalent chromium deposit performed much better than hexavalent chromium
  - Developed a post treatment for the deposit to increase its performance
- VW conducted a survey of automobiles in Russia and determined that micro-cracked chromium deposits performed better than micro-porous systems
  - Micro-porous chromium with 0.3 to 0.5 µ chromium
  - Micro-cracked chromium with > 0.8 µ chromium
    - It was thought that the thick chromium resisted the attack by calcium chloride
- Most of the other automotive companies are monitoring the situation
  - Many are testing trivalent chromium deposits

Calcium Chloride Accelerated Corrosion Test

Nissan's Russian Mud Test

Non-Classical Corrosion of Decorative Nickel / Chromium Deposits

Factors required to produce "Russian Mud" corrosion



Laboratory and field studies established that three factors must be present for rapid "non-classical" accelerated corrosion to occur

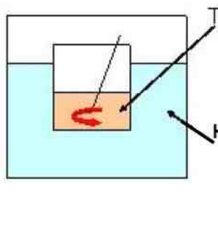
1. Minimum concentration of chloride
   - calcium, magnesium, sodium
2. Moisture
   - Water / humidity
3. Solid particles
   - "Mud"

A paper will be published giving the experimental details

Nissan's Russian Mud Test incorporates these factors

1.Condition

1-1.Make the solution

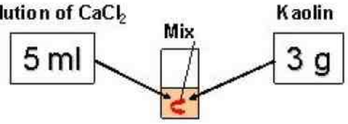


To make the saturated solution of $CaCl_2$

Material:
$CaCl_2$
water pure water (conduction ratio is 2.0 micro-S/cm)

Hot water bath at 40 C

1-2.Making of the Mud

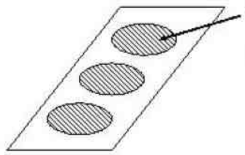


Note1) *Kaolin is white mud which is used in 'Corrodkoat Test] (NES M0139 or JIS H8502')

pH range for Mud is 6.5 to 7.5

Nissan Russian Mud-Test

2.Set the mud to sample



To define the mud thickness, the area (the circle diameter) & weight should be kept. Φ18mm is recommended.

circle diameter	mud weight
18mm	0.12-0.15 g
15mm	0.08-0.10 g
12mm	0.05-0.07 g
10mm	0.04-0.05 g
7mm	0.02 g

3.Test condition

Method A 168 hours at 23 +/- 2 C @ 23% RH … exterior parts

Method B 48 hours at 60 +/- 2 C @ 23% RH … temporary coatings

After test, remove the mud from sample

Some tests go to 336 hours of exposure at 60 C and 23 % RH

4. Evaluation after exposure
Degree of surface corrosion

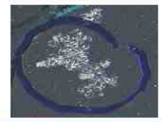
Developing the theory to explain "Russian Mud" corrosion

Influence of Chloride Concentration

Part of the data from a study that will be published in the near future

Influence of Chloride Concentration

Polarographic analysis of chromium over particle nickel

Salt conc.	Initial Open Circuit Potential [V]	Open Circuit Potential after 2 hr / 1 day [V]	Corrosion current after 2 hr / 1 day [nA/cm[2]]	
5.2 M $CaCl_2$ 10.4 M Cl^-	-0.47	-0.46 / -0.48	482 / 653	Significant visible corrosion
2.6 M $CaCl_2$ 5.2 M Cl^-	-0.28	-0.19 / -0.24	79 / 180	NO visible corrosion
5.4 M NaCl 5.4 M Cl^-	-0.31	-0.19 / -0.32	50 / 19	NO visible corrosion

Calcium Chloride has more influence than sodium chloride

23 % Relative Humidity – 24 & 60 °C – 90 minutes

$CaCl_2$

NaCl

Calcium chloride absorbs water even from a low humidity atmosphere while sodium chloride dries

$CaCl_2$ has two moles of chloride
NaCl has one mole of chloride

Developing the theory to explain "Russian Mud" corrosion

Influence of the Presence of Solids

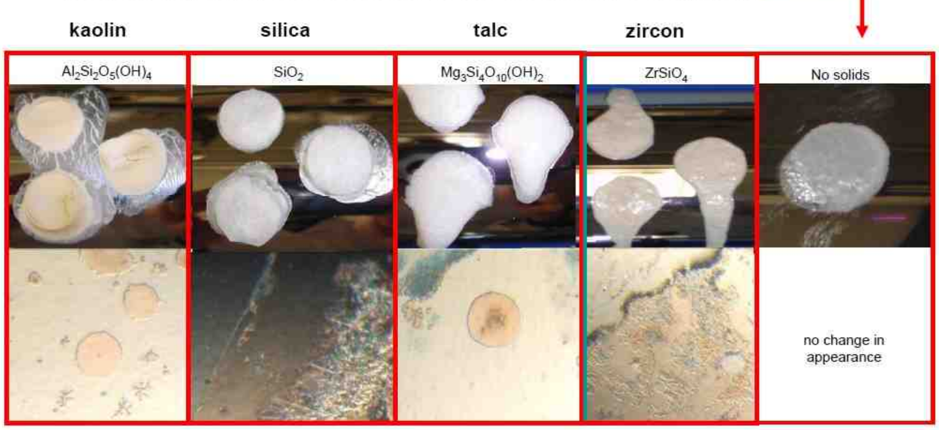
Corrosion after 48 h at 60°C and 23 % humidity

Sat. $CaCl_2$ [ml]	5	1	0	5	1	5	0
Sat. NaCl [ml]	0	0	1	0	0	0	2
DI-water [ml]	0	4.5	4.5	0	4.5	0	3.5
Kaolin [g]	0	5	5	5	3	3	5

Kaolin (solid), chloride and water are needed to produce a visible corrosion of the chromium surface

Similar corrosion was observed when many different solids were used with the Nissan Test

- Kaolin is being used to simulate the dirt from the roads.
- With other solids the corrosion of the chromium is distinctly different, but clearly visible.
- Without any solid, the corrosion of the chromium is negligible.



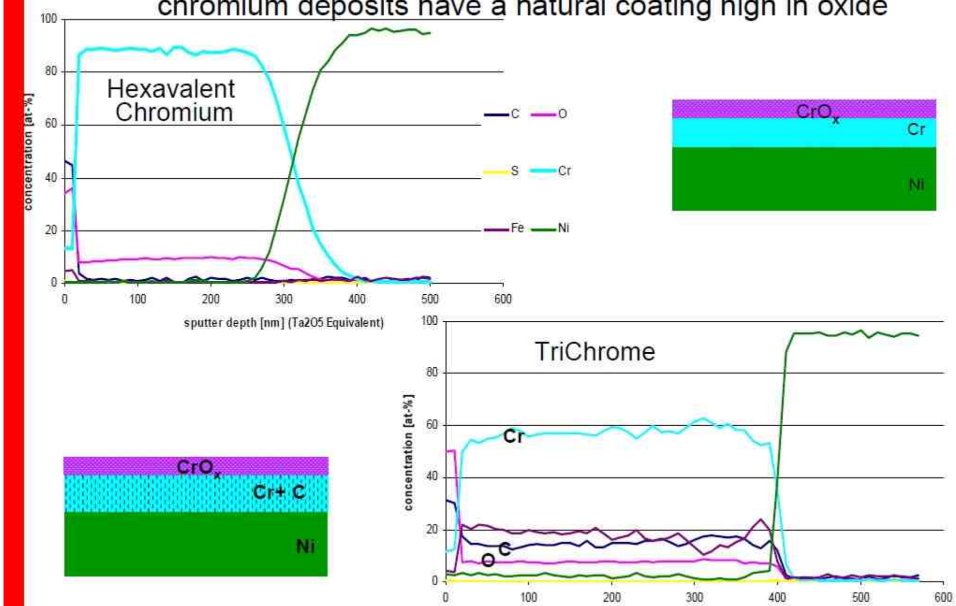
Data indicates that any solid will participate in this form of corrosion

Active Chromium Deposit

Why chromium corroded under the Russian Mud conditions

Depth profile of electroplated chromium

chromium deposits have a natural coating high in oxide

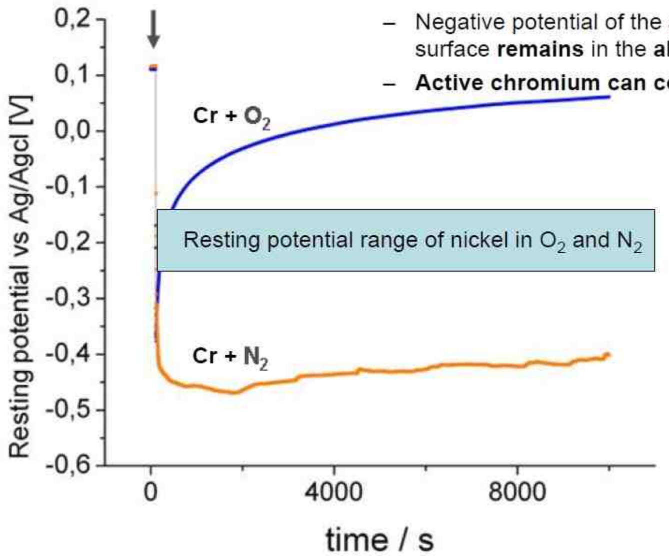


1 nm = 0.001 micron

Generation of an active chromium surface

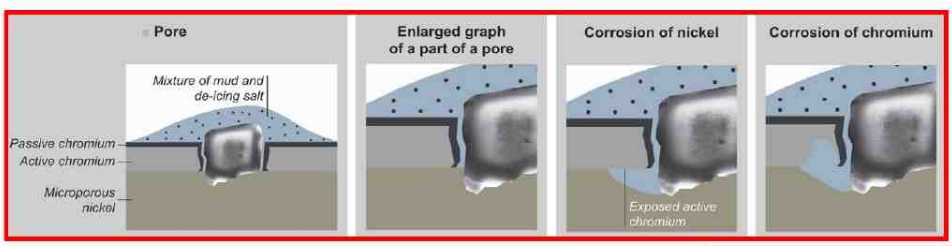
Mechanical damaging of the electroplated chromium surface with a glass pipette in a saturated calcium chloride solution

- **Presence of O_2** leads to **fast re-passivation** of the chromium surface
- Negative potential of the **active chromium** surface **remains** in the **absence of O_2**
- **Active chromium can corrode at** -0.45 V



Active chromium is more reactive than nickel

Theory - Corrosion of Micro-porous Chromium

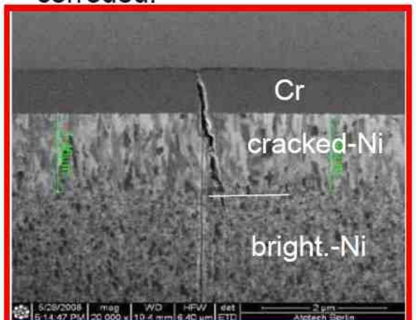


Field damage

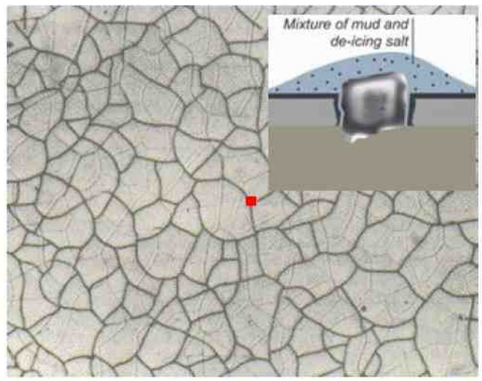
- **Since nickel dissolution in the pore occurs in a lateral direction, active (non-surface) chromium is exposed.**
- **Dirt (e.g. kaolin) in the pore delays the diffusion of oxygen into the pore and thereby prevents the passivation of the active chromium.**
- **The active chromium corrodes lateraly and upward.**
- **Oxygen reduction at the surface of the passive chromium is the counter reaction for both the nickel and the chromium corrosion.**
- **Same reaction takes place with sodium chloride if chloride and moisture are maintained**

Hypothesis: Micro-cracked Nickel / HexChrome

- The nickel corrosion not only takes place directly underneath the chromium layer, but also deeper into the crack towards the bright nickel.
- Continuous cracks can encourage the continuous passivation of the chromium deposit. Easy path for oxygen.
- The bright nickel and micro-cracked layers are preferentially corroded.

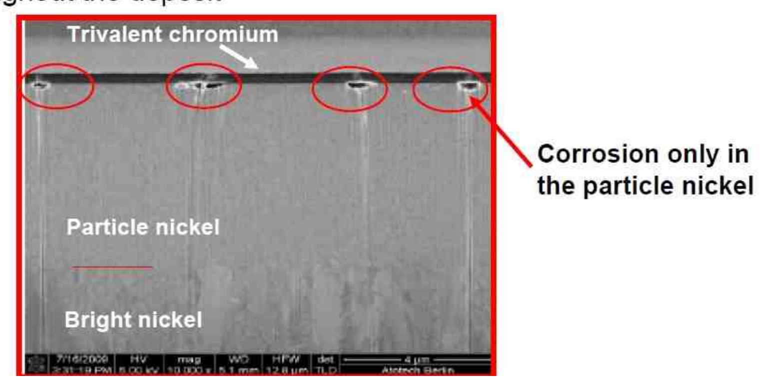


Micro-cracked chromium



Hypothesis: Micro-porous Nickel / Trivalent Chromium

- Tested trivalent chromium deposit is an alloys making it more complex in composition
- Chromium layers from the tested trivalent chromium electrolytes are always more noble than those from hexavalent electrolytes
- Nickel corrosion takes place in the micro porous / noble nickel layer under the passive trivalent chromium
- Corrosion mechanism is similar to traditional one since tested trivalent is passive throughout the deposit



Nissan Russian Mud Test – Hexavalent versus Tested Trivalent

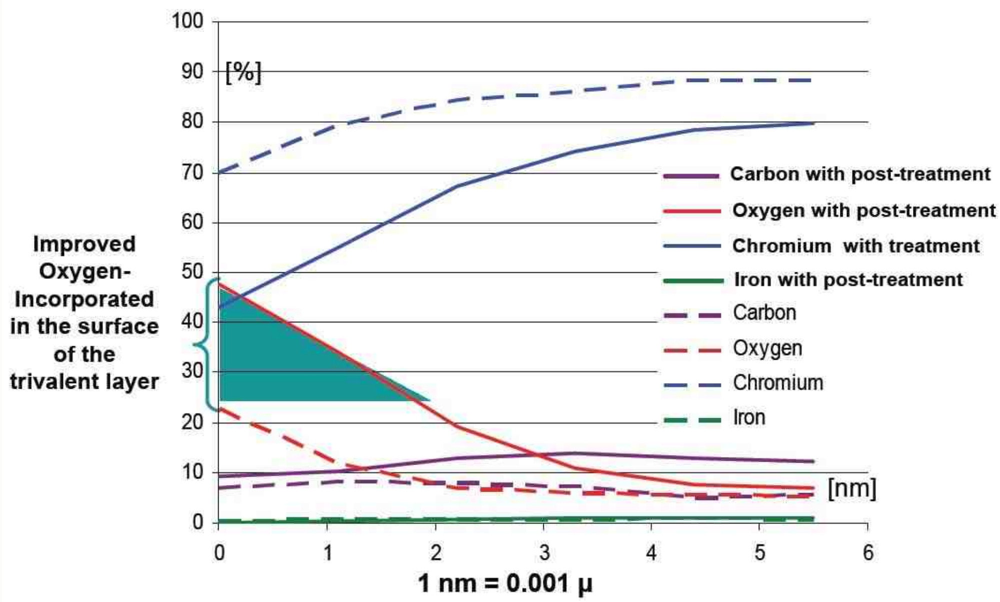
Hexavalent chromium

Hexavalent chromium with clear coat

Trivalent chromium

P Trivalent chromium + Post treatment

Increase the level of oxygen on the surface by the use of a post-oxidizing step



Hexavalent Chromium

Deposits after 168 hours of Nissan Russian Mud Test

Post treatment of hexavalent chromium deposits

Summary

1. Theory proposes that corrosion in the presence of calcium chloride can follow two mechanisms
   a. In the presence of sufficient oxygen the corrosion follows the classical corrosion mechanism
      - Underlying nickel corrodes with chromium staying inert

   b. In the presence of restricted oxygen the corrosion follows a non-classical nickel / chromium corrosion mechanism
      - The bulk of the chromium deposit is low in oxygen and if not exposed to oxygen is more active than nickel
      - Water, chloride and solids must be present for this corrosion mechanism
      - Calcium chloride is an effective source of chloride and water
        – Hydroscopic with two moles of chloride – water always present
        – Under the correct conditions this corrosion can take place with sodium chloride and other sources of chloride
      - Solids restricts oxygen transfer which restricts passivation of the active chromium so the chromium corrodes

Summary

c. Micro-cracked chromium permits oxygen flow for chromium passivation keeping the chromium passive and restricting the non-classical corrosion

d. The tested trivalent chromium deposit is an alloy and is uniformly passive making it the most corrosion resistant chromium

Field Verification

Survey of test automotive grills on OEM vehicles in Moscow during the winter of 2009 – 2010 demonstrated that the tested ….

a. Trivalent chromium system was uncorrroded

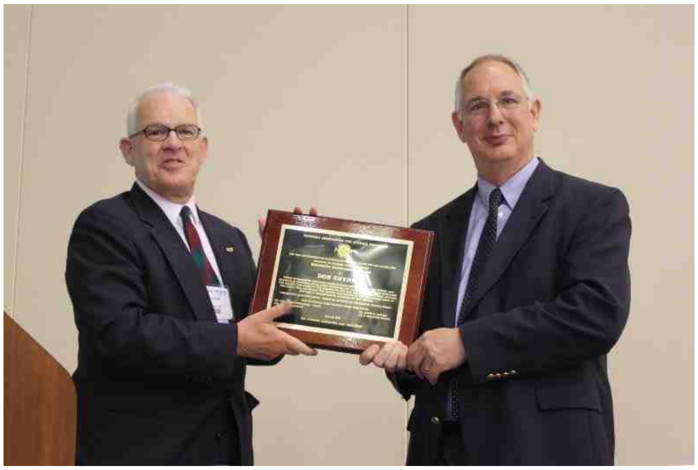
b. Micro-cracked chromium system was slightly corroded

c. Micro-porous chromium system showed extensive corrosion

Seven OEMs have placed the above systems on test vehicles in Moscow, all the companies have not conducted their first year inspection yet.

Other contributors to this work, from Atotech Deut5schland GmbH - Berlin were:

- Günther Bauer
- Dr. Constanze Donner
- Dr. Philip Hartmann
- Dr. Philipp Wachter



Following his talk, Don was presented with the Scientific Achievement Award plaque by Dr. Jim Lindsay, Editor of *Plating & Surface Finishing*. Dr. Lindsay noted that it was a particular pleasure to present the award to Don Snyder. For many years, Don had been Chairman of the Scientific Achievement Award selection committee. Many members had felt that he had been deserving of the award for many years, but they were frustrated in not being able to select him. "It just doesn't look right to give it to the Chair of the selection committee." Lindsay noted. Finally, when Don moved on to other duties, including the Presidency of the AESF Foundation, the selection committee made their move. Clearly, Dr. Snyder's selection was worth waiting for.

About the author

The NASF Scientific Achievement Award is the Association's most prestigious award. Its purpose is to recognize those whose outstanding scientific contributions have advanced the theory and practice of electroplating, metal finishing and allied arts; have raised the quality of products and processes; or have advanced the dignity and status of the profession.

Now a professional consultant, Dr. Donald Snyder, was Worldwide Technical Manager at Atotech, in Rock Hill, South Carolina, when he retired in 2011. Dr. Snyder earned his Ph.D. in physical chemistry from Case Western University and holds an MBA from John Carroll University. He worked in various managerial roles during a more than 40-year career at Harshaw Chemical Co. in Cleveland, Ohio, starting as research director in 1970. Harshaw Chemical was acquired and become Atotech in 1993.

His dedicated service to the AESF and NASF over the years includes the Board of Directors and membership on many Boards and Committees. He has chaired many of these entities as well. He has been Chairman of the Publications Board, a Member of the Research Board and numerous other Committees. More recently, he has served on the AESF Foundation Board of Trustees, including a term as President in 2010-2011. In 2016, he was honored as an NASF Fellow.

He has been active in other groups as well, in particular on ASTM International Committee B08 on Metallic and Inorganic Coatings. In 2015, he received the Frederick A. Lowenheim Memorial Award from that group.