Hexavalent vs. Trivalent
Hard Chromium Plating Processes

An unbiased review of these distinctly different approaches.

Looking at it from both the applicator and end user viewpoints.

While also examining the environmental impact differences.

Everyone agrees that protecting the environment is important.

But we must approach these concerns in a sensible manner, one that actually benefits the overall environment.

Presented By

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Serving the Hard Chrome Industry for over 92 Years

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Presentation Summary

- Chrome Regulations for Electroplating
- Replacing Hex-Cr with Tri-Cr
- Deposit Properties
- Differences in the Processes
- Waste Generation & Zero Discharge
- Process Conversion
- Sustainable Hard Chrome
- Environmental Testing
- Conclusion
- Future Work

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Cr Regulations in Electroplating

Hexavalent Hard Chrome is being attacked for its supposed environmental, workplace and public safety dangers. Some want to further restrict its use or even ban it altogether.

The current federal regulations on Hex-Cr (chromic acid) are:

Air Discharge:	**0.006 mg Cr-6/dscm Cr**
Water Discharge:	**1.0 ppm Total Cr (hex and tri)**
OSHA PEL:	**5 ug/cm3 Cr**

The use of chromic acid may have been abused by some in past years, perhaps due to ignorance of its properties. However, these abuses were corrected long ago.

The existing limits are sufficiently adequate to protect our environment, shop workers and the public. There is no need to further restrict its use because there is no gain from doing so.

In reality, chromic acid is no more hazardous than many other properly managed industrial chemicals are.

Overreacting to the Dangers of Hex-Cr

- **This may be behind the impulse to replace Hex-Cr.**

- **Some think that adopting one of the newer trivalent hard chrome processes (Tri-Cr) is the answer.**

- **We have to be <u>very careful when implementing any change</u> because Hard Chrome is Vital to America's Economy, Defense and Sovereignty.**

- **It is used on Critical Parts like aircraft landing gears, weapon systems and a host of essential industrial components.**

Hex-Cr Replacement Process Must Provide

1) Serve its intended purpose without the risk of critical component failure.
2) Provide an overall environmental and public safety improvement.
3) Be relatively easy to apply, control and operate.
4) Not drastically increase application costs (acquisition and operation).
5) Stand on its own merits and be accepted by the overall market.
6) Undergo having all industry specifications updated such as BAC5709, AMS2460 and Mil-Spec QQ-C-320 (among many others) and all MIL-STD's that call for Hex-Cr.

Hex-Chrome's Application

- Consider that Hex-Cr already meets every one of these needs.
- Hex-Cr has seen widespread use for almost 100 years now.
- The process is refined and all the 'bugs' have been worked out.
- Any replacement would take decades before its finally perfected.

With this background, lets explore the vast differences between the accepted Hex-Cr and the new Tri-Cr Hard Chrome processes.

There is lot to consider.

Deposit Properties

Tri-Cr deposits are claimed to be similar to what's produced by the Hex-Cr process for hardness and wearability.

<u>While this MAY be true for a fresh bath, what happens to the Cr deposit from an aged bath, one with impurities or when the operating conditions vary?</u>

Nobody knows because this has not been reported.

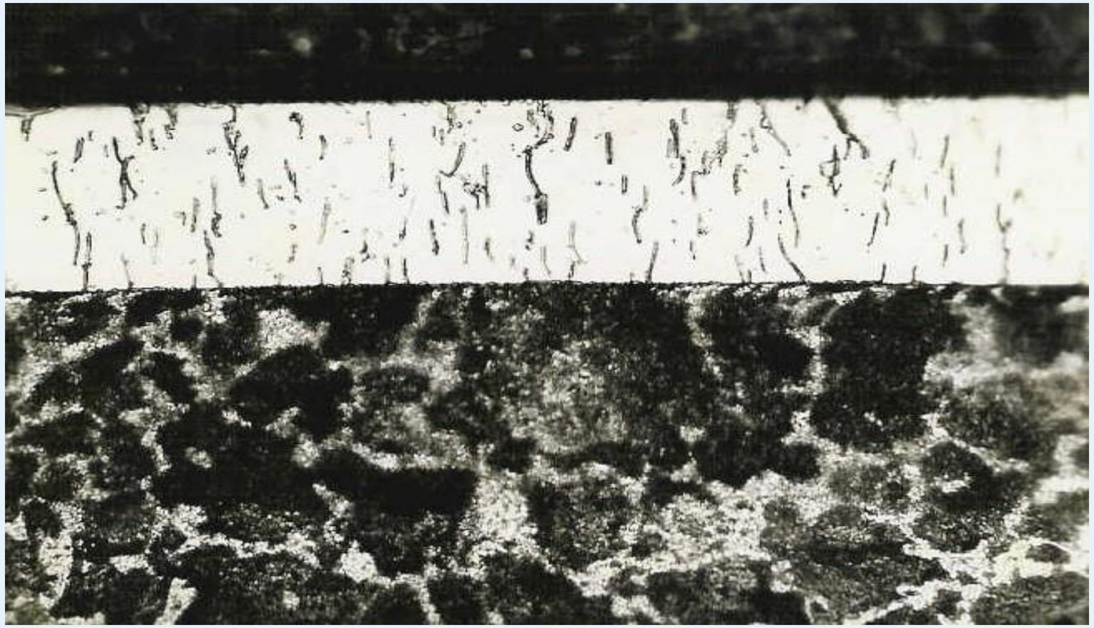
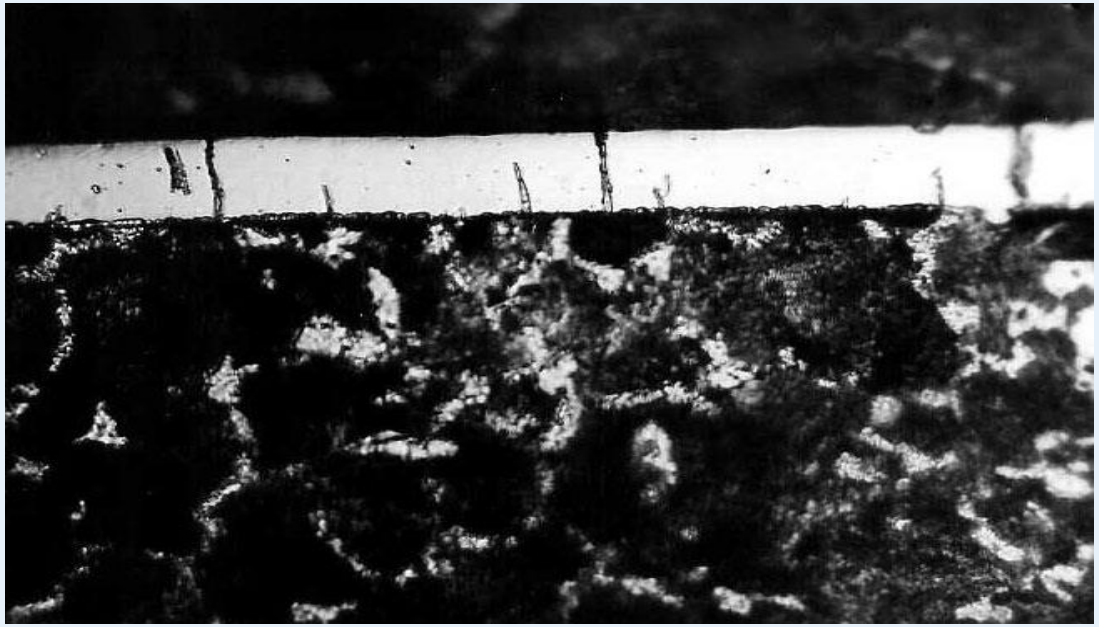
What is known is that the Tri-Cr deposit contains carbon which makes it more brittle. It also has greater internal stress than the Hex-Cr deposit.

There is a considerable difference in the crack structure and corrosion resistance.

Deposit Crack Structure

Tri-Cr's wide deep cracks decrease the corrosion resistance.

The Tri-Cr deposit may require a nickel underlayer.

Hex-Hard Chrome Small Micro-Cracks (small micro-cracks are discontinuous)	Tri-Hard Chrome Larger Macro-Cracks (extend down to the substrate)
	

Plating Bath Properties

Item	Hex-Cr Bath	Tri-Cr Bath
Throwing Power:	**Suitable**	**Reported not as good**
Edge Burning:	**Suitable**	**Much Worse**
Pitting Tendency:	**Suitable**	**May be worse**
Current Interruption:	**Not a problem (if not too long)**	**Unknown**
Plating Cr on Cr:	**Normally done**	**Unknown**
After-Plate Baking:	**Only required for hydrogen embrittlement relief on substrates >RC40**	**May be required for adhesion, stress relief and deposit hardness. But baking opens up the macro-crack structure further and lowers the corrosion resistance**
Chemical Costs:	**Reasonable**	**Considerably Higher**

Substrate Activation

Hex-Cr Process	Tri-Cr Process
Relatively simple process of: **1) Cleaning (often by hand)** **2) Reverse Etching** **3) Hex-Cr Plating** **4) Final Rinsing**	**A much more involved process cycle, similar to Watts nickel plating:** **1) Alkaline Soak Cleaning** **2) Alkaline Electro-Cleaning** **3) Acid Activation** **4) Tri-Cr Plating** **5) Final Rinsing** **(with different rinses between each step)**
(typically involves only 2-3 tanks)	**(typically requires up to 8 tanks)** **(more if a nickel underlayer is required)**

Bath Chemistry

Hex-Cr Bath	Tri-Cr Bath
This bath uses only 2-3 ingredients: **Chromic Acid** **Sulfate** **Sometimes a Secondary Catalyst**	**This bath is more complicated, often containing:** **A Chrome Salt (sulfate or chloride)** **Organic Complexing Agents** **Buffers** **Addition Agents (one or more)** **(and pH Management is Very Important)**
A relatively easy bath to control having a wide range of operating concentrations.	**These ingredients must be closely controlled in order to obtain suitable Cr deposits.**

Analytical Control

Hex-Cr Bath	Tri-Cr Bath
The chromic acid, sulfate and secondary catalyst (if used) have a relatively wide concentration range. **These do not require constant analytical control.** **Many shops operate with only a monthly bath analysis requirement.**	**This bath is much more complicated and sensitive to relatively minor chemical imbalances.** **Some of the bath ingredients (typically 4-5) require daily analytical control.** **Some of these ingredients require chemical dosing.** **In addition, pH management is very important as it changes during plating.**
<u>An easy and inexpensive bath to control.</u> **<u>It does not require an in-house laboratory or daily analysis.</u>** **<u>Bath control costs are lower.</u>**	**<u>These ingredients must all be closely controlled to obtain suitable Cr deposits.</u>** **<u>This requires an in-house laboratory and an on-site lab technician(s).</u>** **<u>Bath control costs are much higher.</u>**

Operating Conditions

The Tri-Cr operating conditions vary with each manufacturer.

Item	Hex-Cr Bath	Tri-Cr Bath
Temperature:	130-140° F, typical	120-150
Current Density:	1 – 10 ASI range	1-4 ASI
Plating Rate/Hour (2 ASI):	0.00125”/hr./side	0.0008-0.002/hr./side
Voltage (2 ASI):	6 VDC, typical	Most are 12-20 VDC (requires more rectification)
Live Entry:	Not required	Typically required
Agitation:	Recommended	Required
Deposit Limit:	Can exceed 0.100”	Some are limited to < 0.008”

Effect Of Impurities

The Tri-Cr bath is more sensitive to common impurities.

Item	Hex-Cr Bath	Tri-Cr Bath
Impurity Tolerance:	**Excellent resistance**	**Very sensitive**
Typical Impurities:	Trivalent Cr, iron, copper and chloride	Cr-6 build-up, iron, copper and several other ions
Effect of Impurities:	Slower deposition rates Deposit problems only if excessive	Causes many plating problems at relatively low concentrations
Source of impurities:	Water supply, chemicals used, fixtures and bussing	Same as the Hex-Cr bath, and the generation of Hex-Cr is a problem
Bath Purification:	Rarely needed if the TCL is kept within reasonable limits	Requires continual purification by ion exchange and decanting

The TCL stands for Total Contaminant Level in Hex-Cr baths. It consists of the percent trivalent, plus the g/l of iron and copper. Ideally it should be below 7.2, but will tolerate a level of 18, i.e.: its very forgiving.

Process Viability

The Tri-Cr bath is considerably more difficult to control.

Item	Hex-Cr Bath	Tri-Cr Bath
Process Window:	Operates well over broad chemical, temperature and current density range. An easy process to control.	Has a very narrow range of operating conditions. This requires much more process control.
Typical Bath Life:	Indefinite when maintained	Likely requires dumping and remaking on a regular basis
Rework Potential:	Not an issue if operated properly	Expected to be much higher
Bath Additions:	Only 2-3 ingredients; easy to make additions	Decanting often needed. More complicated with many chemicals
Water Concentration:	Not an issue	Some baths are very sensitive
Zero Discharge Ability:	Easily Adopted	Not possible
Technology:	Proven and accepted	Developing and unproven

Bath Life

Hex-Cr Bath	Tri-Cr Bath
A very stable bath with an indefinite life if properly maintained. **It rarely (if ever) requires dumping.**	**Considerably less stable and likely requires dumping and remaking on a regular basis, perhaps every 6 months depending upon the ampere hours plated.** **Some data indicates replacing the bath at around 3,000 amp hrs./gallon is needed (estimated).**

The Tri-Cr bath dumping requirement greatly increases hazardous waste.

Waste Generation

Hex-Cr Process	Tri-Cr Process
In most operations chromic acid is the only chemical used that is considered a major pollutant. Chromic acid is easily controlled to prevent its discharge to the land, water and airstreams. The process lends itself to extremely well to full recovery, containment and reuse of the chromic acid.	This process uses more chemicals such as alkaline cleaners, acid activators, an entirely different chromium process and several rinse tanks. These extra baths create additional hazardous waste. While some may be partially recoverable, there are bath dumps to deal with which mandates that a waste treatment system be used. In addition, Tri-Cr baths use chelating chemicals which makes the removal of chrome in the waste stream very difficult and expensive.
Waste treatment is not needed; the result is no Cr discharge to the environment. <u>Properly Used, Hex-Cr has no health or environment issues.</u>	The Tri-Cr process is a hazardous waste generator. <u>The discharge limit for Tri-Cr is only 1 ppm.</u>

Zero Discharge

Hex-Cr Process	Tri-Cr Process
The Hex-Cr process can be Zero-Discharged. A waste treatment is not often needed. This is due to using fewer tanks, the simplified chemistry and elevated bath temperatures. Everything is contained and all process chemicals can be recycled for reuse. Even liquids in the containment system can be reused back in the process. The result is no Cr discharge and no hazardous waste to process giving it a much lower environmental impact.	The Tri-Cr process is a known waste generator. Adopting it actually makes the overall environmental issue worse. It is not possible to recycle all of the additional rinsates used. These baths have a limited life and need decanting and dumping. This creates a large volume of hazardous hydroxide sludge that must be disposed of. The Tri-Cr process actually harms the environment by creating additional hazardous waste.

Process Conversion

Hexavalent hard chrome plating lines can not be easily or inexpensively converted to Tri-Cr processing.

- **The existing Hex-Cr plating tank liner should not be reused.**
- **Many additional tanks must be installed and considerably more floorspace is required.**
- **Special anodes, fixtures and higher-voltage rectifiers are needed.**
- **Additional bath purification, ventilation and support equipment is also required.**
- **An in-house laboratory with a qualified technician is necessary for bath control.**
- **A waste treatment system must be installed and operated.**

Converting from Hex-Cr to Tri-Cr is an expensive endeavor requiring more floorspace, tanks, ventilation, support equipment, electrical power and operating personnel.

Plating Line Layouts - Typical

Hex-Cr	Tri-Cr
A typical Hex-Cr plating system is relatively simple and straightforward. It only requires 2–3 tanks. A reverse etch tank isn’t mandatory, but is beneficial for keeping bath impurities to a minimum. An alkaline cleaner tank is frequently avoided because precleaning is often done by hand. The overall plating line is relatively small and doesn’t require a lot of floorspace.	A Tri-Cr plating line typically requires up to 8 tanks, or more if a nickel underlayer is required for corrosion resistance. Simplifying this line is not possible or plating quality will be sacrificed. The AC electrical power requirement will be much higher for Tri-Cr. The overall plating line requires extra floorspace and is more complicated.

Tri-Cr’s capitalization costs are significantly higher than for Hex-Cr.

Is Hex-Cr Overly Dangerous?

The chromic acid used in Hex-Cr plating is no more hazardous than many other industrial chemicals. The beauty of the Hex-Cr bath is there is only one primary chemical to deal with which is easy to use safely.

This differs from the Tri-Cr plating process where several additional hazardous chemicals are needed. Therefore, the potential safety and environmental dangers are much greater with Tri-Cr than they are for Hex-Cr plating.

<u>Hex-Cr plating poses no dangers to the environment,</u>
<u>the workers or the public if it is handled and used appropriately.</u>

Hex-Cr Plating is Now Sustainable

No Need to Further Restrict or Replace Hex-Cr

Newer Technology has proven that Hex-Cr can be safely used without harm to the workers, the public or the environment.

❖ **The land is protected with specially designed containment.**

❖ **The chemicals and liquids are recycled for reuse.**

❖ **Special mist eliminators remove all Cr from the airstream.**

❖ **There is no Cr discharge. Waste treatment and sewer connection are not required and are eliminated.**

❖ **Chrome misting is controlled without having to use a fume suppressant.**

Adopting Sustainable Hex-Cr Plating

- **Existing Hex-Cr plating operations may require an initial facility review and a brief engineering phase. Some equipment changes will be needed depending on the circumstances.**

- **A special high-efficiency triple-catalyst bath is used which plates faster, but more importantly, reduces the Cr mist generated. Most existing Hex-Cr baths can be converted if they are not overly contaminated.**

The cost of adopting this technology varies with the situation. However, both the CAPEX and OPEX costs will be significantly lower than changing to a Tri-Cr process.

A Tri-Cr user can not compete with a similar Hex-Cr operation.

A Typical Sustainable Hex-Cr Operation

The shop stays clean, the environment and workers are protected.

Designed for Zero Discharge

Plenty of Room for Maintenance

Environmental Testing

Results from a Sustainable Hex-Cr Plating Operation

After 8 hours of operation at 20,000 DC amperes.

EPA Cr Stack Test:		Zero Cr (non-detectable)
OSHA Cr PEL Test:		mg Cr/cm3
	Tank side worker:	0.090 (>55 x below PEL)
	Plating helper:	0.032 (>156 x below PEL)
Dust Wipes:		
	Cr Tank Hoods:	0.004 (the hoods stayed clean)
	Plating shop floor:	0.027 (the surrounding equipment also stayed clean)

The test results were provided by an accredited and a certified environmental laboratory.
(copies are available upon request)

Conclusion

The Sustainable Hex-Cr process has demonstrated that it can now be used safely while protecting the environment, the workers and the public.

- **There is no point in replacing it with an unproven Tri-Cr process that actually creates environmental waste products and increases production costs.**
- **This also means that there is no need to further restrict Hex-Cr's use for hard chrome plating.**
- **Instead, applying the new Sustained Technology will result in saving America's critical aviation, defense and industrial businesses.**

Our task now becomes educating the industry and the regulators on how this can be accomplished.

God gave us Hex-Cr for a purpose; our task is to use it responsively.

Future Work
<u>The Costing Difference</u>

This study would not be complete without also presenting a side by side cost comparison of the Hex-Cr vs. the Tri-Cr Hard Chrome processes, including the:

CAPEX	**(capitalization requirement)**
OPEX	**(operational costing)**

Unfortunately, this data is not available to us as the Tri-Cr bath producers have not responded to our requests for information.

<u>However, you can expect the cost of Tri-Cr to be higher than Hex-Cr for both the CAPEX and the OPEX. This cost difference is expected to be significant, but the extent is unknown at this time.</u>

Anyone interested in Tri-Cr's costing should inquire directly with the producers, explore all aspects and make an informed decision.

Thank You

The staff at Plating Resources, Inc. offers a warm and hardy THANK YOU to all of the hard chrome shops we had the pleasure of working with over the past 92 years.

Your valued input made this presentation possible.
We sincerely appreciate your support.

We look forward to providing you the technology assistance needed to adopt the Sustainable Hex-Hard Chrome method.

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Please email any comments or questions on this report to PlatingResources@Yahoo.com.