Chromium Plating

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1st Edition
with 152 Figures and 90 Tables

Forword

In the periodic system of elements is chromium the metal with physical properties making electrolytic deposited chromium extremely valuable for many engineering and decorative applications. Chromium metal resist most chemicals, is shiny, has a high hardness a low coefficient of friction and beside many other properties a high wear resistance. No other metal can offer such a variety of properties. In this book experience of the best experts and latest technologies are described.

Know how of old foxes has been updated and converted to metric systems. In order to avoid confusion, conversion tables for the most important values have been included. Chromium is at the moment under fire, because it is deposited out of hexavalent chromium solution. Chromium metal itself doesn't cause any problems.Because chromium has so many positive properties it can't be replaced by other metals. So the plating industry found solutions for this problem. The deposition of functional chromium can be handled in closed loop systems which are described in several chaptors. The transport and handling in returnable containers avoid contact of workers with chromic acid. The efficiency of wetting agents and recycling systems avoid emission and ensure clean working conditions.

With the available knowledge it is possible to meet the future REACH requirements. The suppliers of proprietory chemicals know, how to handle dangerous chemicals to make them harmless to apply.

There is no alternative to chromium!

This applies also to its use in stainless steel alloys. The plating supply houses make it possible to apply chromium a safe way.

Stuttgart, November 2006   G.A. Lausmann

1   History

Chromium was not known to the ancients, and credit for discovery of the metal is given to *Nicolas-Louis Vauquelin* in Paris in 1797-1798. *Vauquelin* analyzed a Siberian red lead (crocoite, $PbCrO_4$) and found it to contain an unknown acid in addition to lead. He precipitated the lead as lead chloride and, after evaporating the residue, reduced it with carbon at a high temperature and obtained a network of gray interlacing metallic needles. Because of the many colored compounds *Fourcroy* and *Haüy* suggested the name chromium for the new metal. In just a few years chromite ($FeO \cdot Cr_2O_3$) was identified as a widely distributed and readily available source of chromium chemicals. It appears that known reserves of chromite or chromium ore, particularly in South Africa and Zimbabwe (former Rhodesia), are sufficient to last for the foreseeable future.

Thus, chromium chemicals were something of a 40-years-old novelty when *Antoine Becquerel* speculated on the results to be obtained by electrolyzing their solution in his book in 1843. He said that one would probably succeed in obtaining chromium using chromic chloride; one could also try the chromic sulfate soluble in water, or the green chromic nitrate which dissolves easily.

Probably the first to deposit chromium was *Junot de Bussy* in 1848-1849. *Junot's* patents were not very clear as he claimed to have found ways to deposit a number of metals which we still cannot deposit from aqueous solution. However, his purpose was quite clear. He wanted to break the monopoly of *Ruolz* and *Elkington* on cyanide gold and silver plating by depositing an undercoat of a corrosion resistant metal on the basis metal, and then plating with gold or silver with the corrosive chloride or other baths which were in the public domain, such as those of *Becquerel* or *De la Rive*. Thus, he claimed to deposit undercoats of silicon, chromium, vanadium, tungsten; platinum which was clearly too expensive.

In his patent of addition in 1849, *Junot* disclosed that he used a saturated solution of chromium chloride filtered onto an excess of sodium chloride. The solution was then diluted to 10 % with distilled water, boiled, and filtered again with great care, when it had a beautiful clear amethyst color by transmitted light. At the end of this addition patent, *Junot* commented that when his new deposits were made to some thickness they had a whiteness and brightness that made any subsequent deposit of silver unnecessary, and had the further advantages of resisting the action of hydrogen sulfide completely, and of having greater wear resistance.

In a later French patent in 1855, *Junot* merely reaffirmed that he used a chromium chloride made by dissolving hydrated chromic oxide in hydrochloric acid and evaporating to

dryness to remove excess hydrochloric acid. The British patent of 1852 is uninformative but indicates that he used about 10 g/l of chromium as the double chloride of sodium and ammonia.

At about the same time, in 1854, *Professor Robert Bunsen* in Heidelberg investigated the effect of current density on the electrodeposition of chromium from chromous chloride solutions containing chromic chloride, in a two compartment cell. The cell was made with a carbon crucible as anode and containing some hydrochloric acid in the anode compartment. In the center a small porous ceramic container was placed and contained the solution and a small platinum strip cathode. With this cell and concentrated, boiling hot solutions, *Bunsen* easily obtained small sheets of metallic chromium more than half a square centimeter in area. They were quite brittle; the surface next to the platinum cathode was smooth and bright.

The chromium looked like iron, but was more resistant to damp air. It dissolved with difficulty in hydrochloric acid and dilute sulfuric acid to form chromous salts. Nitric acid, even boiling, scarcely attacked the metal. The specific gravity was about one-seventh higher than previously given in the textbooks, that is, about 6.9 instead of 5.9.

In the second edition of this text book of electrochemistry in 1864, *Becquerel's* only comments on chromium deposition were that chromium salts were difficult to reduce to the metal with electricity, and to give a description of *Bunsen's* work.

In 1856 *Anton Geuther* in Göttingen, Germany, discovered the deposition of chromium from chromic acid solutions while studying elements with more than one valence and trying to disprove *Faraday's* Law. His work and the detailed history of chromium deposition from chromic acid baths are reviewed elsewhere.

Thus it was that more than a century ago some of the main features of the electrodeposition of chromium were anticipated, even though the difficulties of accomplishing this operation postponed the introduction of commercial chromium plating from chromic acid solutions until about 1925, and we are still trying to overcome the difficulties of depositing the metal from trivalent baths. The desirable properties of the metal became known by the 1850s, and concerned with the electrodeposition of metals generally experimented with chromium. Thus, *Isaac Adams Jr.,* who introduced commercial nickel plating in 1869, frequently discussed the possibility of chromium plating in his correspondence in this period.

The basic difficulty of electrodepositing metallic chromium is evident. It can be noted that chromium is not included in the group of metals easily electrodeposited at high current efficiencies from aqueous solutions. Instead, chromium is grouped with metals only reduced from their solutions with difficulty at high cathode potentials, which tend to the evolution of hydrogen simultaneously and give reduction products in the solution such as trivalent chromium in trivalent solutions.

Between 1924 and 1926 *Colin E. Fink* and *Charles H. Eldridge* introduced the use of major catalyst in the electrodeposition of chromium from chromic acid solutions. In the late 1920 *Fink's* patents were issued. It was then more than 125 years after the discovery of the metal that commercial chromium plating was born. United chromium and later

M&T Chemicals who acquired United Chromium discovered the market with the SRHS solutions. SRHS stands for self-regulating high speed.

Gebauer applied in Europe about the same time chromium solutions with H_2SiF_6 as second catalyst. Both systems had disadvantages. The H_2SiF_6 solutions have been too aggressive in terms of corrosion to the substrate.

M&T Chemicals and later *LPW* applied in the 70`s for a patent using alkyl sulphonic acid and their derivates as second catalyst.

Proprietary chromium compounds are successfully sold by *Atotech, Enthone* and *IPT* using these catalysts. *Atotech* and *Enthone* hold the respective patents.

These catalyst are fully soluble and don't etch. Solutions can be operated up to 80 °C and current densities up to 90 A/dm^2 applied. Modern chromium solutions can be recycled and operated in closed loop systems.

No other metal can offer better overall properties then chromium.

References:

[1] R. Guffie: The Handbook of Hard chromium plating, Gardner Publications, Inc., Cincinnati, 1986, p. 6 ff.

[2] G. A. Lausmann, N. Unruh: Die galvanische Verchromung, 2. Auflage, 2006, Eugen G. Leuze Verlag, p. 11 ff.

# 2 The electrolytic deposition of chromium

2.1 Principles of deposition

The debate regarding the mechanism of chromium deposition has been going on since investigations began and continues today. *Liebreich* established that the current density potential curve of chromium deposition from its hexavalent solutions is revealed in four stages. From this he derived a multi-stage deposition process. He assumed that deposition proceeds through the following valency states:

$$Cr^{6+} \rightarrow Cr^{3+} \rightarrow Cr^0$$
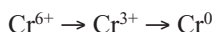
Geuther noticed an increased brown discoloration on the cathode. *Müller*, who worked increasingly on this phenomenon, assumed the following equation to explain the build up of film at the cathode:

$$2\ H_2CrO_4 + 3\ e \leftrightarrow Cr(OH)CrO_4 + 3\ OH$$

E. Müller was also the first to advocate the theory of the direct deposition of chromium from the hexavalent state, i.e.

$$Cr^{6+} \rightarrow Cr^0$$
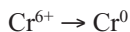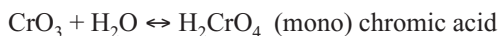
The two theories are still widely discussed today.

Summarized reaction

Most of the described summarized reactions about the deposition of chromium out of chromates describe this process only vagly. Too many single reactions take place the same time. How this single reactions influence each other is difficult to judge.

2.1.1 Deposition by reduction in steps

One of the theories of chromium deposition is the reduction of chromium in steps.

Chromium trioxide (CrO_3) is used as a metal carrier in most commercial chromium baths. As it dissolves in water chromic acid form:

$$CrO_3 + H_2O \leftrightarrow H_2CrO_4 \ \text{(mono) chromic acid}$$
$$2\ CrO_3 + H_2O \leftrightarrow H_2Cr_2O_7 \ \text{dichromic acid}$$

Equilibrium is always established in aqueous solutions:

$$2\ CrO_4^{2-} + 2\ H^+ \leftrightarrow Cr_2O_7^{2-} + H_2O$$
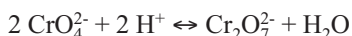
Due to the high chromate content in the chromium baths this equilibrium is pushed strongly to the right, i.e. dichromate is chiefly present in these baths.

If we study the gross reaction of the deposition:

$$2 \text{ Cr} + 7 \text{ H}_2\text{O} \leftrightarrow \text{Cr}_2\text{O}_7^{2-} + 14 \text{ H}^+ + 12 \text{ e}$$
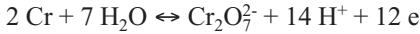
then 27 particles would have to collide simultaneously in one place to deposit 2 chromium atoms. Even if we disregard the electrons, 15 particles, i.e., 1 dichromate ion and 14 hydrogen ions would still have to collide simultaneously. Such a collision is almost impossible and, consequently, in practice the overall reaction cannot proceed. Therefore, partial reactions must take place which involve fewer particles.
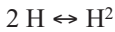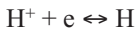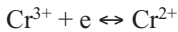
Important information regarding gradual reactions is also gained when intermediates of medium valency appear in the electrolyte or on the electrodes. Trivalent chromium ions accumulate in the chromium baths as electrolysis proceeds. It can be concluded from this that at least this valency state takes part in the reaction.

Before the cathode film has fully formed – in the first section of the current density potential curve – only hexavalent chromium is reduced to trivalent chromium.

$$\text{Cr}_2\text{O}_7^{2-} + 14 \text{ H}^+ + 6 \text{ e} \leftrightarrow 2 \text{ Cr}^{3+} + 7 \text{ H}_2\text{O}$$
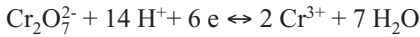
Due to the high consumption of hydrogen ions, the pH in the cathode film increases. This provides the conditions necessary for the formation of the chromium chromate film. If the porosity of the film is increased by foreign anions, then the other reactions proceed with sufficient speed.

Large quantities of hydrogen are released. Besides following reactions:

$$\text{Cr}^{3+} + \text{e} \leftrightarrow \text{Cr}^{2+}$$

$$\text{Cr}^{2+} + 2 \text{ e} \leftrightarrow \text{Cr}$$

$$\text{H}^+ + \text{e} \leftrightarrow \text{H}$$

$$2 \text{ H} \leftrightarrow \text{H}^2$$

As the hydrogen is initially in its atomic state it is highly reactive. This has fuelled further debate among advocates of the theory of gradual deposition about whether all reactions proceed by means of direct transfer of electrons or whether the atomic hydrogen with its high reducing ability participates in the reactions.

References:

[1] G. A. Lausmann, N. Unruh: Die galvanische Verchromung, 2. Auflage, 2006, Eugen G. Leuze Verlag, p. 20 f.

2.1.2   Deposition by direct reduction of chromate

The most important result of the work of *E. Müller* is proposing the formation of chromate(III) chromate film at the cathode. This film should according to *Müller* consist of following composition:

$$\text{Cr} = (\text{OH})_2$$
$$\diagdown$$
$$\text{CrO}_4$$
$$\diagup$$
$$\text{Cr} = (\text{OH})_2$$
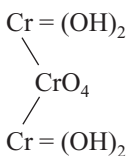
Comparable evaluation with solutions of pure chromic acid and additions of pure chromic acid and additions of sulfuric acid enable *Müller* to concluded:

– chromic acid will be reduced without an intermediate step directly to metallic chromium

– additions of catalyst result in a porous cathode film

C. Kasper has a somewhat different explanation. The first reaction is the formation of $Cr_2(Cr_2O_7)_3$ which will be converted at a later stage into chromium(III) chromate. The presence of sulphate reduce the speed of electrophoreses of these colloids and consequently from a less compact film.

There are many other theories leaving still open questions.

The further role of oxide in the mechanism is that electrodeposited chromium is produced in a passive state due to the residual film on the surface; the practical consequence is that no post-plating passivation is needed. The disadvantage is that electrodeposition can not be interrupted because a passive layer may produce a parting line in the deposit.

References:

[1] G. A. Lausmann, N. Unruh: Die galvanische Verchromung, 2. Auflage, 2006, Eugen G. Leuze Verlag, p. 27 - 28

2.1.3   Anodic reactions

Lead or lead alloys are generally used for chromium plating. Platinised titanium or copper can be used as well. The surface of lead will be converted to lead oxide as soon electrolyses starts.

Water will be oxidised in order to form oxygen.

Chromium(III) reoxidises to chromium(VI). This reaction only takes place up to an anodic current density of about 35 A/dm^2. Lead (IV) may reduce to lead (II) when the current is interrupted.

$$PbO_2 + Pb \rightarrow 2\ PbO$$
$$3\ PbO_2 + 2\ Cr^{3+} + 5\ H_2O \rightarrow 3\ PbO + 2\ CrO_4^{2-} + 10\ H^+$$
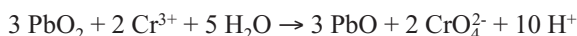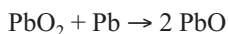
Lead chromate can be formed by reactions of lead oxide with chromates:

$$PbO + CrO_4^{2-} + 2\ H^+ \rightarrow PbCrO_4 + H_2O$$
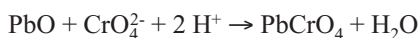
These reactions takes place in all types of solutions based on chromic acid.

The formation of lead chromate should be avoided (see anodes) in order to increase anode life.

The anode erosion takes place when lead oxidises to lead dioxide. Anodes must be therefore carefully selected, sized and applied.

These reactions don't take place when platinised titanium is used. Lead has to be added to the solution in order to form a thin lead film on the surface of the platinised titanium. Supply houses of proprietary chromium compounds can offer respective addition agents suitable for the use of platinised titanium anodes.

An additional lead anode can reduce also the build up of chromium(III), which otherwise may rise.

Depending on the applied anodic current density the formation of chromium(III) can be avoided or reduced by this method.

References:

[1] G. A. Lausmann, N. Unruh: Die galvanische Verchromung, 2. Auflage, 2006, Eugen G. Leuze Verlag, p. 29

2.1.4   Reaction of chromium at the electrodes in aqueous solutions

Chromium and their ions can react in various ways in aqueous solutions.

In aqueous solutions ion of chromium can react different ways. The reactions are shown in *table 2.1*.

Table 2.1: Electrodereactions of chromium

No.	Reactions			Potential (Volt)	
1	$Cr + 2\ OH^-$	$\leftrightarrow$	$Cr(OH)_2$	$+ 2\ e^-$	- 1.4	- 0.0591 pH
2	$Cr + 3\ OH^-$	$\leftrightarrow$	$Cr(OH)_3$	$+ 3\ e^-$	- 1.3	- 0.0591 pH
3	$Cr(CN)_6^{4-}$	$\leftrightarrow$	$Cr(CN)_6^{3-}$	$+ e^-$	- 1.28	
4	$Cr + 4\ OH^-$	$\leftrightarrow$	$CrO_2 + 2\ H_2O$	$+ 3\ e^-$	- 1.2	- 0.0788 pH
5	Cr	$\leftrightarrow$	Cr^{2+}	$+ 2\ e^-$	- 0.913	
6	$CrO + 2\ H_2O$	$\leftrightarrow$	$Cr(OH)_3 + H^+$	$+ e^-$	- 0.785	- 0.0591 pH
7	Cr	$\leftrightarrow$	Cr^{3+}	$+ 3\ e^-$	- 0.744	
8	$Cr + 3\ H_2O$	$\leftrightarrow$	$Cr(OH)_3 + 3\ H^+$	$+ 3$	- 0.654	- 0.0591 pH
9	$Cr + H_2O$	$\leftrightarrow$	$CrO + 2\ H^+$	$+ 2\ e^-$	- 0.588	- 0.0591 pH
10	$CrO + H_2O$	$\leftrightarrow$	$Cr_2O_3 + 2H^+$	$+ 2\ e^-$	- 0.561	- 0.0591 pH
11	$Cr + (3 + n)H_2O$	$\leftrightarrow$	$Cr(OH)_3 \cdot nH_2O + 3\ H^+$	$+ 3\ e^-$	- 0.512	- 0.0591 pH
12	Cr^{2+}	$\leftrightarrow$	Cr^{3+}	$+ e^-$	- 0.407	
13	$Cr + 2\ H_2O$	$\leftrightarrow$	$CrO_2^- + 4H^+$	$+ 3\ e^-$	- 0.213	- 0.0788 pH
14	$Cr^{2+} + H_2O$	$\leftrightarrow$	$CrOH^{2+} + H^+$	$+ e^-$	- 0.182	- 0.0591 pH
15	$Cr^{2+} + 3\ H_2O$	$\leftrightarrow$	$Cr(OH)_3 + 3\ H^+$	$+ e^-$	- 0.136	- 0.1773 pH
16	$Cr^{2+} + 2\ H_2O$	$\leftrightarrow$	$Cr(OH)_2^+ + 2\ H^+$	$+ e^-$	+ 0.185	- 0.1182 pH
17	$2\ Cr + 7\ H_2O$	$\leftrightarrow$	$Cr_2O_7^{2-} + 14\ H^+$	$+ 12\ e^-$	+ 0.294	- 0.0689 pH
18	$Cr + 4\ H_2O$	$\leftrightarrow$	$H_2CrO_4 + 6\ H^+$	$+ 6\ e^-$	+ 0.295	- 0.0591 pH
19	$CrO + 2\ H_2O$	$\leftrightarrow$	$CrO_3^{3-} + 4\ H^+$	$+ e^-$	+ 0.297	- 0.2364 pH
20	$Cr + 4\ H_2O$	$\leftrightarrow$	$HCrO_4^- + 7\ H^+$	$+ 6\ e^-$	+ 0.303	- 0.0689 pH

Table 2.1 (continuation) : Electrodereactions of chromium

No.	Reactions			Potential (Volt)	
21	$CrO_3^{3-} + H_2O$	$\leftrightarrow$	$CrO_4^{2-} + 2\ H^+$ $+ 3\ e^-$	$+ 0.359$	$- 0.0394$ pH
22	$Cr + 4\ H_2O$	$\leftrightarrow$	$CrO_4^{2-} + 8\ H^+$ $+ 6\ e^-$	$+ 0.366$	$- 0.0788$ pH
23	$Cr + 3\ H_2O$	$\leftrightarrow$	$CrO_3^{3-} + 6\ H^+$ $+ 3\ e^-$	$+ 0.374$	$- 0.1182$ pH
24	$CrO + H_2O$	$\leftrightarrow$	$CrO_2^- + 2\ H^+$ $+ e^-$	$+ 0.538$	$- 0.1182$ pH
25	$2\ CrO_2^- + 3\ H_2O$	$\leftrightarrow$	$Cr_2O_7^{2-} + 6\ H^+$ $+ 6\ e^-$	$+ 0.801$	$- 0.0591$ pH
26	$CrO_2 + 2\ H_2O$	$\leftrightarrow$	$CrO_4^{2-} + 4\ H^+$ $+ 3\ e^-$	$+ 0.945$	$- 0.0788$ pH
27	$Cr_2O_3 + H_2O$	$\leftrightarrow$	$2\ CrO_2 + 2\ H^+$ $+ 2\ e^-$	$+ 1.060$	$- 0.0591$ pH
28	$Cr(OH)_3 \cdot nH_2O$	$\leftrightarrow$	$HCrO_{4-} + (n - 1)H_2O + 4\ H^+$ $+ 3\ e^-$	$+ 1.117$	$- 0.0788$ pH
29	$2\ Cr(OH)_2^+ + 3\ H_2O$	$\leftrightarrow$	$Cr_2O_7^{2-} + 10H^+$ $+ 6\ e^-$	$+ 1.135$	$- 0.0985$ pH
30	$Cr(OH)_2^+ + 2\ H_2O$	$\leftrightarrow$	$HCrO_4^- + 5H^+$ $+ 3\ e^-$	$+ 1.152$	$- 0.0985$ pH
31	$Cr_2O_3 + 4\ H_2O$	$\leftrightarrow$	$Cr_2O_7^{2-} + 8H^+$ $+ 6\ e^-$	$+ 1.168$	$- 0.0788$ pH
32	$Cr_2O_3 + 5\ H_2O$	$\leftrightarrow$	$2\ HCrO_4^- + 8\ H^+$ $+ 6\ e^-$	$+ 1.184$	$- 0.0788$ pH
33	$Cr^{2+} + 2\ H_2O$	$\leftrightarrow$	$CrO_2 + 4\ H^+$ $+ e^-$	$+ 1.188$	$- 0.2364$ pH
34	$2\ CrO_2 + 3\ H_2O$	$\leftrightarrow$	$Cr_2O_7^{2-} + 6\ H^+$ $+ 4\ e^-$	$+ 1.221$	$- 0.0886$ pH
35	$2\ Cr(OH)_3 + H_2O$	$\leftrightarrow$	$Cr_2O_7^{2-} + 8\ H^+$ $+ 6\ e^-$	$+ 1.242$	$- 0.0788$ pH
36	$Cr(OH)_3 \cdot nH_2O$	$\leftrightarrow$	$CrO_4^{2-} + (n - 1)H_2O + 5\ H^+$ $+ 3\ e^-$	$+ 1.244$	$- 0.0985$ pH
37	$CrO_2 + 2\ H_2O$	$\leftrightarrow$	$HCr_4^- + 3\ H^+$ $+ 3\ e^-$	$+ 1.246$	$- 0.0886$ pH
38	$2\ CrOH^{2+} + 5\ H_2O$	$\leftrightarrow$	$Cr_2O_7^{2-} + 12H^+$ $+ 6\ e^-$	$+ 1.258$	$- 0.1182$ pH
39	$Cr(OH)_3 + H_2O$	$\leftrightarrow$	$HCrO_4^- + 4\ H^+$ $+ 3\ e^-$	$+ 1.259$	$- 0.0788$ pH
40	$CrOH^{2+} + 3\ H_2O$	$\leftrightarrow$	$HCrO_4^- + 6\ H^+$ $+ 3\ e^-$	$+ 1.275$	$- 0.1182$ pH
41	$Cr(OH)_2^+ + 2\ H_2O$	$\leftrightarrow$	$CrO_4^{2-} + 6\ H^+$ $+ 3\ e^-$	$+ 1.279$	$- 0.1182$ pH
42	$Cr(OH)_3$	$\leftrightarrow$	$CrO_2 + H_2O + H^+$ $+ e^-$	$+ 1.284$	$- 0.0591$ pH
43	$Cr_2O_3 + 5\ H_2O$	$\leftrightarrow$	$2CrO_4^{2-} + 10\ H^+$ $+ 6\ e^-$	$+ 1.311$	$- 0.0985$ pH
44	$CrOH^{2+} + H_2O$	$\leftrightarrow$	$CrO_2 + 3\ H^+$ $+ e^-$	$+ 1.331$	$- 0.1773$ pH
45	$2\ Cr^{3+} + 7\ H_2O$	$\leftrightarrow$	$Cr_2O_7^{2-} + 14\ H^+$ $+ 6\ e^-$	$+ 1.333$	$- 0.1379$ pH
46	$Cr^{3+} + 4\ H_2O$	$\leftrightarrow$	$H_2CrO_4 + 6\ H^+$ $+ 3\ e^-$	$+ 1.335$	$- 0.1182$ pH
47	$Cr^{3+} + 4\ H_2O$	$\leftrightarrow$	$HCrO_4^- + 7\ H^+$ $+ 3\ e^-$	$+ 1.350$	$- 0.1379$ pH
48	$Cr(OH)_3 + H_2O$	$\leftrightarrow$	$CrO_4^{2-} + 5\ H^+$ $+ 3\ e^-$	$+ 1.386$	$- 0.0985$ pH
49	$CrOH^{2+} + 3\ H_2O$	$\leftrightarrow$	$CrO_4^{2-} + 7\ H^+$ $+ 3\ e^-$	$+ 1.402$	$- 0.1379$ pH
50	$CrO_2 + 2\ H_2O$	$\leftrightarrow$	$CrO_4^{2-} + 4\ H^+$ $+ 2\ e^-$	$+ 1.437$	$- 0.1182$ pH
51	$Cr^{3+} + 4\ H_2O$	$\leftrightarrow$	$CrO_4^{2-} + 8\ H^+$ $+ 3\ e^-$	$+ 1.477$	$- 0.1576$ pH
52	$Cr^{3+} + 2\ H_2O$	$\leftrightarrow$	$CrO_2 + 4\ H^+$ $+ e^-$	$+ 1.556$	$- 0.2364$ pH

3 Decorative chromium plating

3.1 Decorative chromium plating at the state of the art

Failures in chromium plating are a great loss because of the high production degree up to the point of chromium plating. White washing (passivation) or insufficient throwing power are the main problems when chromium plating with hexavalent electrolytes. Improvement in at least one of these points is desirable in almost every decorative automatic line. Very awkward for the production is the often suddenly appearance of hazes as initial stage of White Washing effects, which cannot be related to any specific change of process solutions or mode of operation.

Avoiding passive surfaces

Appearance of "white washing" effects is caused by a number of factors. Smaller deviations in the single process steps superpose to a serious failure. A lack of activation of the to be plated surface may result from a high organic content of the bright nickel layer combined with deviations of the rinse water quality, but also from the chemical activation or an insufficient sulphuric acid content of the bright chromium electrolyte.

By application of a new, by the cathodic potential supported activation, such deviations may be reduced evidently. Deviations in the conductivity of the rinse waters or the brightener content of the nickel electrolyte are obviously moderated.

Passivation is so rapid and spontaneous it can occur in a rinse stage.

In production, this benefit of activation may be used as higher protection from "white washing", or the sulphuric acid content in the chromium electrolyte may be reduced, which raises the throwing power.

In addition a chromium electrolyte should be applied which tolerates a higher sulphuric acid content, at comparable or better throwing power.

The mode of operation of the electrolytic activation may be explained as follows: subsequent to nickel deposition, the surface is covered with an active film, if not being immersed electroless in the nickel electrolyte long.

upper production limit (loss of throw)

nickel electrolyte   rinse water   usual activation   chromium electrolyte

lower prodution limit (passivation)

upper production limit (loss of throw)   + 0,1 - 0,2 % H$_2$SO$_4$

nickel electrolyte   rinse water   Ankor NFDS   Ankor 1120 H
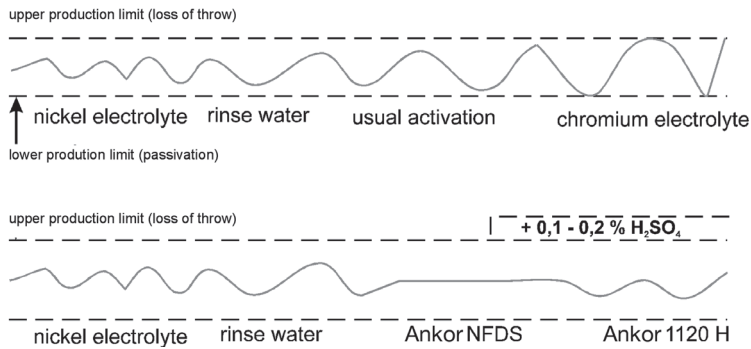
Fig. 3.1: Small variations in single process steps superpose
and production limits are left

The lower the salt content in the rinse waters, the higher the pressure on the solution to absorb this active film. At the same time, the factor time has some influence on the stripping of the active film. (As it is known, "white washing" surely appears after disturbances in the automatic line with racks being exposed in the rinses for a longer period of time). Much better than with usual chemical activation's or still rinses, it is possible to re-produce the required activity by *Ankor*® NFDS activation. The necessary current is only about 10 to 100 mA/dm^2. The activation is based on chromic acid and non critical for drag-in into the actual chromium plating solution.

Improving throwing power of the chromium plating solution

Due to the fact of a relatively high potential being necessary to deposit chromium from hexavalent electrolytes the throwing power of the bright chromium solutions has always been somehow limited. Some improvement to the classic sulfuric acid/chromic acid

Mode of operation of the bright chromium activation Ankor NFDS

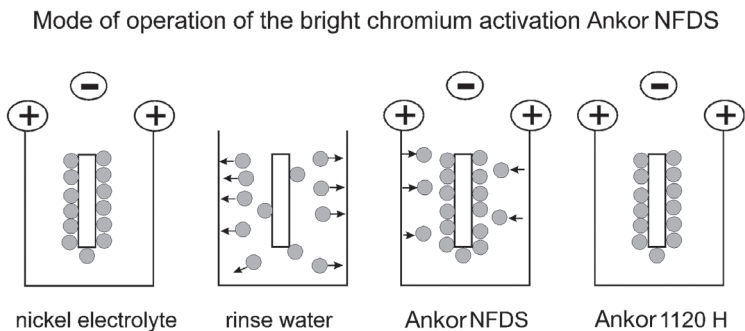nickel electrolyte   rinse water   Ankor NFDS   Ankor 1120 H

Fig. 3.2: Activity film, loss in rinse water and build up
in electrolytical activation to avoid passivation

solutions has been made by the use of Fluorides, which allowed a much lower sulfuric acid content and an improvement in throw. Besides the result on the plated part and some practical tests with hull-cells or similar equipment little information is known how to put throwing power in scientific figures. In this work it has been tried to quantify solutions in throwing power. The solutions which were compared were the *Ankor® 1120* process, a widely used bright chromium electrolyte (300 g/l CrO_3, 0.4 % H_2SO_4, fluorides) and the new *Ankor® 1120 H process* (300 g/l CrO_3, 0.5 % H_2SO_4, new catalyst system) which has been successfully introduced to the marked since 1995.

Potentiometric measurements were carried out at 40 °C with a rotating cathode, which had been nickel plated just before each test run. The area of the cathode was 0.502 cm^2. The potential was measured against calomel electrode in a capillary tube. The third electrode, the anode was platinised titanium.

Three different types of measurements were made:

– current as a function of the potential
– potential as a function of the current
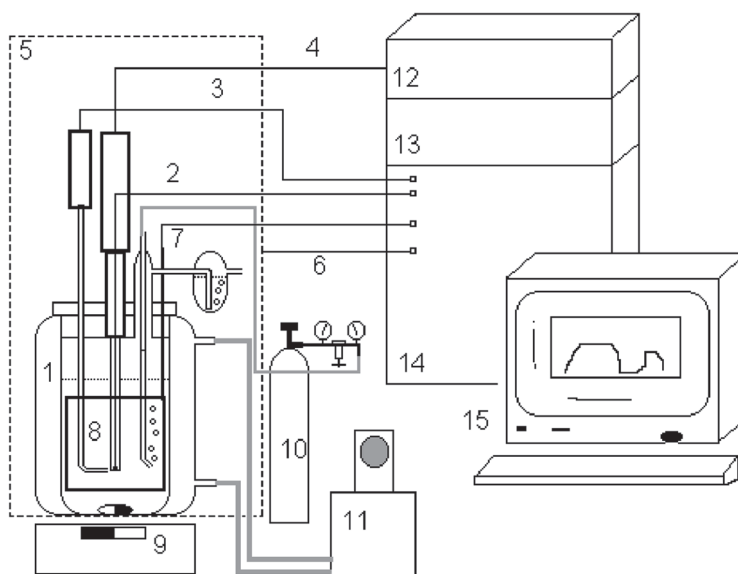– measurement of the potential at constant current

Fig. 3.3: Equipment for potentiometric measurements
1 - double wall heat exchanger, 2 - contact rotating electrode,
3 - contact reference electrode, 4 - rotating electrode contact, 5 - Faraday box,
6 - contact earth, 7 - contact anode, 8 - capillary tube
9 - magnetic agitation, 10 - argon supply, 11 - temperature control,
12 - control unit rotating electrode, 13 - frequency analyser,
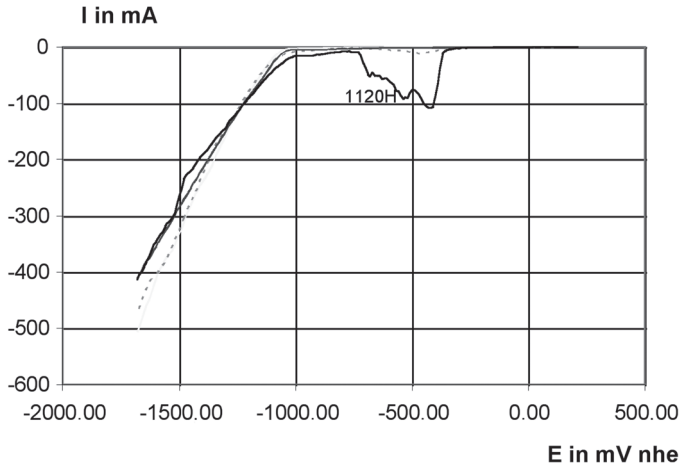14 - potential measurement unit, 15 - computer

I in mA

Fig. 3.4: Current as a function of the potential, speed 10 mV/s

Results of the measurement

Starting on the right at the open circuit voltage all samples show a reaction at about -1 V. Previous to that reaction the samples with *Ankor® 1120 H* show a strongly oscillating reaction which was able to be reproduced. Probably because of a potential drop related to the reaction. To investigate more detailed about this behaviour the next measurement was carried out with a constantly rising current.
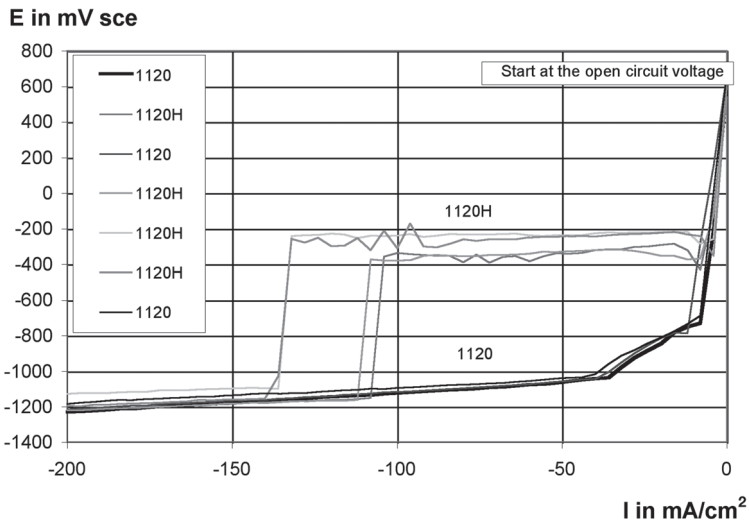
E in mV sce

Fig. 3.5: Potential as a function of current, speed 2 mA/s

4   The hard chromium plating

4.1   Choice of the basic material and its surface treatment

The conditions of the basic material largely determine the result of the plating.

Substrate conditions affect adhesion appearance and corrosion resistance. Chromium deposits magnify and exaggerate imperfections in the surface of the basic material. Suggestions how to plate a variety of substrates can be found at *chapter 4.3*.

Basis metal prefinishing are all processes that occur before plating. These include grinding, polishing, electrocleaning and etching. All machined surfaces are damaged. Machining- and grinding produced defects will be magnified by chromium plating especially on thick deposits. Since levelling does not occur in chromium plating solutions, the plated part is never smoother than the substrate. The preferred surface for plating should be free from tool marks, slivers, gouges, and inclusions. Removing substantial stock from the steel will significantly improve the substrate.

The finishing wheel grit acts like small ploughs when removing material and forms ridges at the grooves. This plowing often leaves metal slivers on the surface. Prefinishing should progressively proceed with finer and finer grit material to produce a less damaged surface and smaller slivers. The metal slivers will be removed eventually or reduced to insignificant size. The metal slivers may be removed during chemical or electrochemical activation of the steel before plating.

One of the keys to good prefinishing is the selection of the initial grit size and the final grit size. The initial grit size should be coarse enough to remove all machining lines, unevenness, pores and surface oxides, etc. The final grit size should produce a surface that is suited for plating or polishing is required. Basis metal improvement may occur in electrocleaning and etching before plating. The grain or grit size of the intermediate steps must be appropriate to remove the scratches and slivers of the proceeding step and produce finer defects for the next step to remove or reduce. Each grinding step should be at 90° angle relative to the prior step to obtain optimum results.

During the grinding process plastic deformation of the steel occurs and metal is bent over and embedded into the substrate. Some chips which are not removed can thus

cause slivers in the basis metal. The plastic condition caused by the high pressures of grinding also can cause grit material to be embedded in the substrate. Both of these conditions cause base metal defects.

Grit material should be as uniform as possible. Cost is usually related to quality. Cheap media may have larger grit material in with the finer media. Low quality media will produce a poor quality finish. It is also possible to contaminate media. One must especially prevent coarse media from contaminating fine media.

	Appearance	*Ra µm* Before Plating	After Plating
Factory finish	Bright	0.77	4.5
Finish with 400 and 600 grit SiC	semi-bright, grind lines visible	0.82	1.4

Mechanical finishing

The table shows that a bright substrate is not necessarily a good substrate. The parts are motorbike shock absorbers.

The factory-finished part and the part refinished with 400 and 600 grit paper had about the same Ra before plating. However, the refinished part had a much smoother finish after plating and a lot less nodules. The surface finish Ra is of great importance in obtaining a good chromium plated part. However, as noted above the Ra does not measure slivers that have been bent over into the substrate.

Deposit quality is a function of basis metal smoothness and freedom from defects.

The above samples were plated in a high efficiency etch-free chromium solution at 60 °C and a current density if 60 A/dm^2. The samples were plated for 30 minutes to a thickness of 50 microns. Samples were plated in 1.4 litres of solution that was magnetically stirred and thermostatically temperature controlled. A constant current, constant voltage power supply with a very low ripple was used in the constant current mode. These samples were electrocleaned in an alkaline electrocleaner for one minute at 15 A/dm^2 and etched for 30 seconds at 15 A/dm^2 in the plating solution.

Etching in chromic acid

The anodic etch of the part in chromic acid or in the plating solution, will influence the nodularity of the chromium deposit. Reduced nodularity will occur with a very low short time and low current etch or a high coulomb moderate time and high current etch. An electrocleaner will stand up the slivers as will a moderate etch. A very light (low coulomb) etch will not stand up the slivers. However, a light etch may not be adequate for good adhesion. A long etch, typically one minute and 60 A/dm^2 will raise up slivers and etch them off. The high current density makes the solution act like an electro-polish. The etch intensity drastically affects the surface roughness of the as received samples.

The following experiments show the effect of pretreatment cycle or etch on surface roughness and corrosion resistance. The following pretreatments were used.

Pretreatment A:

–   Anodic electroclean for two minutes at 10 A/dm^2

–   Cold water rinse

–   Immersion in 5 % sulfuric acid at room temperature for 15 seconds

–   Cold water rinse

Pretreatment B:

–   Anodic electroclean for one minute at 15 A/dm^2

–   Cold water rinse

–   Etch in bath one minute at 60 A/dm^2

The parts were plated in a high efficiency etch-free chromium solution to a thickness of 35 microns. The samples were plated at 60 °C and 45 A/dm^2. The table below shows the basis metal finish and the finish of parts processed with pretreatment A and B. Also shown is the neutral salt spray test corrosion resistance of these samples. Corrosion resistance improved as nodules were decreased and surface finish was improved. No finishing was done after plating. Post finishing usually improves the corrosion resistance.

	Substrate	Pretreatment	
		A	B
Ra μm	1.25	5.25	2.25
Hours in NSST		24 - 48	96 - 122

Chemical and electrochemical finishing

Chemical and electrochemical polishing can be used to improve the substrate before plating. These processes are designed to remove metal and make the substrate smoother. The chemical polish is a proprietary solution containing 10 % by volume of the concentrate and 10 % by volume of 35 % hydrogen peroxide. The parts have to be immersed in this solution for five minutes at room temperature.

The electropolish contains 15 % sulfuric acid, 63 % phosphoric acid, 10 % chromic acid and 12 % water. This solution can be used at a temperature of 70 °C for 6 minutes at 45A/dm^2. After the chemical or electrochemical polishing, the rods can be plated to a thickness of 50 microns.

Cast aluminium and cast iron substrate defects

Cast materials are subject to the same grinding and finishing defects as for steel substrates. However, cast materials are more likely to have inclusions and voids than

non-cast steels. Defects of basis metal will be discussed below for chromium plated cast aluminium and cast iron parts.

A comparison of lab and factory casting quality highlights sources of aluminium substrate defects. The laboratory cast sample had no voids or inclusions while the plant cast material had many inclusions. The aluminium is contaminated in the casting process; the following sources of voids in the casting department are considered significant.

– Putting oily scrap into the pots

– Contacting the aluminium directly with flame in the pot

– Infrequent cleaning the bottom of the pot

– Not emptying the ladle on each run

By eliminating the above practices, the rejects can be reduced.

Chromium plated cast iron can have pits in the chromium. A four micron wide pit in the basis metal will cause a pit in the chromium. Electroplated chromium has very good microthrowing power. When the defect becomes too large, chromium cannot bridge over or fill it in and a pit in the chromium occurs. Since graphite or carbon particles in cast iron have low hydrogen overvoltages hydrogen is formed at the graphite particle before chromium is electrodeposited. A graphite particle on the cast iron surface should therefore cause a pit in the chromium deposit. Pitting can be caused by voids or inclusions.

If inclusions of sulphur occurred on the surface, they can over-catalyze the localized area and prevent plating. In a fluoride-based plating system low current density etching could occur and form a pit where the sulphur inclusion was located. This pit would appear to be caused by a basis metal pit but may have been caused by a surface inclusion.

Cast iron contains voids which can have several origins. Voids can be caused by: a graphite nodule being removed from the surface, torn metal due to dull machine tools, and microshrinkage. Microshrinkage occurs during casting and can cause the information of small cracks in the cast iron.

Inclusions in the cast iron can cause pits. Inclusions of non-metallic dross will cause pits or pores because the dross can not be plated. Magnesium silicate dross has also been observed in cast iron. Graphite can become segregated to the surface and could cause pitting. Voids and inclusions can be controlled by casting procedures and control of the cast iron chemistry.

The selection of high quality base material is the key for good deposits. The identification and optimization of these prefinishing methods improved the basis metal of both steel and cast aluminium and subsequent plated parts. Appropriate mechanical finishing and an anodic etch produces a surface that can be plated with a minimum of nodules. Optimum casting practices can produce substrates with produce acceptable plated parts.

References:

[1] A. Jones: Atotech, USA