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DEVELOPMENT OF CHROME PLATING PROCESS ON FUEL INJECTORS USED IN GASOLINE ENGINES

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LIST OF SYMBOLS

°C	Celsius
dyn/cm	Dyne/Centimetre
€	Euro
lt/h	Litre/Hour
µm	Micrometre
ml	Millilitre
mN/m	Millinewton/Metre
mm²	Square Millimetre
HV	Vickers Hardness

LIST OF ABBREVIATIONS

8D	Eight Disciplines
DC	Direct Current
EDS	Energy-Dispersive X-ray Spectroscopy
FEM	Finite - Elemente - Methode
FMEA	Failure Mode and Effects Analysis
HDEV4	High-Pressure Piezo Injector
HDEV5	High-Pressure Solenoid Injector
PDCA	Plan – Do – Check - Act
PTFE	Politetrafloroetilen, Teflon
R&D	Research and Development
XRF	X-ray Fluorescence

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ABSTRACT

DEVELOPMENT OF CHROME PLATING PROCESS ON FUEL INJECTORS USED IN GASOLINE ENGINES

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Department of Metallurgical and Materials Engineering

MSc. Thesis

Adviser: Assoc. Prof. Dr. Cem AKCA

Hard chromium plating is produced by electrodeposition from a solution containing chromic acid and a catalytic anion in proper proportion. The metal produced is extremely hard and corrosion resistant. The process is used for applications where excellent wear and/or corrosion resistance is required.

In this study, which was carried out in collaboration with Robert Bosch Gasoline Systems, determination and solution of white spot defects on Bosch's high-pressure solenoid injector HDEV5 were aimed. Formation of white spots (or white patches) reduces the coating thickness resulting in poor abrasion resistance. In order to eliminate the formation of white spots; anode changing times were optimized, thickness of Pt coating on anode was increased, electrolyte flow rate was optimized, chemical properties of plating bath were examined (surface tension, pH, concentration, etc.) and finally the age and quality of bath were optimized.

Keywords: Coating, hard chromium plating, electrodeposition, white spot.

ÖZET

BENZİNLİ ARAÇLARDA KULLANILAN YAKIT ENJEKTÖRLERİNİN KROM KAPLAMA PROSESİNİN GELİŞTİRİLMESİ

Behiye Aybike YALCINYUZ

Metalurji ve Malzeme Mühendisliği Anabilim Dalı

Yüksek Lisans Tezi

Tez Danışmanı: Doc. Dr. Cem AKCA

Sert krom kaplama, kromik asit iceren bir cözelti de belli bir oranda katalizor yardimiyla elektrolitik biriktirme yöntemiyle iyonlarinin ayrismasi ile edilir. Üretilen metal son derece sert ve korozyona karsi dayaniklidir. Mükemmel asinma ve/veya korozyon direnci gerektiren uygulamalarda kullanilir.

Robert Bosch Benzinli Sistemleri ile calisilan bu tezle; Bosch`un yüksek basincli solenoit enjektörlerinde, sert krom kaplama ile üretilen parcalarinda görülen beyaz lekeye cözüm bulmasi amaclanmistir. Beyaz lekenin olusmasi kaplama kalinliginin düsmesine böylelikle düsük asinma direncine neden olmaktadir. Beyaz leke olusumunu engellemek icin; anota yapilan Pt kaplamanin kalinliginin arttirilmasi, anot degisim zamanlarinin ve elektrolitik debinin optimize edilmesi, banyonun kimyasal özelliklerini incelemek (yüzey gerilimi, pH, konsentrasyon vb.), son olarak banyo yasi ve kalitesinin optime edilmesi gibi calismalar yapilmistir.

Anahtar Kelimeler: Kaplama, sert krom kaplama, elektrolitik biriktirme, beyaz leke

CHAPTER 1

INTRODUCTION

1.1 Literature Review

1.1.1 Surface Engineering

Surface engineering is treatment of the surface and near-surface regions of a material to allow the surface to perform functions that are distinct from those functions demanded from the bulk of the material [1]. The required properties or characteristics of surface-engineered components include:

- Improved corrosion resistance,
- Improved oxidation and/or sulfidation resistance,
- Improved wear resistance,
- Improved mechanical properties,
- Improved electronic or electrical properties,
- Improved thermal insulation,
- Improved aesthetic appearance,
- Reduced frictional energy losses [2].

Surface engineering which is a discipline of science, encompasses the total field of research and technical activity aimed at the design, manufacture, investigation and utilization of surface layers, both technological and for end use, with properties better than those of the core, such as mainly anti-corrosion, anti-fatigue, anti-wear and decorative. Other applications include properties such as optical, electrical, magnetic, adhesive, ablation, passivation, inhibition, catalytic, diffusion, biocompatibility [3].

Surface engineering has a lot in common with fundamental and applied science in the meaning as defined above. Figure 1.1 shows the relationship of surface engineering with other multidisciplinary sciences.

- Fundamental sciences: Physics, chemistry, partially mathematics and constitutes their application to material surface.
- Applied sciences:
    - Sciences dealing with materials science and material engineering, with special emphasis on heat treatment,
    - Construction and use of machines, with special emphasis on material strength, primarily fatigue, tribology and corrosion protection,
    - Electrical engineering, electronics, optics, thermos kinetics, the science of magnetism [3].

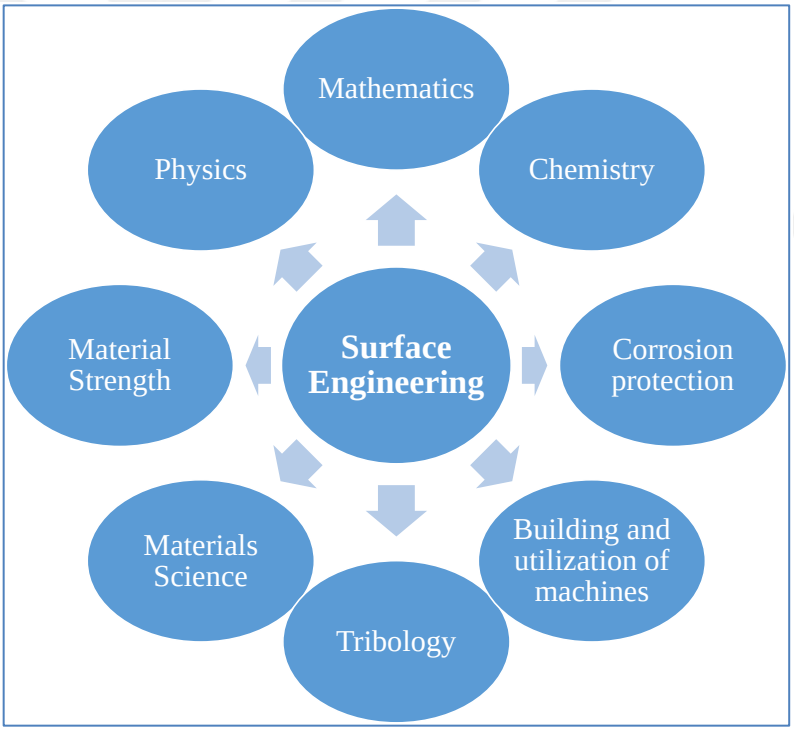


Figure 1.1 Connection of the multidisciplinary on surface engineering [3]

Today, important industrial sectors such as the automotive industry, the aviation industry and the power engineering industry depend on modern surface engineering processes. At the same time, the newer industrial sectors, such as medical engineering, micro-systems technology and micro-electronics, would not have been able to grow as rapidly without the methods of surface engineering [4].

A coating has no end in itself, as a coating development will always depend on the intended application (Figure 1.2). The surface engineer must not only be able to think in terms of the application, but also be capable, in collaboration with the customer, to describe the load complex as completely as possible: only then can a theoretical choice of material for the surface be made [4].

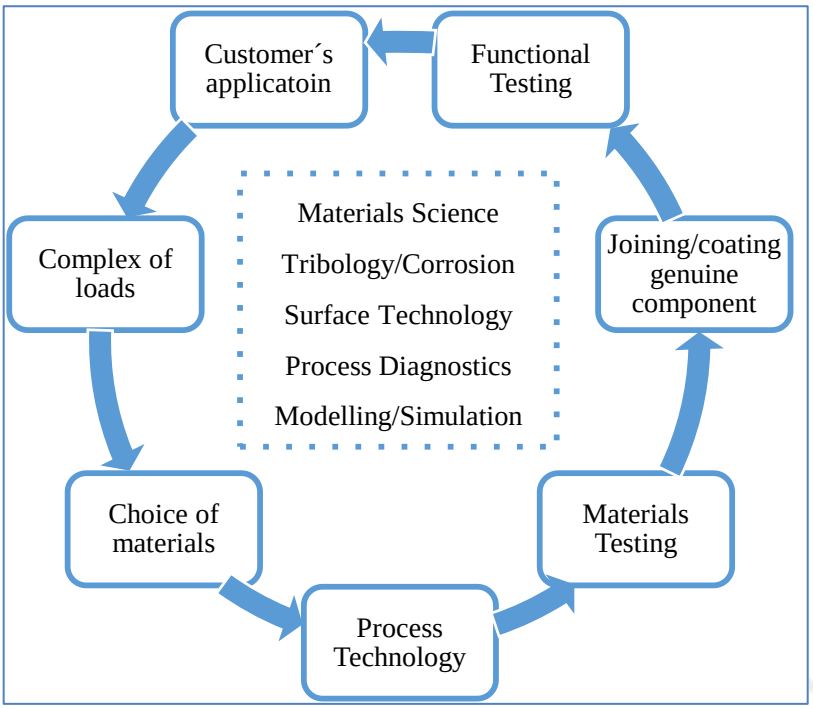


Figure 1.2 Methodical development approaches in surface engineering [5]

Equally as varied as the functions of surfaces are the processes of surface engineering which has a distinction can be made between surface modification processes and surface-coating processes (Figure 1.3):

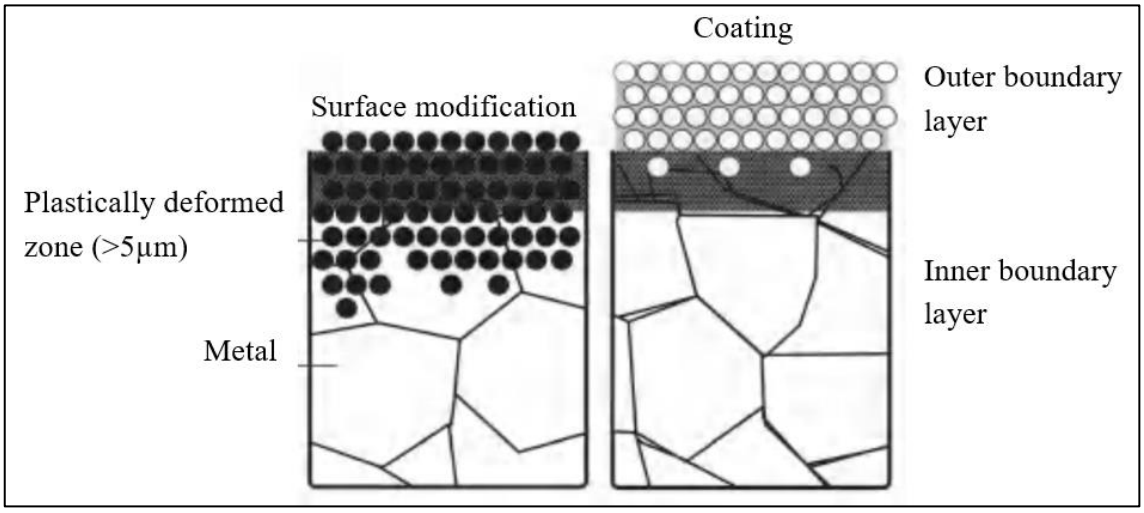


Figure 1.3 The surface modification and the surface coating [5]

- Surface modifications are processes which penetrate into the material and thus alter the surface properties; this can be in the form of thermal (e.g. by diffusion, as with nitration or carbonization), chemical, or also mechanical processes (e.g. by shot blasting) to achieve residual compressive strengths.
- For surface-coating processes, new materials are applied to the surface. The coatings can be applied as single layers and as a rule, layer systems, alloy layers, composite layers or even gradient layers are produced [4].

Figure 1.4 illustrates a scheme under which coating processes may be categorized.

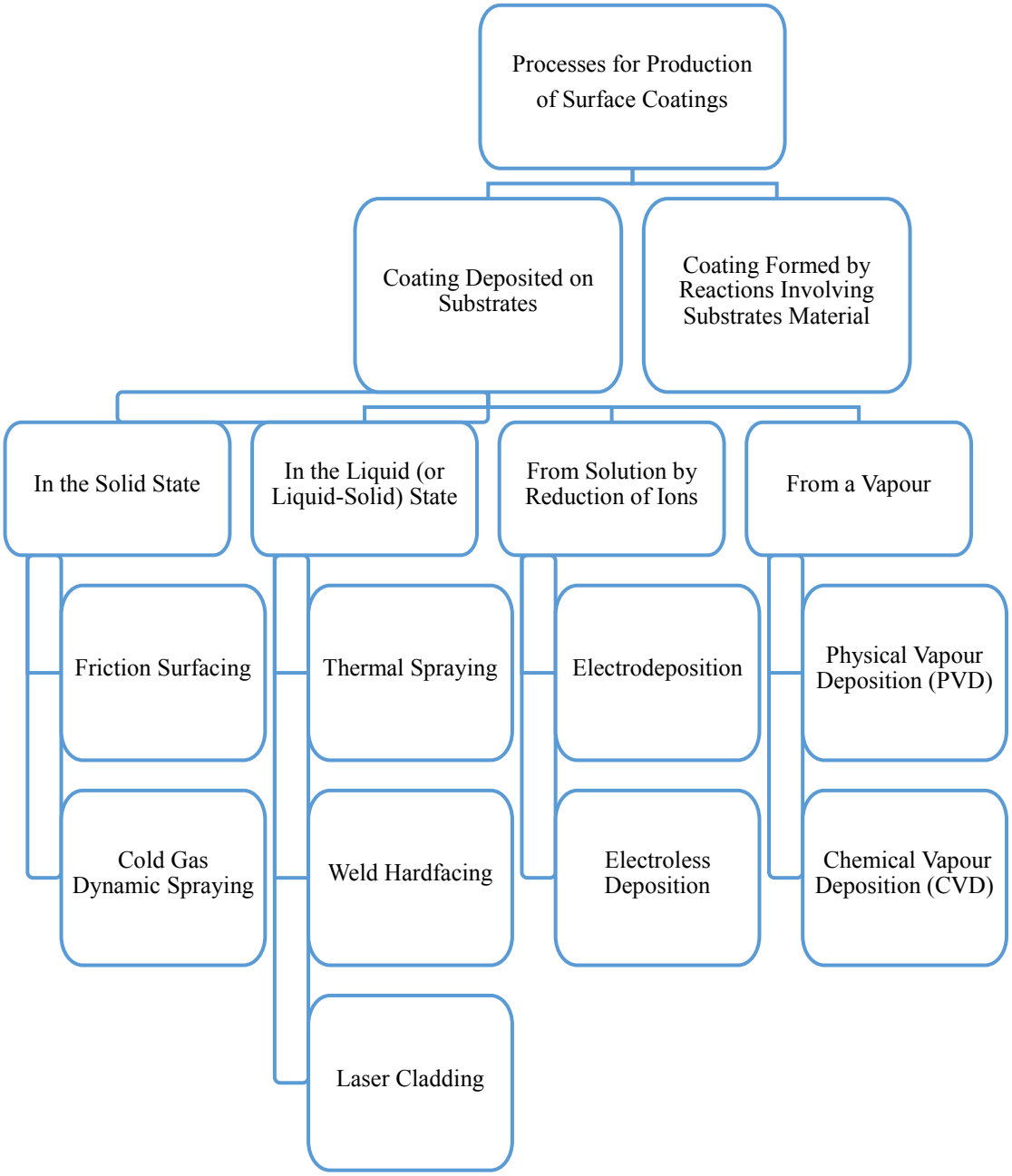


Figure 1.4 Basic classification of coating types [6]

1.1.2 Electrodeposition

Electrodeposition refers to film growth process which consists in the formation of a metallic coating onto a base material occurring through the electrochemical reduction of metal ions from an electrolyte [7]. These processes follow the laws of electrochemistry and may be classified as;

- Electroplating, metal deposition processes with an external current,
- Chemical metal deposition, metal deposition processes without an external current [4].

Michael Faraday first put forward the laws of electrolysis in 1833 and they still form the basis of the technology, such as the amount of chemical change produced is proportional to the quantity of electricity which passes and the amounts of substances liberated by a given quantity of electricity are proportional to their equivalent weights [8]. The electrolyte contains the depositing metal ions and usually also complexing agents, buffering agents, inert salts and organic additives. Electrodeposition is particularly well suited for coating of large numbers of small pieces such as screws, using continuous barrel plating [9].

The metal ions for the formation of the coating are made available either by the dissolution of an anode or by the electrolyte. The component to be coated is switched as the cathode, and the reduction of the metal ions takes place here. The required electrons are produced by oxidation at the anode (Figure 1.5) [4].

Electrodeposits are applied to metal substrates for decoration, protection, corrosion resistance, chemical inertness, wear resistance, build-up of substrate dimensions, electrical properties, magnetic properties, solder ability, reflectance, and reduction of friction. Electrodeposited coatings are sometimes applied for two or more reasons. For example, decorative and protective plating and combined in such applications as steel automobile bumpers, trim items made of zinc die castings or steel, trim items on large and small appliances, costume jewellery, electronic circuits, piano strings, construction and architectural hardware, plumbing fittings, electrical contacts, plastic items, and magnetic memory devices [10]. Many metals can be electrodeposited; Cu, Ni, Cr, Zn, Cd, Sn, Au, Ag, Pd, Pt and as well as many alloys; bronze (Cu-Sn), brass (Cu-Zn), Sn-Pb, Sn-Zn, Sn-Ni, Fe-Ni, Zn-Ni, Zn-Fe, Au-Cu, Ag-Pd, Ni-Pd, Co-Ni [9].

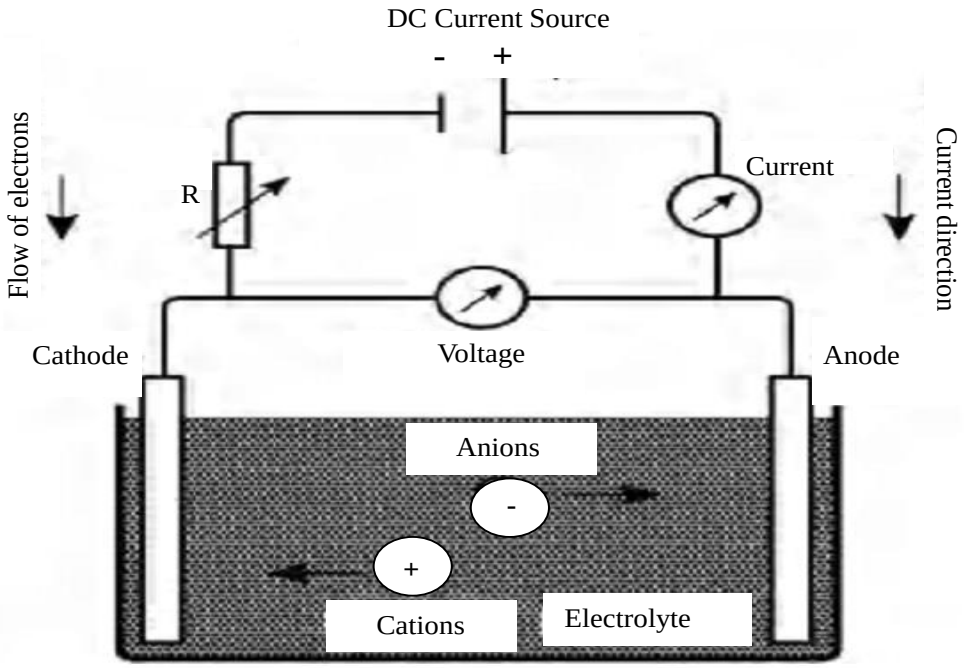


Figure 1.5 Principle of the electrochemical metal deposition process with external DC current source [5]

1.1.3 Hard Chrome Plating

Hard chromium plating is produced by electrodeposition from a solution containing chromic acid (CrO_3) and a catalytic anion in proper proportion. The metal so produced is extremely hard and corrosion resistant. The process is used for applications where excellent wear and/or corrosion resistance is required. This includes products such as piston rings, shock absorbers, struts, brake pistons, engine valve stems, cylinder liners, and hydraulic rods. Other applications are for aircraft landing gears, textile and gravure rolls, plastic rolls, and dies and molds. The rebuilding of mismachined or worn parts comprises large segments of the industry [1]. In the automotive industry, applications include not only engine parts, but also large metal form dies for auto body parts [11].

Hard chromium plating can be used in almost any situation where resistance to abrasion wear is vital. Here are some areas of applications:

- Agricultural; chain saw aluminium cylinders, chain saw teeth, hydraulic equipment shafts, cotton-picking spindles.
- Aircraft; rocker arms, valves, piston rings, turbine blades, cylinders, crankshafts, undercarriage rams, landing gear shafts, camshaft journals.
- Automotive; valve stems, shock-absorber rods, camshafts, power steering shaft, crankshafts.

- Chemical; hydraulic rams, glass molds, perforated plates.
- Electrical; turbine shafts, X-ray columns, wire drawing dies, wire drawing cones, relay components, non-magnetic parts.
- Engineering mechanical; inspection tools and gauges, cutting tools, machine tools, concrete pumps.
- Motors; cylinders, rocker arms, stub axles, fork axles, bearings, camshaft journal, cams, ball pins, piston rings, pivot pins, crank shafts, brake shafts, differential shafts, gear level shafts, gasoline pump shafts, transmission shaft, sliding pinion shafts, valves, spindle, water pump, valve tappets [12].

Hard chromium plating is also known as industrial, functional, or engineering chromium plating. It differs from decorative chromium plating in the following ways:

- Hard chromium deposits are intended primarily to increase the service life of functional parts by providing a surface with a low coefficient of friction that resists galling, abrasive and lubricated wear, and corrosion. Another major purpose is to restore dimensions of undersized parts.
- Hard chromium normally is deposited to thicknesses ranging from 2,5 to 500 μm and for certain applications to considerably greater thicknesses, whereas decorative coatings seldom exceed 1,3 μm.
- With certain exceptions, hard chromium is applied directly to the base metal; decorative chromium is applied over undercoats of nickel or of copper and nickel [1].

1.1.3.1 Advantages

The chromium plating process has been widely used for many years, is inexpensive and easy to perform. On the other hand;

- Cr films have high hardness, much larger than the corresponding bulk metal, and provide a sharp increase in wear resistance of the surface being coated. High hardness is retained up to about 350°C, but Cr can operate up to 480°C.
- Cr retains its corrosion resistance at high temperature. It is stable at high air temperature, in cool sulfuric or nitric acids solutions, in oxidizing media, and it does not tarnish in sulfur (II)-containing atmospheres up to 400°C.

- Chromium provides good adhesion with steel, nickel and copper; no peeling is observed. Additionally, it has good diffusion barrier properties.
- The friction coefficient is relatively low, especially when using lubricant.
- Micro-cracked chromium retains oil and its lubricating abilities are enhanced.
- The deposition of both very thin and thick coatings (up to 0,5 mm) is possible.
- Chromium has excellent brightness and pleasant appearance [1], [7].

1.1.3.2 Disadvantages

Several disadvantages of chromium plating are its high fatigue life debit, marginal corrosion resistance due to micro cracking, high power consumption, nonuniform coverage, poor penetration into holes and tube bores and the evolution of hydrogen in the process. Because of the hydrogen evolution, misting occurs, which leads to high air emission rates and associated adverse health, safety, and environmental risks [1]. Therefore, disadvantages could be sorted like these;

- Low ductility and possibility of cracking; the fatigue limit of Cr-plated steel is consequently reduced.
- It corrodes in HF and HCl.
- Internal stresses are rather high; embrittlement, hydrogenation and cracking are observed.
- Solderability and weldability are low; electrical conductivity is also poor.
- Current efficiency of chromium deposition is very low; in combination with the necessity of six electrons transfer it results in very high electricity consumption at low deposition rate.
- Poor deposit distribution: Cr solutions have very low throwing power and covering power.
- The deposition conditions should be very closely controlled.
- The solutions and waste water are toxic and corrosive. Chromium acid “mist” is produced by gas evolution at the electrodes [7].

1.2 Objective of Thesis

1.2.1 Robert Bosch Turkey

The Bosch Group is a leading global supplier of technology and services. Its operations are divided into four business sectors: Mobility Solutions, Industrial Technology, Consumer Goods, and Energy and Building Technology. The Bosch Group started its operations in Turkey with its branch office established in 1910 and its first factory was found in Bursa in 1972 [13]. There are three plants for injector produced in Bursa which one is for gasoline systems and another two are for diesel systems.

This thesis was carried out with the collaboration Robert Bosch Turkey Gasoline Systems. There are two types of injector which are produced. These are high-pressure piezo injector HDEV4 and high-pressure solenoid injector HDEV5 (Figure 1.6).

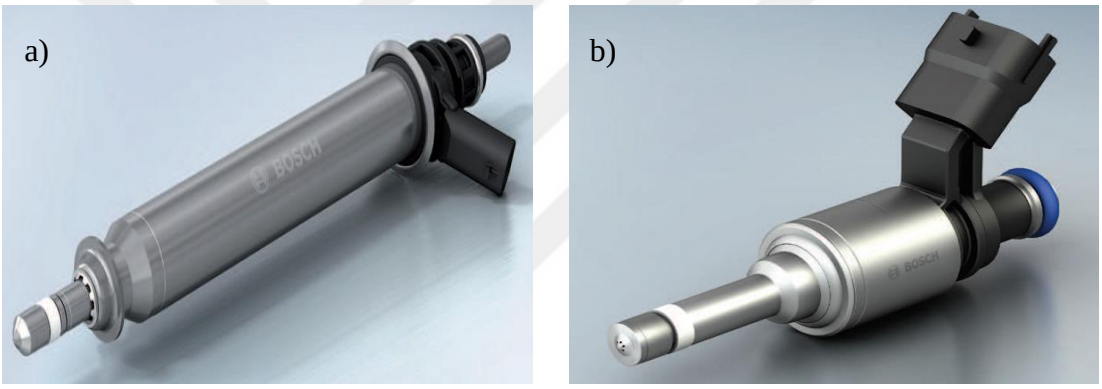


Figure 1.6 High-pressure piezo injector HDEV4 (a) and High-pressure solenoid injector HDEV5 (b) [14], [15]

HDEV4 is used for all engines of Mercedes Automotive and HDEV5 is used for another all engines of automotive industry. The aim of the thesis is to solve a problem seen on a part of HDEV5 which is hard chrome coated.

1.2.2 HDEV5 and Solenoid Armature

It is the function of the high-pressure fuel injector (HDEV) on the one hand to meter the fuel and on the other hand by means of its atomization to achieve controlled mixing of the fuel and air in a specific area of the combustion chamber. Depending on the desired operating mode, the fuel is either concentrated near the spark plug (stratified charge) or evenly distributed throughout the combustion chamber (homogeneous distribution) [16]. The high-pressure injector (Figure 1.7) comprises the following components:

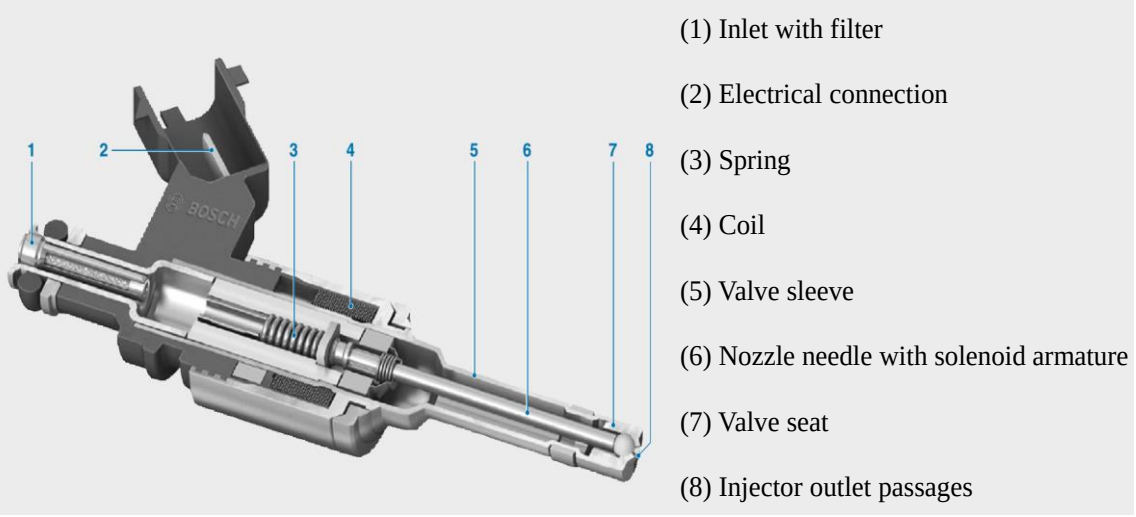


Figure 1.7 Design of HDEV5 high-pressure injector [16]

A magnetic field is generated when current passes through the coil. This lifts the valve needle off the valve seat against the force of the spring and opens the injector outlet passages [16]. When the injector opens, the solenoid armature (magnetanker) moves up and hits the stop ring. At the same time, the solenoid armature heads all needle group from to the innenpol. Because of hitting the innenpol, surfaces of solenoid armature and innenpol are coated with hard chrome coating for wear and adhesion of hydraulic (Figure 1.8). When the injector closes, it moves down and spreads that the magnet coil makes magnetic force. There are four holes on the solenoid armature which passes coming fuel. According to customer request, the surface of hard chrome coating could be one side or two side (Figure 1.9).

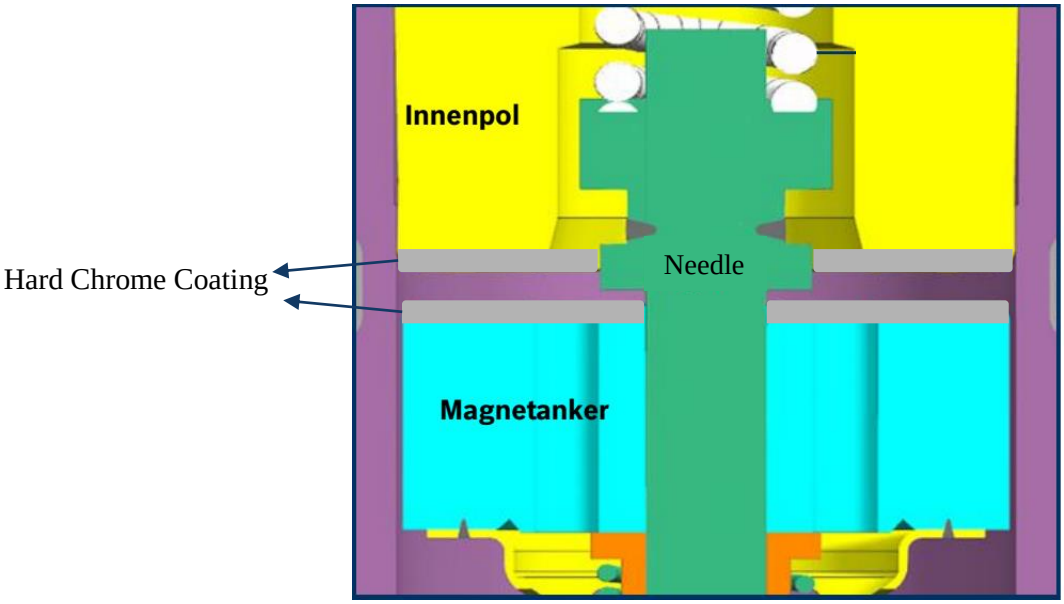


Figure 1.8 Solenoid armature, Innenpol and Needle group [17]

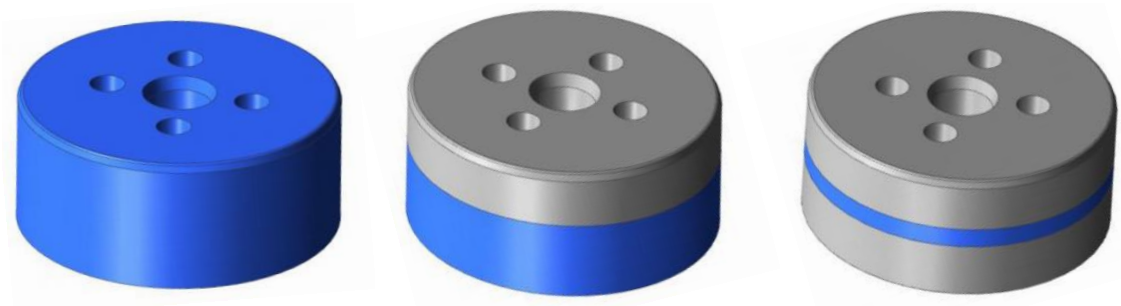


Figure 1.9 Without coating, one and two side coating of solenoid armature

The coating thickness of solenoid armature must be average 8,5 µm ± 3 µm. However, the thickness which is not planar, should be dome-shaped. The middle of the big hole where is around the thickness, must be bigger than 4 µm and the edges must be bigger than 7 µm. Yet, the problem which shows that itself on these important areas, is not fully chrome plated as required on surface. There are two type of failures which are called center and edge (Figure 1.10). The failures are detected by visual inspection and called "white spot".

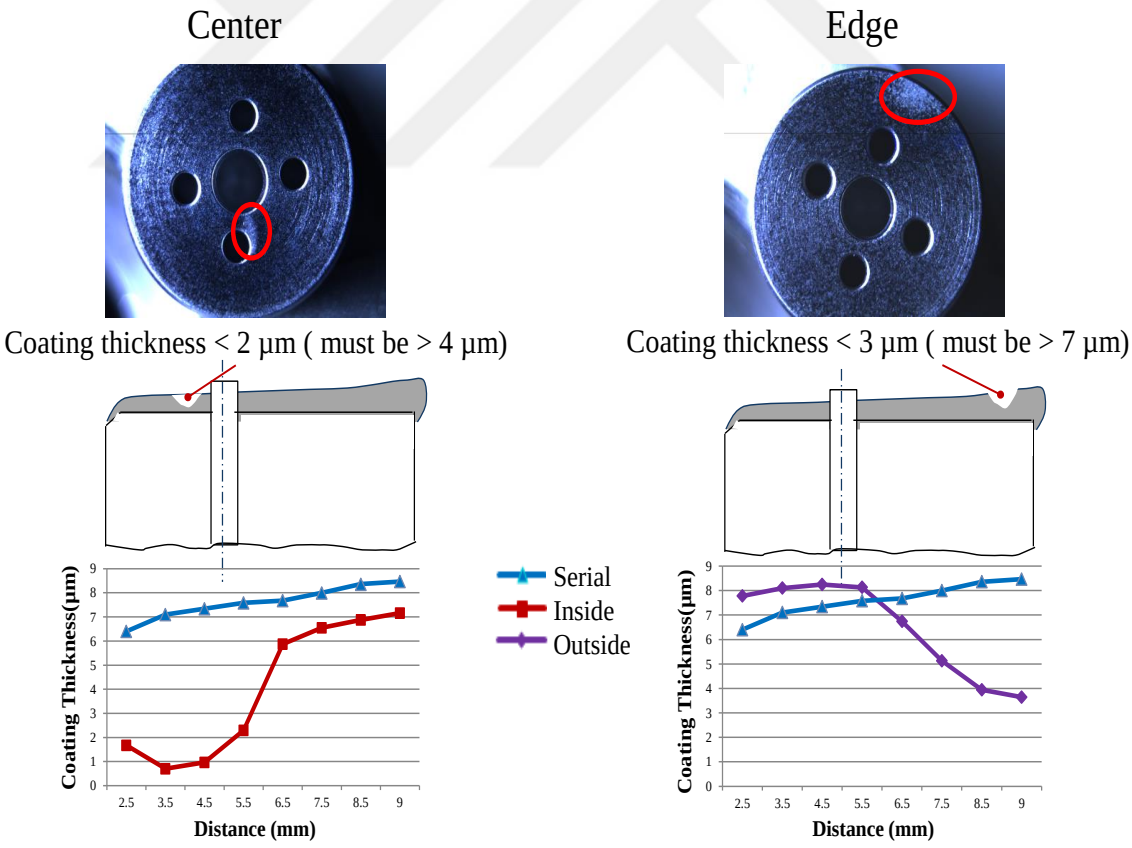


Figure 1.10 Failures of solenoid armature

If the solenoid armature with white spot assembles an injector, the injector could have a problem when it works. First aim of using hard chrome coating is improve abrasion resistance by high surface hardness, but white spot gets lower coating thickness and lower abrasion resistance so the injector might be get broken when the engine is running. Because of these, the aim of the thesis was decreasing scrape amounts as possible as minimum level.

The thesis was projected to reduce scrape rate from 2,3 to 2,07 (decreasing min %10). In short, the company produces 13,5 million solenoid armuture in a year and have to put 320000 scrapes in a scrape box. If a scrape cost is 36 cent, in yearly 112000 Euro will waste. It is also an economic side why the project was done (Figure 1.11).

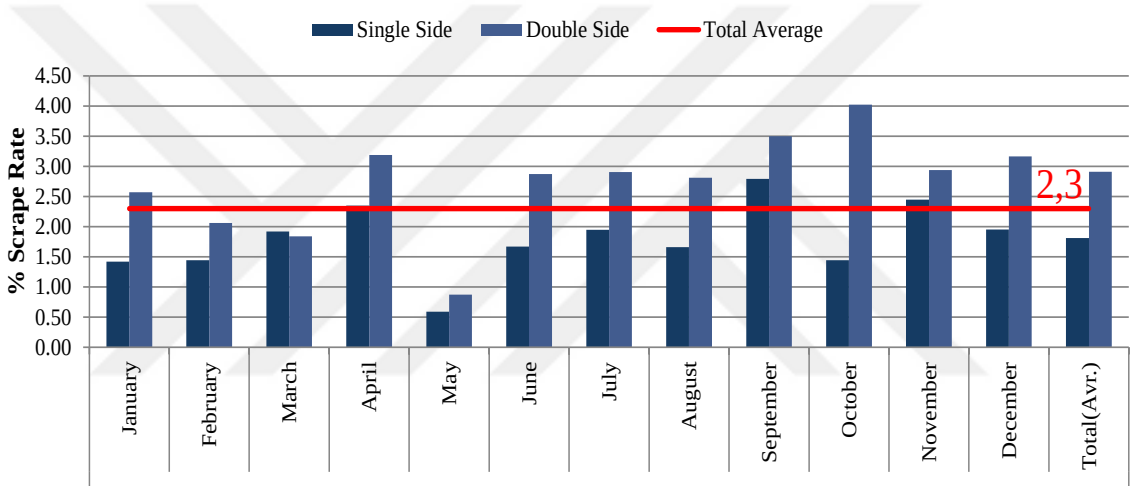


Figure 1.11 Scrape rate of solenoid armature

1.3 Hypothesis

When the finding solutions of the problem was tried, similar problems on literature and quality management methods show to ways for solving. The PMBOK® Guide [18] explains that quality management processes "…include all the activities of the performing organization that determine quality policies, objectives, and responsibilities so that the project will satisfy the needs for which it was undertaken."

There are many methods of quality management which are used on automotive and another industry. The most commonly used methods are PDCA, FMEA, 6 Sigma, Fishbone, 8D, Shainin etc. For example, Kanji and Asher [19] refer PDCA (Plan-Do-Check-Action) is used for the development of a new product based on the requirements of the customer and FMEA (Failure Mode and Effect Analysis) is used for searching a

process to describe possible causes of failure or examining a product or service to look for what can go wrong. However, these methods are not enough for analysing this problem. Therefore, “Fishbone (Cause and Effect Analysis)” was used for trying to find potential solutions to a problem and looking for the root cause [19].

Figure 1.12 shows that how to use fishbone diagram on the hard chromium plating process and which factors could be effective on the problem. According to fishbone diagram and literature searching lead the following researches and experiments:

- Optimization of anode life time
- Thicker Pt coating on anode effect on better coating and/or anode life,
- Effect of flowrate,
- Controlling and changing the chrome bath parameters;
    - Adding surfactant and changing surface tension,
    - The chrome bath age and quality,
    - Following H_2SO_4/CrO_3, Cr^{+3} concentration and conductivity values
    - The chrome bath cleanliness
- Effects on raw part geometry and quality;
    - First and second side differences,
    - Two different suppliers’ samples.

Figure 1.12 Fishbone analysis and probable effective factors in the process

CHAPTER 2

EXPERIMENTAL STUDIES

2.1 Hard Chrome Plating Process at Robert Bosch Turkey

Chromium solution firstly should be prepared for refers to electrolyte for a hard chrome plating process. Then the material and geometry of the anode and the current density should be determined for formed an electrical field.

Chromium trioxide is the most common source of hexavalent chromium ions. Even though chemically incorrect, chromium trioxide is usually referred to as chromic acid. The acid is formed in aqueous solution [20]. Chromium solutions consist of chromic acid and catalysts. Modern solutions with two catalysts have a current efficiency of more than %20 and in case of high speed plating up to %50. The basic solution made up with 250 g/l CrO_3 and 2,5 g/l H_2SO_4. These solutions are cheap to make up, but expensive to operate. The current efficiency is usually just above %10. Consequently, a longer plating time is required and more electricity used. Hardness is lower and brightness hardly appears [21]. Because of this lower performance, different type of catalysts is added to chromium solutions for help to electrodeposition of chromium. Also, current density and temperature could be changed to high performance.

In the hard chrome plating process at Bosch Turkey, CrO_3 with water, % 1-1,5 H_2SO_4 and a make-up solution was prepared for the electrolyte. The make-up is a kind of catalyst and is produced by Enthone GmbH. The company explains their catalyst in Figure 2.1, when make-up adds to step by step it can be seen the hardness and efficiency increase till 50 ml/l, maximum hardness is 1064 HV and maximum efficiency is %25. Therefore, crack density goes up to continue.

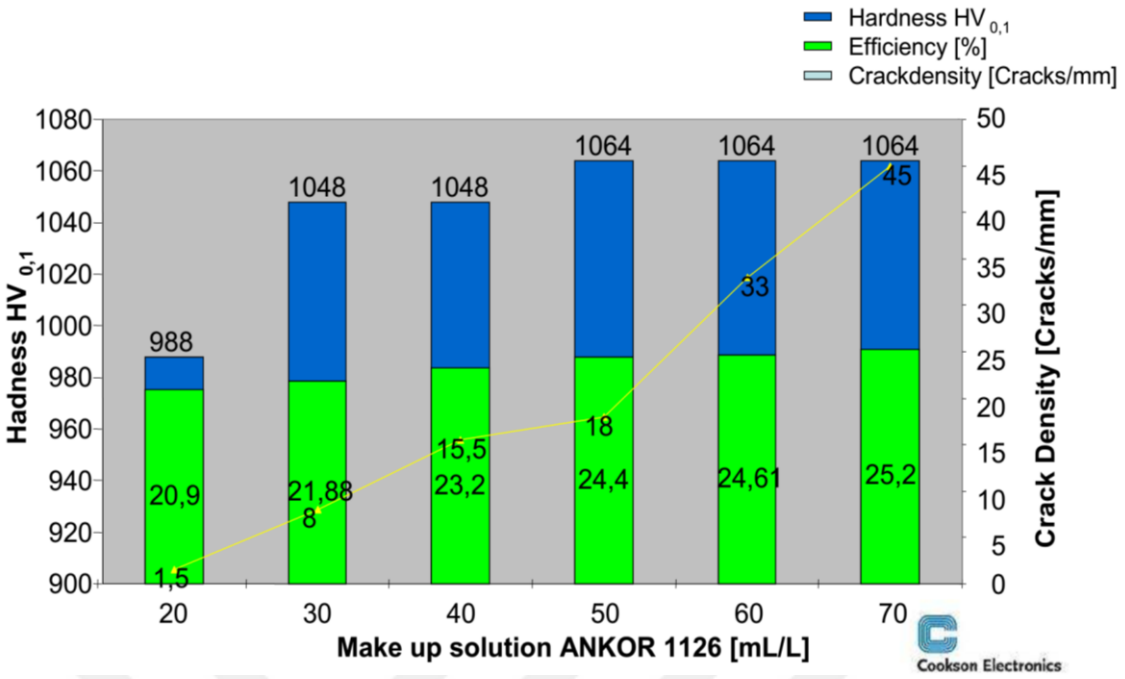


Figure 2.1 Effect of make-up solution [22]

According to Lausmann [21], micro cracks are covetable characteristics of hard chromium electrodeposits. Micro cracks form during electrodeposition when the tensile stress exceeds the cohesive strength of the chromium. The sulphate concentration, current density, temperature also the concentration of other catalyst (e.g. make-up) effects the micro crack density. If the micro crack density is too low, then the micro cracks will become larger and may expose basis metal. Because of these reasons, the crack density is as important as efficiency and hardness. So, the make-up solution of 70ml/l concentration is used in the hard chromium process at Bosch Turkey.

Before coating which is called surface preparation, is as important as coating process. Newby [1] and Tracton [11] define that, all impure (oil, grease) and passive films (oxides and sulphides) must be removed from substrate before hard chrome plated. In addition to cleaning, surface-activating processes are also significant in preparing the base metal for hard chromium plating.

Figure 2.2 illustrates that circle of hard chromium process in Robert Bosch Turkey. Firstly, the parts are loaded, before coating they should be cleaned and etched by current for activated the surface. Cleaning and etching of steel before plating is needed to ensure adherence of the chromium deposits. When the parts are started to plating; the chrome tank pumps the electrolyte on surface of parts, at the same time current is started to going on them. Table 2.1 shows that parameter of hard chromium plating

process. After coated, rinsing, drying, X-Ray measurement for coating thickness and visual inspection for separate scrap are followed to finish process respectively.

Table 2.1 Parameter of hard chromium process

Flow Rate	10000 l/h
Current Density	1,8 A
Efficiency	% 20 - 25
Area of Surface	74,79 mm^2
Current Density	48 - 60 A/dm^2
Time	160 - 170 seconds
Temperature	68 ± 2 °C
Thickness	8,5 µm ± 3 µm

The electron current is additionally provided from an external source in the hard chrome coating process. Generally, lead or lead alloys are used for that however because of toxic lead slurries in modern systems are used platinised titanium [4], [21]. That is why, the platinised titanium is used in the hard chrome plating process at Bosch Turkey. Yet, the platinised titanium has also important disadvantages such as, limited life and inadequate in indication of when they are becoming inoperative [20].

The solenoid armature consists of a ferromagnetic material, which makes a magnetic field when an electrical current comes. The material of solenoid armature which is X12CrS13 (1.4005), elemental composition is given in Table 2.2.

Table 2.2 Elemental composition of solenoid armature

Element	C	Si	Mn	P	S	Cr	Mo	N
%	Max. 0,025	0,5 – 1,0	0,7 – 1,54	Max. 0,045	0,25 – 0,35	11,9 – 12,6	0,3 – 0,6	Max. 0,025

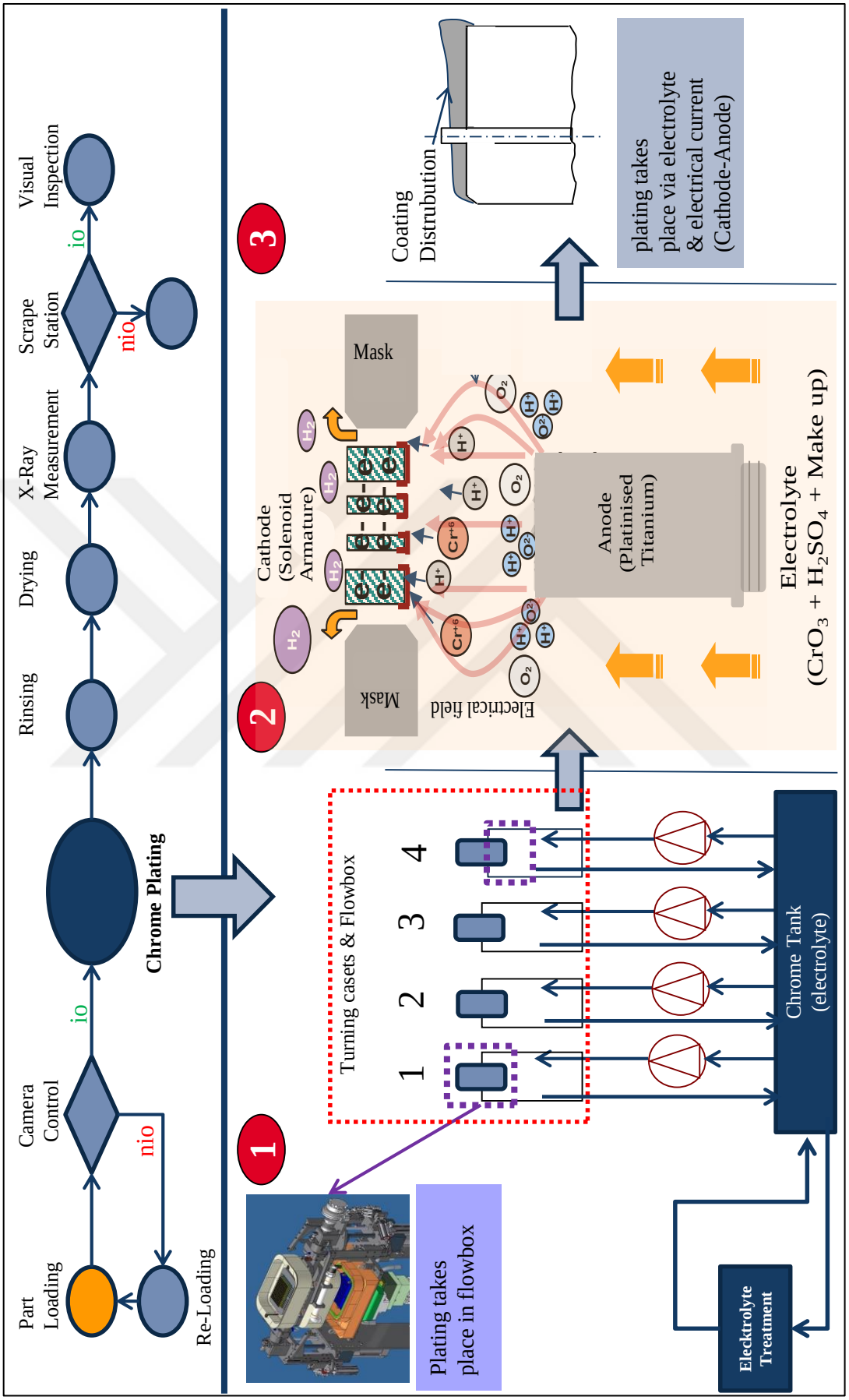


Figure 2.2 Hard chrome plating process at Robert Bosch Turkey

2.1.1 Principles of Deposition

There are two theories for the mechanism of chromium deposition since investigations began and continues today. First one, 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 [21]:

$$Cr^{+6} \rightarrow Cr^{+3} \rightarrow Cr^{0} \quad (2.1)$$

However, E.Müller was also support the theory of direct deposition of chromium from the hexavalent state. But for this theory has still many open questions [21].

$$Cr^{+6} \rightarrow Cr^{0} \quad (2.2)$$

The two theories are still widely discussed today. The first theory which is in steps, accepted for hard chrome process in Bosch Turkey.

Deposition by reduction in steps explain like that, chromium trioxide (CrO_3) is used as a metal carrier in most commercial chromium baths. As it dissolves in water chromic acid form [21]:

$$CrO_3 + H_2O \leftrightarrow H_2CrO_4 \text{ (mono) chromic acid} \quad (2.3)$$

$$2\ CrO_3 + H_2O \leftrightarrow H_2Cr_2O_7 \text{ dichromic acid} \quad (2.4)$$

Equilibrium is always established in aqueous solutions:

$$2\ CrO_4^{-2} + 2\ H^{+} \leftrightarrow Cr_2O_7^{-2} + H_2O \quad (2.5)$$

Due to high chromate content in the chromium baths this equilibrium is pushed strongly to the right, i.e. dichromate is chiefly present in these baths [21].

If it is studied the gross reaction of the deposition:

$$2\ Cr + 7\ H_2O \leftrightarrow Cr_2O_7^{-2} + 14\ H^{+} + 12e^{-} \quad (2.6)$$

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.

$$Cr_2O_7^{-2} + 14\ H^{+} + 6e^{-} \leftrightarrow 2\ Cr^{+3} + 7\ H_2O \quad (2.7)$$

Due to the high consumption of hydrogens 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 [21]:

$$Cr^{+3} + e^- \leftrightarrow Cr^{+2} \quad (2.8)$$

$$Cr^{+2} + 2\ e^- \leftrightarrow Cr \quad (2.9)$$

$$H^+ + e^- \leftrightarrow H \quad (2.10)$$

$$2\ H \leftrightarrow H^2 \quad (2.11)$$

Figure 2.3 the resulting potential-pH diagram (Pourbaix diagram) is shown for hydrated compounds. Table 2.3 shows the most important equilibration reactions of chromium without participation of electrons. The equilibration is adjusting itself in the electrolyte. The pH dependencies for these reactions with a participation of hydrogen ions [23].

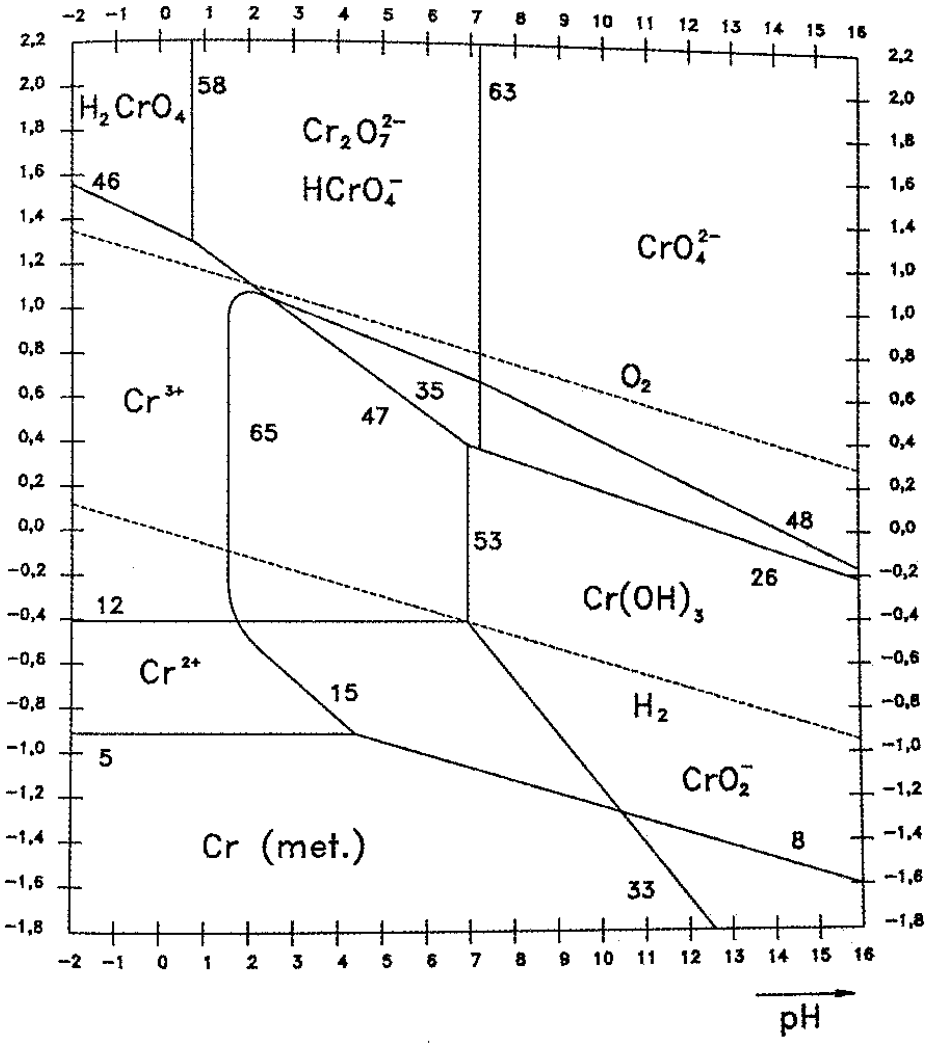


Figure 2.3 Potential-pH-Diagram [23]

Table 2.3 Equilibrium reactions of chromium with water [23]

No	Equilibrium Reactions	Concentration
1	$H_2CrO_4 \leftrightarrow HCrO_4^- + H^+$	$log\frac{[HCrO_4^-]}{[H_2CrO_4]} = -0.75 + 1\ pH$
2	$2\ H_2CrO_4 \leftrightarrow Cr_2O_7^{-2} + H_2O + 2\ H^+$	$log\frac{[Cr_2O_7^{-2}]}{[H_2CrO_4]} = 0.18 + 2\ pH$
3	$H_2CrO_4 \leftrightarrow CrO_4^{-2} + 2\ H^+$	$log\frac{[CrO_4^{-2}]}{[H_2CrO_4]} = -7.20 + 2\ pH$
4	$HCrO_4^- \leftrightarrow CrO_4^{-2} + H^+$	$log\frac{[CrO_4^{-2}]}{[HCrO_4^-]} = -6.45 + 1\ pH$
5	$Cr_2O_7^{-2} + H_2O \leftrightarrow 2\ HCrO_4^-$	$log\frac{[HCrO_4^-]^2}{[Cr_2O_7^{-2}]} = -1.68$
6	$Cr_2O_7^{-2} + H_2O \leftrightarrow 2\ CrO_4^{-2} + 2\ H^+$	$log\frac{[CrO_4^{-2}]^2}{[Cr_2O_7^{-2}]} = -14.59 + 2\ pH$

Evaluating the reactions 1 to 6, various conditions can be deriveded from the situation in the electrolyte and the cathode film. The equilibration is self-adjusting (after make-up) in the solution according to the reaction shown in Figure 2.4 [23].

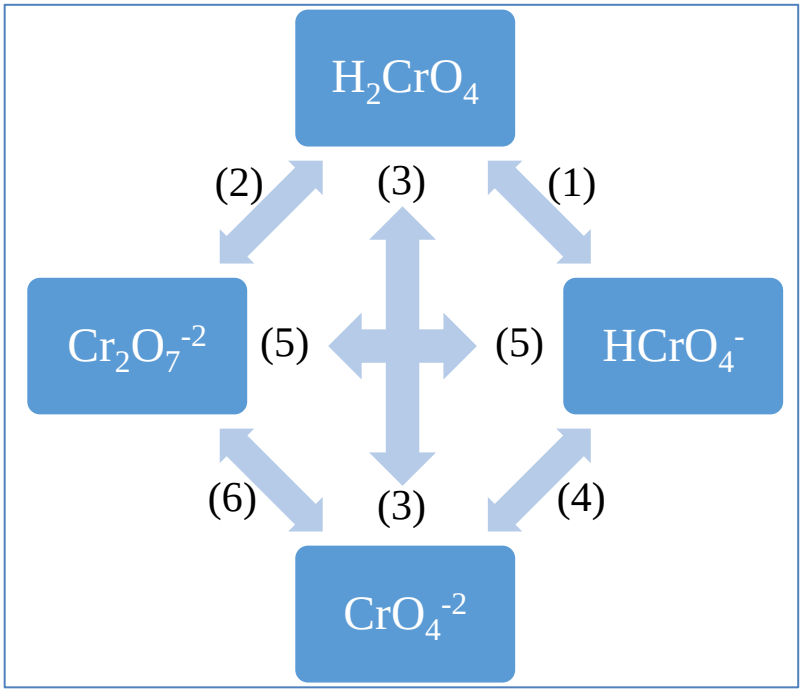


Figure 2.4 Equilibration after make-up [23]

Insoluble lead alloys serve as anodes, although in modern systems platinum-plated titanium has replaced the lead anodes in order to prevent the creation of toxic lead slurries [4]. The surface of lead will be converted to lead oxide as soon electrolyzes starts. Water will be oxidized in order to form oxygen. Lead chromate can be formed by reactions of lead oxide with chromates [21]:

$$PbO + CrO_4^{-2} + 2\ H^+ \rightarrow PbCrO_4 + H_2O \quad (2.12)$$

$$2\ H_2O + 4e^- \rightarrow O_{2(g)} + 4\ H^+ \quad (2.13)$$

These reactions take place on all types of solutions based on chromic acid. The formation of lead chromate should be avoided in order to increase anode life. The anode erosion takes place when lead oxidizes to lead dioxide. Anodes must be therefore carefully selected, size and applied. These reactions do not take place when platinized titanium is used. Lead has to be added to the solution in order to form a thin lead film on the surface of the platinized titanium. Supply house of proprietary chromium compounds can offer respective addition agents suitable for the use of platinised titanium anodes [21].

2.1.2 Surface Tension of the Chrome Bath

The surface tension of liquid is defined as the inward force acting on the surface of the liquid due to the attraction of the molecules below the surface, or the property, due to molecular forces, existing in the surface film of all liquids which tends to contract the volume into a form with the least surface area; the particles in the surface film are inwardly attracted, thus resulting in tension [24].

Baths of electroplating systems generally contain surfactants, also known as wetting agent. Surfactant are surface active species because of this they move by accumulating at an interface or a surface. They are oriented with hydrophilic head into solution at an air-electrolyte interface and the hydrophobic tail to the air side. In this way, they reduce the surface tension of a liquid [25].

Surfactants requirements for the electroplating industry include:

- Chemically stable surfactants without side effects for chromium solutions,
- Low surface tension,
- Low foam formation,
- Chemically pure surfactants with no free ions,

- The reduction of the surface tension should take place by speedy diffusion of the surfactants soluble in water and electrolyte so that no undissolved particles impair the chromium deposit [21].

Chromium deposition is accompanied by a considerable evolution of hydrogen gas at the cathode surface. These bubbles rise to the electrolyte surface and explode, hence a mist of the electrolyte is formed which is extremely hazardous to health, and indeed to nearby equipment. However, if a surfactant is added, the surface tension can be reduced from 70 to 20 mN/m and then extent of chromic acid mist formation is greatly reduced [25]. Generally, fluorinated surfactants which are used in the process, consist of the major types are amines of perfluoralcyl-sulphonic-acids ($C_8F_{17}SO_3N(C_2H_5)_4$) [21].

The size of the uprising gas bubbles becomes smaller with lower surface tension (Figure 2.5). This small gas bubbles do not bring enough kinetic energy to the solution surface to generate chrome coating mist when compared to bigger bubbles. The size of the gas bubbles determine the amount of energy released by the blowing bubbles. Smaller diameter gas bubbles virtually eliminate chrome misting of the plating solution [21], [26], [27].

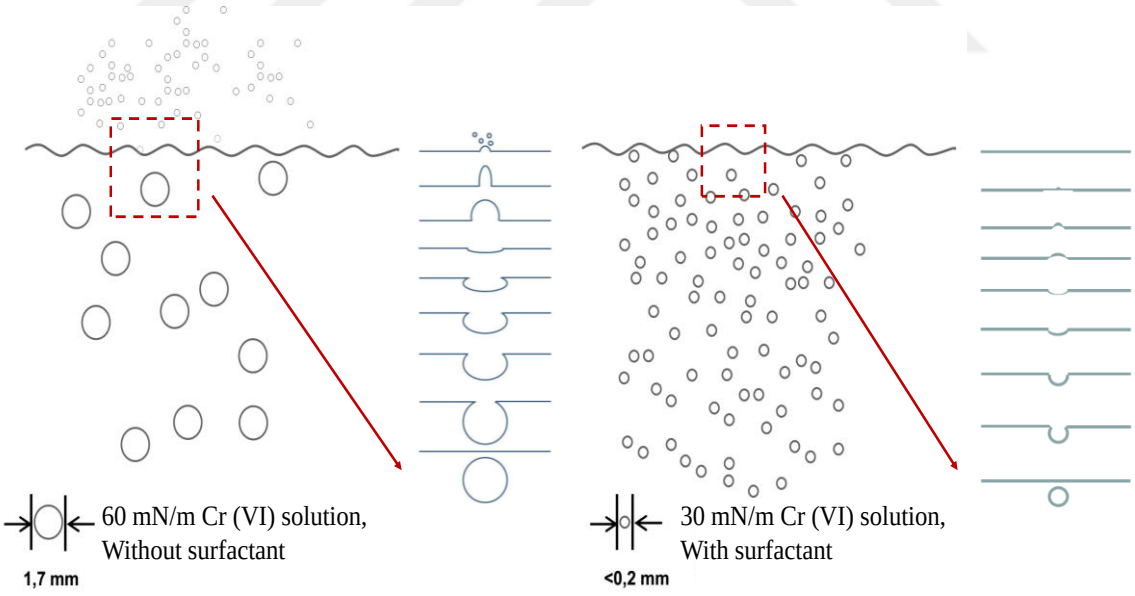


Figure 2.5 Effect of surfactant on gas bubbles [27], [23]

However, the surfactants were not used in the hard chrome plating at Robert Bosch Turkey. It could be affected the white spot problem when processing the chrome bath without this kind of surfactants. ANKOR® Dyne 30 MS which was used for this experiment, was supplied from Enthone GmbH who was also provided the chrome bath

and make-up solution. They explain that their product [26], "ANKOR® Dyne 30 MS is production proven to lower surface tension to 30 dyne/cm (mN/m) or below, eliminating air borne Cr(VI) emission." (Figure 2.6).

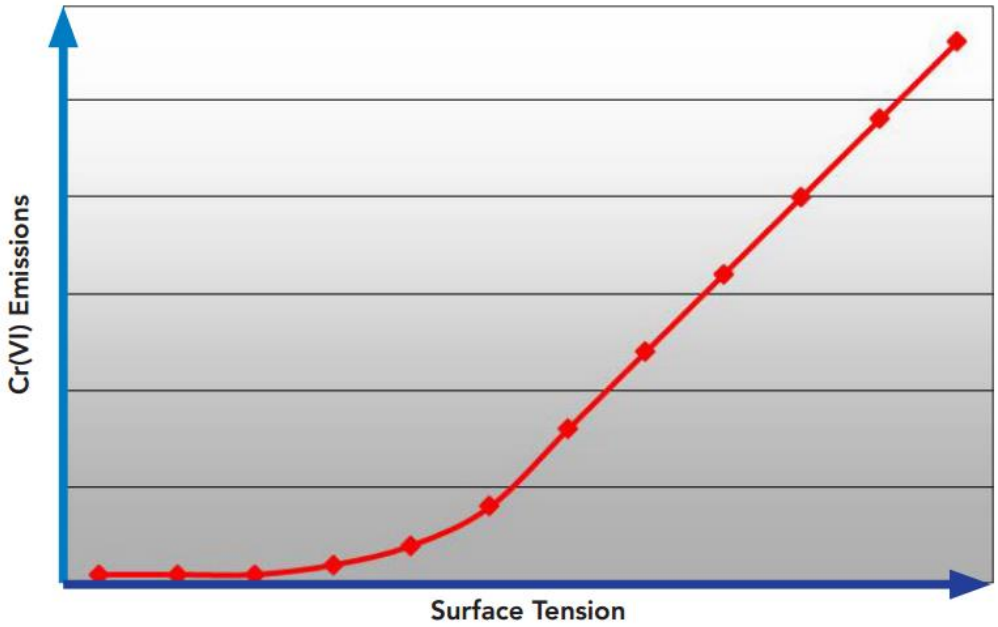


Figure 2.6 Effect of surface tension on chrome mist elimination [27]

2.2 The used Devices and Programs

Energy dispersive spectroscopy (EDS) is used for the chemical characterization or elemental analysis of a sample. EDS makes use of the X-ray spectrum emitted by a solid sample bombarded with a focused beam of electrons to obtain a localized chemical analysis. All elements from atomic number 4 (Be) to 92 (U) can be detected in the principle [28].

The coating thickness is measured with X-ray fluorescence (XRF) which is a coating thickness measurement method used by bombarding with gamma rays or high energy X-rays. The device is supplied by Helmut Fischer GmbH, Germany. The device has advantages than other the coating thickness measurement of methods:

- Simple sample preparation,
- Short measurement times,
- No chemicals are used [29].

Nanoindentation is a new method to characterize material mechanical properties on a very small scale. Test methods include indentation for comparative and quantitative hardness determination and scratching for evaluation of wear resistance and thin film adhesion. The coating thickness which is bigger than 5 nm, can be evaluated [30].

Sita bubble pressure is a way for measure the surface tension of the chrome bath (Figure 2.7). The principle of the method is the air is bubbled into the solution through a PTFE capillary. After the pressure of the bursting bubble is measured and calculated to surface tension. The device is supplied by Sita Mess-Technik GmbH, Germany.



Figure 2.7 The SITA pro line t15

Laser interferometer is used for measurement the very small values which are not achievable any other way. It works by merging two or more sources of light to create an interference pattern, which can be measured and analysed. The device is supplied by AMETEK (Zygo) Germany GmbH [31].

Finite Element Method (FEM) is a numerical technique for finding approximate solutions to boundary value problems for differential equations [32]. The hard chrome plating process is a closed system, so it cannot be seen inside when the plating is gone. Because of this, the FEM is helped for the closed system.

CHAPTER 3

EXPERIMENTAL RESULTS

3.1 Preliminary Tests

Some analyses were done at the white spot as the EDS analyse, the coating thickness and hardness measurement lastly take pictures on the light microscope. First of all, the EDS analyse demonstrated that there was no another element at the white spot (if atomic number is higher than three). Then, the coating thickness showed that the area of white spot thickness was lower than as required. On the other hand, the hardness showed also there were no differences between the area of the serial and the white spot. At the last, the light microscope pictures of the white spot were looked different as usual (Figure 3.1, Table 3.1).

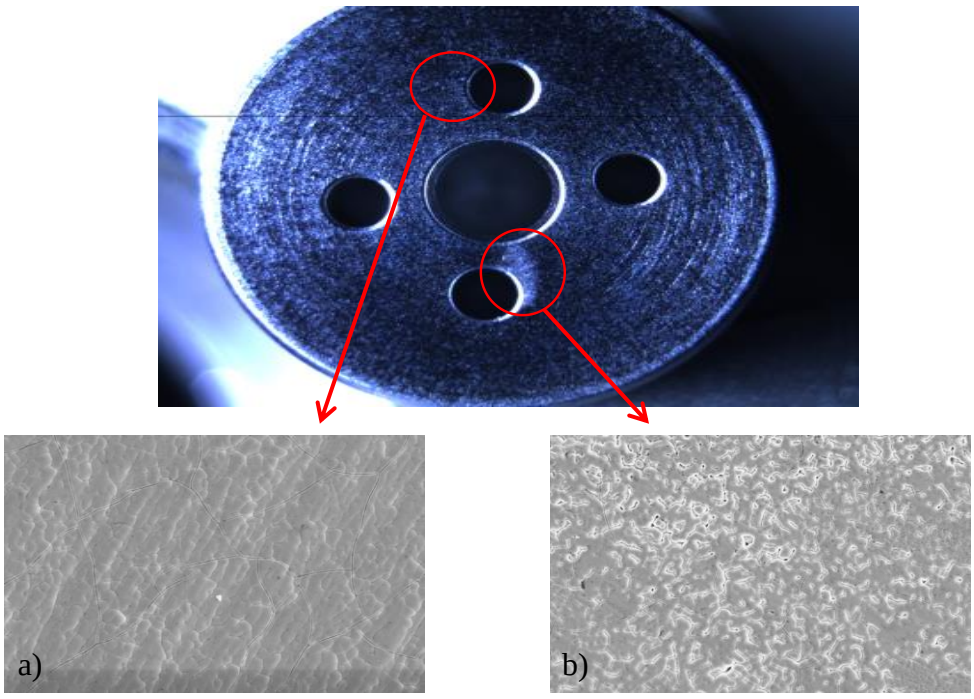


Figure 3.1 Photos of light microscope at the hard chrome coated surface
a) serial b) white spot

Table 3.1 The EDS analyse, the coating thickness and hardness measurement of the hard chrome coated surface at serial and white spot

	Serial	White Spot
EDS	% 100 Cr	% 100 Cr
Coating Thickness	7,2 µm	1,1 µm
Hardness	1200 - 1300 HV	1200 - 1300 HV

3.2 Anode Life Time

New anodes were started to use in each flow-box, the scrape rate showed a quite decrease (Figure 3.2). The scrape rate results were calculated before and after changed anode on ten days.

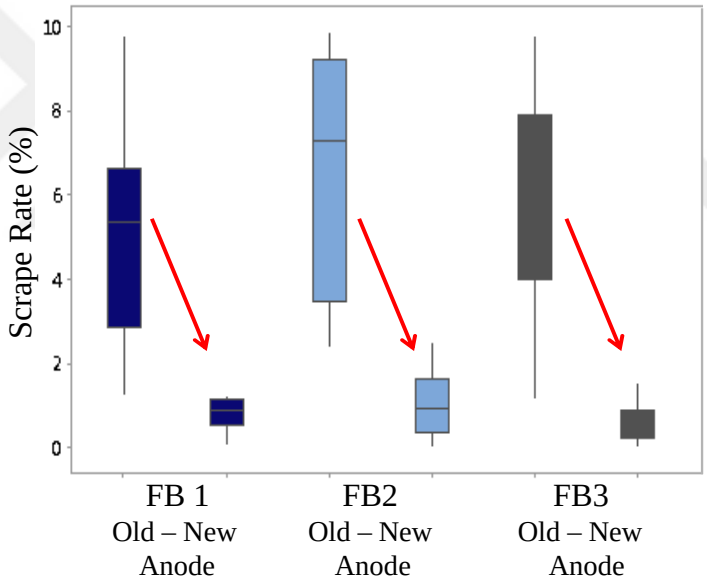


Figure 3.2 Effect of changed anode

According to the effect of changed anode, when the coating amount increase how to change the scrape rate was analysed. Figure 3.3 shows that except of other effects in the process the scrape rate goes up dramatically from % 2,4 to % 4,5 between eight hundred thousand coating times to one million. It can be clearly seen that the anode has a life time and when the coating amount increases over time, the efficiency of anode decreases.

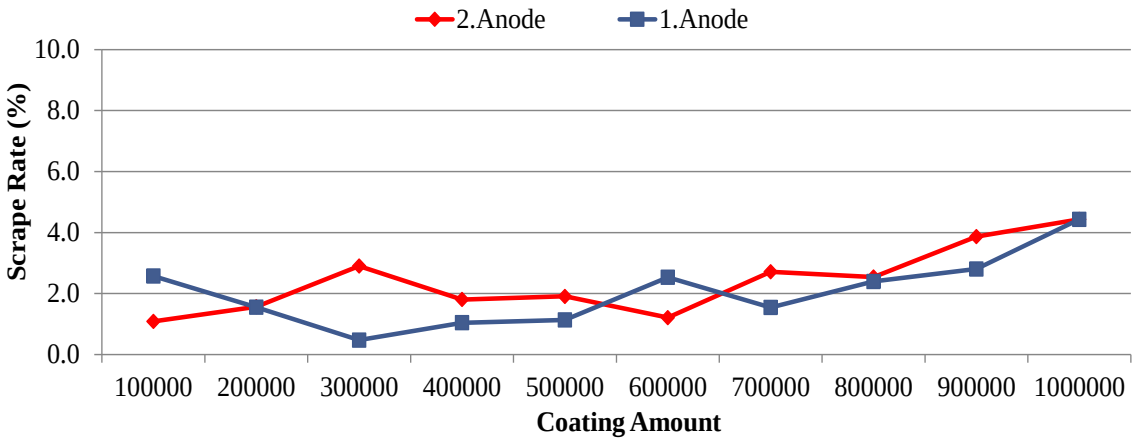


Figure 3.3 Relationship between the scrape rate and the coating amount

The anode life time could be optimized regarding the anode cost and the scrape amount. Every flow-box has 104 anodes and one of the anode cost is 68 €, a scrape is 0,36 cents. (3.2) equant shows that when the scrape amount is 19645, the anodes cost of flow-box is amortised. Figure 3.4 shows that the anodes should not been continued to use after one million coating.

$$68 \times 104 = 7072€ \tag{3.1}$$

$$7072 \div 0{,}36 = 19645\ scrape \tag{3.2}$$

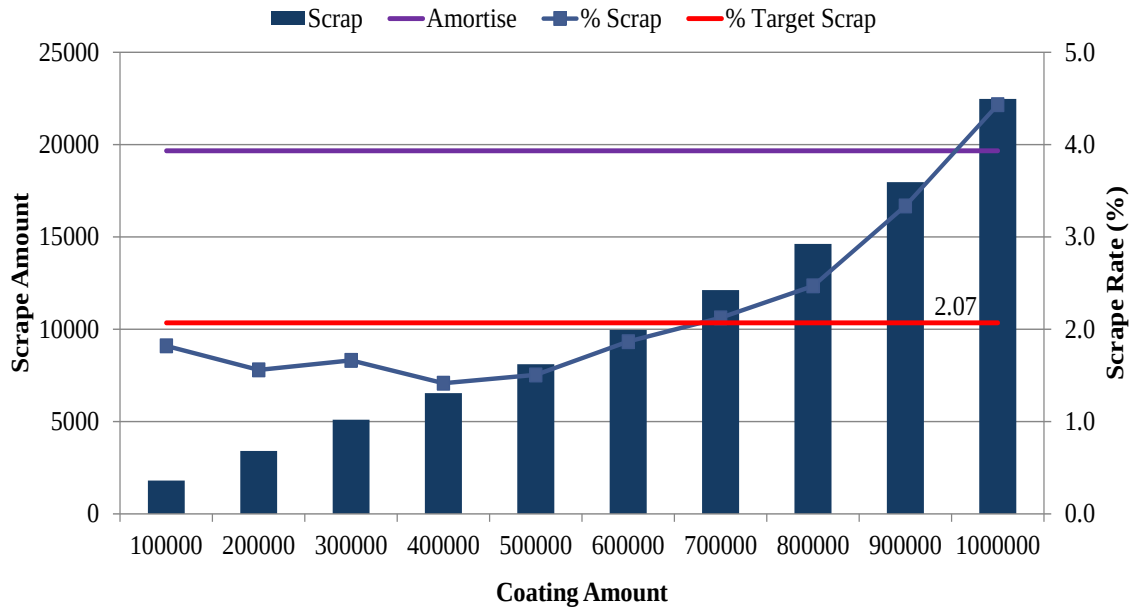


Figure 3.4 The amortise of the anode cost

Therefore, the innenpol (Figure 1.8) is coated in the same process. There is no white spot on the innenpol of the hard chrome coated surface. However, when the efficiency of the anode counteracts, a white hole is seemed on its. The coated area of an innenpol (≈94mm^2) is more extensive than a magnetic armature´s. Therefore, the anode life of the innenpol is shorter. Normally a 10-micron platinised titanium anode is used in the process. It means that the titan anode has 10 µm thick platinum coated and is able to coated approximately 300000 coating times. When the platinum coating thickness of the anode was increased to 20 µm, the anode life significantly increased approximately two times more (Figure 3.5).

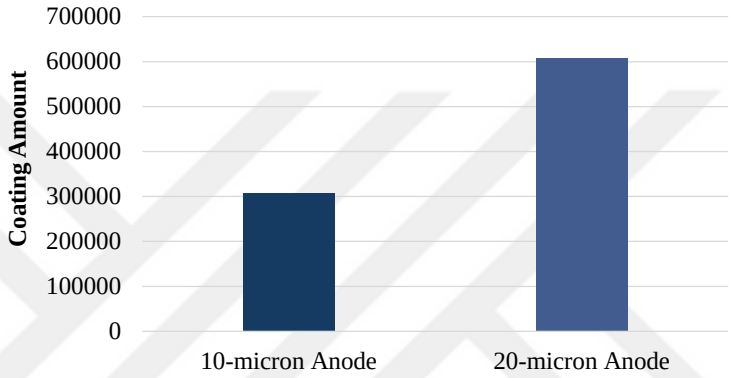


Figure 3.5 Relationship between the coating amount and using different platinum coating thickness of the anode

3.3 Flowrate

The common chrome tank pumps the electrolyte every flow-box with a flowrate. The electrolyte should cover the all surface of magnetic armature homogenous and as required coating form. So, the flowrate is one of the most important parameter for the process. Because of this, firstly the parameter of flowrate should be checked it was enough for covered or not.

As the mentioned before, the hard chrome process is a closed system so before the main experiments the FEM simulation is used for show a way. First step was created different values of the flowrate simulation. The serial parameter was 10000 lt/h so according to this, one of different value should be higher and another one should be lower than serial´s. In the process when the electrolyte comes to flow-box after it branches to tubes which are reached the magnetic armature. Normally, mouth of the pipe should be opened and incident electrolyte should reach over the cathode surface.

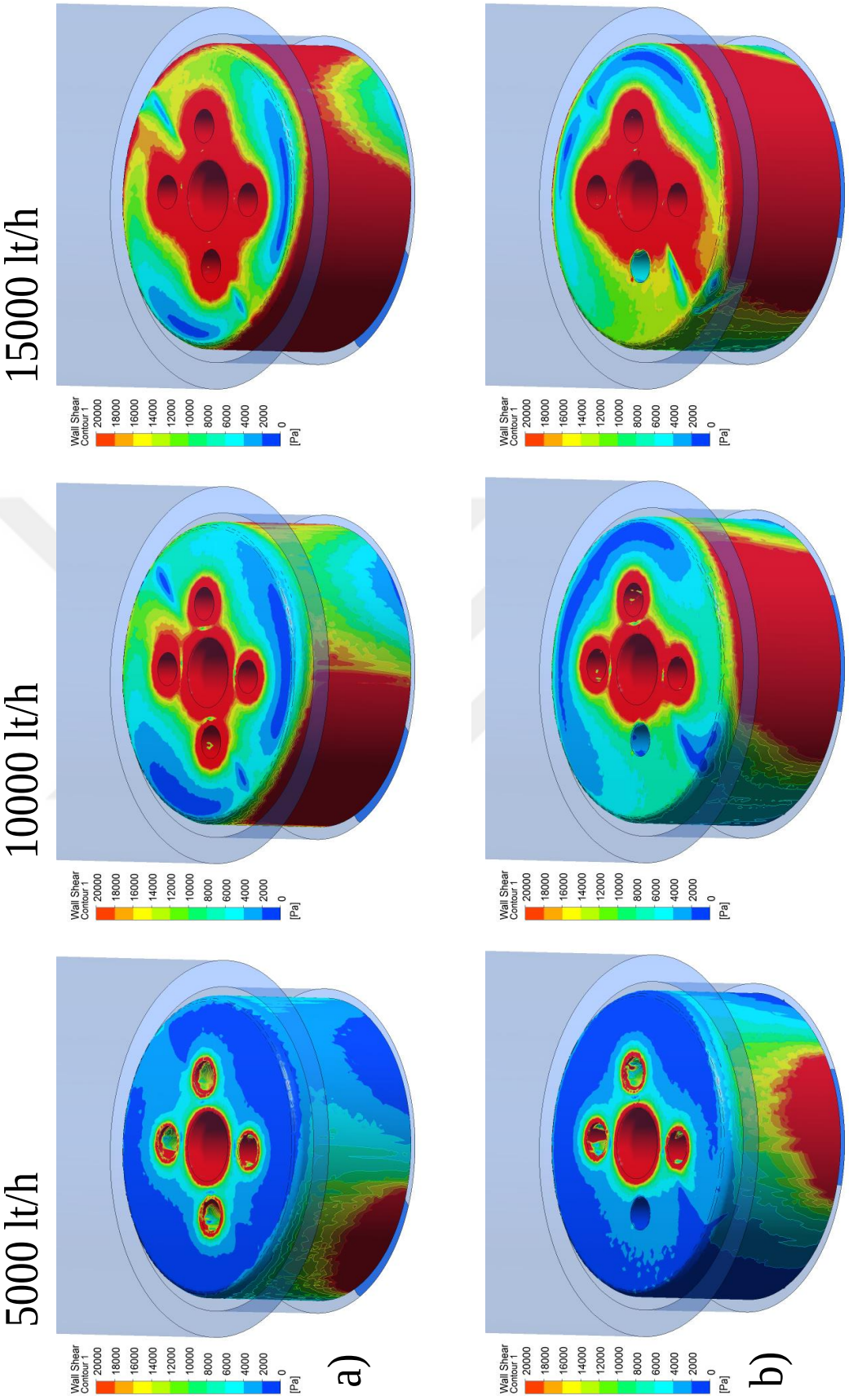


Figure 3.6 Effects of flowrate with using FEM on first side of solenoid armature
a) Best case b) Worst case

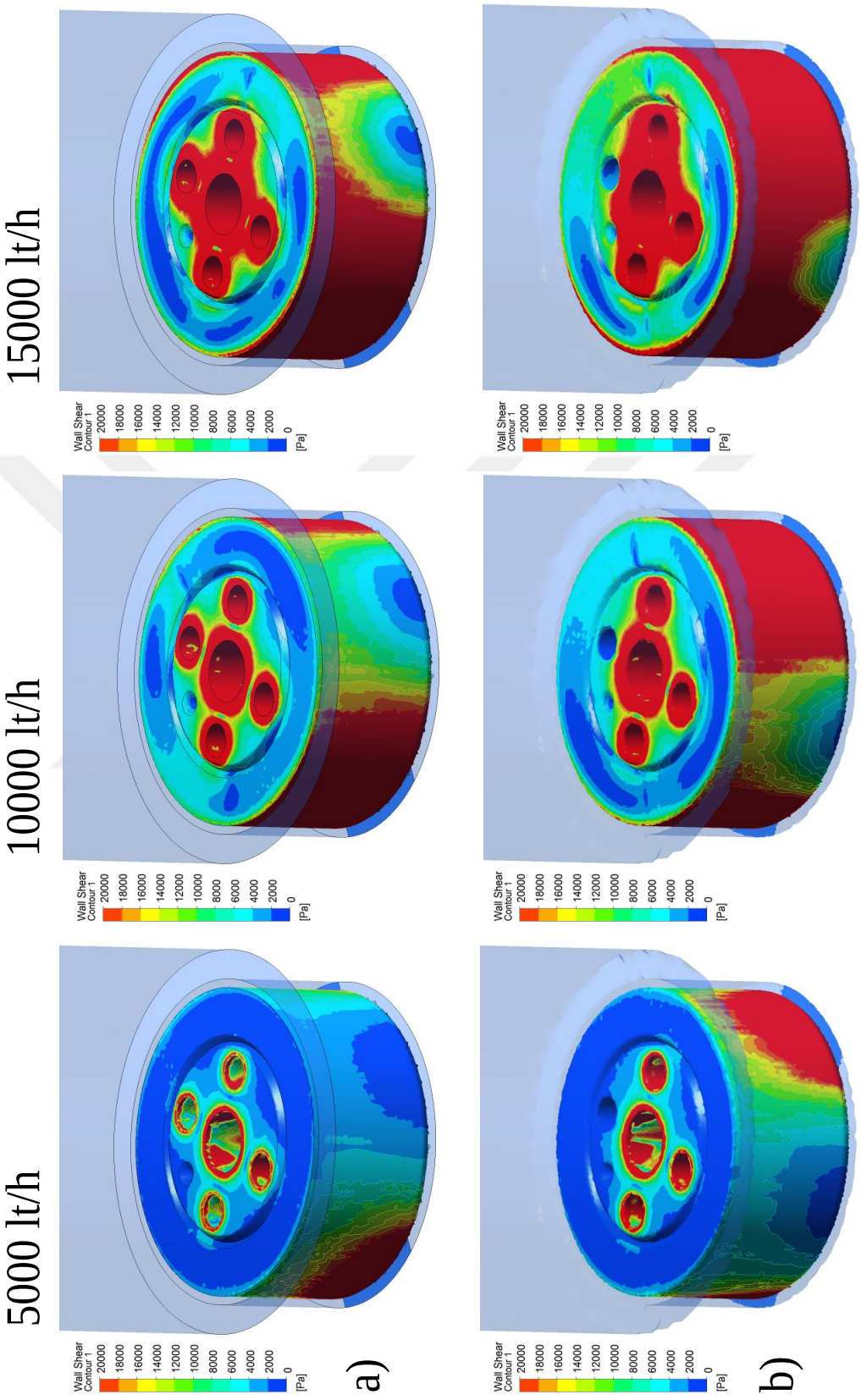
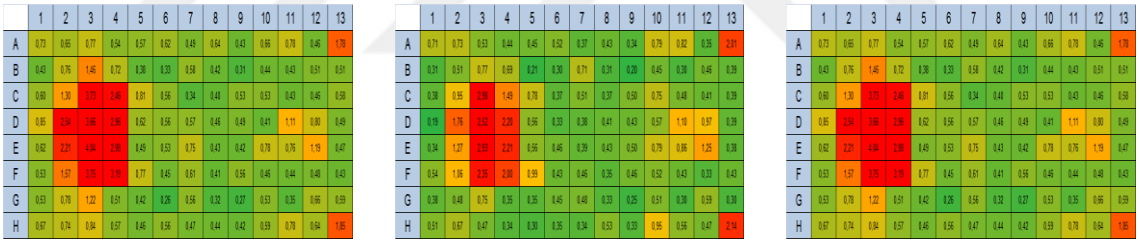


Figure 3.7 Effects of flowrate with using FEM on second side of solenoid armature a) Best case b) Worst case

On the other hand, it is possible to solenoid armature could revolve around left or right and one of mouth of pipes might be closed. One of the failures which is white spot seems on between big hole to one of small holes, is called center failure. In addition, FEM can be simulated situation of closed one of mouth of tubes then is showed that this situation. Therefore, it can be seen the inside failure have a connection or not with the closed pipe. If all mouths of pipes open which is called best case, if one of mouth of pipe closes which is called worst case.

Figure 3.6 and Figure 3.7 show that the different values of the flowrate as lower is 5000 lt/h, serial is 10000 lt/h and higher is 15000 lt/h effect on first and second side of the solenoid armature with using FEM at the best and worst case. It can be seen clearly that, the higher flowrate covers the first and second side of the solenoid armature at both cases and more effective than the lower flowrate. Nevertheless, even though the worst case is happened, the higher flowrate is eliminated the worst case.

Every flow-box can be coated 104 samples in a coating time. The failures appear which position in flow-box was analysed in Figure 3.8. It is clear to see that most of scrapes seem almost same positions in all flow-boxes.



FB 1 FB 2 FB 3

Figure 3.8 The scrape distribution in each flow-boxes at serial parameter 10000 lt/h

The main experiment was done in the process according to the results of FEM simulation and the scrape distribution in each flow-boxes. It was planned, the lower flowrate was near the serial parameter (8000 lt/h) and the higher flowrate was outstanding of the FEM simulation and the serial parameter (20000 lt/h). Therefore, it can be seen clearly differences effect of between the higher and lower flowrate in the process.

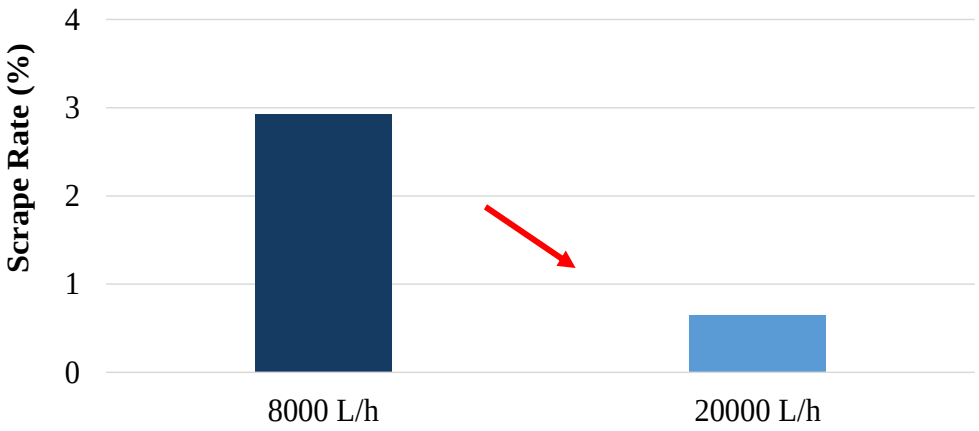


Figure 3.9 Relationship between the scrape rate and the higher and lower flowrate

Figure 3.9 shows evidently that, higher flowrate had less scrap than the lower flowrate. At the same time the scrape distribution was changed with higher flowrate, which is shown in Figure 3.10. In addition, the scrape distribution of the lower flowrate had similar picture as serial.

a)

	1	2	3	4	5	6	7	8	9	10	11	12	13
A	0.84	0.00	0.00	0.84	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
B	0.00	0.00	3.36	0.00	1.68	0.00	0.00	0.00	0.00	6.72	0.00	1.68	0.00
C	0.00	0.84	0.00	5.88	0.00	1.68	0.00	0.00	0.00	0.00	2.52	0.00	0.00
D	0.00	0.00	10.92	0.00	9.24	0.00	0.00	0.00	0.00	9.24	0.84	0.00	0.00
E	0.00	0.84	0.00	1.68	0.84	4.20	0.00	0.00	2.52	0.00	4.20	0.00	0.84
F	0.00	0.00	1.68	0.84	2.52	0.84	0.00	0.00	0.00	5.04	0.84	0.00	0.00
G	0.00	0.00	4.20	2.52	0.00	0.00	0.00	0.00	0.00	0.00	1.68	0.00	0.84
H	0.00	4.20	0.84	2.52	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

b)

	1	2	3	4	5	6	7	8	9	10	11	12	13
A	0.00	0.84	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
B	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.84	0.00	0.00	0.00
C	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
D	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
E	0.00	0.00	0.00	0.00	0.00	0.00	0.84	0.00	0.84	0.00	0.00	0.00	0.00
F	0.00	0.00	0.00	0.84	0.00	0.00	0.00	0.84	0.84	0.00	0.00	0.00	0.00
G	0.00	0.00	0.00	0.00	0.00	0.84	0.00	0.00	0.00	0.84	0.84	0.00	0.00
H	0.00	0.84	0.00	0.84	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Figure 3.10 Scrape distribution in flow-boxes a) 8000 lt/h and b) 20000 lt/h

Moreover, the FEM simulation was done again after the main experiment with using these parameters. In this case, the FEM simulation was calculated the flowrate how to come on the surface of the solenoid armature. It can be seen clearly that the last simulation demonstrates the same results as before and supports the main experiment (Figure 3.11).

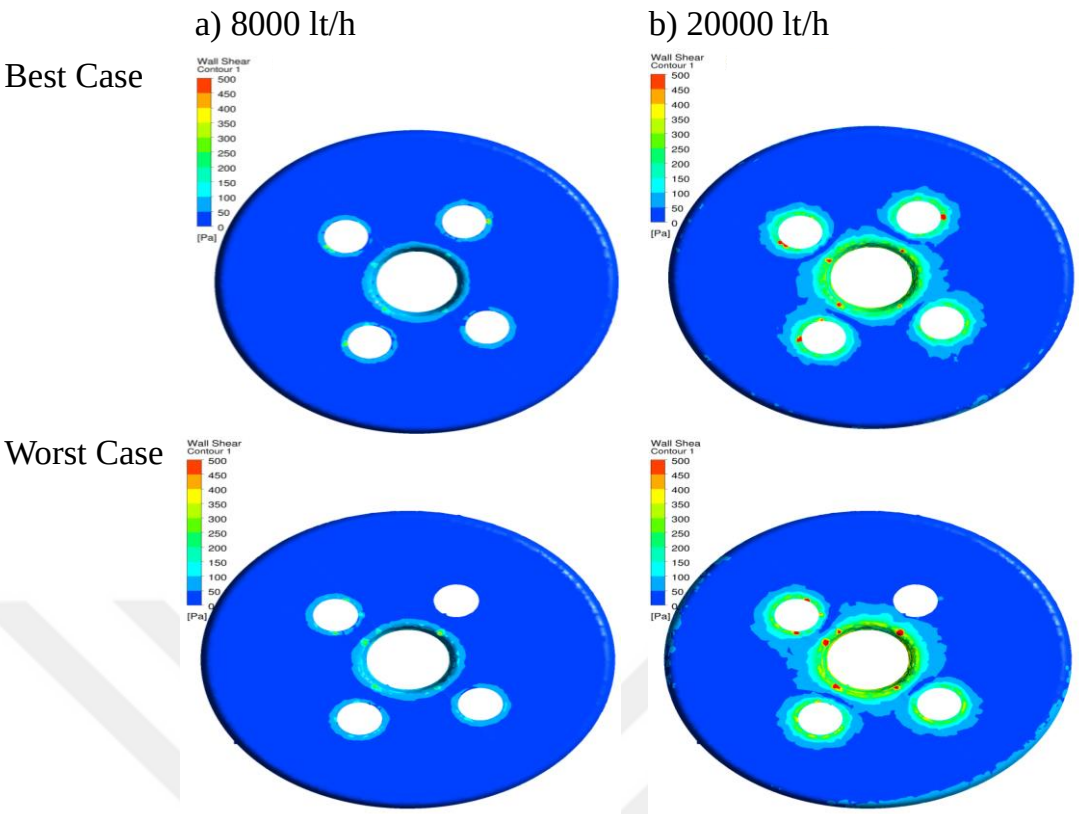


Figure 3.11 Effects of the different flowrate on first side of surface solenoid armature a) 8000 lt/h and b) 20000 lt/h

3.4 Chrome Bath Parameters

3.4.1 Surface Tension

First of all, the first experiment was done in a pilot plant of Robert Bosch R&D Center in Stuttgart. Normally, the surface tension of the chrome bath which was 71 Nm/m, was reduced with added surfactant to 33 Nm/m. Figure 3.12 illustrates that when the surface tension was reduced to 33 Nm/m, the scrape rate was almost zero. It shows there was no reason occurring white spot on surface of solenoid armature.

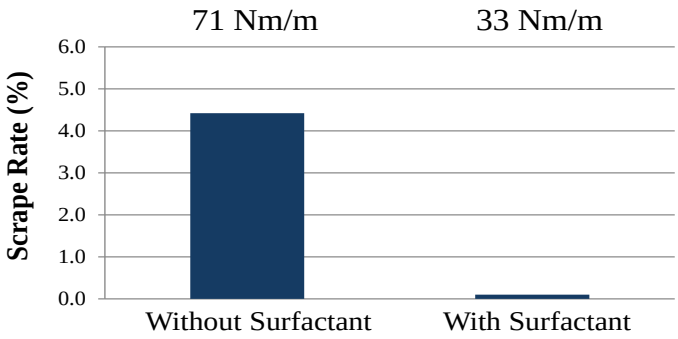


Figure 3.12 Effect of the surfactant on the scrape rate

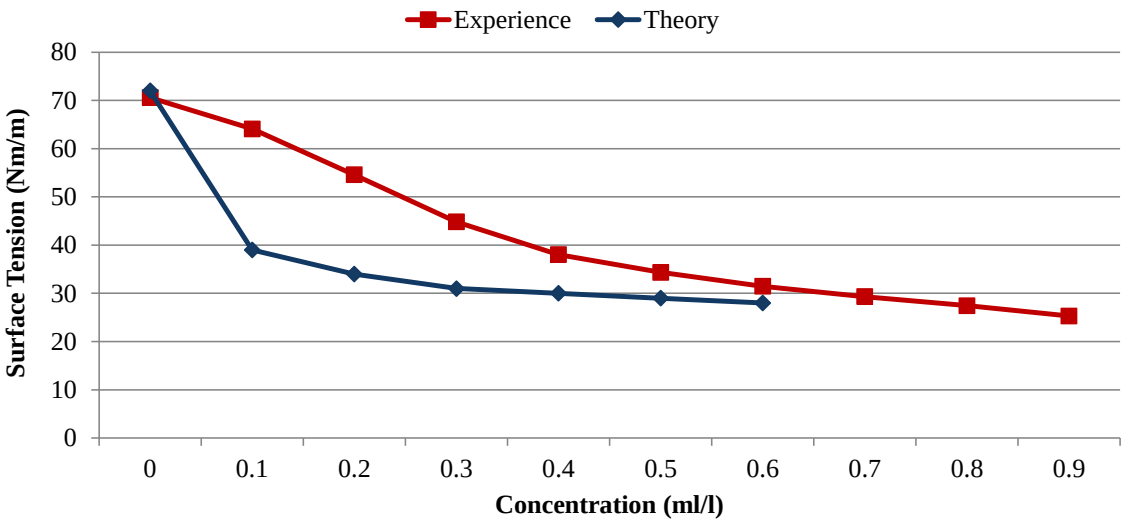


Figure 3.13 Changing the surface tension with amount of the surfactant

According to the first experiment, the effect of the surface tension was wanted to see in the main process. Firstly, it should be known how many quantity use in the tank and how to measure surface tension. Therefore, The SITA pro line t15 was used for the measurement. The results of the measurement of the surface tension in the chromium bath are illustrated in Figure 3.13. There are two measurements; the theory line shows that Enthone GmbH explained the surface tension should be reduced with their product ANKOR® Dyne 30 MS. But, when the chromium bath with ANKOR® Dyne 30 MS was measured in the laboratory with the same method, the experience line is seen.

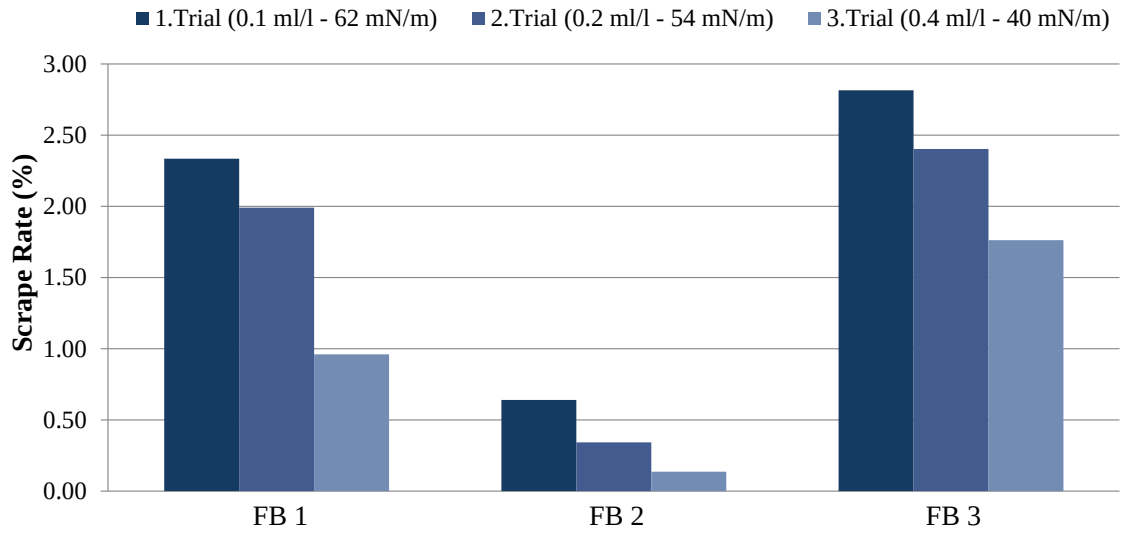


Figure 3.14 Results of main experiment of surface tension with different amount of surfactant

The surface tension of the chromium bath was normally 71,3 mN/m in the process. The main experience was started firstly with added to 0,1 ml/l concentration of the surfactant and the surface tension reduced 62mN/m after it was continued with 0,2 ml/l and 0,4 ml/l then the surface tension reduced 54 and 40 mN/m, respectively. Thus, there was considerably a decrease on scrape rate with this reduction (Figure 3.14).

3.4.2 Chrome Bath Age and Quality

As Chapter 3.3 is explained, the source of the electrolyte in every flow-box comes from the common chrome tank. Each flow-boxes were analysed at scrape rate in longer time, it can be seen clearly that the increases and the decreases go along with the same time in Figure 3.15. Although every single flow-box had different anode life. For example, the anodes of the FB 1 had been just changed and the FB 2 came to end of the anode life.

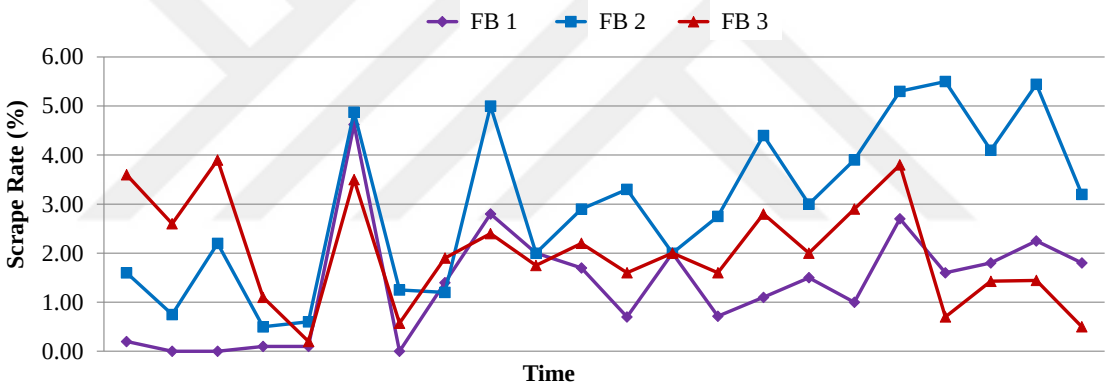


Figure 3.15 Daily scrape rate in each flow-box

According to the analyse, when something is changed in the common chrome bath, the coating quality is similarly effected in the different flow-boxes with this changing. Figure 3.16 shows the comparing of the scrape rate in a flow-box using with the new anodes in the old and new chrome bath. There was apparently a significant decline when the chrome bath was changed.

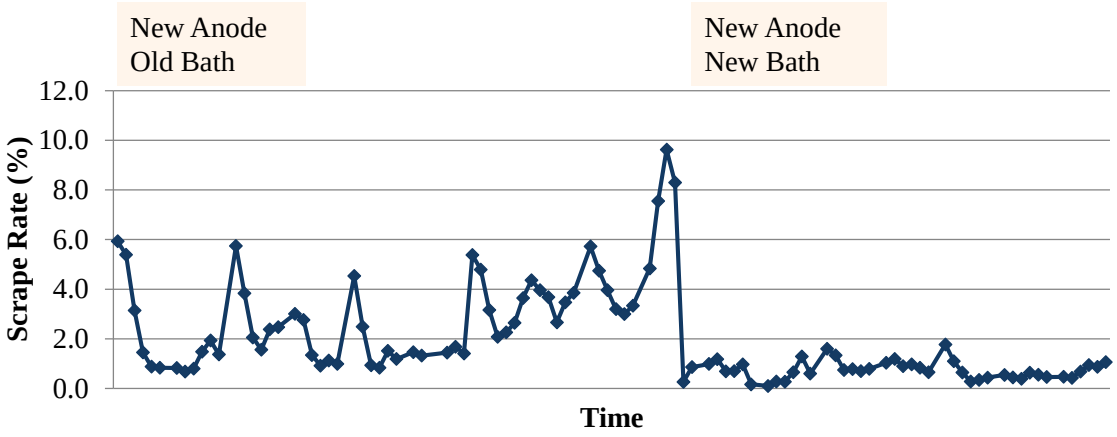


Figure 3.16 The relationship with the scrape rate at a flow-box and the different quality of the chrome bath with the new anodes

3.4.3 Others

Every parameter of the chrome bath was followed and controlled during the project. The surface tension, the quality and the age of the chrome bath were straight effected on the coating quality. On the other hand, according to literature the concentration of H_2SO_4/CrO_3 and Cr^{+3} in the chrome bath are influenced the coating quality. The daily data showed that the concentration of H_2SO_4/CrO_3 and Cr^{+3} was stable as required the process parameter between % 1,10 - 1,40 and smaller than 17 gl/l, respectively. However, when the chrome bath had just changed, the Cr^{+3} concentration was 0 and in time was decreased. At the same time, the conductivity of the chrome bath was checked. The conductivity values were seen always between 460 - 480 m/s. At the last, the particles were found sometimes on the surface of the solenoid armature during the visual inspection. That is why, the parts of the process were checked and so many particles were found in the different parts of the process such as, the chrome tank, the flow-box, the rinsing-box. The particles were searched at EDS and the results showed they were chrome, titanium and platinum particles (Figure 3.17).

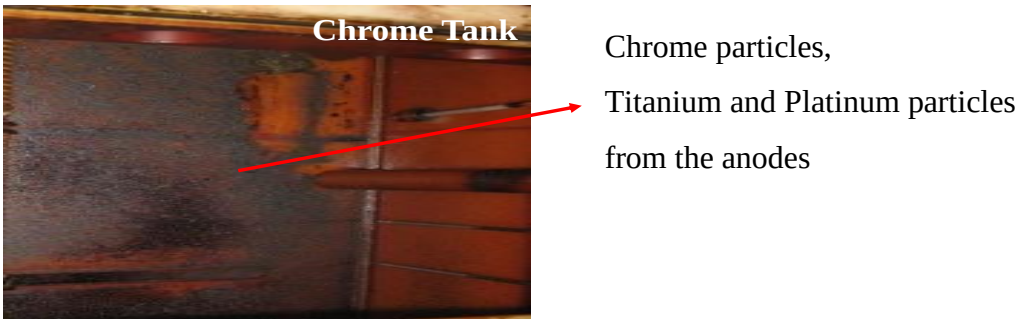


Figure 3.17 The particles in the chrome tank

3.5 Raw Material Geometry

As mentioned Chapter 1.2.2 the solenoid armature is coated by two different types according to the costumer request. Even though, the same solenoid armature was coated the same conditions in the process, the scrape rate of the different side coated was changed (Figure 3.18).

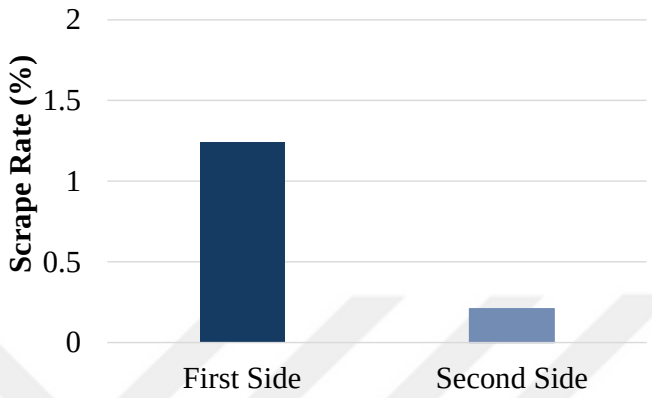


Figure 3.18 The scrape rate of the first and second side of the solenoid armature in a year

This differences was taken the different surface geometry. At the same time, Bosch Turkey had two suppliers for the raw materials. That is why, the surface geometry of the raw materials was searched with laser interferometer for two suppliers. Then, the results showed that there were no differences on the first side of the solenoid armature by two suppliers. However, on the other hand there were differences on second side of the solenoid armature by two suppliers (Figure 3.19). It can be seen clearly; the concave of the surface topography (a) was a bad effect for the coated quality. Also, there were two kinds of the second side of the surface topography from two different suppliers.

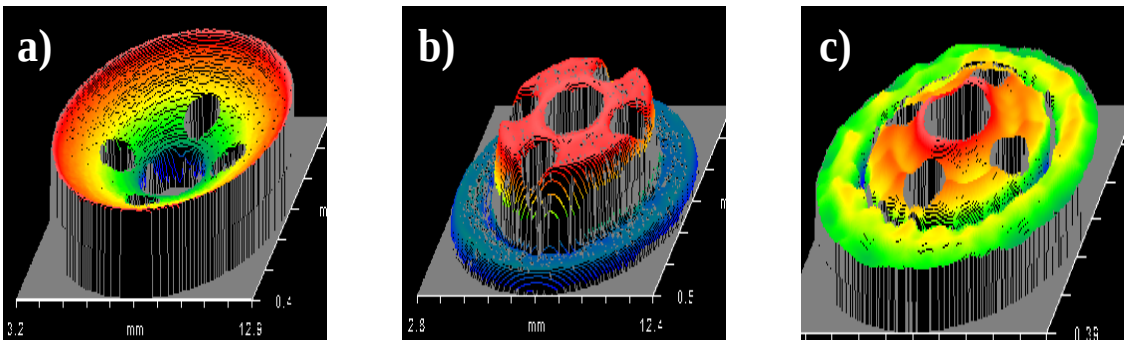


Figure 3.19 The surface topographies of the raw materials by two suppliers
a) The first side of A and K company b) The second side of A company
c) The second side of K company

The analysis of the second side of the topography on both companies shows in Figure 3.20. The tolerance of the height of the hole on the second side is 50 µm. According to the results, it can been seen the company A was produced the distance near the tolerance. Then, the different distance also was effected the flatness.

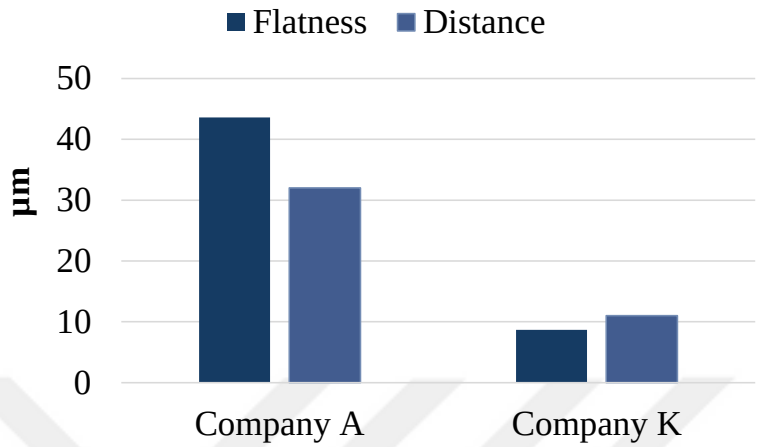


Figure 3.20 The analysis of the second side on both companies

After the results, an experiment had planned for the differences effect on the coating quality. The process was worked with the raw materials of company A in first 10 days then in second 10 days with company K. The results of the experiment demonstrate although the both companies had totally the same scrape rate (≈ % 1,0) after 10 days, the company A had clearly more the scrape rate of the second side than company K (Figure 3.21).

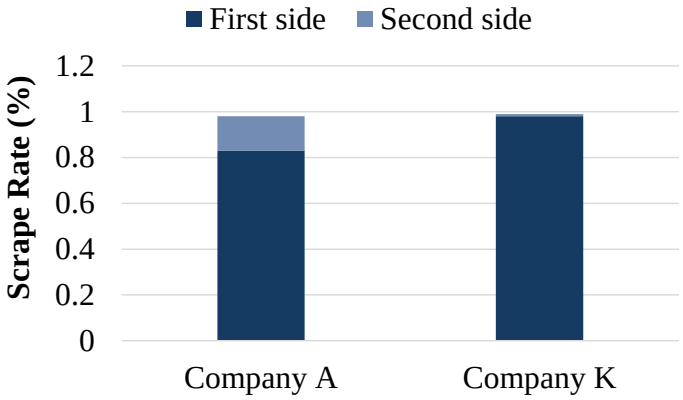


Figure 3.21 Differences scrape rate between company A and K

After the experiment, the FEM simulation was prepared for the first side and the different second sides on worst case (Figure 3.22). The results of the simulation were also supported the process experiment.

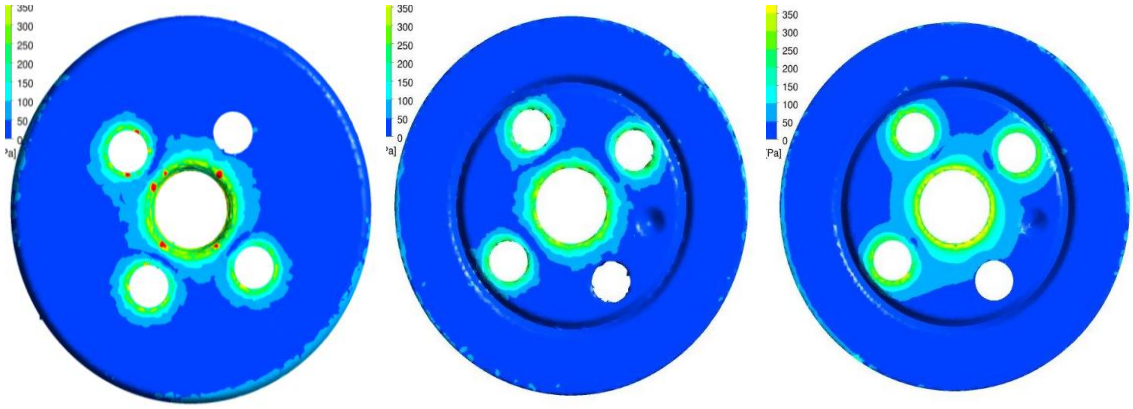


Figure 3.22 The FEM simulation of the different surface sides on worst case
a) The first side of A and K company b) The second side of A company
c) The second side of K company

CHAPTER 4

RESULTS AND DISCUSSION

After the experiments, there were not just only one solution of the project. It should be optimized and change some process parameters. Figure 4.1 shows that the changing of the scrape rate in a year. The project was searched to start in December. After two months, the optimization had will started.

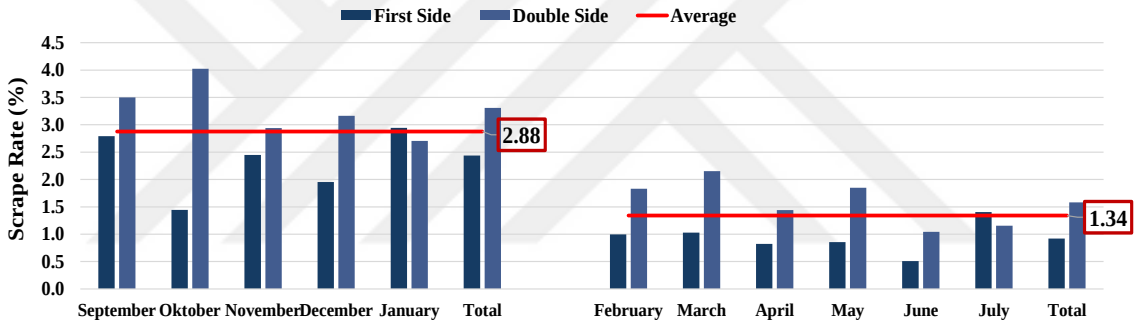


Figure 4.1 The changing of the scrape rate in a year

The first effect of the project was the anode life time. In the literature, it is mentioned about the life time but there were not exactly real experiments. For the hard chrome process of the solenoid armature at Bosch Turkey in their conditions, the anode life time should be constant at 1 million coated amount. On the other hand, it can be seen when the anode coating thickness became thicker, the anode life time also increased according to the experiment of the hard chrome process of the innenpol.

The second effect of the project was the flowrate. According to the flowrate experiments, the flowrate parameter decreased from 10000 l/h to 13000 l/h. During the experiment it could be gone up 20000 l/h but normally the process could not continue with it. Because the pump which is between the chrome tank and the flow-box, was not sufficient this higher flowrate. The maximum value was allowed 13000 l/h.

The other effect was the raw material geometry. Considering the pictures of the laser interferometers of the first and second side solenoid armature, the form of the raw material was effected on coating quality. For example, the concave form for first side or the second side of the height could be raised the scrape rate. Everything aside, it can be estimated the three-above effects could be grouped the side-reasons. The effects were effected on the coating quality but not directly.

The experiments of the increasing surface tension and the using new chrome bath showed that the scrape rate dramatically decreased. The new anode and the chrome bath system can be named the best case in the process. The process had good performance with the best case. In time, both parameters became older. Changing the anode was not sufficient only. Something inside the chrome bath was changed and was effected directly the coating quality.

On the other hand, when the surfactant was used in the process, the surface tension of the chrome bath and the scrape rate decreased step by step. If the effects of the chrome bath age and the surface tension were associated, it can be estimated the surface lower tension could be positive effect on the older chrome bath. Also, the surfactant effected on the gas bubble in the bath and H_2 gas were formed during the process were known. At the same time, there were no differences hardness between the serial and the white spot area. If all these results were combined, it can be estimated:

- Producing the big gases (H_2 gases) during the process were negative effect on the coating quality,
- The process was started and the coating was formed but the gas bubbles came to on surface of the samples,
- The gas bubbles were blocked the coating around where it came to the area,
- The area could not be continued to coat and seemed lighter than serial,
- When the surfactant was used in the process,
- The surfactant could be eliminated these bigger gases.

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PUBLISHMENTS

Conference Papers

1. Yalcinyuz, B. A., Akca C., (2016). "Investigation of White Spot Formation During the Hard Chromium Plating of Fuel Injectors Used in Gasoline Engines", MeTal2016, May 25th - 27th 2016, Brno, Czech Republic, EU.

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