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**ÇUKUROVA UNIVERSITY
INSTITUTE OF NATURAL AND APPLIED SCIENCES**

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MSc THESIS

Beytullah ONAT

**THE EFFECT OF PROCESS PARAMETERS ON
THICKNESS AND BRIGHTNESS OF CHROMIUM PLATING**

DEPARTMENT OF MECHANICAL ENGINEERING

ADANA, 2004

ÇUKUROVA ÜNİVERSİTESİ
FEN BİLİMLERİ ENSTİTÜSÜ

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AND BRIGHTNESS OF CHROMIUM PLATING**

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YÜKSEK LİSANS TEZİ

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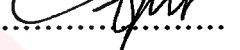
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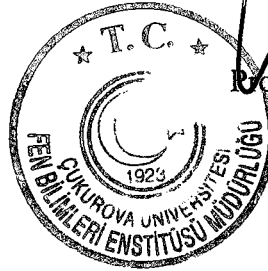
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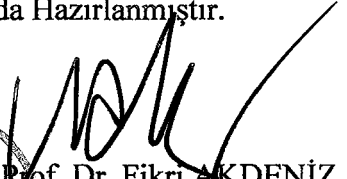
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ABSTRACT

MSc THESIS

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**DEPARTMENT OF MECHANICAL ENGINEERING
INSTITUTE OF NATURAL AND APPLIED SCIENCES
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In many instances, the properties of the materials could be insufficient to meet some of the functional demands especially those, which arise from the environmental conditions. It could be a very corrosive atmosphere or an excessive wear condition. As the high quality materials may turn out to be too costly, designers should seek a solution, which will either protect the base material against hostile environment or improve properties of base material only at the surface. Chromium plating process is the most effective way of solving all of these problems.

The aim of this study is, defining the process parameters of the chromium plating process, effects of these parameters on brightness and thickness of the chromium plating and defining the optimum process parameters which will provide the best thickness and brightness. During this study all material preparation and preliminary works before chromium plating process carried out in the plating workshop of Medikar Co. Inc. and chromium plating process done in the Mechanical Engineering Laboratory of Çukurova University.

Keywords: Hard and Bright Chromium, Corrosion, Electroplating, Response Surface Methodology (RSM), Plating Thickness and Plating Brightness.

ÖZ

YÜKSEK LİSANS TEZİ

KROM KAPLAMADA İŞLEM PARAMETRELERİNİN KAPLAMA KALINLIĞI VE PARLAKLIĞINA ETKİLERİ

Beytullah ONAT

ÇUKUROVA ÜNİVERSİTESİ
FEN BİLİMLERİ ENSTİTÜSÜ
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Birçok uygulamada malzemelerin özellikleri ortam şartlarından dolayı istenilen fonksiyonları karşılamakta yetersiz kalmaktadır. Bu ortam çok korozif veya aşırı aşınmanın olduğu bir ortam olabilir. Çok kaliteli malzemelerinde maliyetinin yüksek olmasından dolayı tasarımcılar parçaları veya malzemeleri bu tür istenilmeyen etkilerden korumak için, malzemelerin özelliklerini arttıracak yüzey işlemlerine yönelmişlerdir. Krom kaplama işlemi bu metotlar arasında en yaygın olarak kullanılan metottur.

Bu çalışmanın amacı, krom kaplama işlemindeki işlem parametrelerinin tanımlanması, bu parametrelerin kaplama kalınlığına ve parlaklığına etkileri ve en kalın ve parlak kaplamanın hangi koşullarda elde edilebileceğinin saptanmasıdır. Çalışma süresince krom kaplama işlemi öncesi yapılması gereken işlemler Medikar A.Ş.'nin kaplama tesislerinde, krom kaplama işlemi ise Çukurova Üniversitesi Makine Mühendisliği Laboratuvarında yapılmıştır.

Anahtar Kelimeler: Sert ve Parlak Krom Kaplama, Korozyon, Elektro Kaplama, Yüzey Tepki Yöntemi (RSM), Kaplama Kalınlığı ve Kaplama Parlaklığı.

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NOMENCLATURE

i	Current Density (A/dm ²)
T	Bath Temperature (°C)
t	Plating Time (sec)
α	Radius
n	Number of Factors
d _i	Desirability

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1. INTRODUCTION

In many instances, the properties of the materials could be insufficient to meet some of the functional demands especially those, which arise from the environmental conditions. It could be a very corrosive atmosphere or an excessive wear condition. As the high quality materials may turn out to be too costly, a designer should seek a solution, which will either protect the base material against hostile environment or improve properties of base material only at the surface.

Financial losses caused by corrosion is about £17 billion a year in Britain alone and 8 billion \$ (U.S. Dollars) in Turkey in a year. Friction and abrasion account for a further £4 billion in losses in Britain. These figures accentuate the significance and necessity of surface finishing. Today, the focus is on preserving raw materials and natural resources, protecting the environment and saving energy wherever possible. Some examples are given in Table 1.1 about corrosion lost in USA.

Table 1.1. Economical Losses Caused by Corrosion in USA

Corrosion in fuel system of Automobiles	100 million \$ / Year
Corrosion in cooler system of Automobiles	52 million \$ / Year
Corrosion in exhaust system of Automobiles	500 million \$ / Year

Over the past two decades, increasing attention has been given both to an understanding of corrosion processes and to the development of methods of prevention.

Electroplating is one of the most effective ways of preventing corrosion and increasing wear resistant of base material. Extremely thin layers of just a few microns are deposited onto base materials, so valuable resources are used very sparingly and only in places where they are really needed. The chemical processes involved in electroplating have also been rapidly developed and adapted to modern demands. Energy-saving automation, closed water circuits and highly advanced

waste water treatment and resource recovery systems now represent the state of the art.

Electroplating is the term given to the process of depositing one metal on another entirely different metal by means of an electric current. The process was first applied by Elkington in 1840. The metal to be deposited is held usually in an acid or alkaline solution called electrolyte, practically all metal lending themselves to electro-deposition with more or less ease, among the easiest to deposit being copper, nickel, brass, gold, silver, zinc, iron, tin, cadmium. It is however difficult of any to deposit with even a moderate degree of success.

Electroplating consists of passing an electric current of low voltage through the electrolytic solution, the positive terminal being termed the anode usually composed of a flat plate of the metal being deposited, though not necessarily always of like composition, while the negative terminal is termed the cathode, and is the article to be plated. The anodes, when made of similar metal to that which is being deposited are known as soluble anodes, owing to the fact that they dissolve into the electrolyte and deposit on the cathode. Anodes in this category are those used for silver and nickel plating. Those, which do not dissolve, are called insoluble anodes such anodes being the lead ones used in chromium plating.

Chromium plating made an almost instantaneous entry into the electroplating industry in about 1923, and there are very few modern technical processes, which became so quickly and universally commonplace that they could not be ignored. This remarkable success is purely the result of the outstanding properties, which are possessed by the thinnest deposits of chromium.

Chromium plating soon established itself commercially, despite the deficiencies of the production process, and not only held its ground, but constantly enlarged its field of applications.

Chromium plating operations are categorized based upon the thickness of the chromium metal layer applied. It can be divided roughly into "hard chromium" and "bright (decorative) chromium". The first practical application of chromium plating was the production of white, bright deposits of hitherto unattainable tarnishes resistance and hardness so that with these deposits it was possible to improve on all

other methods of improving the appearance of metal surfaces. In decorative plating, a layer of nickel is first plated over a metal substrate. Following this step, a thin layer of chromium is deposited over the nickel layer to provide a decorative and protective finish, for example, on faucets and automotive wheels. Hard chromium plating is a process in which a thicker layer of chromium metal is deposited directly on metal substrates such as engine parts, industrial machinery, and tools to provide greater protection against corrosion and wear. Chromic acid anodizing is an electrochemical conversion process that creates a wear and corrosion resistant surface on metal objects but does not result in a metallic chromium layer.

The description “hard chromium” as opposed to “bright chromium” is in a sense erroneous, since hard chromium is in no way harder than bright chromium. Its great hardness is a consequence only of the greater thickness of the deposit. In itself bright chromium may indeed be harder than some hard chromium although this hardness cannot be made use of in practice owing to the thin deposit. Therefore, for bright (decorative) chromium plating, the most important property is the perfect brightness of the deposit and for hard chromium plating; the most important property is the thickness of the deposit since thicker deposit gives greater hardness.

The process parameters that affect the brightness and thickness of conventional chromium plating are the followings.

1. Chromic acid content of the bath
2. Type and amount of the catalyst
3. Current density
4. Bath temperature
5. Plating time

In electroplating industry, electro-platers face with many problems and undesirable results on chromium plated materials. Problems such as matt deposition, milky white chromium deposition, rough or sandy chromium deposition, insufficient thickness and hardness are the most faced problems in the electroplating industry. Most of these problems caused since the effect of the process parameters and their optimum values are not known exactly.

This study has been performed to investigate the effect of process parameters on brightness and thickness of the chromium plating and to define the optimum values of these parameters, which will provide maximum brightness and thickness. During this study, an experimental setup for chromium plating process was constructed and MS58 brass materials were chromium plated under different process conditions to define the effects of the process parameters. After experiments completed, results were analyzed and optimized based on central composite design of response surface methodology by a statistical software program called Design Expert.



2. PREVIOUS STUDIES

2.1. Historical Evaluation of Chromium Plating

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. The lead is precipitated 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 (M. E. Weeks, 1956).

In just a few years chromite ($\text{FeO}\cdot\text{Cr}_2\text{O}_3$) was identified as a widely distributed and readily available source of chromium chemicals. Thus, chromium chemicals were something of a 40 years old novelty when Antoine Becquerel speculated on the results to be obtained by electrolyzing their solutions in 1843. It is observed 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 (M. I. Udy, 1956).

The history of chromium electroplating has been reviewed by many authors, notably by Junot de Bussy, R. Schneidewind, O. Macchia, O. Bauer, N. Arndt and W. Krause, G. Dubpernell and C. Kasper (A. H. Sully, 1967).

The first reference to the electroplating of chromium is in the 1848 patent of Junot de Bussy. Junot's patents were not very clear as he claimed to have found ways to deposit a number of metals, which still cannot be deposited from aqueous solution. Junot 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, it is claimed to deposit undercoats of silicon, chromium, vanadium, tungsten, titanium, molybdenum, tin and tantalum to replace platinum, which was 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 filtered. 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 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 1854, Robert Bunsen investigated the effect of the current density on the electroplating of chromium from chromous chloride solutions containing chromic chloride, in a two compartments 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 (G. Dubpernell, 1977).

In 1856, Anton Geuther published the first detailed account of the electroplating of chromium in Goettingen, Germany. In the study, chromic acid solution, which presumably contained some residual sulphuric acid has been used (J. K. Dennis, 1993). For 75 years from this time onwards there were many attempts to electroplate chromium from many different kinds of bath and although some success was achieved, contradictory results were obtained and no process was developed which was sufficiently well controlled and reproducible to be commercially developed (A. H. Sully, 1967).

The use of lead anodes with a trivalent bath to which additions of alkaline earth or alkali chlorides were made has been mentioned by E. Placet and J. Bonnet in France. Another researcher, M. LeBlanc observed that chromium cannot be electroplated from the solutions of chromium sulphate. In 1905 H. R. Curveth and B. E. Curry have concluded that not only were some of the findings of E. Placet and J. Bonnet correct but they have also readily produced plate from chromic acid baths.

This study has led Bancroft to state in 1906 that the real solution from which to deposit chromium is neither chrome alum nor sulphate, it is chromic acid.

F. L. Salzer has worked on solutions of chromic acid and reported the benefits of adding chromium sulphate to obtain electrodeposits of chromium.

From 1912 to 1914 Sargent has worked at Cornell, also under Bancroft, carrying out a systematic investigation into the electrolytic behaviour of various mixtures of chromic acid and chromium sulphate (J. K. Dennis, 1993).

Evaluation of the chromic acid bath and the effect on its deposition characteristics of changes in solution composition and operating parameters has been studied by Haring & Barrows in 1927. Since that time many advances have been made in chromium coatings. One of the biggest advances was the use of silicofluoride ions as catalysts in addition to sulphate ions. This type of solution has about 18 to 20% of the chromic acid bath containing only sulphate as catalyst (M. J. Udy, 1956).

2.2. Principles of Chromium Plating Process

Chromium plating is different in many aspects to other electroplating processes. In the majority of cases the articles to be plated are placed in a solution containing dissolved salts of the metal to be deposited, electrolytic conduction then causing the metal ions to be discharged at the cathode. Chromium deposition on the other hand is achieved in several reduction steps of the hexavalent chromic acid. With most electroplating processes the deposited metal ions are mainly replaced from the anodes. However, this is not possible with chromium plating baths, since the anodes would dissolve as trivalent chrome, and once a certain concentration of trivalent chrome is reached considerable trouble would occur. For this reason hard lead, or special lead alloy anodes are used in chrome electrolytes, which do not dissolve, and upon which an active, conductive lead oxide film forms during electrolysis. As it is seen in Figure 2.1 chromium plating process involve several operations for the modification of the surface properties of metallic products, based on three main stages: surface preparation, electroplating and post-treatment processes (RIEDEL Galvanotechnik, 1994).

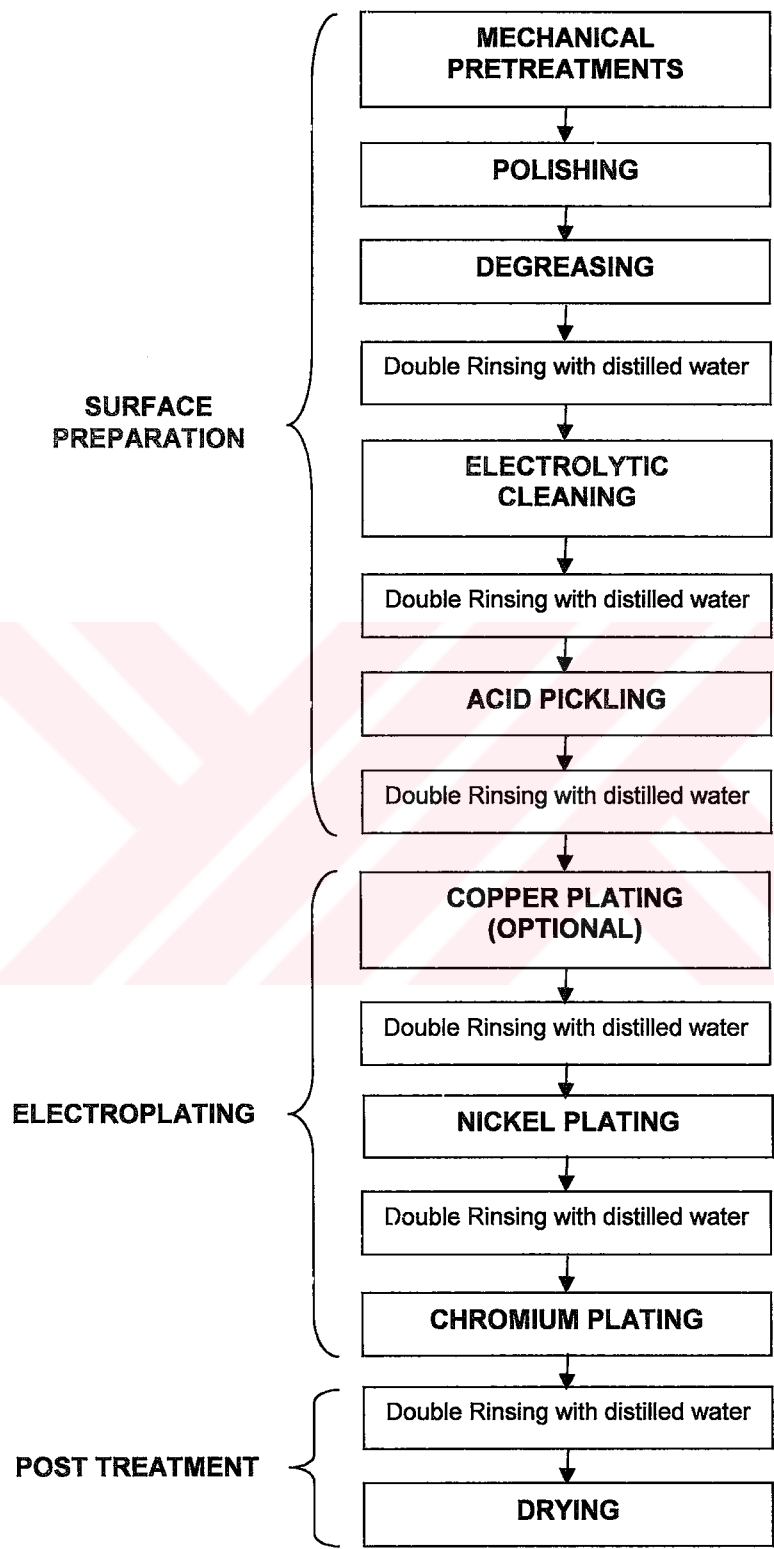


Figure 2.1. Surface Preparation and Chromium Plating Process

Where the chromium plating is mainly required for protection against corrosion, value is naturally laid on a chromium deposit as free from pores as possible. Normally the application of at least 20 μm is necessary to withstand atmospheric corrosion. For stronger chemical attack, still heavier coatings of 50 μm or more are needed. When it had been established that thin, highly porous chromium deposits were not able to provide the required corrosion protection, efforts were increased to produce more durable deposits, and have lead to notable success. The improvements were achieved on the one hand by use of special underlayers, e.g., multilayer nickel, and on the other by improvements in the chromium deposit itself.

Chromium plating processes are categorized based upon the thickness of chromium metal layer applied. Therefore, chromium plating can be divided roughly into “hard chromium” and “bright (decorative) chromium”.

2.2.1. Bright (Decorative) Chromium Plating

Bright (decorative) chromium plating is one action in a series of plating steps that result in a thin layer of chromium being deposited on a base material. It is the process by which a thin layer of chromium (typically 0.003 to 2.5 microns) is electrodeposited on a base metal, plastic, or undercoating to provide a bright surface with wear and tarnish resistance.

Bright (decorative) chromium is almost exclusively plated over a nickel electrodeposit, which can easily be plated over substrates such as plastics, steel, aluminium, copper alloys, brass and zinc die castings. Nickel plating is preferred because it protects the substrate from corrosion, helps to give chromium a white color, and is protected from surface oxidation by the chromium layer. Stainless steel is the only substrate that is frequently plated directly with chromium, but a nickel preplate before chromium is also used. Multiple or single layers of nickel and copper can precede the nickel/chromium deposits depending upon the intended use of the part (D. L. Snyder, 1996).

2.2.2. Application Fields of Bright (Decorative) Chromium Plating

One of the earliest and widest fields of application of bright chromium plating was in the tableware industry. For this purpose, iron or steel articles were chromium plated directly or with an undercoat. Nickel silver was particularly good for direct chromium as this metal readily polished to a high gloss. Knife blades were always directly plated due to the risk of peeling of other undercoats on the flexible substrate.

The main application fields of chromium plating nowadays are the automotive industry, motorcycles, medical instruments, power tools and hand wrenches. Many of these items are made up of parts that have been bright chrome plated (J. Stockemer et al., 1999).

Bright chromium plating is widely employed in many kitchen and bathroom fittings, on washing machines, cookers, and also for surgical, hospital and dental instruments where the good chemical resistance of the chromium to different medicaments, sterilizing solutions and biological fluids, combined with the ease of cleaning of the smooth and poorly wetted surfaces are highly desirable. Since such instruments are often subject elastic loads, care should be taken to ensure that the nickel is deposited in as ductile a condition as possible (National Metal Finishing Resource Center, 2002).

Bright Chromium plating is also commonly used in jewellery, domestic appliance, photographic and many other industries, both in the fully bright and matt forms (L. Fedrizzi et al., 2002).

2.2.3. Hard Chromium Plating

Hard Chromium plating is also known as industrial or functional chromium plating. This is a process by which a thick layer of chromium is deposited on a base material. An appreciable hardening of the surface only occurs with thicker coatings, and, the necessary thickness being determined entirely by the nature and size of the mechanical load. Development over several years enabled the production of heavy chromium deposits in the form of so called “hard chromium plating” to become large

scale production practice over a very wide field. The description “hard chromium” as opposed to “bright chromium” is in a sense erroneous, since hard chromium is in no way harder than bright chromium. Its great hardness is a consequence only of the greater thickness of the deposit. In itself bright chromium may indeed be harder than some hard chromium although this hardness cannot be made use of in practice owing to the thin deposit. Hard chromium plating has a greater thickness than bright chromium plating and has a large variability, going up to 500 μm (L. Fedrizzi et al., 2002).

Hard chromium plating has properties similar to the solid metal, the most important are: high hardness levels (with thick deposits), low coefficient of friction (high lubricity), good corrosion resistance, high heat resistance, low coefficient of linear expansion and high thermal conductivity. Any differences in plating practices will inevitably cause major variations in the hardness of the electroplated material. Hardness of the hard chromium plating can range from 550 to 1250 HBN (J. Simão and D. K. Aspinwall, 1999)

Essentially both bright and hard chromium plating can be produced from the same baths, namely, chromic acid solutions with the addition of a foreign anion. Slight differences between the compositions of the bright chromium and hard chromium baths are usual in practice; thus for preference 200-400 g/l as compared with a lower concentration of about 250 g/l for hard chromium plating.

There are two basic requirements, which have to be met for the use of hard chromium coatings.

1. The base or substrate material must be such that it is capable of resisting externally applied forces without undergoing extensive deformation, i.e. the strength and hardness properties of the base material must be matched to some extent, to those of the hard chromium coating applied. The pairing of martensitic base materials with hard chromium coatings has proved to be a particularly successful combination.
2. The coating thickness should be restricted to a minimum where deformation or shock loading of the composite can be expected in the application concerned.

The typical hardness of chromium coatings for the metal working industries lies in the range 800-1000 HV (0.1). Coatings deposited by modern electroplating techniques may reach hardness values up to 1200 HV. The achievable hardness values depend on a number of operating variables such as electrolyte bath temperature, current density and chromic acid/sulphate ratio (H. Klein and H. H. Urlberger, 1992).

Residual stresses and crystallographic texture in hard-chromium electroplated coatings have been investigated by J. Pina et al., (1997). The X-ray diffraction method has been used to study the structural and mechanical state of electrodeposited chromium coatings. Experiments have been performed on layers of various thicknesses, plated on different types of substrates, and the evolution of the stress state as a function of depth has been studied. The dependence of the texture on the thickness of the coatings and the substrate material has been also studied by the authors.

Chromium coatings have been electroplated by direct current and exhibited a strong crystallographic texture that increases in the core of the coating with the growth in thickness. This increase depends on the substrate material (slight for copper, important for ferritic steel and intensive for stainless steel). The profile of residual stresses showed tensile values up to 800 MPa at the surface of the coating. Values fell in the core till 200 to 300 MPa and increased in the interface in a manner, which depends on coating thickness and mechanical strength of the superficial layer of the substrate.

A survey study has been conducted by Paul J. Cote and Christopher Rickard, (1999) on erosion damage in chromium-plated gun bore surfaces using specimens of three erosion-damaged, chromium plated, 120 mm M256 gun barrels and two erosion-damaged, 155 mm gun barrels (M199 and XM297). Specimens have been examined by optical microscopy, laser scanning confocal microscopy (LSCM), and electron microprobe analysis.

They have observed that hard chromium shows a high density of embedded microcracks between the major cracks in the chromium. These embedded microcracks were absent in low contractile (LC) chromium specimens. With the

155mm, where lower temperature propellants were used, there has been evidence that sliding wear causes damage to the chromium plate.

It is often assumed that fracture is the mode of damage initiation into chromium-plated steel. However, this survey of five different gun tubes has indicated that chemical attack is the precursor to erosion damage into the steel.

E. O. Cobo et al. (1999) analyzed the causes of hard chromium layer spalling in the rotor of a downhole hydraulic motor. They stated that hard chromium deposits normally have a cracked structure that may vary from 15 to more than 200 cracks/cm² depending on plating bath chemistry, current density and temperature.

Zones with lost coating and base metal attack have been also observed along the whole rotor. Microscopic examination has shown typical macrocracks that run through the whole chromium layer. From the results obtained, they concluded that chromium plated steel and base steel have shown similar electrochemical behavior in mud aqueous phase, whereas pure chromium remained passive up to the transpassive region because the microprobe analysis of the metal-coating interface have shown no metallic deposit between the steel and the chromium layer. As the steel substrate was corroded, chromium coating lost adherence and became detached under the influence of frictional forces.

J. Simão and D. K. Aspinwall (1999) studied on the effects of hard chromium plating on electrical discharge textured (EDT) roll surface topography (“roughness” and “waviness”). In the study, X-ray diffraction techniques have been used to measure the surface residual stresses.

Industrial experience with hard chromium plated mill rolls clearly indicates that coatings applied to a particular type of roll surface texture achieved either by shot blasting (SB), electrical discharge texturing (EDT), extend roll service life and performance.

It has been claimed that roll change times have been reduced significantly when compared with similar uncoated rolls. Also according to the experiments, the chromium deposit not only increased the surface roughness of the EDT roll but also retained some “weak” peaks normally lost in the early stages of rolling with uncoated

rolls. 3-D topographical maps shown in Figure 2.2 (a) and (b) illustrate that with chromium plating, a well-defined surface is achievable.

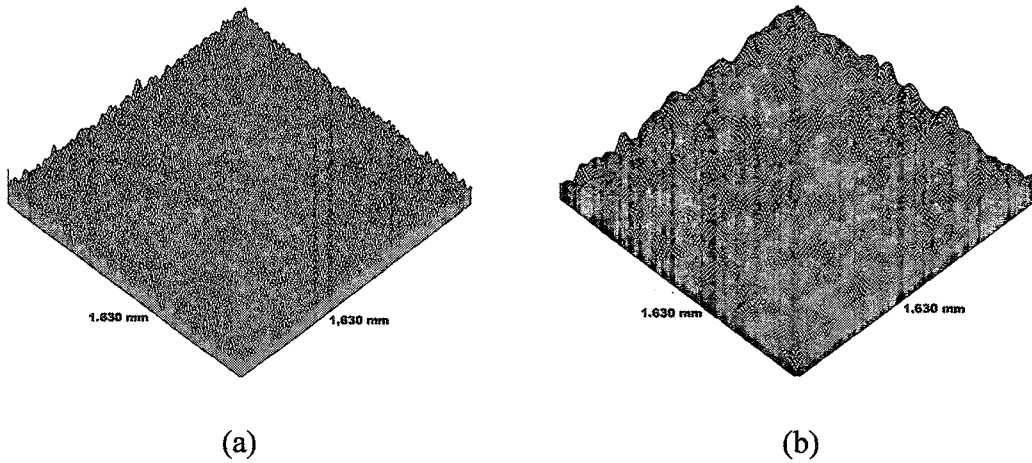


Figure 2.2. Sample 3-D Topographical Plots of the Hard Chromium Plated EDT Specimen Bands: (a) A: $1.02\mu\text{m } R_a$; (b) K: $10.23\mu\text{m } R_a$ (Simão ,1999)

Pascal Negre (2001) studied and developed processes allowing to obtain harder, thick coatings of chromium and more resisting to the corrosion than the traditional coatings, from a new and non-toxic electrolytic solution.

A solution of chromium plating of which the chromium is at the same moment under free shape and under complex shape has to behave as one finds ions under two forms; a complex shape (mainly by lactic acid) and a free shape (resulting from some nickel sulphate) has been planned to be prepared. It is expecting to obtain a hardness of about 1700 to 1900 HV_{100g} after a thermal treatment of 20 minutes at 300°C is applied by this developed bath.

The effect of contact pressure on the wear behavior of AISI H13 tool steels with chromium nitride and hard chromium coatings has been investigated by L. H. Chiu et al., (2002).

Hard chromium and chromium nitride coatings have been applied to a hardened and tempered AISI H13 tool steel by using electroplating and cathodic arc plasma deposition, respectively. As it is seen in Figure 2.3 the microhardness of the applied hard chromium and the chromium nitride coatings and the base steel has been found 890, 2150, and 510 HV_{0.01}, respectively. When subjected to a lighter load

of 3.3 MPa, both hard chromium and chromium nitride coatings have been provided excellent wear resistance better than that of uncoated H13 steel. When the applied contact pressure has been increased to 11 MPa, the thick hard chromium coating exhibited a satisfactory long-term wear resistance but the thin CrN coatings can only provide a short-term protection against the heavy contact pressure wearing (See Figure 2.4).

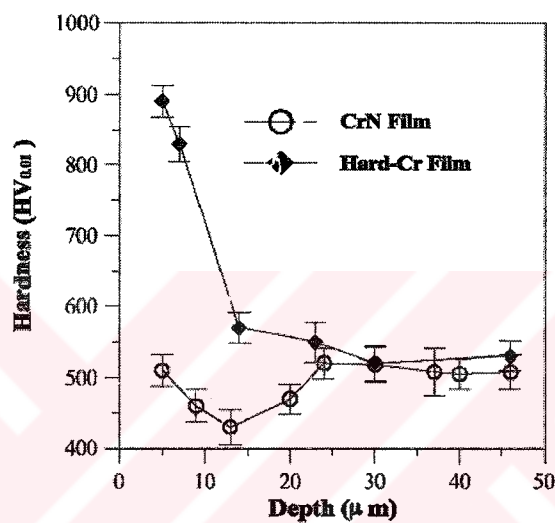


Figure 2.3. Microhardness Profiles of H13 Steel Specimens with given Coatings (Chiu, 2002).

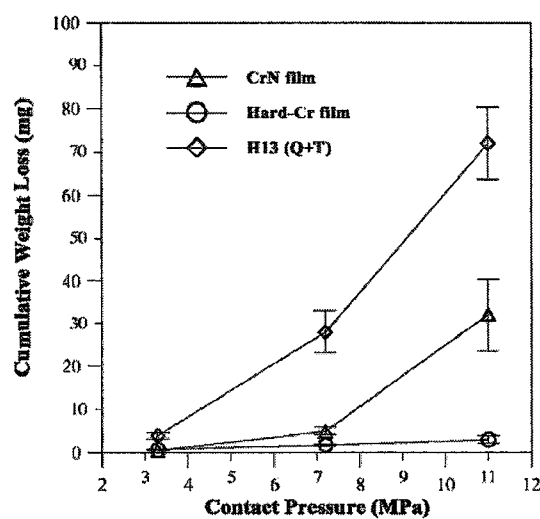


Figure 2.4. Cumulative Weight Loss Characteristics of H13 Steel Specimens in given Conditions as a Function of the Applied Contact Pressure (Chiu, 2002).

The literature dealing with wear-corrosion problems of chromium coatings shows only qualitative and partial results, analyzing the involved damage phenomena from a mechanical point of view, or from an electrochemical one. Hard chromium is a coating suitable to working conditions where a continuous sliding of the metal components is combined with the presence of an aggressive environment, as an example in earthmovers, in mining transport system or in moulds for plastics.

L. Fedrizzi et al., (2002) studied the mechanisms of tribocorrosion of hard chromium coated steel bars in a sodium chlorides solution under sliding wear. By this study it has been tried to combine and integrate two different kinds of damage through a proper experimental approach in order to obtain an overview of the problem.

They concluded that, weight loss due to wear has been found to be very important, and the wear mechanism is mainly of an adhesive type. Damages of secondary importance have been due to abrasive wear (at test beginning) and localized corrosion (pitting-like). Electrochemical data suggested that the corrosion rate of chromium coatings has been increased by almost one order of magnitude by the mechanical damage. Coating degradation has been increased as the rotational speed and the applied load on the counterface increased.

Another investigation, to compare the microstructure, wear resistance and potentials of HVOF sprayed $\text{Cr}_3\text{C}_2\text{-NiCr}$ and WC-Co coatings for a possible replacement of hard chromium plating in gas turbine components repair has been made by Tahar Sahraoui et al., (2003). They showed that coatings exhibit high hardness with a high volume fraction of carbides being preserved during the HVOF spraying process. Hardness and wear resistance of the WC-Co coatings have been better than those of the $\text{Cr}_3\text{C}_2\text{-25NiCr}$ coatings. Compared to HVOF sprayed $\text{Cr}_3\text{C}_2\text{-25NiCr}$ coatings, WC-Co coatings exhibit a low porosity. Considering the economical and ecological requirements, HVOF sprayed carbides based cement coatings can be used for a possible replacement of hard chromium plating in gas turbine shafts repair.

2.2.4. Application Fields of Hard Chromium Plating

Hard chromium plating has several properties such as high hardness (with thick deposits), low coefficient of friction (high lubricity), good corrosion resistance, high heat resistance, low coefficient of linear expansion and high thermal conductivity. Because of these features, it is used throughout many industries in a number of different types of applications. Firstly, it can be applied to a new component to provide a durable hard wear-resisting coating such as wire wound rods for paper coating, seal areas on pump or drive shafts, conveyer wear rails and rollers, plastic extruder screws, print rollers.

Another application for Hard Chromium plating is for the refurbishment of worn components where the metal has been lost through wear or been manufactured undersize or, even if there has been excessive distortion during a hardening process. This application usually requires a thicker deposit and components are pre-Chrome ground then a suitable deposit of hard chrome is deposited before they are ground back to original sizes and tolerances. Examples of this process are: machine spindles or housings, motorcycle forks, cardboard tube formers, pump shafts or rotors, hydraulic rods and cylinders, any sliding or rotating shafts.

Moreover, hard chromium coating suitable to working conditions where a continues sliding of metal components is combined with the presence of an aggressive environment, as an example in earthmovers, in mining transport systems or in moulds for plastics (L. Fedrizzi et al., 2002).

The applications of hard chromium plating in the plastics tooling industry grow daily as new ideas occur for the use of the deposit. The following list is given as a guide for the successful use of the deposit in the more established applications.

1. Tooling Components

- Core pins

- Mold inserts (shim deposit)

- Heater probes

- Ejector pins

2. Plastics Inspection Tooling

Plug gauges

Slip gauges

Support fixtures

3. Plastics Cutting Tools

Drills

Taps

4. Plastics Process Equipment

Sealers

Mixing shafts

Extruder screws

Nozzles

Hard chromium plating applications in the engineering discipline are by far no new toy. It is almost now 60 years since deposition was offered to the engineering industry, and during this time the importance of the process has steadily increased. The application of hard chrome is now a recognized means of prolonging the life of all types of metal parts subject to corrosion, friction and abrasion. And it should be well borne by the mold designer, mold maker and molder that they will benefit by learning a little more about the practical side of the job. There is no doubt that many applications have reached a point where hard chromium plating has become an indispensable tool (M. DeLaPuenta, 2003).

2.3. Effects of Chromium Plating Process on Properties of Base Metal

Guojin Lu et al., (2004) have investigated the effect of chromate conversion coatings on the corrosion resistance of Ni-based alloys. The influence of thin (10-50nm) chromate conversion coatings (CCC) on the corrosion performance of Ni-P based alloys in 0.5 M H_2SO_4 has been investigated by using potentiodynamic sweeping techniques. It is found that CCC film can improve the corrosion resistance of Ni-P alloys. However, the improvement in corrosion resistance of Ni-W-P or Ni-Mo-P coating has been minimal. CrO_3 concentration, solution PH and immersion

time have significant effects on the corrosion resistance of Ni-P. And it has been found that all those variables cause an enhancement in both the growth rate of the CCC and dissolution rate of the Ni layer.

Influence of chromium structure on corrosion-protective properties of coatings in severe conditions (marine and mine atmosphere) were studied by L. N. Solodkova et al. (2004). Protective properties of chromium coatings were studied by accelerated and atmosphere corrosion tests in marine and mine atmosphere.

They stated that the choice of most suitable chromium coating for the protection of steel in marine atmosphere or in mines should be based on the service conditions. For severe conditions (wear in an aggressive media, containing dust and gases) a single-layer semi-bright crack-free chromium deposited from the conventional bath or a double-layer coating deposited from the baths with lower CrO_3 concentration, containing dichromates or using pulse current instead of direct current is preferable. If high wear resistance is not essential a single layer crack-free milky coatings (hardness 650 kg/mm^2) may be suitable.

2.4. Factors Affecting the Properties of Chromium Plating

The most important factors which influence the properties of electrodeposited chromium are the chromium content of the bath, the type and amount of catalyst, the type and amount of cations, the impurities in the solution, solution temperature, time and the current density at which the electrolysis is carried out.

A comprehensive investigation of the variation of the appearance of chromium deposits in a standard bath containing 250 g/l CrO_3 and $2,5 \text{ g/l SO}_4$ with current density and the temperature of the bath has been made by W. Hume-Rothery and M. R. J. Wyllie, (1944). They have studied the appearance of deposits on $0,5 \text{ mm}$ thick annealed steel sheet of random crystal orientation, all the specimens being prepared in a standard way and anodically degreased before plating.

Similar to that of Hume-Rothery and Wyllie for sulphate bath, has been carried out by E. A. Brandes and J. A. Whittaker, (1967). Current density was varied between 200 and 1500 A/ft^2 and temperature up to 85°C . The texture of the deposits

under the various conditions was determined by x-rays. As shown in Figure 2.5 and the results showed that the degree of texture increased as the temperature increased. They also concluded that whereas in the sulphate bath there is a fall of current efficiency with increasing temperature, the opposite is true for the fluoride bath.

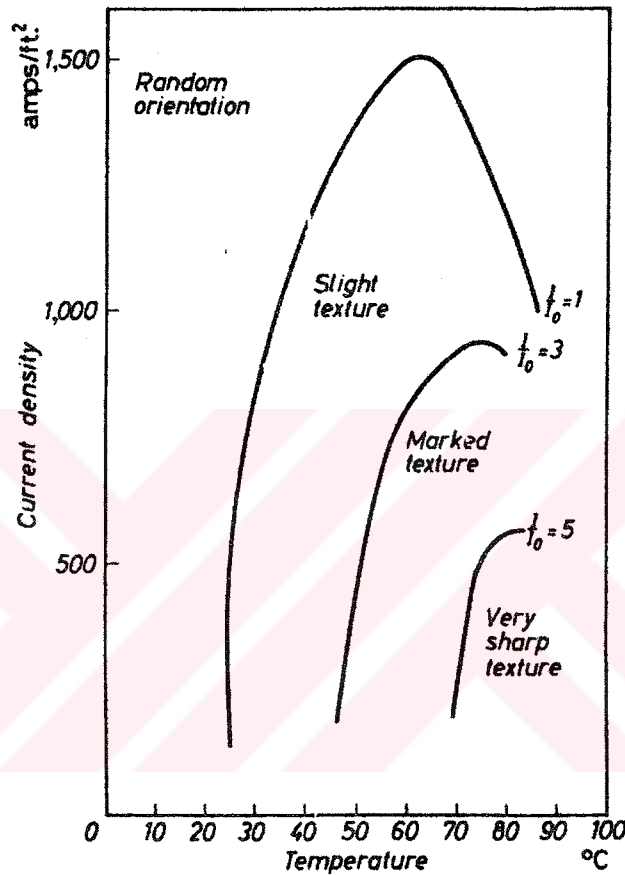


Figure 2.5. Variation of Crystal Orientations of Chromium Plated from a Fluoride Bath under Various Conditions (Brandes, 1967)

It has been shown that high hardness, low wear rate, good corrosion and oxidation resistances of chromium coatings can be improved by the introduction of nitrogen in the deposit by S. J. Bull et al., (1990).

J. Stockemer et al., (1999) prepared chromium and chromium nitride layers by non-reactive and reactive (in a mixture of Ar and N₂ gas) D.C. magnetron sputtering of a 90mm diameter target, respectively. All coatings have been deposited onto pre-cleaned substrates: a silicon substrate for the deposition rate determination, 430 stainless steel for the layer tribological testing and 304 stainless steel for the

characterization and corrosion properties of the deposits. The variable process parameters considered in their work are: the applied power on the target, the gas composition and finally the deposition time.

They showed that the deposition rate decreases with increasing N_2 content as seen in Figure 2.6. The grain size has been always lower for the CrN coating (5 nm) than for the Cr coating (30 nm). The hardness of the CrN coating has been higher than the hardness of the uncoated substrate. The increase in hardness is linked to a better wear resistance. Wear resistance of the CrN coating has been observed due to its high hardness and low friction coefficient.

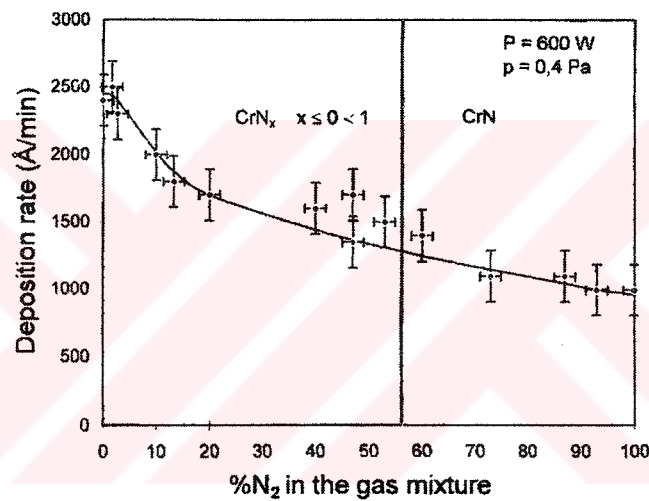


Figure 2.6. Deposition Rate versus Gas Composition at Constant Target Power (Stockemer, 1999)

T. Marek et al., (2000) have studied the effects of pre-treatment and composition of substrates on the quality and defect structure of electrodeposited thick chromium coatings. In their study, two sets of samples have been prepared on all the substrate materials. In one set, the substrates have been mechanically polished (MP), while in the other set, the substrates have been electropolished (EP). The mechanical polishing has been consisted of a 10 min treatment with p2500 polish paper, then a 10 min chromium-oxide (grain size: 1 μ m) polishing and finally a 5 min metal polish. The electropolishing has been carried out at 7V with a current density of 15 A/dm² for 2 min. It has been shown that the quality of the electrodeposited chromium coatings depends not only on the conditions of preparation, but also on the

composition onto which it has been deposited. Also results have been shown that the mechanical polishing results in more defective layer than the electropolishing.

S. Survilienė et al., (2001) have investigated the effect of MoO_2 and TiO_2 on electrodeposition and properties of chromium coating. Chromium coatings have been plated from aqueous hexavalent baths of two versions (A and B). Electrolyte A has been composed of 120 g/l of chromic acid (CrO_3) and 2 g/l of the additive Limeda Ch-3, electrolyte B (conventional) has been composed of 250 g/l of chromic acid (CrO_3) and 2.5 g/l of sulphuric acid (H_2SO_4). In addition, the baths of both types also contained the suspension of highly dispersed particles of MoO_2 or TiO_2 .

It has been shown that incorporation of MoO_2 and TiO_2 particles into the Cr coating leads to the decrease in hardness as seen in Figure 2.7. The use of fine-dispersion suspension of MoO_2 enhances the reduction of hydrogenation of the substrate and incorporation of these dispersion particles into the Cr deposit leads to the reduction of the coating internal stresses.

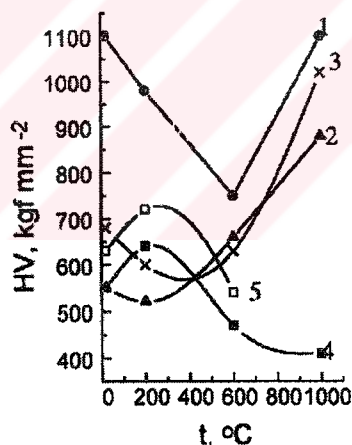


Figure 2.7. Dependence of HV (kgf/mm^2) on temperature of annealing of Cr (1), of Cr- TiO_2 (2, 5) and of Cr- MoO_2 (3, 4) coatings deposited from: Bath A (1), Bath A+1.0 g/l TiO_2 (2), Bath A+4.2 g/l MoO_2 (3), Bath B+4.2 g/l MoO_2 (4), Bath B+1.0 g/l TiO_2 (5). Temperature, 60°C , $i_c = 60\text{A/dm}^2$. Thickness of coating $20\mu\text{m}$ (1-5) (Survilienė, 2001)

Wang Deqing et al., (2004) have investigated the effects of temperature, current density and time on thickness of nickel, copper and hard chromium coatings produced by a multiple electroplating process.

1 mm thick plate of aluminum (0.01% Cu, 0.22% Si, 0.25% Fe, balance Al in weight percent) has been used as the substrate. Prior to deposition, the substrate has

been degreased in a 100 g/l sodium hydroxide solution at 60 °C for 1 min and rinsed with deionized water. Then, the specimen has been immersed in a nickel plating bath (pH = 3.8–4.6) containing 250 g/l of nickel sulfate hexahydrate, 40 g/l of boric acid, 10 g/l of sodium chloride, brighteners and a wetting agent at 45–55°C and 2–3 A/dm² for different time. The copper plating has been carried out first in a hydroxyl ethydenes diphosphate (HEDP) solution at 10–55 °C and 0.5–1.5 A/dm² for varied time, rinsed with deionized water, and then in an acidic bright copper plating solution at 10–40 °C and 2–3 A/dm². After the specimen being rinsed with deionized water, the specimen has been immersed in a chromium plating bath containing 300 g/l of chromium trioxide, 3 g/l of sulphuric acid at 50–65 °C and 25–35 A/dm² for different time. The anodes for the nickel, copper and chromium plating were electrolytic grade nickel, copper and lead, respectively. For all the preplates of nickel and HEDP and acidic copper before the following plating, the plating temperature and current density have been optimized and the plating time has been maintained in 5 min.

The microstructure of the composite coatings on the aluminum substrate is shown in Figure 2.8.

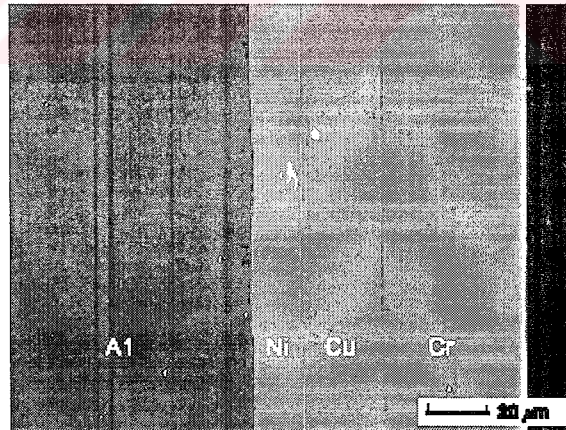


Figure 2.8. SEM Image of the Composite Coatings (Deqing, 2004)

Figure 2.9 shows the effect of current density on thickness of the chromium coating electroplated for 5 min at different temperatures.

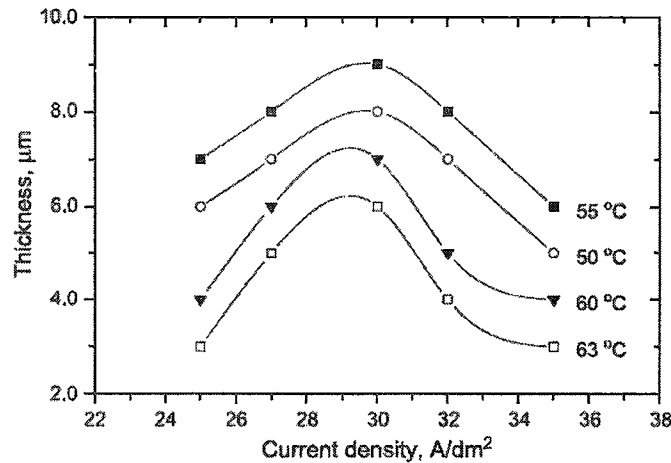


Figure 2.9. Effect of Current Density on Thickness of the Chromium Coating Electroplated for 5 min at Different Temperatures (Deqing, 2004)

As shown in Figure 2.10, the relationship of the chromium coating thickness and plating temperature at different current densities also indicates that the overheating of the plating bath beyond 55 °C causes a rapid decline of the coating thickness.

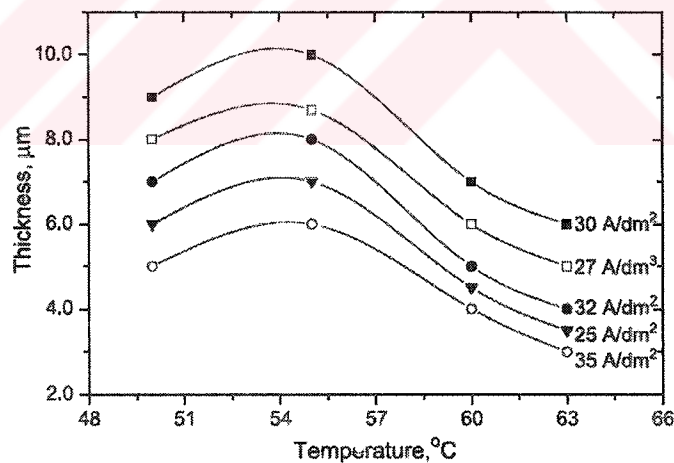


Figure 2.10. Effect of Temperature on Thickness of the Chromium Coating Electroplated for 5 min at Different Current Densities (Deqing, 2004)

Experiments have shown that the optimized plating conditions to obtain the thickest coatings are at 2.5 A/dm² and 49 °C for nickel, 0.8 A/dm² and 20 °C for HEDP copper, 2.6 A/dm² and 30 °C for acid copper and 29 A/dm² and 54 °C for hard chromium. Under the optimized composite electroplating conditions, a sound

adhesion between any plated materials over the aluminum base has been achieved, and a bright, uniform and flawless chromium coating has been obtained with a microhardness of HV1029. Finally, they claimed that the hard chromium coating layer has a much higher anti-pitting property in 3.5 wt. % sodium chloride solution than that of the 1Cr13 steel.

2.4.1. Effects of Operating Conditions

In all commercial baths containing chromic acid, constant attention to maintenance of the correct ratio of chromic acid to catalyst addition is essential to ensure constant plating conditions. This ratio is being expressed in grammes CrO_3 and grammes SO_4 or its equivalent. The so-called concentrated bath of commerce contains 400 g/l CrO_3 and 4 g/l SO_4 while the standard bath contains 250 g/l CrO_3 and 2,5 g/l SO_4 .

A. Brenner, P. Burkhead and C. Jennings (1947) have experimented with a dilute bath containing 50 g/l CrO_3 and 0,5 g/l SO_4 . Particular attention has to be given in all types of baths to keeping the $\text{CrO}_3 / \text{SO}_4$ ratio balanced against the loss of SO_4 due to the removal of the plated articles or its addition when new articles which may have been acid dipped are inserted into the bath.

The conditions of temperature and current density required for bright plating and the current efficiencies obtained have been defined for the various commercial baths. Data for bath temperatures up to 65°C have been given by G. Dubpernell while A. Brenner, P. Burkhead and C. Jennings gave data for a bath temperature of 85°C for both sulphate and fluoride baths.

A recent improvement in chromium plating practice has been the introduction of chromium plating bath known as the "Self Regulating High Speed Chromium Plating Bath". This is of the standard type 200 to 300 g/l CrO_3 , but the catalyst used is of the silicofluoride type and is of only limited solubility so that, by providing an excess of it the bath concentration is automatically regulated. The current efficiency claimed for this bath is 4 to 10 % higher than that obtained in conventional solutions

of the same concentration. Some normal and some self-regulating hexavalent chromium plating baths given by P. A. Pepchuk (1963) are listed in Table 2.1.

Table 2.1. Comparison of Hexavalent Chromium Plating Baths (Pepchuk, 1963)

Chromic Acid CrO_3 g/l	Catalysts or additives g/l	Temperature $^{\circ}\text{C}$	Current Density A/dm^2	Current Efficiency %	Remarks
Bath 1. 250	H_2SO_4 2.5	30-70	15-105	12-20	
Bath 2. 250	SrSO_4 6.0 K_2SiF_6 18	30-70	15-105	15-24	Self-Regulating
Bath 3. 250	CaCO_3 50.0 Sugar 2.0 CaSO_4 5.0	10-45	15-75	14-34	
Bath 4. 300	H_2SO_4 2.0 Sugar 2.0 NaOH 40.0	10-45	15-75	20-36	Self-Regulating
Bath 5. 280	SrSO_4 6.0 NaOH 40.0	10-45	15-75	22-38	Self-Regulating

Note: Hardness increases with deposit thickness $30\mu\text{-}700\text{ kg/mm}^2$, $40\mu\text{-}1200\text{ kg/mm}^2$. For restoring worn parts working at loads $>25\text{ kg/cm}^2$ use bath 2 at 50°C and $60\text{-}75\text{ A/dm}^2$ for lower loads use baths 3, 4, or 5 at $18\text{-}22^{\circ}\text{C}$.

The microstructure, texture and hardness of electrodeposited hard, direct current (DC) chromium and pulsed reversed chromium have been investigated by C. Bergenstorf Nielsen et al. (1998). In this study, two samples were used for microstructural investigation, one direct current (DC) chromium and one pulsed reversed (PR) chromium. The microstructure of direct current (DC) electrodeposited chromium and pulsed reversed (PR) electrodeposited chromium have been investigated using X-ray diffraction and cross-sectional transmission electron microscopy.

Investigations have shown that, the DC Cr that was chosen was the one with the highest crack density. It also had the highest Vickers hardness ($\text{HV}_{0.1} = 11\text{ GPa}$) (see Figure 2.11) The PR chromium chosen was the one which was deposited without microcracks (see Figure 2.12) this specimen also had the lowest hardness of the series of PR Cr coatings ($\text{HV}_{0.1} = 5.5\text{ GPa}$). As shown in Figure 2.11 upper right part of the micrograph is as-deposited Cr and lower left part of the micrograph shows the electropolished Cr surface with easily identified cracks. For PR chromium coating, as shown in Figure 2.12 upper part of the micrograph is as-deposited Cr and

lower part of the micrograph shows the electropolished Cr surface. The electropolishing has removed the rough surface of the coating, but it has not revealed any cracks.

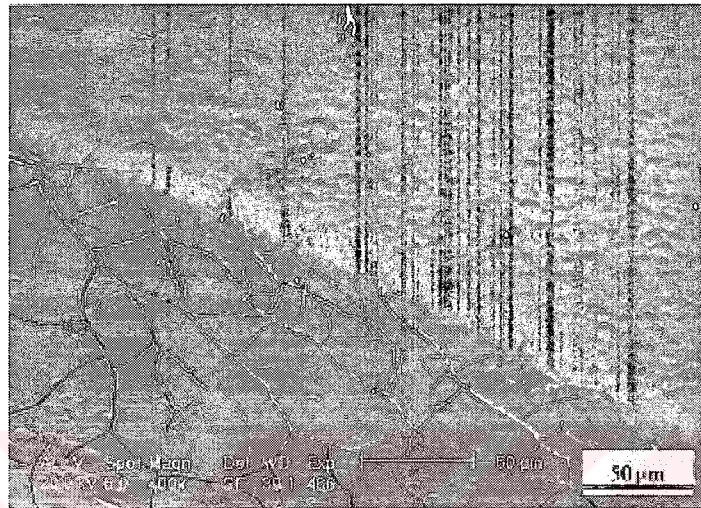


Figure 2.11. SEM Micrograph of the Surface of the DC Cr (Nielsen, 1998)

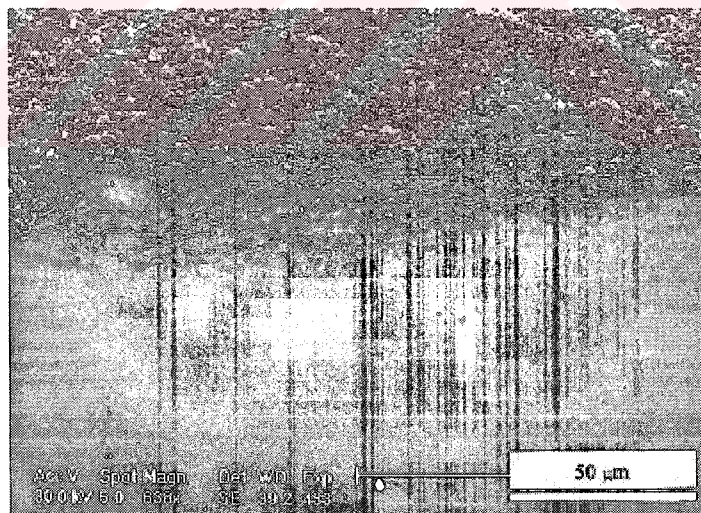


Figure 2.12. SEM Micrograph of the Surface of the PR Cr (Nielsen, 1998)

K. M. Yin and C. M. Wang (1999) have investigated the controlling operating parameters that effect the deposit uniformity in axial and circular directions of hard chromium plating on the interior of small tubes. The study has been consisted of two

parts. (1) copper tubes and lead-tin alloy anodes, (2) steel gun tubes and lead-coated carbon steel.

They have found that for the deposition on the copper tube the use of a small-diameter central anode improved the circular uniformity of the deposited chromium. Also, at a low flow rate, the chromium deposition efficiency decreased with increasing applied current, whereas the efficiency was proportional to the applied current if a high fluid velocity was used. On chromium plating for open systems, the surface roughness decreases with increasing current, flow rate and cathode/anode ratio. The deposit hardness increases with applied current, flow rate and width of the annular gap. For the study of plating on barrels, it has been observed that circular uniformity and hardness can be improved significantly by rotating the tube.

For decorative chromium plating, the most important property is the perfect brightness of the deposit. In the early days of chromium plating, since it was not practical to polish the chromium deposit after plating owing to the absence of a suitable polishing medium, the direct production of a bright coating from the bath was an essential pre-requisite for the practical application of the process.

Nowadays it is in fact possible to polish matt chromium deposits to a high finish, although this post-treatment involves additional expense and also produces a less attractive effect than the directly deposited chromium, so that the emphasis is still on the direct production of bright chromium. For the usual chromium solutions with a chromic acid content of 150 to 400 g/l and about 1% of catalyst, definite current density and temperature ranges exist within which chromium is deposited in the bright state. Bright chromium is deposited within the hatched section; whilst below this area, matt, brittle deposits are obtained; above it, on the other hand, milky, soft deposits are produced.

At average current densities there is a wider tolerance than at extreme current densities because of the permissible bath temperature. Too high a bath temperature in relation to the current density, or rather too low current density for the temperature normally leads to chromium deposits having a milky appearance. If the temperature rises further, the deposits become completely matt, and finally dark and rough (i.e. burnt). Excessively high current densities or too low a temperature soon lead to fully

matt deposits. At too high current densities the formation of rough and nodular deposits also manifests itself.

Since bright chromium is only deposited in very thin films, the quality of the undercoat plays an important role. In order to produce bright deposits, the presence of an equally bright underlayer is obviously essential. Moreover, the chemical nature of the base is also important; thus, for example, the bright range is of considerably greater importance in the chromium plating of copper and its alloys than in the case of nickel, iron or steel (R. Weiner and A. Walmsley, 1980).

In the baths of average composition containing from, say 200 to 400 g/l CrO_3 (preferably 300-400 g/l) with sulphate ions as the catalyst in the ratio of 1:95 to 1:115 in relation to chromic acid, bright chromium plating can be carried out at a current density of about 7 to 20 A/dm^2 at 30 to 55 °C (a mean of about 10 A/dm^2 at 40). At lower temperatures the bright range of the current density is appreciably lower.

Increasing the chromic acid concentration generally results in a narrowing of the bright current density range. Increasing the sulphate content at constant chromic acid content displaces the bright plating range towards higher current densities. In fluoride-containing baths, the bright zone is somewhat different from those with sulphate, the main difference being the fact that a rather higher degree of brightness can be obtained from cooler solutions. In mixed acid electrolytes containing both sulphate and silico-fluoride, an excess of silico-fluoride reduces the brightness. Contaminants, mainly too high trivalent chromium and iron content, reduce the bright range just as much, and may ultimately prevent the formation of bright deposits completely.

It can therefore be seen that all the factors interact, including the bath composition with respect to absolute concentration as well as the relative ratio of the constituents, the current density and the temperature. A bath cannot therefore be characterized by one single parameter, but all the separate conditions must be left constant if reproducible results are to be obtained. In order to obtain as bright a color as possible, the most important point is to plate onto the best fully bright polished

base. Particularly good is anodically polished base metal, or an undercoat produced from a perfectly operating bright plating bath.

2.4.1.1. Effect of Anodes and Cell Equipment

Insoluble lead anodes are almost always used in chromium plating from chromic acid baths. The film of lead peroxide, which is formed on the anodes, fulfils the useful function of oxidizing trivalent chromium, which is continuously formed in the bath, to chromic and so maintains the trivalent ion concentration at the desired low level. Anodes of chemical lead are not recommended as they are attacked by the solution and result in the formation of sludge of lead chromate. Antimonial lead is better and has a greater strength and resistance to corrosion. Lead-tin alloys containing about 7% tin are said to be the best available materials according to the investigations of Dubpernell in 1941.

Iron anodes have occasionally been used when a strong and rigid anode is required. Pure iron, either electrolytic or Armco, resists corrosion much better than mild steel, but it is usually recommended that if iron anodes are used they should be coated with lead.

Tanks for chromium plating are usually made of lead lined steel. The linings may be of antimonial lead but tin-lead linings are even better. It is preferable in all cases to lead line wooden tanks, as this prevents decomposition of the wood by the various chemicals used, with resultant leakages at the joints. The lead lining should be lead-burned at the joinings, and finally lined with reinforced glass to prevent rupture of the lead by careless handling, and also to avoid short circuit by metallic contact with the anodes.

The use of plasticized PVC sheets cemented to steel tanks and welded at seams and corners has been reported by H. R. Carveth, in 1945, although those must not be used above 60 °C. Also is observed that for small baths polyethylene tanks are a possibility.

2.4.1.2. Effect of Chromic Acid Concentration

The simplest factor, which influences the properties of chromium plating is the chromic acid (CrO_3) concentration. If the CrO_3 concentration is increased at a constant ratio of CrO_3 to SO_4 , the hardness of the chromium is reduced to some extent.

According to the investigations of R. J. Piersol, by reducing the chromic acid content from 300 to 250 g/l, the hardness (more correctly the abrasion resistance) has been so greatly increased that it takes almost three times as long to grind off a specific thickness of the chromium deposited from the more dilute bath as that deposited from the stronger one.

In case of bright chromium, the occurrence of greater internal stress does not play such an important role because of the very much lower coating thickness. But increasing the chromic acid concentration generally results in a narrowing of bright current density range.

2.4.1.3. Effect of the Catalyst

Investigations of M. Cymbaliste, (1938) have shown that an increase in the sulphate content of the bath under constant conditions has produced a decrease in hardness. And investigations of R. Bilfinger have shown that the observation of M. Cymbaliste was only correct to some extent. R. Bilfinger has varied the sulphate addition over very wide limits, namely 1 to 20% of the chromic acid concentration, and has shown in this way that an increase in the sulphate content first lowers the hardness of the chromium deposits as it is also stated by Cymbaliste, but by raising the solution temperature and current density at the same time, this reduction in hardness has been reversed.

E. Winniwarter and J. Orban have studied the effect of sulphate ion concentrations to the bright chromium plating. They have shown that even within the range of the usual sulphate ion concentrations, increasing the percentage of sulphate

present displaces the bright range towards higher temperatures, whilst at the same time elevates the current density range and gradually narrows the band.

Investigations carried out by A. Brenner, P. Burkhead and C. Jennings (1947) have shown that chromium deposits of considerably greater hardness can be obtained from solutions containing fluoride instead of sulphate under similar conditions of current density and temperature, as shown in Table 2.2.

Table 2.2. Hardness(Knoop) of chromium deposits from sulphate and fluoride containing solutions at 85°C (Brenner, 1947)

Current Density A/dm ²	Solution Composition	
	300 g CrO ₃ + 3 g H ₂ SO ₄	300 g CrO ₃ + 7.5 g KF
20	325	470
40	425	836
60	475	885
80	550	800

The work of H. Wahl and K. Gebauer (1951) has shown that the hardness differences between chromium from an electrolyte of 250 g of chromic acid with 1% sulphuric acid on the one hand, and 0,6% sulphuric acid and 1% fluosilicic acid on the other have not been very significant, whilst no appreciable differences have been occurred in the wear resistance either. Table 2.3 shows some results of these researches.

Table 2.3. Hardness (Vickers) of chromium deposits from sulphate and from sulphate plus silico fluoride containing solutions at 50°C (Wahl, 1951)

Current Density A/dm ²	Solution Composition	
	250 g CrO ₃ + 2,5 g H ₂ SO ₄	250 g CrO ₃ + 1,5 H ₂ SO ₄ + 2,5 g H ₂ SiF ₄
20	1,000	1,120
40	1,065	1,150
60	1,110	1,150
80	1,190	1,180

In general, the brighter plating range and greater hardness alter at approximately the same rate, so that it is often possible to draw conclusions about the hardness from the appearance. Too low a sulphate content gives matt, grey deposits, which also have reduced hardness.

2.4.1.4. Effect of Various Cations

The trivalent chromium content in the chromium solution is often difficult to control, since it is influenced by the prevailing operating conditions, notably by the ratio of anodic to cathodic current densities.

According to the Investigations of R. J. Piersol only grey, soft chromium deposits have been produced from solutions completely free of trivalent chromium. A small amount of Cr^{+3} improves the appearance and increases the hardness of the chromium. Research results have shown that 5 to 10 g/l represents about the optimum value. In higher amounts, over 15 to 20 g/l, trivalent chromium again has adverse effect on the appearance of the current density and temperature.

2.4.1.5. Effect of Current Density and Temperature

The hardness of electrolytic chromium deposits is considerably affected by the prevailing current density and temperature at which the electrolysis is carried out.

Findings of H. Wahl and K. Gebauer (1951) given in Figure 2.13 in solid line curves indicate the results of the experiments which chromium plated balls have exhibited on abrasion under constant conditions for a specific time.

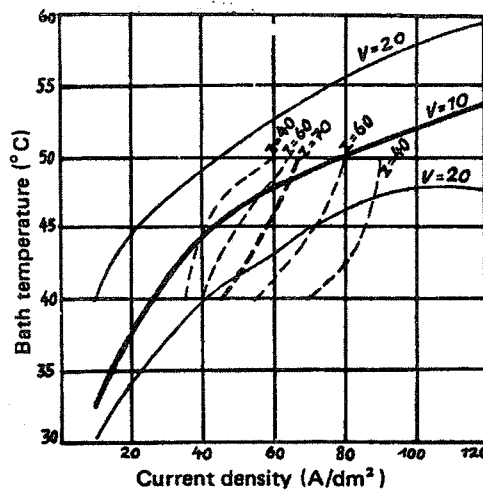


Figure 2.13. Curves of equal resistance to wear according to Wahl & Gebauer(—) and Piersol(---) in relation to current density and temperature of the chromium solution. V = Abraded volume, z = time to chromium deposit cut through

As seen in Figure 2.13, it is evident that, for every temperature or current density value there is a corresponding current density or temperature value at which the greater abrasion resistance of the chromium will be reached and the smallest loss ($V=10$) indicates high abrasion resistance. Also the findings of R. J. Piersol are shown in Figure 2.13 with dashed lines. In the findings of R. J. Piersol, the time needed for a chromium deposit of constant thickness to be worn through is taken as a measure of the abrasion resistance. In this study, the longest time ($z = 70$ min.) has indicated the highest abrasion resistance.

J. M. Hosdowich (1949) has investigated on the abrasion resistance of the chromium deposits that is constantly ground for short periods of time (e.g. 2 seconds) by wear testing method. The number of grinding periods required for a definite thickness to be worn through has been taken measure of the wear resistance.

According to the investigations of M. Cymbaliste (1938), the maximum hardness, which can be achieved for all current densities in a chromium solution of 300 g/l CrO_3 , and 6 g/l SO_4 has been lain at about 50°C . At the temperature of 55°C , the hardness has been equally high at all current densities, and all equal hardness curves have been crossing one another at a single point. It has been conclude that, at higher temperatures, increasing the current density produces a rise in the hardness, whilst at lower temperatures, raising the current density lowers the hardness.

Researches of W. Eilender, H. Arend and E. Schmidtman (1948) have established that at all current densities there always exists a most favorable temperature at which the greatest hardness is produced, above and below this value, the hardness values fall with increasing current densities.

3. MATERIALS AND METHOD

3.1. Experimental Setup

For chromium plating there are several requirements, whether the plant is large or small, obsolete or modern. All these conditions can be defined according to the dimensions, quantity of the articles to be plated and economical conditions. Generally, a chromium plating plant composed of electroplating tanks, electronically conducting anodes, electronically conducting cathode (the workpiece to be plated), the source of electric current or energy, the means of control of this current, heating coils (resistance), temperature controller and several smaller details.

In this study, a small modern chromium electroplating experimental setup has been built. It consists of a plating tank, heating coils, digital thermostat, tin-lead anodes containing 7% tin and a programmable DC electrical power supply, as shown in Figure 3.1 and 3.2. Agitation of the electrolyte performed by hand stirring before and after each experiment. Other laboratory tools such as glass pipe, glass funnel, weight measuring device etc. were also used during experiments to handle chemicals.



Figure 3.1. Experimental Setup of Chromium Electroplating

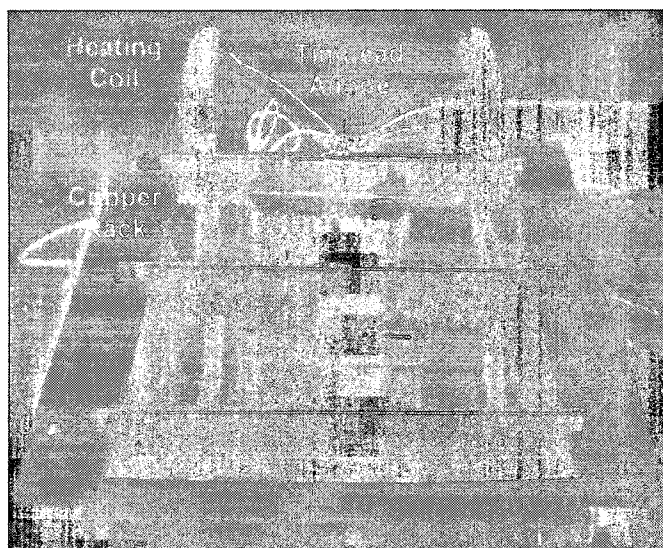


Figure 3.2. Upper View of Plating Bath

3.1.1. Plating Tank

It is particularly important that the tank should have no electrical contact with the anodes since this can greatly accelerate corrosion. It is nowadays possible to coat the inside of the tank with chromic acid resisting paint, but this is seldom practiced. Fluoride containing solutions can apparently attack the glass lining, so that for such solutions, lining of plastic sheet, such as polyvinyl chloride, Hypalon (chloro-sulphonated polyethylene), or Teflon (PTFE) are recommended.

Recently, it has also become possible to apply sprayed plastic linings, which are pore-free and very firmly adherent. They are applied to a thickness of about 2.5 mm and a further advantage is that it is possible to increase the thickness locally at areas where increased attack is expected, e.g. at solution level.

The plating tank should be of such a size that the articles being plated are positioned at a distance 15 to 20 cm from the sides and bottom of the tank as well as from the surface. In deciding on the dimensions of the tank, and of its rectifier capacity, consideration should be given to an ideal current loading of 1 to 1.5 ampere per liter of the tank content.

In this study, polyethylene plating tank was used since polyethylene can withstand chromic acid solutions, which includes %98 sulphuric acid. Dimensions of

the plating tank are 280x280x275 mm as shown in Figure 3.3 and capacity of the plating tank was approximately 21000 ml. Two plastic jars, with a capacity of 850 ml were used for double rinsing operation of the specimens after chromium plating process.

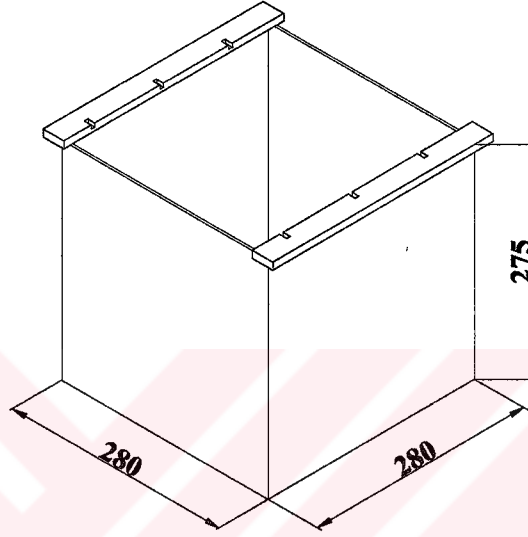


Figure 3.3. Technical Drawing of Polyethylene Plating Tank

3.1.2. Heating Coils

The heating of electrolytic solution can be carried out using different sources of heat such as a water or steam jacket, which can be heated in any desired manner, heating coils or immersion heaters. The heat transfer efficiency of a plastic or plastic lined tank is, however poor. Because of this reason for the plants, which comprised of plastic based tanks heat transfer efficiency should be considered.

In this study, internal heating of the electrolytic solution was carried out by means of an immersion heater, which is made of lead pipe. The diameter of the lead pipe was 15 mm. The power of the heater was selected as 1000 W and it is determined according to the maximum operation temperature of plant (70 °C). The size and shape of the heater were designed according to the size of the plating tank and aimed to provide homogenous heat distribution in the electrolytic solution (See

Figure 3.4). PTFE supports, with 15 mm height, were used to prevent contact between the bottom of the tank and heater.

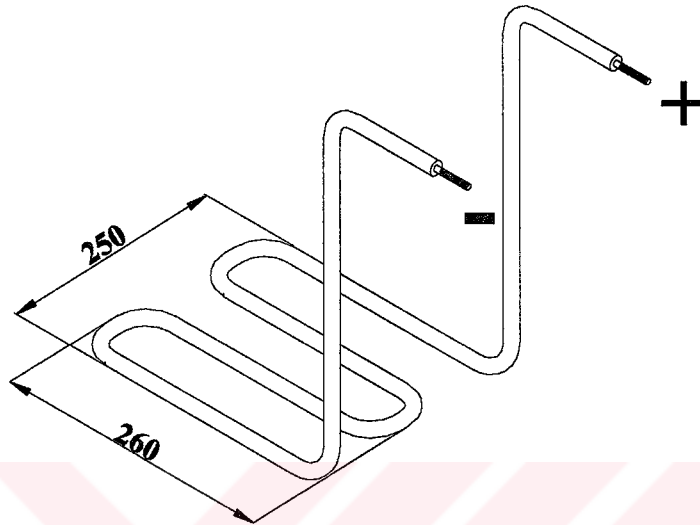


Figure 3.4. Heater Made of Lead Pipe

3.1.3. Anodes

The usual anode material is lead. Pure lead is strongly attacked in chromic acid producing considerable amounts of lead chromate; it coats the anodes with a non-conducting film which must be removed occasionally or the anodes build up high resistance and cease to function. For this reason, hard lead containing 6 to 8% antimony is generally employed. Alloys of lead and tin (6 to 10%) or containing small amounts of silver (0.5 to 1.5%) or tellurium (0.2%) have been proposed. Tin containing lead anodes have been particularly recommended instead of antimonial lead for fluoride-containing baths. It is most essential that a vat contains anodes of all the same composition, as differing alloys on the same bus bar in a vat can dissolve at differing rates even without impressed current, and if, for instance, both tin-lead and antimonial-lead anodes are present together, the more expensive tin-lead anodes will be corroded badly.

Regardless of which alloy is used, a high degree of purity is a basic requirement for the anode metal. The pure lead should contain 99.9% lead. Antimony

must be completely free from arsenic, which can cause roughness in the chromium deposit even when present in traces. Hard lead with low silver content, e.g. 94% lead, 5% antimony and 1% silver exhibits a lower tendency towards the formation of chromate films.

The anode area should be about the same, or rather greater than that of the area of the work, although variations of between half and double this area are common. The relative areas can determine the proportion of trivalent chromium in the bath, and the life of the anodes is higher if they are used at higher anode current densities.

In this study, tin-lead anodes, which contain 93% lead and 7% tin were used. Dimensions of the anodes were selected as 150x120x20 mm according to the size of the work (See Figure 3.5).

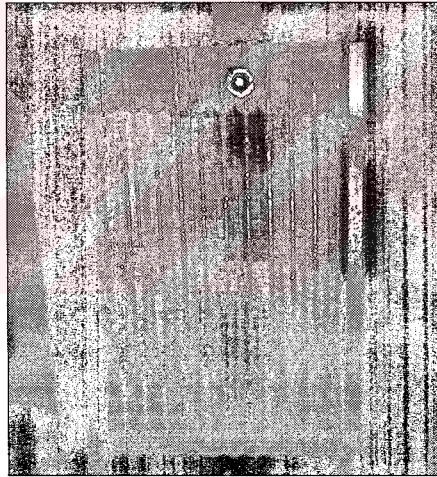


Figure 3.5. Tin-lead Anode, Which Contains 93% Lead and 7% Tin.

3.1.4. Cathode (Test Specimens)

MS58 (CuZn40Pb2) brass was used as a cathode material in this study. MS58 brasses are frequently hot-worked and extruded. They are low in cost, mildly corrosion-resistant and used commonly for many engineering applications. The shape and dimensions of the test specimen used in the chromium plating processes are shown in Figure 3.6 and chemical compositions of MS58 brasses are given in Table 3.1.

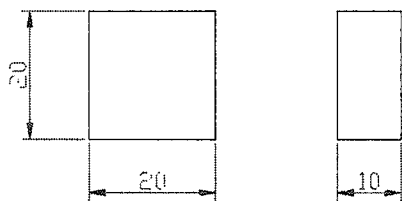


Figure 3.6. The Shape and Dimensions of the Test Specimens Used in Chromium Plating Process

Table 3.1. Chemical Composition of MS58 Brass Test Specimens

Symbol of Alloy	Number of Alloy in DIN	% Cu	% Pb	% Zn	% Al	% Fe	% Ni	% Sn	%Other	Density gr/cm ³
CuZn40Pb2	2.0402	57.0 59.0	1.50 2.50	Rest	Max. 0.1	Max. 0.4	Max. 0.4	Max. 0.3	Max. 0.2	8.43

3.1.5. Temperature Controller

The aim of using temperature controller is to keep the bath temperature precisely at the setpoint during experiments without any changes. An on-off controller is the simplest form of temperature control device. The output from the temperature control device is either on or off, with no middle state. An on-off controller will switch the output only when the temperature crosses the setpoint. For heating control, the output is on when the temperature is below the setpoint, and off when it is above the setpoint.

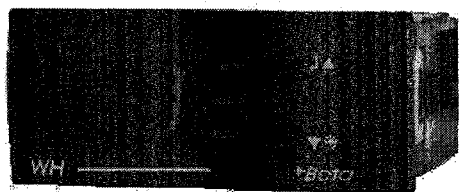


Figure 3.7. Temperature Controller Used During Experiments

In this study, an on-off WH31-DISPLAY temperature control device, shown in Figure 3.7, was used to control bath temperature.

The WH31-DISPLAY is a digital thermostat with temperature visualized on a LED-type display. Measuring range of the device varies between -50 °C to +99 °C and operates as an ON/OFF heating regulator. This means that the heater stops when set point temperature is reached and restarts at a temperature equal to the set point one minus a differential. Amount of differential can be set from keyboard and it was set to the minimum value of device as 1 °C to be more precisely. Technical specifications of WH31-DISPLAY temperature control device, used in this work, are given in Table 3.2.

Table 3.2 Technical Specifications of WH31-DISPLAY Temperature Control Device

Housing	Self-extinguish UL94V0 ABS plastics, black colour
Size	Frontal 32x74mm; depth 78mm (including terminal cover)
Mounting	Flush-panel on hole 28x70 mm (with "fast-lock sliding brackets)
Protection	IP 64 for the front panel
Connections	On screw terminal board for wires with cross section are < 2.5 mm ²
Display	2 ½ digit LED display 12.5 mm high
Data Storing	Not volatile memory
Operating Temperature	Between -5 °C to 65 °C (23 °F to 149 °F)
Stocking Temperature	Between -30 °C to 75 °C (-22 °F to 167 °F)
Relative Humidity	20 to 85% (not condensing)
Measurement Range	Between -50 °C to 99 °C for PTC probe
Output	1 on a SPDT 8 (3) A 250 Vac relay
Analogue input	1 for PTC thermostatic probe
Resolution	1 °C (1 °F)
Accuracy	Better than 1.0% f.s. ±1 digit
Power Supply	Standard 12 Vac/dc ± 15%; available 230 Vac +5/-10% 50/60 Hz through built-in transformer

3.1.6. Power Supply

The source of current in the early days of plating was a battery consisting of a negative element and a positive element, the former usually being some metal, or carbon, and the latter invariably zinc. The discovery by Faraday of the principles of the electric dynamo obviated the use of batteries, and today dynamos are used in their place. These yield a current in every way more suitable to plating, and they generate a steady flow whenever wanted.

In recent years a type of electrical plant, known as the metal rectifier, has been developed for the conversion of the almost universal alternating current into the necessary low-voltage direct current. There are no dynamos or revolving generators necessary, the rectifier equipment consisting essentially of a transformer consuming alternating current from the electricity mains, and delivering alternating current at a voltage approximating to the low voltage required for plating, this alternating current being then converted into the low-voltage direct current by means of rectifier.

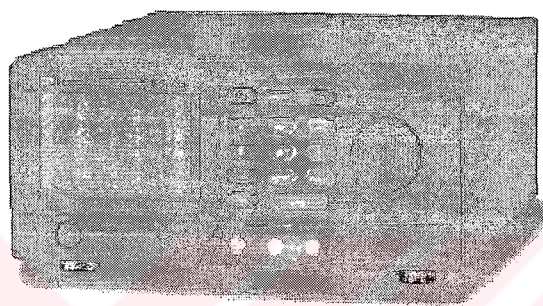


Figure 3.8. DC Electrical Power Supply Source Used in Experiments

A supply of 4 to 6 volts is quite suitable for most copper, nickel, silver, etc. plating, but for chromium the higher current necessary will demand a higher voltage. In general, the actual requirements of electrical equipment are based on the size of the piece to be plated and the desired thickness.

In this study, electrical requirements of experiments were low due to size of test specimens. The dimensions of the specimens were selected as 20x20x10 mm, which requires maximum electrical demand of 180 VA. For this reason, Instek-PSP 603 (60 V – 3.5 A) model “Programmable Switching DC Power Supply” was used as electrical power supply (See Figure 3.8). Technical specifications of Instek-PSP 603 are given in Table 3.3.

In electroplating process, the current allowed to flow to the cathode (test specimen) is in proportion to the area going to be plated, so that the current is expressed as current density or quantity of current per unit area. In commercial plating, the current density is expressed as amperes per decimeter square (A/dm^2). In this study, the operating range of the current density was selected between 8 A/dm^2 and 40 A/dm^2 where surface area of the test specimen to be plated was 0.04 dm^2 .

Table 3.3. Technical Specifications of PSP-603 Programmable Power Supply

Operating Voltage	115/230 V AC $\pm 15\%$		
Power Frequency	50/60 Hz		
Power Consumption	Approximately 420 VA maximum		
Power Output	200 W maximum		
Output Voltage	0 ~ 60 V DC 20mV resolution	0 ~ 40 V DC 10mV resolution	0 ~ 20 V DC 10mV resolution
Program Accuracy	$\pm 0.05\% \pm 4$ digits	$\pm 0.05\% \pm 3$ digits	$\pm 0.05\% \pm 4$ digits
Output Current	0 ~ 3.5 A 2mA resolution	0 ~ 5 A 2mA resolution	0 ~ 10 A 5mA resolution
Program Accuracy	$\pm 0.1\% \pm 5$ digits	$\pm 0.1\% \pm 5$ digits	$\pm 0.3\% \pm 10$ digits
Voltage Load Regulation	≤ 10 mV		
Current Load Regulation	≤ 5 mA		
Voltage Line Regulation	$\leq 0.05\%$		
Current Line Regulation	$\leq 0.05\%$		
Ripple Voltage	≤ 20 mV rms		
Ripple Current	≤ 10 mA rms		
Readback Resolution (Meter)	20 mV 2 mA	10 mV 2 mA	10 mV 5 mA
Readback Accuracy (Meter)			
Voltage	$\pm 0.05\% \pm 4$ digits	$\pm 0.05\% \pm 3$ digits	$\pm 0.05\% \pm 3$ digits
Current	$\pm 0.1\% \pm 5$ digits	$\pm 0.1\% \pm 5$ digits	$\pm 0.1\% \pm 10$ digits
Digital Display	Multi-line LCD with background lighting		
AC Fuse	Slow-Blow T6.3A/250V for 115V, T3.15A/250V for 230V		
Weight	Approximately 4 kgs		
Dimensions	Approximately 225x100x305mm (without stand and power cable)		

3.2. The Preliminary Works for the Experiments

Quality of the chromium plating is primarily depending on the reaction that takes place at the cathode during deposition. This reaction can only be favorable if the plating plant has been properly prepared and adjusted. Even though the conditions are right in the plating bath and at the cathode, there is no guarantee that the deposit will be satisfactory since the quality of the deposit also depending on the conditions and quality of the equipments and the preparatory steps of the plant.

3.2.1. Preparation of Test Specimens

Surface contaminants such as oils, greases, waxes and metallic debris are almost always present on materials as a result of production processes that have been

carried out prior to receipt. Therefore, before any process of metallic coating is applied to a metal substrate it is essential that the latter's surface shall be in a suitable condition to receive the coating. In order to achieve this, one or more pretreatment processes must be employed. Broadly, pretreatments fulfill one or more of these purposes:

- Removal of surface contaminants
- Removal of superficial corrosion
- Control of the physical nature of the metal surface

The presence of surface contaminants always seriously hinders the successful application of a coating process for the following reasons.

- They can scar the metal surface during any polishing treatments that may be required, or may even be driven into the surface of the metal so that they cannot easily be removed.
- They can provide a physical barrier that will prevent access of a processing solution to the metal surface so that the requisite reaction cannot occur.
- They can react with a processing solution, altering its chemical composition and hence its reactions with the metal to be coated.
- In the presence of an electrolyte (such as processing solution) they can react with the substrate metal or with the coating metal, causing corrosion of the surface or producing insoluble products that will further contaminate the surface.
- They can be incorporated in a coating system, producing a region where coating adhesion may be defective or interfering with the homogeneity or growth of the coating itself so that a physical defect may develop. Any such defects produced during the early stages of the processing sequence may provide a region where subsequent processing solutions can become entrapped; these pockets of entrapped solution can themselves produce corrosion at a later time.

It follows from the above possibilities that surface contaminants should always be removed before subsequent processing is attempted. The principal way in

which contaminant of this nature is removed from metals is by the use of cleaner-degreaser.

3.2.1.1. Mechanical Pretreatments

The test specimens shown in Figure 3.6, were manufactured from a 3 m length 20x20 mm brass bar stock. Electrical connections of the test specimens were provided by copper-wires, which have 2.2 mm diameter. After that, all specimens coated by polyester in order to prevent electrolyte/test specimen interactions except the surface of the specimen, which is going to be plated. Test specimens were mechanically abraded with five different grit numbers (400/600/800/1000/1200) SiC abrasive papers in order to obtain smooth surface on plated specimens. The abrading process carried out by hand on a smooth leveled surface and performed in lubricated state with water.

3.2.1.2. Polishing

Polishing is used to improve appearance, leveling, reflective properties or closeness of fit with mating components or to reduce friction between moving components. Mechanical, chemical and electrolytic methods may be used. In this study, mechanical, chemical and electrolytic polishing methods were applied to the specimens before nickel plating process, to obtain smooth surface, specimens were subjected to mechanical polishing process.

This method may be considered as an extension of the abrading process at the finest end of scale; metal removal is reduced and smoothing action accentuated. When applied in its final stages to produce the greatest luster and smoothness it is known as buffing.

In this study, very fine grades of silicon carbide polishing paste was used as polishing abrasives and were applied to the test specimens by means of buff, which is rotated by an electrical motor. After mechanical polishing has been finished all specimens immersed in a tank, which contains gasoline. The specimens are then

cleaned by a soft brush in order to remove impurities formed on the surfaces during polishing and finally, all specimens were rinsed by fresh water.

3.2.1.3. Degreasing

Degreasing was carried out to ensure complete removal of particles of metal, abrasive and the residue of greases or waxes used for lubrication, during polishing process.

An organic solvent called as carbon tetrachloride was used as a cleaner-degreaser in this study. Solvent was filled in a plastic tank and specimens, which were appropriately suspended from copper handling devices were immersed in the solvent and kept in the tank for 10 minutes. Oils, greases and lacquers were softened by the solvent and taken into solution, and entrapped insoluble dirt and metal particles were loosened so that they fell away to the bottom of the tank.

3.2.1.4. Rinsing

After degreasing operation, double rinsing of the test specimens were carried out in order to clean remaining degreaser solvent from the surface of the specimens.

In this study, a static drag-out tank which has 50 lt water capacity was used for first rinsing operation. The work leaving the plating, degreasing or polishing tank was first rinsed in a static drag-out tank by immersing and taking them out 5 or 6 times. After the first rinsing operation in static drag-out tank, all specimens were exposed to second rinsing operation. Continues flow water from a sprinkler was used as seen in Figure 3.9 for the second rinsing operation. Double rinsing operation was applied with fresh water after each stage of polishing and nickel plating as described in this section. However, after chromium plating process, since each specimen was subjected to double rinsing operation separately two plastic jars, with a capacity of 850 ml were used with the same procedure.

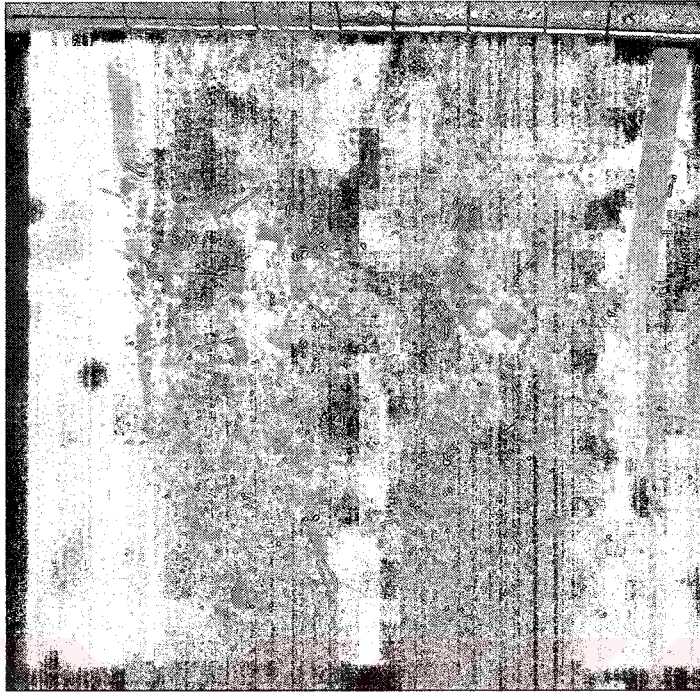


Figure 3.9. Second Rinsing Operation of Nickel Plated Specimens

3.2.1.5. Electrolytic Cleaning

Electrolytic cleaning is an electrochemical cleaning process by which surface metal is removed by anodic dissolution and will effectively prepare the surface of a material for further processing. Electropolishing leaves a smooth, clean surface ideal for conversion coating, plating, anodizing, or welding. Sometimes referred to as "reverse plating", electropolishing actually removes metal starting with the high points within the microscopic surface texture. By removing these points, electropolishing will improve the surface finish, leaving a smoother and more reflective surface.

Electropolishing was accomplished by altering the electrode potential of metal piece within a heated electrolyte bath. A cathode is assembled to mirror the surface of the specimen. When current is supplied, the electrical charge causes metal ions to be dissolved from the surface of the working piece. The key to the process is the differences in the current density across the microscopic surface. The current density is greatest at high points and lowest at the low points. The rate of the

electrochemical reaction is directly proportional to the current density. The increased current density at the raised points causes the metal to dissolve faster at these points and thus levels the surface material.

In this study, a bath consists 80 g/l nitric acid was used for electro chemical cleaning. Specimens were suspended to the anode of the cell and stainless steel cathodes were used for cathodic reaction. After immersing the specimens into the solution, 5 A/dm² current density were applied to specimens for 5 minutes, and then specimens were rinsed.

3.2.1.6. Acid Pickling

Acid pickling process is a chemical polishing process. This stage of polishing consists of acid dissolution of the metal from the surface, the rate of attack being limited by controlling the rate of diffusion of soluble salts from the surface and the replenishment of free acid in the region. Chemical polishing was applied to improve the brightness and reflectivity of the test specimens but it is not possible to achieve a true mirror surface. Acid pickling is one of the most widely used method and it has been reported that scale and oxide removal consumes 5% of all sulphuric acid, 25% of the hydrochloric acid, most of the hydrofluoric acid, and large quantities of nitric and phosphoric acids.

Although the hydrofluoric acid is an effective pickling material for many metals at room temperature, a hydrochloric acid solution at a concentration of about 15% was preferred for this study. After preparation of solution, all specimens were immersed into the solution and kept for 5 minutes in the bath and finally specimens were rinsed as rapidly as possible in order to prevent further reaction of solvent retained on the surface of the specimens.

3.3. Nickel Plating Process

Nickel plating process was performed using the facilities of Medikar Co. Inc. For nickel plating process, a Watts nickel plating bath containing chemical

compounds given in Table 3.4 was prepared. The capacity of the bath was 250 lt. The anodes used during nickel plating were consisting of 99% nickel. They were immersed into the bath within cotton bags to prevent fine particles from being dispersed in the solution and thus causing roughness by incorporation in the specimens' surfaces. Bath temperature was 50 °C and 4 A/dm² current density was maintained for 15 minutes. Following to nickel plating process, specimens were rinsed.

Table 3.4. Chemical Composition of Nickel Plating Bath

Chemical	Concentration
Nickel Sulphate (NiSO ₄ .7H ₂ O)	250 g/l
Nickel Chloride (NiCl ₂ .6H ₂ O)	60 g/l
Boric Acid (H ₃ BO ₃)	40 g/l
Nickel Brightener	0.5 ml/l
Nickel Leveller	12 ml/l
Nickel Humidifier	12 ml/l

3.4. Chromium Plating Process

After nickel plating and double rinsing operations, test specimens were subjected to chromium plating process in the experimental setup prepared for this study. Bath composition and values of other process parameters are defined by the software Design Expert 6.0 which was used for the design of experiments. Different experimental conditions were defined by software for each set of experiment and order of the experiments was randomized. Each experiment was carried out by two replications, that is, two specimens were chromium plated under the same experimental conditions.

During chromium plating process, lead anodes attack by chromic acid and an insulating layer of lead chromate (yellow in color) can be formed if the working surfaces of the anodes are not transformed into the lead peroxiding process. The oxide layer prevents the formation of lead chromate, whilst allowing the passage of plating current.

Therefore, before starting chromium plating process of test specimens, peroxiding of the anodes were carried out by using following sequence:

- 5% solution of sulphuric acid in 15 lt. water was prepared.
- Surfaces of the lead anodes were cleaned by scrapping.
- Lead anodes were connected to DC power supply, one negative and the other one positive.
- Current was adjusted to 3.5 A and maintained for 15 minutes.
- The polarity of the DC power supply was reversed.
- Current was adjusted to 3.5 A and maintained for 15 minutes.
- The polarity of the DC power supply was reversed.
- Finally, the current was adjusted to 3.5 A and maintained for 20 minutes.

After peroxiding process, a dark brown coating on the lead anodes was observed. This was because of protective layer of lead peroxide.

Following to the peroxiding of the anodes, chromium plating process was carried out. Experiments were carried out using the following sequence of operation.

- Plating tank was filled with 14 lt fresh water.
- Required amount of chromic acid was added to the fresh water.
- Mixture of chromic acid and water was stirred by hand with a glass rod.
- Required amount of sulphuric acid was added to the bath.
- Mixture was stirred by hand with a glass rod.
- Bath temperature was set by temperature controller and heating coils.
- Amount of current density was set.

After bath temperature was maintained, adjusted current was applied and chromium plating process finalized. Following to the chromium plating of the test specimens, they were rinsed in two plastic jars, which have 850 ml. water capacity.

3.5. Drying

Test specimens were subjected to the compressed air first and then suspended on a rod for an hour during drying operation.

3.6. Methods of Testing

Measuring the film thickness and determining the visual appearance of chromium plated surfaces are primarily concerned for quality control of plated components. There are many test methods available for identification of deposit, and other properties of coatings such as corrosion resistance, wear resistance, hardness, surface smoothness, brightness, porosity and etc. In this study, test specimens were subjected to the various test methods such as measurement of film thickness and measurement of reflectivity (brightness) in order to investigate the effect of process parameters on the thickness and brightness of chromium plated surfaces.

3.6.1. Film Thickness Measurement

In many industrial applications, the special structure of electrodeposited chromium is responsible for the hardness and thickness of chromium plating. The hardest chromium deposits attain the hardness of corundum, and are twice as hard as other metals such as iron, cobalt and nickel. They are much harder than nitrided or case-hardened steel. Also thickness control is of particular importance where the work is to be dyed or where close dimensional tolerances have to be obtained together with adequate protection. Therefore, thickness of deposit may be thought as one of the most important features of the chromium plating process.



Figure 3.10. (a) The Measured Points. (b) The Points, which Extremely High Film Thicknesses Were Observed

In this study, film thickness measurements were made at the points shown in Figure 3.10 (a). The arithmetic average of these values was taken to determine the

average film thickness of plated parts. The measurements taken at the points shown in Figure 3.10 (b) were not used due to high thicknesses observed at these points because of non-uniform current distribution.

The thickness measurement of the specimens was performed using DCFN 2000 model coating thickness gauge. The device has a double-sided probe and digital indicator as seen in the left side of Figure 3.11 and before each measurement the device was calibrated. One side of the probe is used for ferrous application and the other side of the probe is used for non-ferrous application. In this study, the non-ferrous applications side was used for thickness measurements.

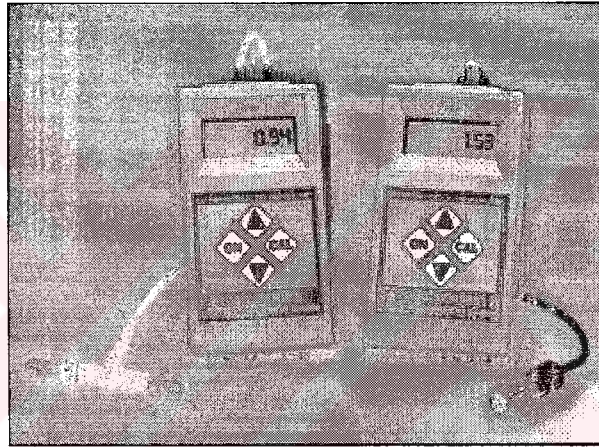


Figure 3.11. Film Thickness Measurement Device

Operating principle of DCFN 2000 model coating thickness gauge based on creating eddy-currents. When an eddy-current producing probe is brought into direct contact with a bare metal surface, a magnetic flux circuit is created. The amount of flux created depends on the frequency and strength of the eddy-current force and the magnetic reluctance of the bare metal. A non-metallic, non-conducting coating placed in the path of a magnetic flux circuit creates a “magnetic gap” which increases the circuit reluctance and causes a decrease in the circuit flux, proportional to the thickness of the coating or plating. The DCFN 2000 model coating thickness gauge measures this decrease to provide an accurate, direct indication of the coating thickness being measured.

3.6.2. Brightness (Reflectivity) Measurement

For the measurement of the brightness, the reflectivity of the coated surfaces was measured since the reflectivity of the surface is directly proportional with the brightness of the surface. This method is suitable for a broad range of applications where surface reflectivity enables measurement of brightness such as coatings, plastic films, extrusions, coil coatings, liquid crystal displays, magnetic and optical disks, optical fibers, beverage cans. Reflectivity can be defined as, the optical property of a material defining what ratio of light is reflected compared to the incident light.

The color of chromium is bluish-white. The reflectivity of polished chromium surfaces is actually 55% that of freshly polished silver in the visible light range, although these reflectivity properties are maintained in the atmosphere, whereas silver, as is well known, tarnishes relatively quickly. Silver loses its reflecting properties particularly rapidly in sulphur-bearing atmospheres, whilst chromium remains unchanged.

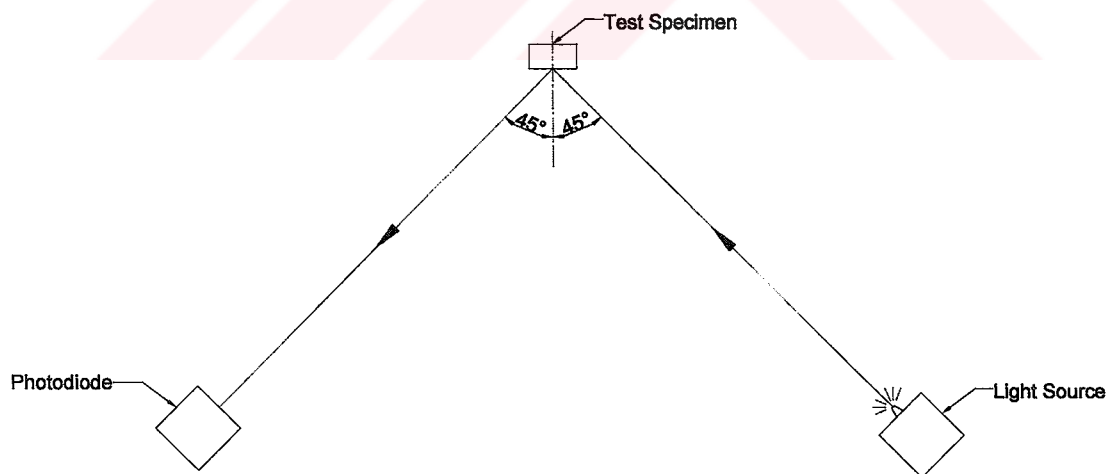


Figure 3.12. Experimental Setup of Reflectivity Measurement

The experimental setup for the measurement of the reflectivity was rather simple, a linear polarized light source was set-up at a constant distance and angle

from the surface of the test specimens and the photodiode of the reflectivity measurement device which measures the intensity of the reflected light from specimen surface was located at the symmetry of the light source. The intent was to compare measurements of the amount of reflected light gathered by the photodiode. The luxmeter gives a numerical readout in Lux. A white LED with lens was placed 20 cm away to the surface of the test specimen with an angle of 45° to the normal of the surface and the photodiode of the device was located to the symmetry of the light source. Test set-up is shown in Figure 3.12 schematically. For the measurement of the reflectivity, luxmeter feature of CONRAD VOLTcraft 5 in 1 Multi-Tester was used (See Figure 3.13). The device measures the intensity of the light source by a built-in silicon photodiode with filter; this filter lets light pass between 400 nm and 700 nm. This is the range visible for the human eye. For the comparison of the reflected light, initially light source was located 20 cm away from luxmeter and illuminated, the intensity of the light was measured without test specimens. Then, each specimen located as shown in Figure 3.12 and intensity of reflected light from chromium plated surface was measured.



Figure 3.13. Reflectivity Measurement Device

3.7. Design, Analysis and Optimization of the Experiment

3.7.1. Response Surface Methodology (RSM)

In the early stages of experimental work, experimenters typically use screening experiment designs that normally consist of trials run at the extreme lower- and upper-bound level setting combinations of the variable study ranges. They provide information on the direct additive effects of the study variables and on pairwise (two-variable) interaction effects. Screening designs enable experimenters to select the best materials and equipment from available alternatives and to focus on the correct variables and ranges for further study.

In the later stages of the experimental work, the goal shifts from screening to product and process optimization. The statistical experiment designs most widely used in optimization experiments are termed "response surface designs." In addition to trials at the extreme level settings of the variables, response surface designs contain trials in which one or more of the variables are set at the midpoint of the study range (other levels in the interior of the range may also be represented). Thus, these designs provide information on direct effects, pairwise interaction effects and curvilinear variable effects. Response surface methodology (RSM) is the combination of mathematical and statistical techniques used in empirical study of relationships and optimization, where several independent variables influence a dependent variable or response, the goal being to secure the optimal response. In applying the RSM, the response or dependent variables influence on an independent variable is viewed as a surface to which a mathematical model is fitted. The eventual objective of the RSM is to determine the optimum operating conditions for the system or to determine a region of the factor space in which the operating conditions for the system or to determine a region of the factor space in which operating requirements are satisfied.

3.7.2. Central Composite Design (CCD)

Most practitioners of RSM generate experiment designs and analyze their data using a statistical software program running on a computer. Many of these programs can generate many classes of RSM designs and, in some cases, offer several varieties of each class. However, the central composite design is the most popular of the many classes of RSM designs due to the following three properties:

- A central composite design (CCD) can be run sequentially. It can be naturally partitioned into two subsets of points; the first subset estimates linear and two-factor interaction effects while the second subset estimates curvature effects. The second subset need not be run when analysis of the data from the first subset points indicates the absence of significant curvature effects.
- CCDs are very efficient, providing much information on experiment variable effects and overall experimental error in a minimum number of required runs.
- CCDs are very flexible. The availability of several varieties of CCDs enables their use under different experimental regions of interest and operability.

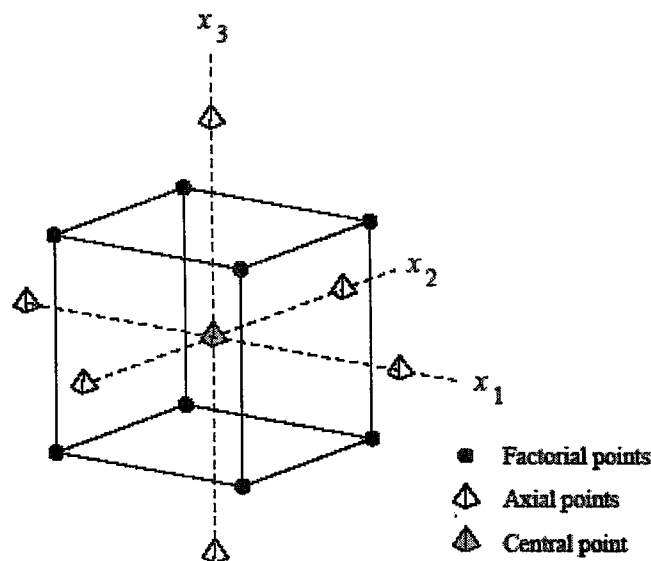


Figure 3.14. Central Composite Designs for 3 Design Variables at 2 Levels (Montgomery, 1997)

A second-order model can be constructed efficiently with central composite designs (CCD). CCDs are first-order (2^n) designs augmented by additional centre and axial points to allow estimation of the tuning parameters of a second-order model. Figure 3.14 shows a CCD for 3 design variables.

As shown, in Figure 3.14, the design involves 2^n factorial points, 2^n axial points and 1 central point. CCD presents an alternative to 3^n designs in the construction of second-order models because the number of experiments is reduced as compared to a full factorial design (15 in the case of CCD compared to 27 for a full-factorial design). Hence, in the case of problems with a large number of design variables, use of central composite design may be time-consuming.

In most statistical software programs, there are three main varieties of CCD. These are face-centered, rotatable (circumscribed) and inscribed CCD. Many experimenters are uncertain about the best variety to use in a given study. To make the right selection, the differences between these varieties should be understood in terms of the experimental region of interest and region of operability, according to the following definitions.

Region of interest: A geometric region defined by lower and upper limits on study-variable level setting combinations that are of interest to the experimenter.

Region of operability: A geometric region defined by lower and upper limits on study-variable level setting combinations that can be operationally achieved with acceptable safety and that will output a testable product.

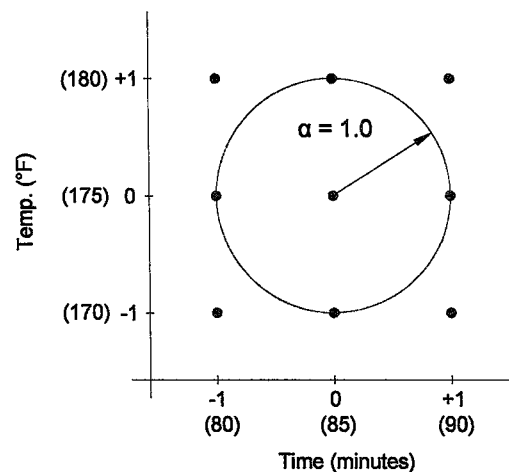


Figure 3.15. Two-Variable Face-Centered CCD (Montgomery, 1997)

Figure 3.15 presents a face-centered CCD for two study variables: time and temperature. Both coded and natural variable level settings for time and temperature are shown in the figure. The design consists of a center point, four factorial points (the intersection points of the ± 1 coded variable bounds) and four axial points (points parallel to each variable axis on a circle of radius equal to 1.0 and origin at the center point). The dots in Figure 3.15 identify the variable level setting combinations that constitute the nine design points (experiment runs).

The radius, designated α , determines the geometry of the design region. An α of 1.0 defines a square design geometry (a cube for three variables, a hypercube for four or more variables, etc.). As the value of α increases, the axial points extend beyond the faces of the square and the design region becomes more spherical.

To successfully carry out any designed experiment, the region of operability must encompass the region of interest. In this example, this means that the process must be able to be operated at all time and temperature level setting combinations in the region of interest described by the variable ranges. Therefore, the first step in selecting the right variety of CCD is to compare the region of interest to the region of operability. If the process cannot be operated at one or more of the extremes of the region (in this case the corners of the square), then a face-centered CCD is inappropriate.

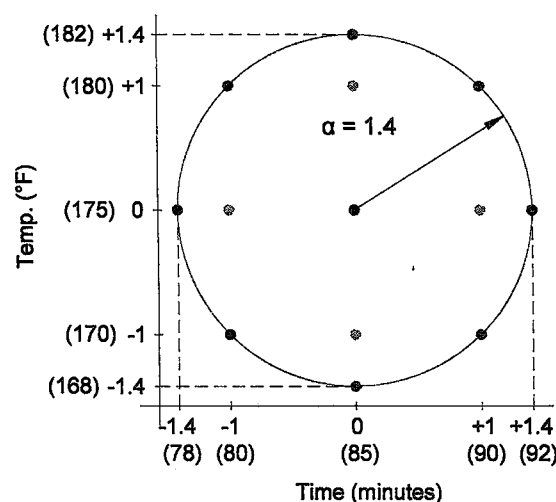


Figure 3.16. Two-Variable Rotatable (Circumscribed) CCD (Montgomery, 1997)

Rotatable (circumscribed) designs are the original form of the central composite design. Figure 3.16 presents a rotatable CCD for time and temperature using the previously defined lower and upper variable bounds. As the figure shows, the rotatable CCD uses an α value of 1.4 to describe a circular design geometry (a sphere for three variables, a hypersphere for four or more variables, etc.).

For a given number of variables, α value required to achieve rotatability is computed as $\alpha = [2^n]^{1/4}$ where n is the number of study variables or factors. Rotatability refers to the uniformity of prediction error. In rotatable designs, all points at the same radial distance (r) from the center point have the same magnitude of prediction error. In most rotatable designs the factorial points and axial points lie on different concentric geometric spheres and thus have different magnitudes of prediction error. For example, in the 2^3 rotatable CCD, the factorial points are located on a sphere of radius 1.73, while the axial points are located on a sphere of radius 1.68. Setting α to 2^n changes the design from a rotatable CCD to a spherical CCD. In spherical CCDs, all design points occur on the same geometric sphere. These designs are not exactly rotatable, but they are near-rotatable.

The value of making rotatability (or near-rotatability) a design goal becomes clear when you consider that the location of the optimum point within the region of interest is not known before the experiment is conducted, so it's desirable that all points a given distance (r) from the center point in any direction have the same magnitude of prediction error.

Relative to the α value of 1.0 in the face-centered design, the rotatable design α value of 1.4 has extended the design region beyond the defined variable bounds. Thus, predicted responses at or near the axial points, which would have been extrapolations in a face-centered design, are within the design region in rotatable design. This is an important consequence, because the magnitude of prediction error increases geometrically with distance outside the design region.

However, extending the axial points beyond the defined variable bounds when using rotatable CCDs requires operating the process at five level settings of each variable. The face-centered CCD, in contrast, requires operating the process at

only three level settings of each variable. This makes the face-centered CCD a simpler design to carry out.

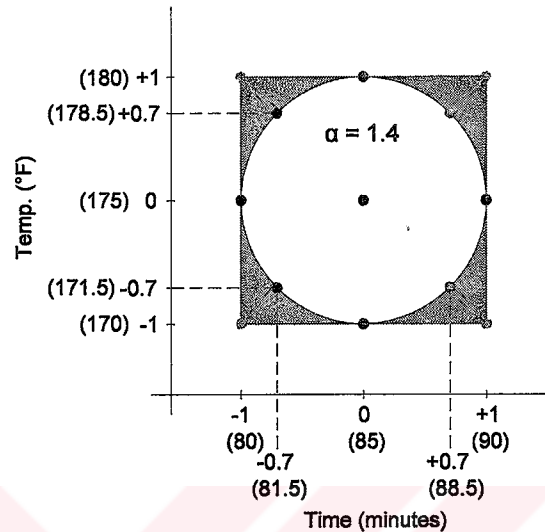


Figure 3.17. Two-Variable Inscribed CCD (Montgomery, 1997)

Figure 3.17 presents an inscribed CCD for time and temperature, again using the previously defined lower and upper variable bounds. The inscribed CCD also uses an α value of 1.4 to describe a circular geometric region (a sphere for three variables, a hypersphere for four or more variables, etc.). However, inscribing restricts the actual design region to the defined variable ranges by locating the axial points at the lower and upper bounds of the variable ranges. The factorial points are brought into the interior of the design space (inscribed) and set at a distance from the center point that preserves the proportional distance of the factorial points to the axial points. For example, given a rotatable CCD for two variables ($\alpha = 1.4$) with coded variable bounds of ± 1 , the factorial points would range between -1 and +1 and the axial points would range between -1.4 and +1.4. In the corresponding inscribed design, the factorial points would range between -0.7 and +0.7 and the axial points would range between -1 and +1.

As a summary, the inscribed option is a convenient way to generate a rotatable CCD that enables to study the full ranges of the experiment variables while excluding nonallowable operating conditions at one or more of the extremes of the

design region. Face-centered CCD, should be used whenever the region of operability encompasses the full region of interest as described by the variable ranges or when nonallowable operating conditions exist at only one of the extremes of the design region. In rotatable and near-rotatable CCDs, each experiment variable is represented at five levels. The face-centered CCD requires only three levels of each experiment variable, making it the simplest variety of CCD to carry out as well as the least prone to corruption due to sources of experimental error associated with setup and operation. Compared to face-centered CCDs, rotatable or near-rotatable CCDs offer reduced prediction error for, and improved estimation of, quadratic (curvature) effects. However, given a reasonable magnitude of overall experimental error, say a 5-percent RSD, these benefits do not outweigh the added complexity of requiring each variable to be run at five levels.

3.7.3. Design Expert 6.0

In this study, for the design of experiments (DOE), analysis and optimization of the process, version 6 of Design Expert software was used. Design-Expert software features and analyzes two-level factorial, general (multilevel) factorial, fractional factorial, Taguchi orthogonal arrays, Plackett-Burman, and combined mixture/process designs, as well as response surface methods (RSM) analysis for up to 10 process factors or 24 mixture components. Software offers powerful evaluation capability for generations of various statistical measures on the design matrix. The analysis includes standard ANOVA as well as various diagnostic plots on the residuals. The regression engine handles up to a full cubic polynomial model with forward, backward or stepwise algorithms. The program generates 2D contour plots and rotatable 3D graphs. The program's numerical optimization function finds the most desirable factor settings for up to 12 responses simultaneously. Unique tools for generating and graphing propagation of error (POE) make it possible to reach goals for reducing variation.

Design of experiments (DOE) methods use probability and statistics to define the minimum number of experiments needed to identify significant cause-and-effect

relationships between a given number of factors and one or more responses. Mathematically, DOE methods are well developed to identify efficient experimental designs. The three major components of DOE are design, analysis, and optimization. The strength of Design Expert 6.0 is the ease with which these tasks can be carried out and the usefulness of information provided in the displays. Principally, program provides many powerful statistical tools.

- Standard two-level full and fractional factorials (up to 256 runs) for testing up to 15 factors simultaneously, now also with minimum aberration blocking choices.
- General (multilevel) factorial designs (up to 32,000 runs) using factors with mixed levels.
- Taguchi orthogonal arrays.
- High-resolution irregular fractions, such as 4 factors in 12 runs.
- Plackett-Burman designs for 11, 19, 23, 27 or 31 factors in 12, 20, 24, 28 or 32 runs respectively.
- Response Surface Method (RSM) designs, including central composite (small, face-centered, etc.), Box-Behnken (3-level), hybrid and D-optimal.
- Mixture designs, such as simplex-lattice, simplex-centroid screening (for up to 24 components) and D-optimal.
- Combined mixture and process designs.
- Ability to graph any two columns of data on the XY graph (this is a great way to view a blocked effect)
- Easy-to-use automatic or manual model reduction.
- Ability to easily analyze designs with botched or missing data.

3.7.4. Design of Experiments (DOE)

The underlying goal of this study is to correlate thickness and brightness of the chromium coating to a set of factors such as amount of chromic acid, ratio of chromic acid to sulphuric acid, bath temperature, current density and time. In this

study, rotatable (circumscribed) central composite design of Response Surface Methodology was chosen for the design of experiments. For this purpose, initially upper and lower values of the experiment factors (process parameters), given in Table 3.5, were determined.

Table 3.5. Lower and Upper Values of Experiment Factors

Factors	Units	Minimum Value	Maximum Value	Low Level (-1)	High Level (+1)
Amount of Chromic Acid	g/l	175	400	240.2	334.8
Chromic Acid/Sulphuric Acid	-	0.005	0.010	0.006	0.009
Bath Temperature	°C	30	70	42	58
Current Density	A/dm ²	8	40	17.27	30.73
Time	sec	300	1200	561	939

Number of factors and their low level (-1) and high level (+1) values were then entered as seen in Figure 3.18.

	Name	Units	Low	High
A:	Amount of Chromic Acid	g/l	240.2	334.8
B:	Chromic Acid/Sulphuric Acid	-	0.006	0.009
C:	Bath Temperature	C	42	58
D:	Current Density	A/dm2	17.27	30.73
E:	Time	sec	561	939

Figure 3.18. Design Expert Response Surface Design Tab

As shown in Figure 3.19 at the bottom of the central composite design form type of the design were set to “Full” and value of blocks were entered 1 since all test specimens were manufactured from the same block of brass and the number of experiments were given by software. The default selection of “Alpha” set at 2.37841 in coded units is the axial distance from the center point and makes the design rotatable.

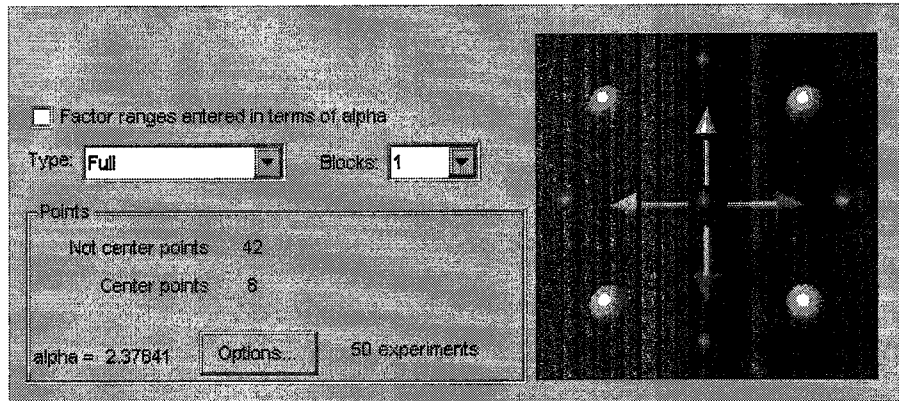


Figure 3.19. Central Composite Design Dialog Box

Then the program asks for the number of the responses and their definitions together with units as shown in Figure 3.20.

After identifying the names and units of the responses, to get the design layout of experiments, the continue button was pressed and then completed design layout was given by program as seen in Figure 3.21. The three columns on the left of the design layout identify the experimental runs. Experimental runs were randomized by Design Expert. Five columns at the right side of these columns identify the values of the process parameters at each experiment.

	Name	Units
☐	Thickness	mm
☐	Brightness (Reflectivity)	%

Figure 3.20. Completed Response Form

After completing experiments according to the design layout given by Design Expert, the values of responses were entered to the columns and then analysis and optimization of the results were carried out. Analysis and optimization of each response were made separately.

Notes for Next										
	Std	Run	Block	Factor 1 A:Amount of Chromic Acid g/l	Factor 2 B:Chromic Acid/Sulfuric Acid	Factor 3 C:Bath Temperature C	Factor 4 D:Current Density A/cm2	Factor 5 E:Time sec	Response 1 Thickness mm	Response 2 Brightness (reflectivity) %
Status	32	1	Block 1	334.81	0.006	58.41	30.73	938		
Evaluate	42	2	Block 1	287.50	0.007	50.00	24.00	1200		
Analysis	47	3	Block 1	287.50	0.007	50.00	24.00	750		
Thickness	44	4	Block 1	287.50	0.007	50.00	24.00	750		
Brightn	34	5	Block 1	400.02	0.007	50.00	24.00	750		
Optimizati	10	6	Block 1	334.81	0.006	41.59	30.73	561		
Number	15	7	Block 1	240.19	0.008	58.41	30.73	561		
Graph	46	8	Block 1	287.50	0.007	50.00	24.00	750		
Point P	19	9	Block 1	240.19	0.009	41.59	17.27	938		
	9	10	Block 1	240.19	0.006	41.59	30.73	561		
	50	11	Block 1	287.50	0.007	50.00	24.00	750		
	30	12	Block 1	334.81	0.008	58.41	30.73	938		
	2	13	Block 1	334.81	0.008	41.59	17.27	561		
	12	14	Block 1	334.81	0.008	41.59	30.73	561		
	23	15	Block 1	240.19	0.008	58.41	17.27	938		
	8	16	Block 1	334.81	0.009	58.41	17.27	561		
	37	17	Block 1	287.50	0.007	30.00	24.00	750		
	24	18	Block 1	334.81	0.008	58.41	17.27	938		
	6	19	Block 1	334.81	0.006	58.41	17.27	561		
	1	20	Block 1	240.19	0.008	41.59	17.27	561		
	5	21	Block 1	240.18	0.006	58.41	17.27	561		
	22	22	Block 1	334.81	0.008	58.41	17.27	938		
	29	23	Block 1	240.19	0.008	58.41	30.73	938		
	13	24	Block 1	240.19	0.008	58.41	30.73	561		
	3	25	Block 1	240.19	0.009	41.59	17.27	561		
	35	26	Block 1	287.50	0.007	50.00	8.00	750		

Figure 3.21. Completed Design Layout

3.7.5. Analysis of the Results

Analysis of the thickness and brightness were carried out individually once the response data has been entered. Initially, thickness was analyzed. Before the analysis of responses, data of each response were checked whether transformation required or not. Transformations apply a mathematical function to all the response data. Transformation of the responses is an important component of any data analysis. Transformation is needed if the error (residuals) is a function of the magnitude of the response (predicted values). Unless the ratio of the maximum response to the minimum response is large, transforming the response will not make much difference. For both responses transformation was not required, since the ratios of the maximum to minimum thickness and brightness values are lower than 10. Because a ratio greater than 10 indicates that transformation is required. Therefore, the data of the responses will be analyzed as they are, without transformation.

Then regression calculations were done to fit linear, two-factor interaction (2FI), quadratic and cubic polynomial models to the selected responses. The program

calculates the effects for all model terms and produces statistics such as F-values, lack of fit and R-squared values for comparing the models. If a statistically significant model is detected, the program will underline and note the "Suggested" model and becomes the default model.

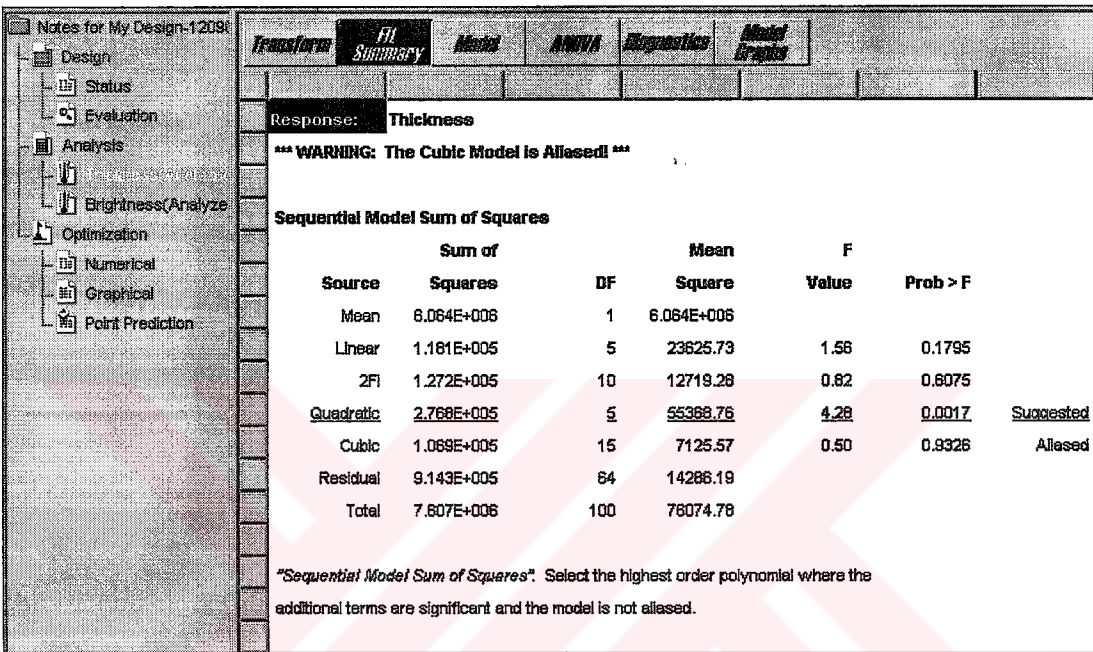


Figure 3.22. Summary Table for Sequential Model Sum of Squares

The “Sequential Model Sum of Squares” summary table shows how terms of increasing complexity contribute to the total model (See Figure 3.22). The model hierarchy is described below:

- “Linear”: the significance of adding the linear terms to the mean and blocks.
- “2FI”: the significance of adding the two factor interaction terms to the mean, block and linear terms already in the model.
- “Quadratic”: the significance of adding the quadratic terms to the mean, block, linear and two factor interaction terms already in the model.
- “Cubic”: the significance of the cubic terms beyond all other terms.

For each source of terms (Linear, 2FI, etc.), the probability (“PROB>F”) value was examined to see if it falls down 0.05. The quadratic model for thickness

analysis and 2FI (Two Factor Interaction) model for brightness analysis would be the logical choices since their probability values smaller than 0.05 and for both response analysis the cubic order terms will not significantly improve the fit. The lack of fit tables were then examined as shown in Figure 3.23.

Lack of Fit Tests						
Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Linear	6.021E+005	37	16273.98	1.13	0.3369	
2FI	4.749E+005	27	17590.53	1.22	0.2612	
<u>Quadratic</u>	<u>1.981E+005</u>	<u>22</u>	<u>9004.57</u>	<u>0.62</u>	<u>0.8888</u>	<u>Suggested</u>
Cubic	91217.03	7	13031.00	0.90	0.5111	Aliased
Pure Error	8.231E+005	57	14440.33			

"Lack of Fit Tests": Want the selected model to have insignificant lack-of-fit.

Figure 3.23. Summary Table for Lack of Fit Tests

The "Lack of Fit Tests" table compares the residual error "Mean Square" to the "Pure Error" from replicated design points. If there is significant lack of fit, as shown by a low probability value ("PROB>F"), then we have to be careful about using the model as a response predictor. In the lack of fit tests, the model, which has not so small F value and probability value greater than 0.1 is desirable. If a model shows lack of fit, it should not be used to predict the response. The quadratic model, identified earlier as the likely model for thickness, and 2FI model for brightness do not show significant lack of fit. Since the cubic model was aliased, so it should not be chosen.

The "Model Summary Statistics" table lists other statistics such as Standard Deviation (Root MSE), R-Squared, Adjusted R-Squared, Predicted R-Squared and the PRESS statistic useful in comparing models. The model which has low standard deviation, R-Squared near 1 and relatively low PRESS is the best. The predicted residual sum of squares (PRESS) is a measure of how well the model fits each point in the design. As seen in Figures 3.24 and 3.25, the quadratic model for thickness and 2FI model for brightness analysis come out the best models. They exhibit low

standard deviation ("Std. Dev."), high "R-Squared" values and a low "PRESS." Based on these comparisons the program automatically underlined the quadratic model and 2FI model as "Suggested" model.

Model Summary Statistics						
Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	123.13	0.0765	0.0274	-0.0212	1.576E+006	
2FI	124.31	0.1590	0.0088	-0.1048	1.705E+006	
<u>Quadratic</u>	<u>113.70</u>	<u>0.3383</u>	<u>0.1708</u>	<u>0.0069</u>	<u>1.533E+006</u>	<u>Suggested</u>
Cubic	119.52	0.4076	0.0836	-0.2994	2.005E+006	Aliased

"Model Summary Statistics". Focus on the model maximizing the "Adjusted R-Squared" and the "Predicted R-Squared".

Figure 3.24. Model Summary Statistics of Thickness Analysis

Model Summary Statistics						
Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	8.91	0.2183	0.1767	0.1148	8443.54	
<u>2FI</u>	<u>8.53</u>	<u>0.3597</u>	<u>0.2453</u>	<u>0.0732</u>	<u>8840.02</u>	<u>Suggested</u>
Quadratic	8.43	0.4114	0.2624	0.0685	8884.43	
Cubic	8.51	0.5138	0.2478	-0.1849	11301.36	Aliased

"Model Summary Statistics". Focus on the model maximizing the "Adjusted R-Squared" and the "Predicted R-Squared".

Figure 3.25. Model Summary Statistics of Brightness Analysis

After models were selected, ANOVA tables for each model were investigated. The ANOVA table displays all the statistical details necessary for analysis with text providing brief explanations and guidelines. The ANOVA tables obtained for this study are shown in Figures 3.26 and 3.27.

Transform	Fit Summary	Model	ANOVA	Diagnostics	Model Effects
Use your mouse to right click on individual cells for definitions.					
Response: Thickness					
ANOVA for Response Surface Quadratic Model					
Analysis of variance table [Partial sum of squares]					
Source	Sum of Squares	DF	Mean Square	F Value	Prob > F
Model	5.222E+005	20	26108.26	2.02	0.0148
A	17242.99	1	17242.99	1.33	0.2516
B	69.95	1	69.95	5.411E-003	0.9415
C	86966.79	1	86966.79	6.73	0.0113
D	4181.36	1	4181.36	0.32	0.5711
E	9667.57	1	9667.57	0.75	0.3898
A ²	1.199E+005	1	1.199E+005	9.27	0.0032
B ²	1430.49	1	1430.49	0.11	0.7403
C ²	12756.48	1	12756.48	0.99	0.3235
D ²	1.278E+005	1	1.278E+005	9.88	0.0023
E ²	73732.95	1	73732.95	5.70	0.0193

Figure 3.26. ANOVA Table for Quadratic Model of Thickness (Partially shown)

Transform	Fit Summary	Model	ANOVA	Diagnostics	Model Effects
Response: Brightness					
ANOVA for Response Surface Quadratic Model					
Analysis of variance table [Partial sum of squares]					
Source	Sum of Squares	DF	Mean Square	F Value	Prob > F
Model	3923.87	20	196.19	2.76	0.0007
A	128.19	1	128.19	1.80	0.1831
B	273.78	1	273.78	3.85	0.0532
C	1321.81	1	1321.81	18.60	< 0.0001
D	342.37	1	342.37	4.82	0.0311
E	15.58	1	15.58	0.22	0.6410
A ²	11.34	1	11.34	0.16	0.6907
B ²	107.69	1	107.69	1.52	0.2220
C ²	219.18	1	219.18	3.08	0.0829
D ²	38.88	1	38.88	0.55	0.4617
E ²	54.28	1	54.28	0.76	0.3848

Figure 3.27. ANOVA Table for 2FI Model of Brightness (Partially shown)

The ANOVA in this case confirms the adequacy of the quadratic model for thickness and 2FI model for brightness (The model $PROB>F$ is less than 0.05). In addition to these tables, software provides coefficients for quadratic and 2FI models, final equations for responses in coded form, residuals and diagnostics of models.

The diagnostic details provided by Design-Expert could best be analyzed by inspection of various plots. The most important diagnostic is the normal probability plot of the studentized residuals. The normal probability plot indicates whether the residuals follow a normal distribution, in which case the points will follow a straight line. The data points should be approximately linear. A non-linear pattern (such as an S-shaped curve) indicates non-normality in the error term, which may be corrected by a transformation.

The diagnosis of residuals revealed no statistical problems as shown in Figures 3.28 and 3.29, so the response surface plots of the factors can be generated. Design-Expert software provides various graphs to help for the interpretation of the selected models.

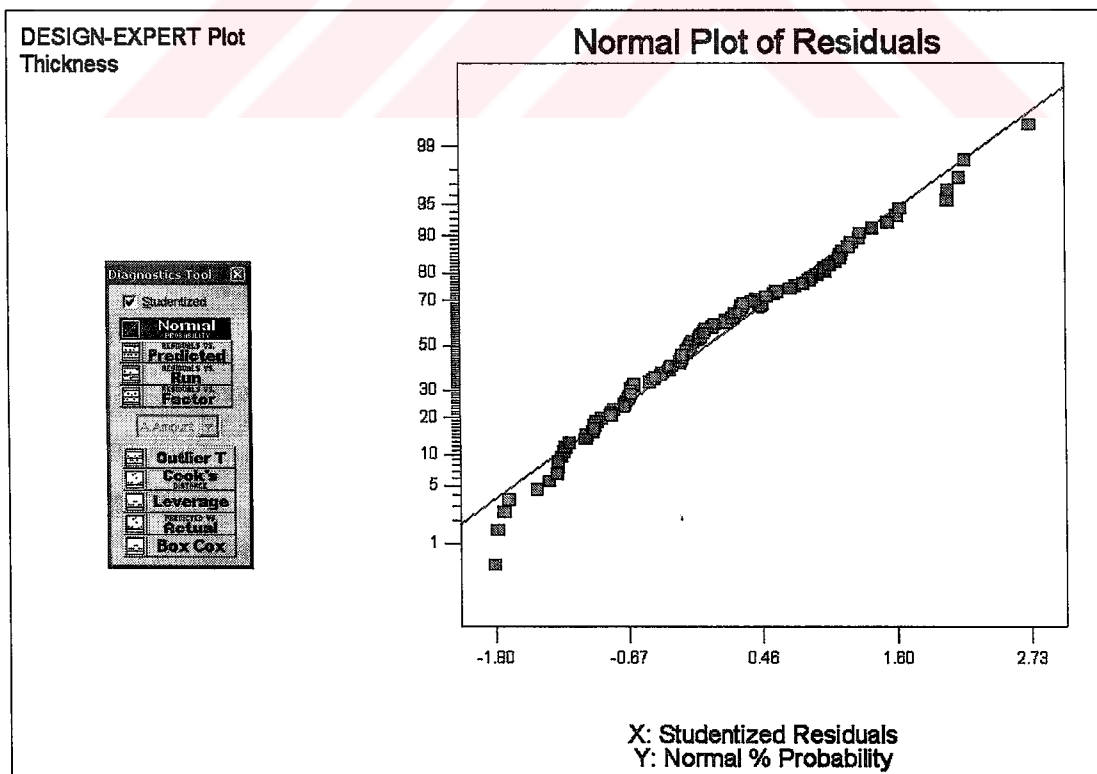


Figure 3.28. Normal Probability Plot of the Residuals for the Model of Thickness

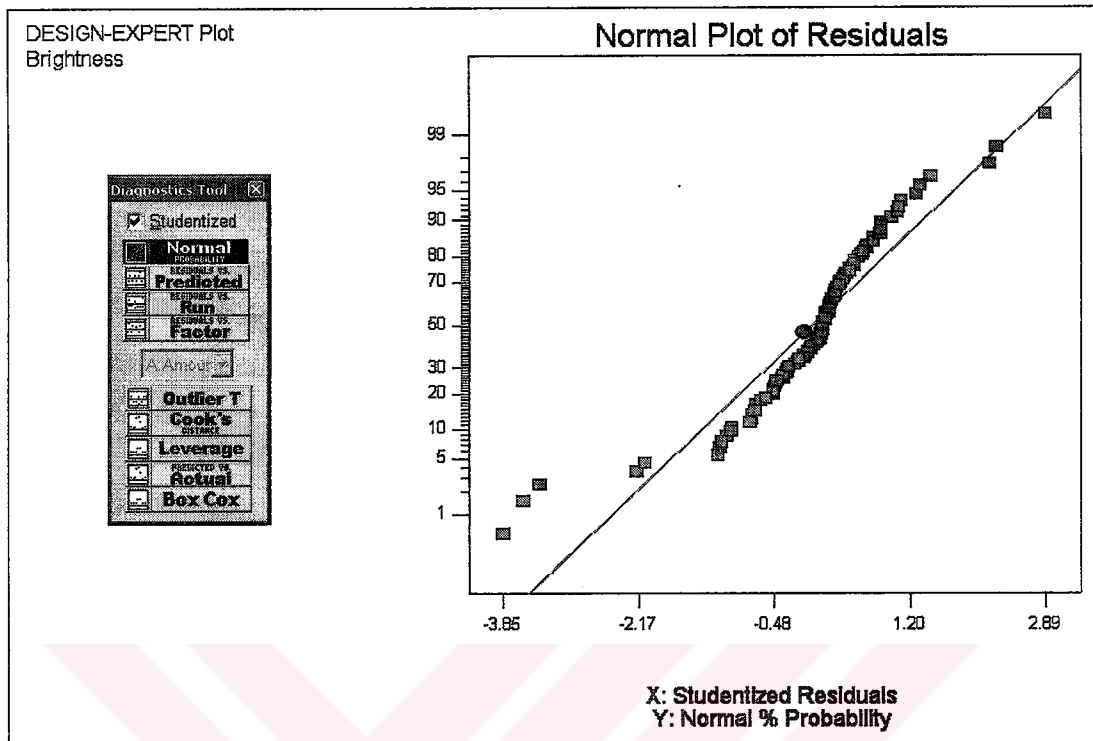


Figure 3.29. Normal Probability Plot of the Residuals for the Model of Brightness

3.7.6. Optimization Method

The optimization module in Design-Expert searches for a combination of factor levels that simultaneously satisfy the requirements placed on each of the responses and factors. Optimization of one response or the simultaneous optimization of multiple responses can be performed graphically or numerically.

Numerical Optimization optimizes any combination of one or more goals. The goals may apply to either factors or responses. The possible goals are: maximize, minimize, target, within range, none (for responses only) and set to an exact value (factors only). A minimum and a maximum level must be provided for each parameter included in the optimization. A weight can be assigned to a goal to adjust the shape of its particular desirability function. Desirability is an objective function that ranges from zero outside of the limits to one at the goal. A value of “1” represents the ideal case; a value of “0” indicates that one or more responses fall outside desirable limits. The numerical optimization finds a point that maximizes the

desirability function. The characteristics of a goal may be altered by adjusting the weight or importance. For several responses and factors, all goals get combined into one desirability function. The default value of one creates a linear ramp function between the low value and the goal or the high value and the goal. Increased weight (up to 10) moves the result towards the goal. Reduced weight (down to 0.1) creates the opposite effect. The “importance” of a goal can be changed in relation to the other goals. The default is for all goals to be equally important at a setting of 3 pluses (+++). If it is necessary one goal to be most important, importance value can be changed to 5 pluses (+++++).

For this study, the goals of the factors were obtained between their lower (-1) and upper (+1) values as seen in Figure 3.30. For thickness and brightness; the goal “maximize” were selected since the optimum values of the factors which will provide the maximum thickness and brightness are desired.

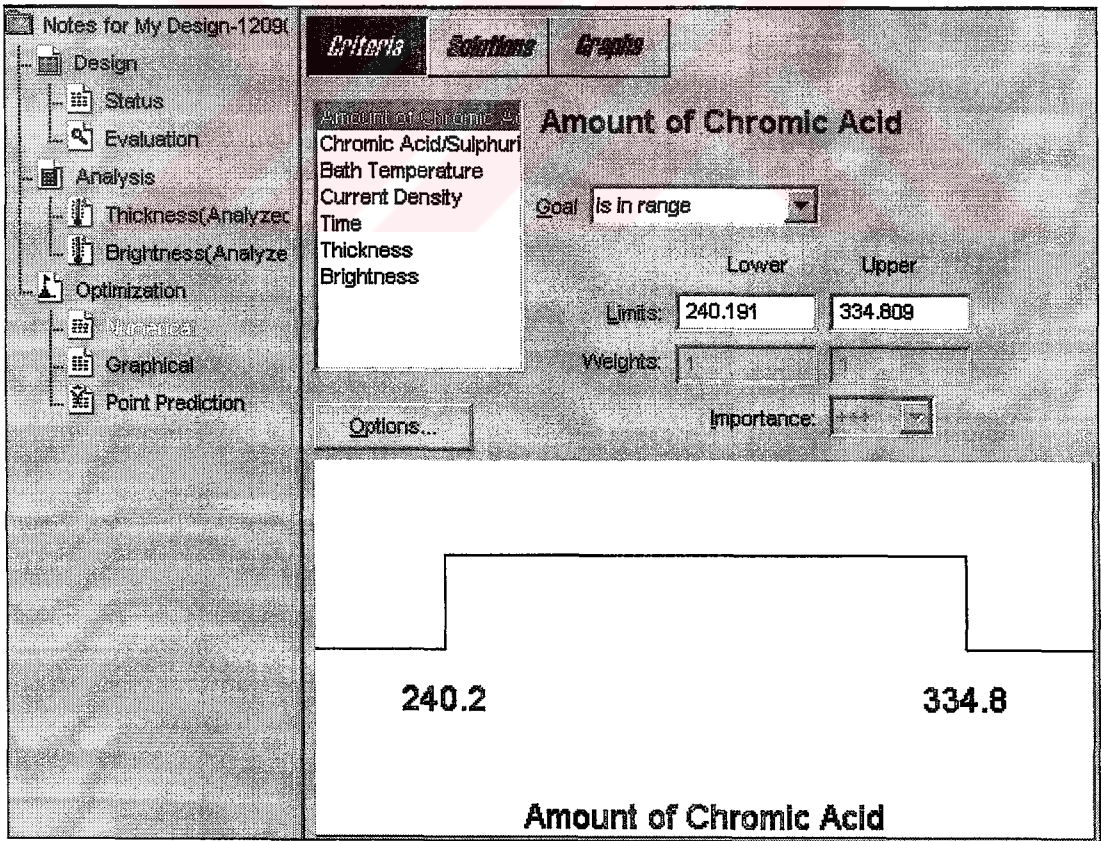


Figure 3.30. Setting Numerical Optimization Criteria

The lower and upper limits of thickness value were entered as 1 μm and 500 μm as shown in Figure 3.31 (a), since the thickness of chromium coating varies between these values in industrial applications. Lower limit of brightness was set to 20% since the minimum brightness value taken from results was 22,51%, and for the maximum limit of the brightness theoretical high of 100% was set as shown in Figure 3.31 (b).

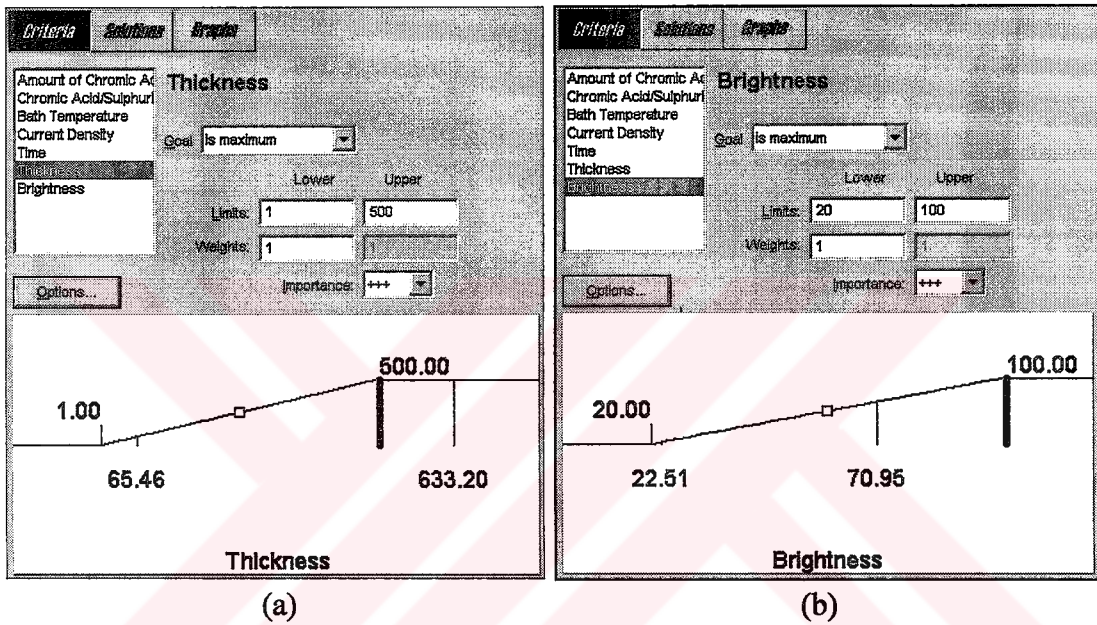


Figure 3.31. (a) Thickness Criteria Settings, (b) Brightness Criteria Settings

These settings create the following desirability functions

1. Thickness:

- If less than 1 μm , then desirability (d_i) equals to zero
- From 1 μm to 500 μm , d_i ramps up from zero to one
- If over 500 μm , then d_i equals to one

2. Brightness:

- If less than 20%, then desirability (d_i) equals to zero
- From 20% to 100%, d_i ramps up from zero to one
- If over 100%, then d_i equals to one

Weights give added emphasis to upper or lower bounds or emphasize a target value. With a weight of 1, the d_i will vary from 0 to 1 in linear fashion. Weights

greater than 1 (maximum weight is 10) give more emphasis to the goal. Weights less than 1 (minimum weight is 0.1) give less emphasis to the goal. For this study, weights of both responses were determined in its default value 1.

Importance is a relative scale for weighting each of the resulting d_i in the overall desirability product. For this study, importance fields of both responses were determined at 3 pluses (+++), a medium setting.

For the optimization of the responses, the program randomly picks a set of conditions from which to start its search for desirable results. Multiple cycles improve the odds of finding multiple local optimums, some of which will be higher in desirability than others. After 10 cycles of optimization, the results appear for each response.

Graphical optimization was carried out after numerical optimization. By making numerical optimization an area of satisfactory solutions has been found. Graphical optimization displays the area of feasible response values in the factor space. The requirements are essentially the same as in numerical optimization. Any "window" that is not shaded satisfies the multiple constraints on the responses. Unless the default color settings are not reconfigured, the area that satisfies the constraints will be yellow, while the area that does not meet the criteria is gray.

4. RESULTS AND DISCUSSION

The production of good-quality chromium coated articles depends partly on control of coating process and partly on control of the articles themselves. Indication of good quality for a chromium coated article can be defined according to its coating thickness, hardness, brightness, corrosion resistance and wear resistance depending on the application area.

Since main applications of chromium plating are based on decorative and protective purpose, the principal properties, which determine the quality of the coating are thickness and brightness of the coating. In this respect, effects of process parameters on the thickness of chromium coated specimens were investigated firstly, and then effects of process parameters on the brightness of chromium coated specimens were investigated. In the following sections the experimental results, obtained in this study, were given and discussed.

4.1. Effect of Process Parameters on the Thickness of Chromium Plating

It has been known that the corrosion protection, wear resistance and hardness of chromium plating depend primarily on the thickness of deposit. Also, thickness is the distinguishing factor between hard and decorative chromium plating. For hard chromium coating the thickness, which provides satisfactory hardness to the substrate is the most important feature and for decorative chromium plating the thinnest coating, which provides best appearance to the substrate is the most important feature.

Experiments were performed under different conditions in order to investigate the effect of process parameters on the thickness of chromium plating. For each experiment two test specimens were plated under the same conditions. The effect of main process parameters, such as amount of chromic acid (CrO_3), ratio of chromic acid (CrO_3) to sulphuric acid (H_2SO_4), bath temperature, current density and plating time, on the thickness were discussed in the following sections.

4.1.1. Amount of Chromic Acid

The effect of chromic acid amount on the thickness was investigated by using the graph taken from the analysis of Design Expert software. The results of the experiments obtained at different conditions were plotted in Figure 4.1. As shown in this figure, thickness of the plating increased up to a certain amount of chromic acid (approximately 275 g/l), then the thickness of chromium deposit was decreased after 275 g/l while the amount of chromic acid was increased. However, the variation of thickness between 265 g/l and 285 g/l was so small. This phenomenon is taught to be caused due to current efficiency, which is high at low chromic acid concentration. Thus, increase in coating thickness at low chromic acid concentration can be explained by Faraday’s Law, the quantity of material deposited or dissolved at an electrode is directly proportional with the quantity of electricity, which flows through electrolyte. Therefore, for hard chromium plating process, the amount of chromic acid should be taken in between 265 g/l and 285 g/l to obtain maximum thickness.

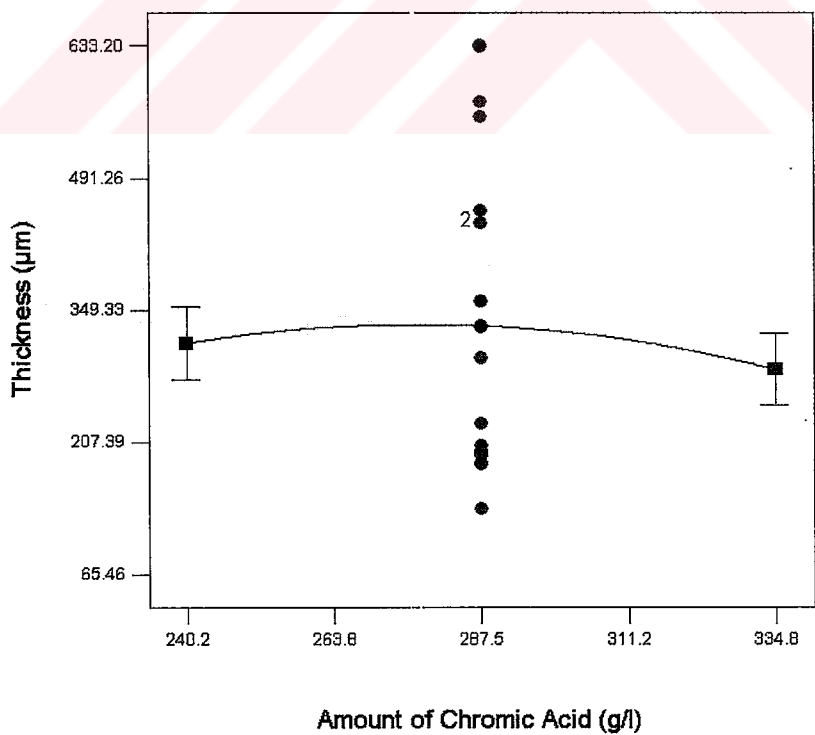


Figure 4.1. The Effect of Amount of Chromic Acid (CrO₃) on Thickness

Measurements made on the two test specimens plated under the same conditions showed variations in the thickness values. This is because of deposition of Cr ions to substrate, which causes reduction on the concentration of chromic acid in the bath after plating the first specimen. Therefore, the differences between two specimens were varied according to the amount of chromic acid in the plating process of the first and second specimens. Lower thickness values were obtained when the amount of chromic acid was less than the optimum value (275 g/l).

Also it has been observed that the thickness of the plated specimens were extremely different at the center points indicated by red points in Figure 4.1 (287.5 g/l), despite the plating conditions of these specimens were the same. The reason of these extremities may be caused because of the following reasons:

- The concentration of the baths may be different since the agitation of the baths was made by hand stirring.
- The surface of the anodes may be dirty and because of the lead chromate coating on the anodes electrical conductivity from the anodes may decrease (Aydonat, 2002).

In chemical processes, the effect of the parameters on the results may depend on the process conditions. Interaction between amount of chromic acid and other process parameters and the effect of these to the thickness of the chromium plating are shown in Figures 4.2, 4.3, 4.4, and 4.5. Actually, interaction is not a desirable feature since it creates difficulties to predict the effect of each factor on the process.

The obtained curves shown in Figures 4.2 and 4.3 are approximately parallel to each other, and in Figures 4.4 and 4.5 there are slight differences between the curves and these effects are negligible. The differences in the curves may be caused because of the effects of other parameters to the thickness of coating not due to the effect of amount of chromic acid. So, it may be concluded that these factors have no significant effect compared to the effect of chromic acid amount on the coating thickness. This shows that, there is no interaction between amount of chromic acid and other process parameters.

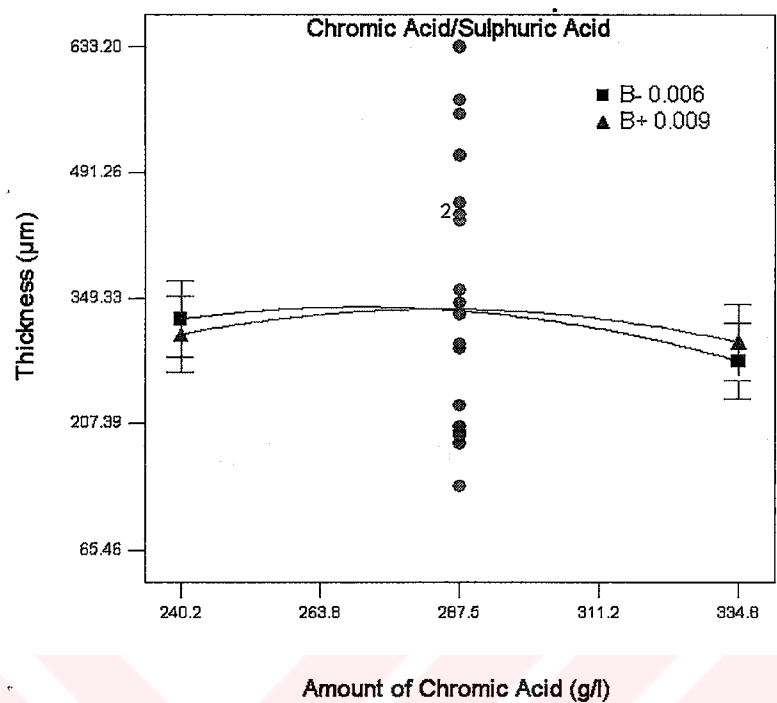


Figure 4.2. Interaction between Amount of Chromic Acid and Chromic Acid/Sulphuric Acid Ratio and their Effects to the Coating Thickness

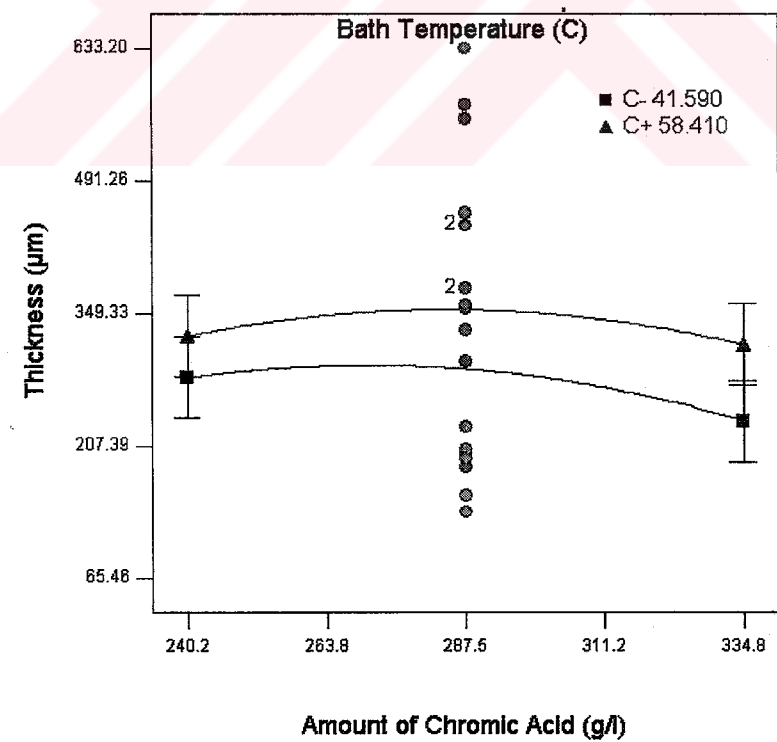


Figure 4.3. Interaction between Amount of Chromic Acid and Bath Temperature and their Effects to the Coating Thickness

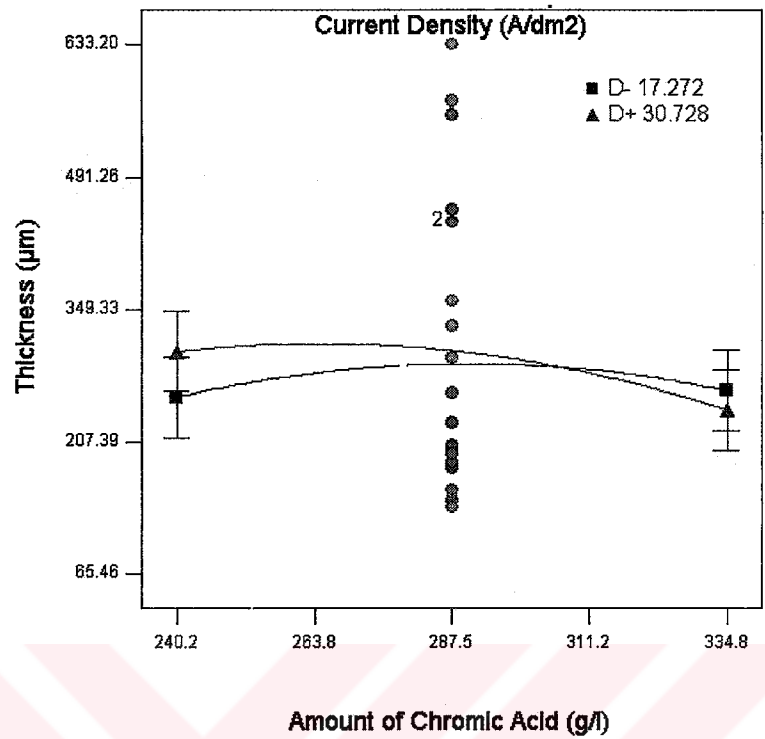


Figure 4.4. Interaction between Amount of Chromic Acid and Current Density and their Effects to the Coating Thickness

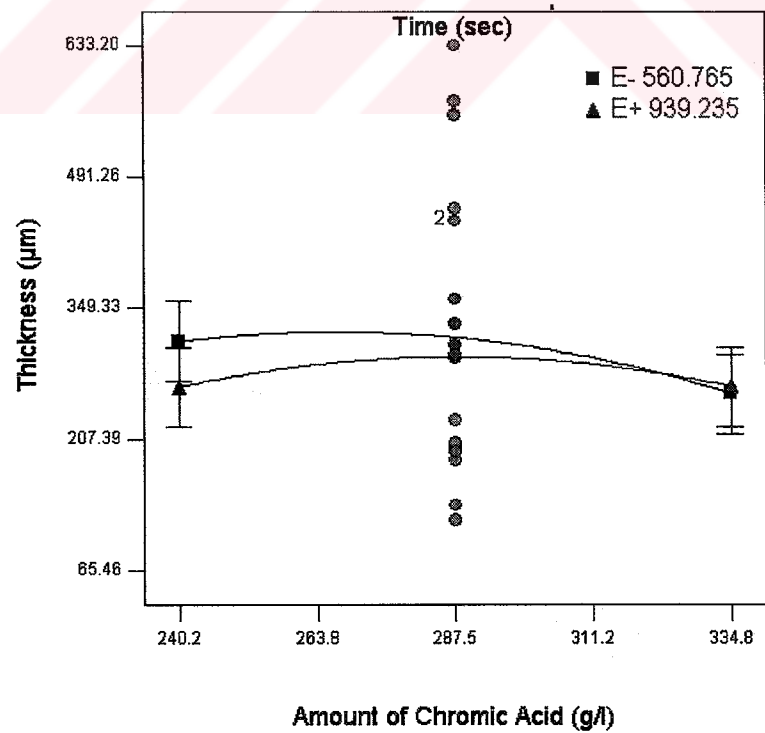


Figure 4.5. Interaction between Amount of Chromic Acid and Plating Time and their Effects to the Coating Thickness

4.1.2. Ratio of Chromic Acid to Sulphuric Acid

The effect of chromic acid to sulphuric acid ratio on the thickness of the chromium plating was plotted in Figure 4.6. As shown in this figure, an increase in the ratio of chromic acid to sulphuric acid results in a slight decrease in the coating thickness. The minimum thickness is reached when the ratio of chromic acid to sulphuric acid is approximately 0.0075. The thickness of the coating increases slightly with the further increasing in the ratio of chromic acid to sulphuric acid. Finally, it was observed that changing the ratio of chromic acid to sulphuric acid between 0.005 (1/200) and 0.010 (1/100) has no significant effect on the coating thickness. Because the addition of sulphuric acid (catalyst) to the plating bath is used to provide higher penetration rate of deposits on the surface of the substrate and prevents the burning of coating during electroplating. No metallic coatings can be obtained without using catalyst in chromium plating process.

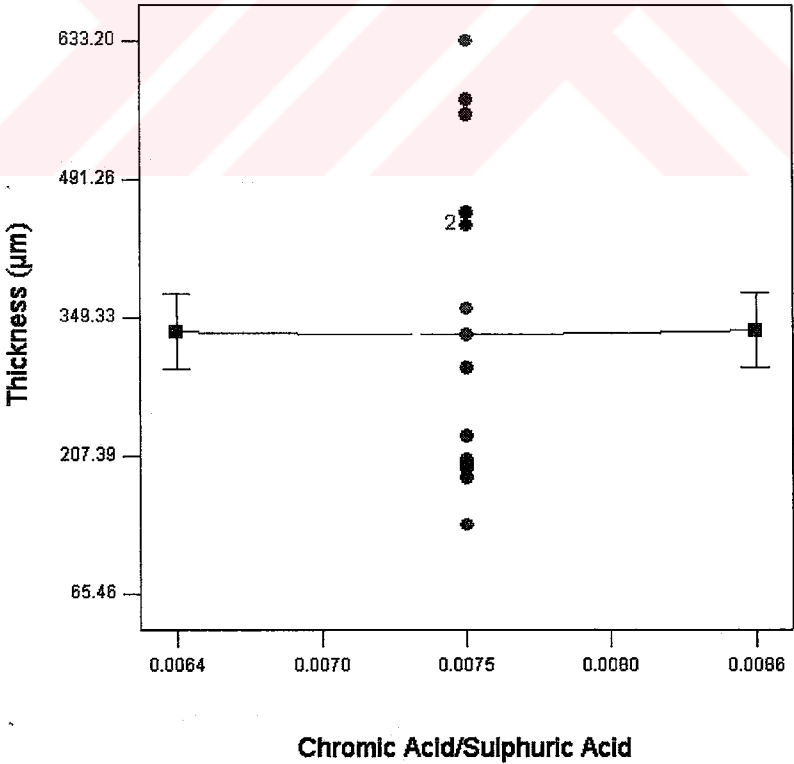


Figure 4.6. The Effect of Chromic Acid/Sulphuric Acid Ratio on Thickness

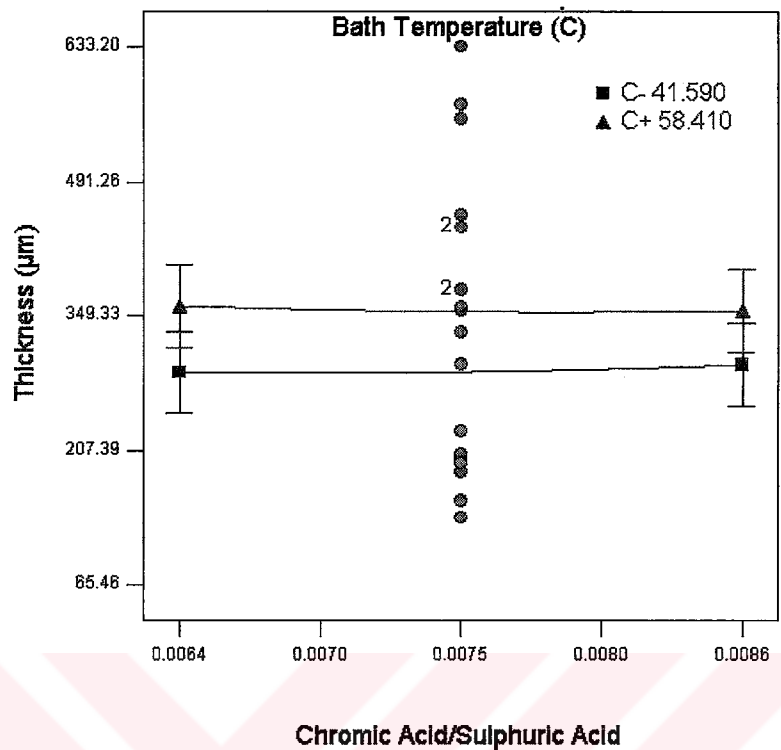


Figure 4.7. Interaction between Chromic Acid/Sulphuric Acid Ratio and Bath Temperature and their Effects to the Coating Thickness

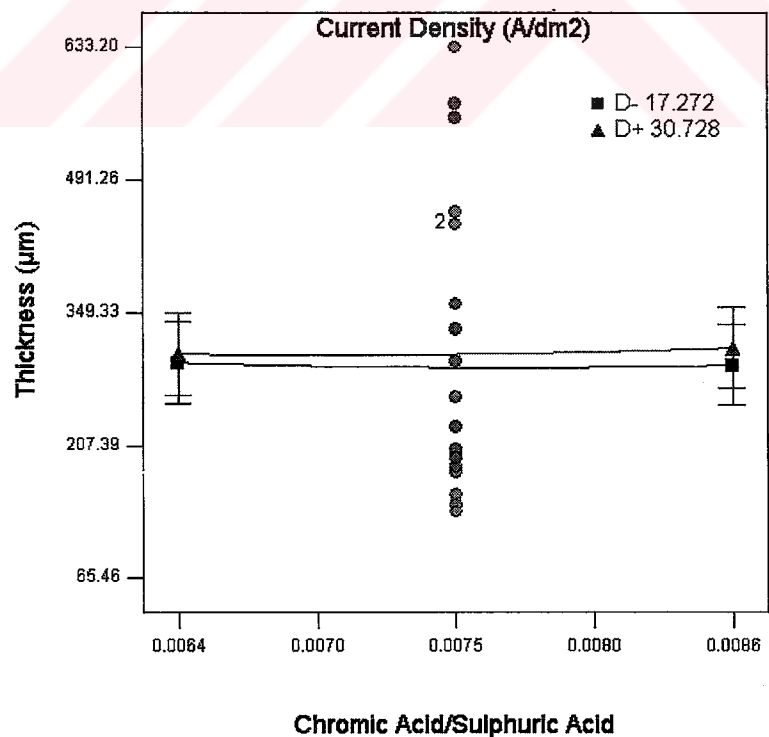


Figure 4.8. Interaction between Chromic Acid/Sulphuric Acid Ratio and Current Density and their Effects to the Coating Thickness

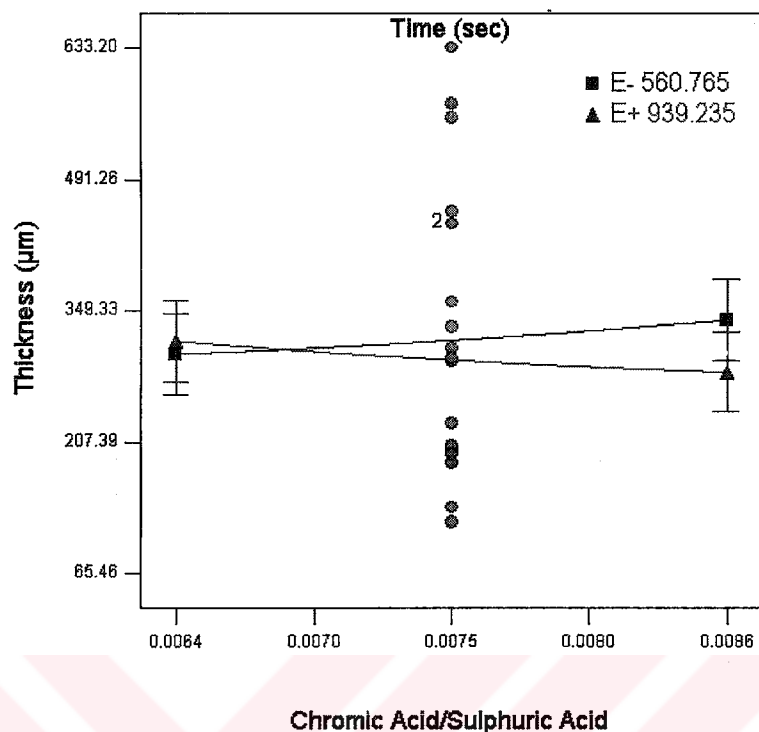


Figure 4.9. Interaction between Chromic Acid/Sulphuric Acid Ratio and Plating Time and their Effects to the Coating Thickness.

Interaction graphs between ratio of chromic acid to sulphuric acid and other process parameters and effect of these on the thickness of the chromium plating are shown in Figures 4.7, 4.8, and 4.9.

As shown in Figures 4.7, and 4.8, bath temperature and current density were not changed the relation between coating thickness and ratio of chromic acid to sulphuric acid since two curves in each figure are parallel to each other. This indicates that there is no interaction between these parameters.

The interaction between plating time and the effect of chromic acid to sulphuric acid ratio on the coating thickness is shown in Figure 4.9. Figure indicates that, at a constant plating time 561 sec increasing the ratio of chromic acid to sulphuric acid results in an increase of the coating thickness, however, by increasing the plating time to 939 sec the relation between the ratio and thickness was changed. Then, at long plating times, coating thickness decreases with increasing ratio of chromic acid to sulphuric acid. Thus, it is concluded that, there is an interaction between plating time and ratio of chromic acid to sulphuric acid.

4.1.3. Bath Temperature

The variation of coating thickness with bath temperature is shown in Figure 4.10. It is clear that the plating thickness increases with the increase in bath temperature. This is not the case as indicated in the investigation of Wang Deqing et al., 2004. The difference may be caused due to constant plating time (5 min) and the interaction between plating time and bath temperature, which was not considered in their investigation. On the contrary of results obtained by Wang Deqing et al., the results obtained in this study, is more realistic since it is known that in chemical processes, increasing temperature, accelerates the reaction and increases conductivity. Thus, increasing bath temperature in plating process, increases the deposition rate of chromium ions and hence the coating thickness.

Interaction graphs between bath temperature and other process parameters and effect of these on the thickness of the chromium plating are shown in Figures 4.11, and 4.12. As shown in Figure 4.11, there is no interaction between current density and bath temperature since change in current density were not changed the relation between bath temperature and coating thickness.

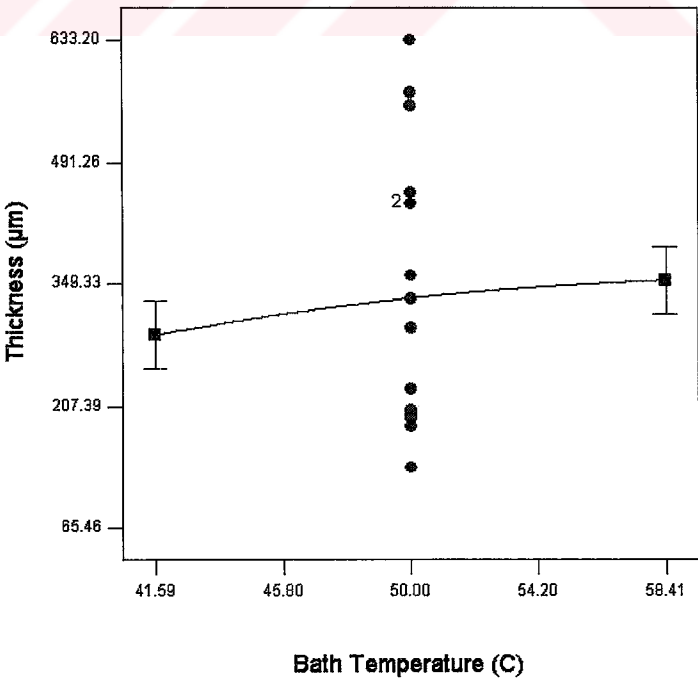


Figure 4.10. The Effect of Bath Temperature on Thickness

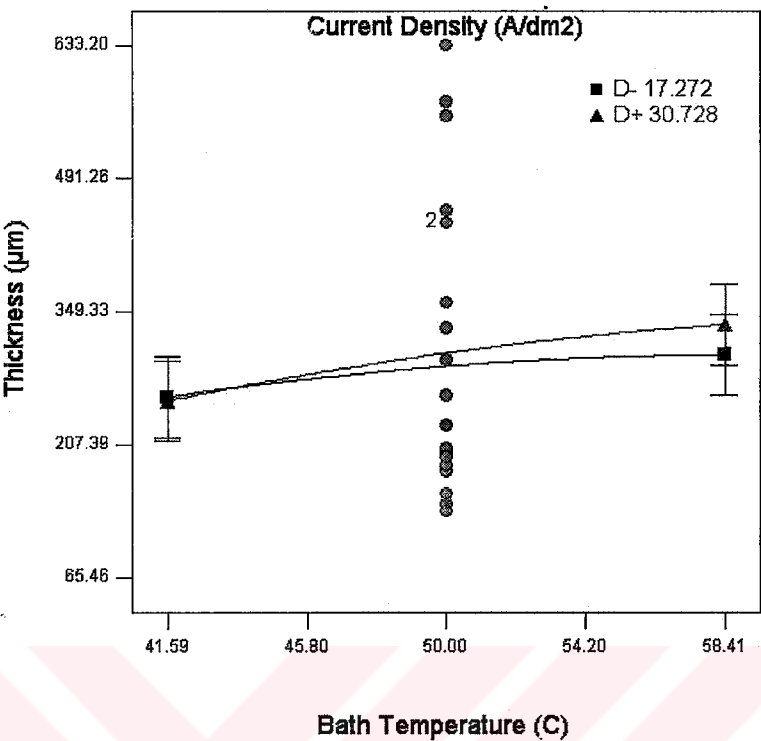


Figure 4.11. Interaction between Bath Temperature and Current Density and their Effects to the Coating Thickness

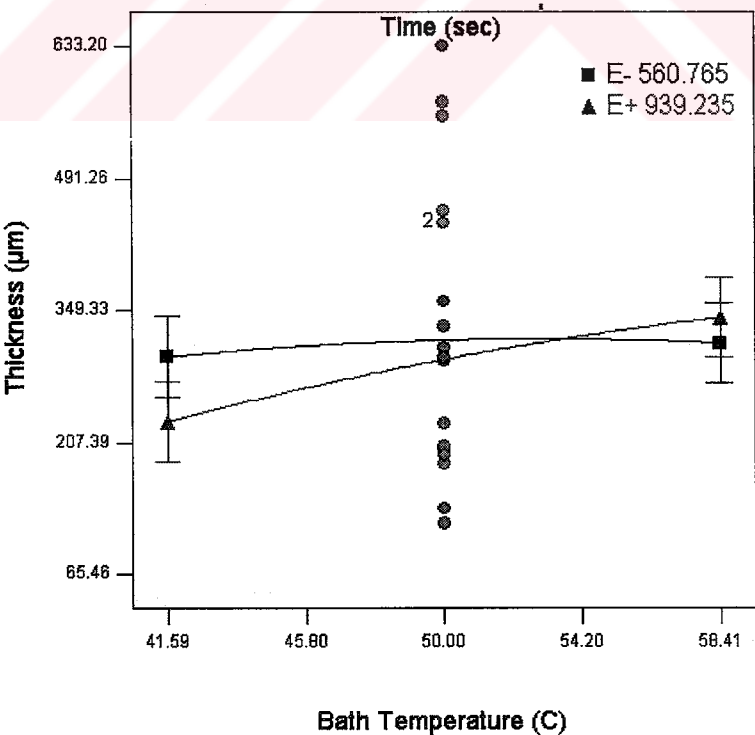


Figure 4.12. Interaction between Bath Temperature and Plating Time and their Effects to the Coating Thickness

Figure 4.12 indicates that an increase in bath temperature increases the thickness of the chromium plating slightly to some extent and then decreases slightly. However, increasing the plating time and bath temperature at the same time resulted an increase in the coating thickness. Therefore, it has been concluded that there is an interaction between plating time and bath temperature.

4.1.4. Current Density

The effect of current density on the coating thickness was plotted in Figure 4.13. The influence of current density on the coating thickness has the same trend as obtained by the amount of chromic acid as shown in Figure 4.13. By increasing current density, the thickness of coating increases first, and reaches a maximum value while current density is between 24 A/dm^2 and 25 A/dm^2 and beyond this point, the thickness of chromium deposit decreases. This is the case as indicated by Wang Deqing et al., 2004. According to the investigations of Wang Deqing et al., the thickest coating can be obtained at a current density of 29 A/dm^2 . In this study, however the optimum current density value, which gives the thickest coating has been found in between $24\text{-}25 \text{ A/dm}^2$.

As stated by Faraday's law, the mass of the deposit is proportional to the current strength. Therefore, an increase in current density should result in an increase of coating thickness theoretically. However, lead chromate layer occurred on the surfaces of the anodes decreases the covering power of the bath since electrical conductivity between anodes and electrolyte decreases. Thus, different current densities may exist on the surface of the substrate after the points, which lead chromate layer occurred.

Another reason to this phenomenon may be the amount of hydrogen absorbed by the cathode during electroplating. With increasing current density, the amount of hydrogen absorbed increases and this causes to less deposition of chromium ions on the surface of substrate.

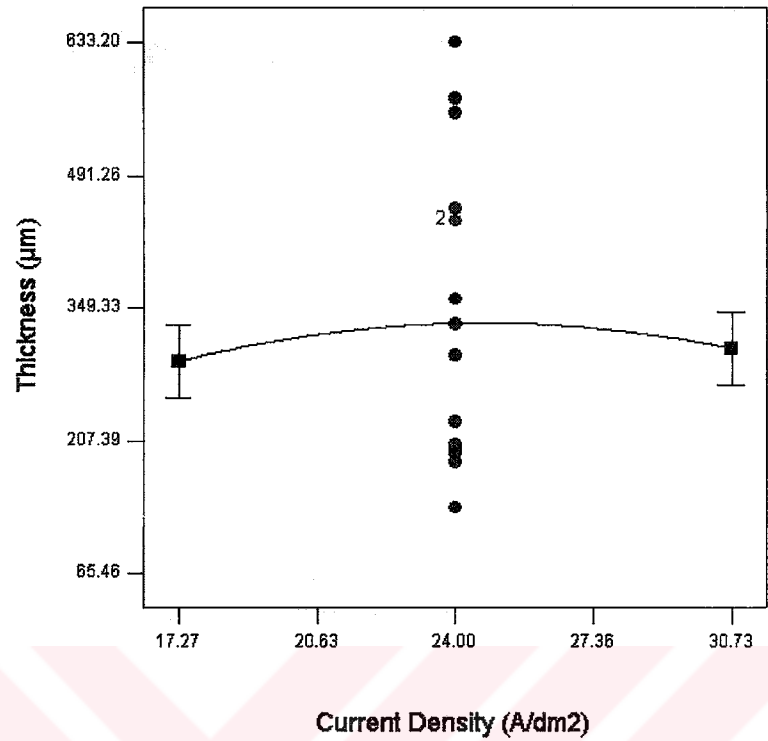


Figure 4.13. The Effect of Current Density on Thickness

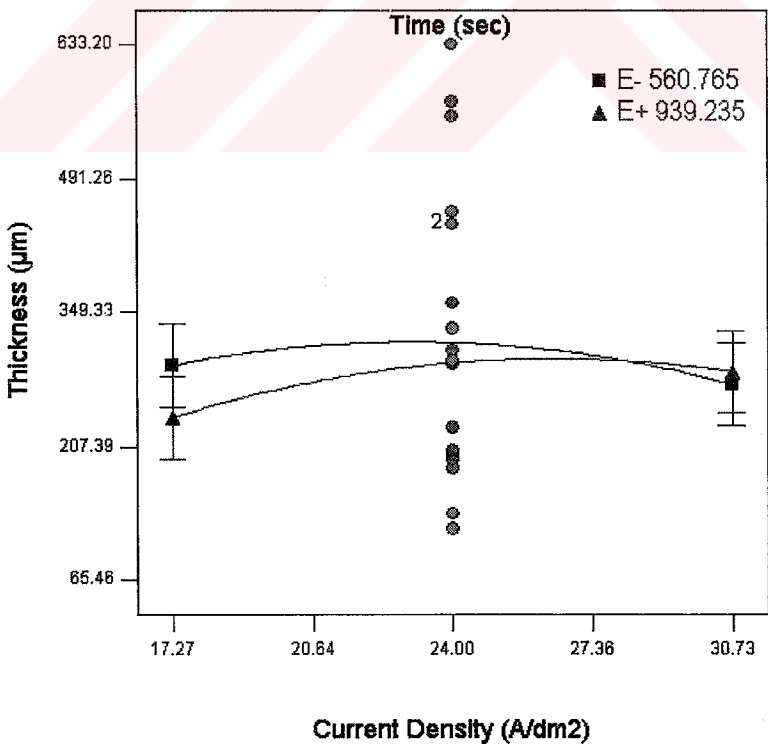


Figure 4.14. Interaction between Current Density and Plating Time and their Effects to the Coating Thickness

Interaction graph between the current density and plating time and their effects on the thickness of the chromium plating are shown in Figure 4.14. As shown in this figure, increasing plating time was changed the relation between current density and thickness. Therefore, it is concluded that there is an interaction between plating time and current density.

4.1.5. Plating Time

The effect of plating time on the coating thickness was plotted in Figure 4.15. As shown in this figure, the thickness of the chromium plating increased up to a certain value of plating time (approximately 730 sec) however, the thickness of chromium deposit was decreased after 730 sec while plating time increased. This is not the case as indicated by Wang Deqing et al., that the thickness of the chromium plating increases while plating time increases.

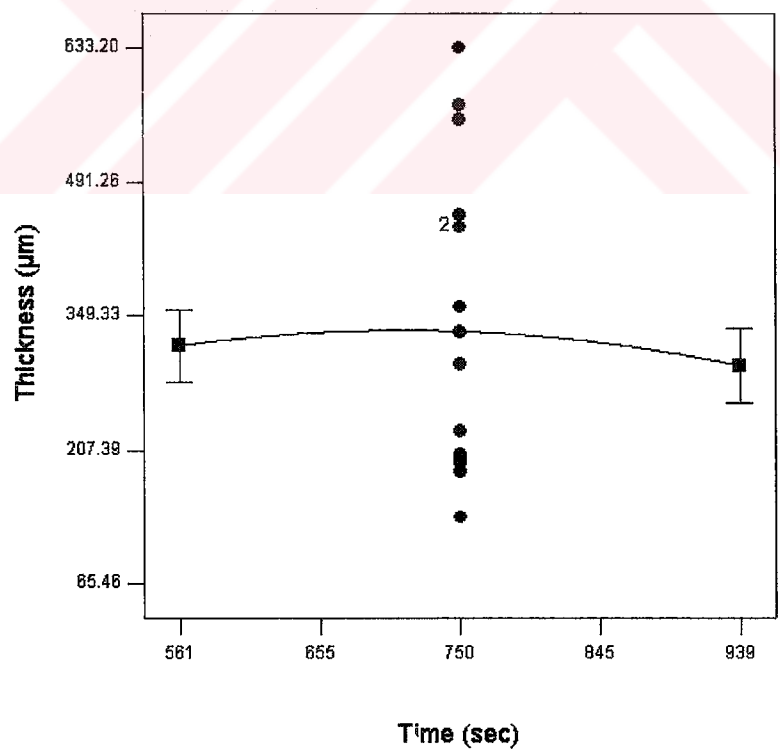


Figure 4.15. The Effect of Plating Time on Thickness

This may be caused due to the interactions of plating time with ratio of chromic acid to sulphuric acid (Figure 4.9), bath temperature (Figure 4.12) and current density (Figure 4.14). As it is seen in the figures, increasing plating time decreases the coating thickness in certain values of chromic acid/sulphuric acid ratio, bath temperature and current density.

4.2. Optimum Values of Process Parameters for Thickest Plating

Optimization of responses and factors was performed using the optimization module of Design-Expert. 10 possible solutions were found for the optimum chromium plating thickness. The values of process parameters, their corresponding plating thicknesses and desirability values are given in Figure 4.16.

One of the solutions given in Figure 4.16 can be used to obtain optimum chromium plating thickness but the most desirable solution is the one which has the highest desirability value. This solution is automatically selected by software in the first line of the figure. Thus, the optimum chromium plating conditions, which produce the thickest coatings are given in Table 4.1.

Table 4.1. Optimum Plating Conditions for Thickest Plating

Amount of Chromic Acid (g/l)	CrO ₃ /H ₂ SO ₄	Bath Temperature (°C)	Current Density (A/dm ²)	Plating Time (sec)
278.6	0.006	58	26.9	875

The ramp display combines the individual graphs for easier interpretation. The dot on each ramp reflects the factor setting or response prediction for that solution. The height of the dot shows how desirable it is. The ramps report of first solution is given in Figure 4.17. The histogram shows how well each variable satisfied the criteria: values near one are good.

The desirability histogram of the best solution is given in Figure 4.18. As it is shown in Figure 4.19, overlay plots of all factors were not shaded so for this study, all regions satisfy the multiple constraints on the responses of thickness and brightness.

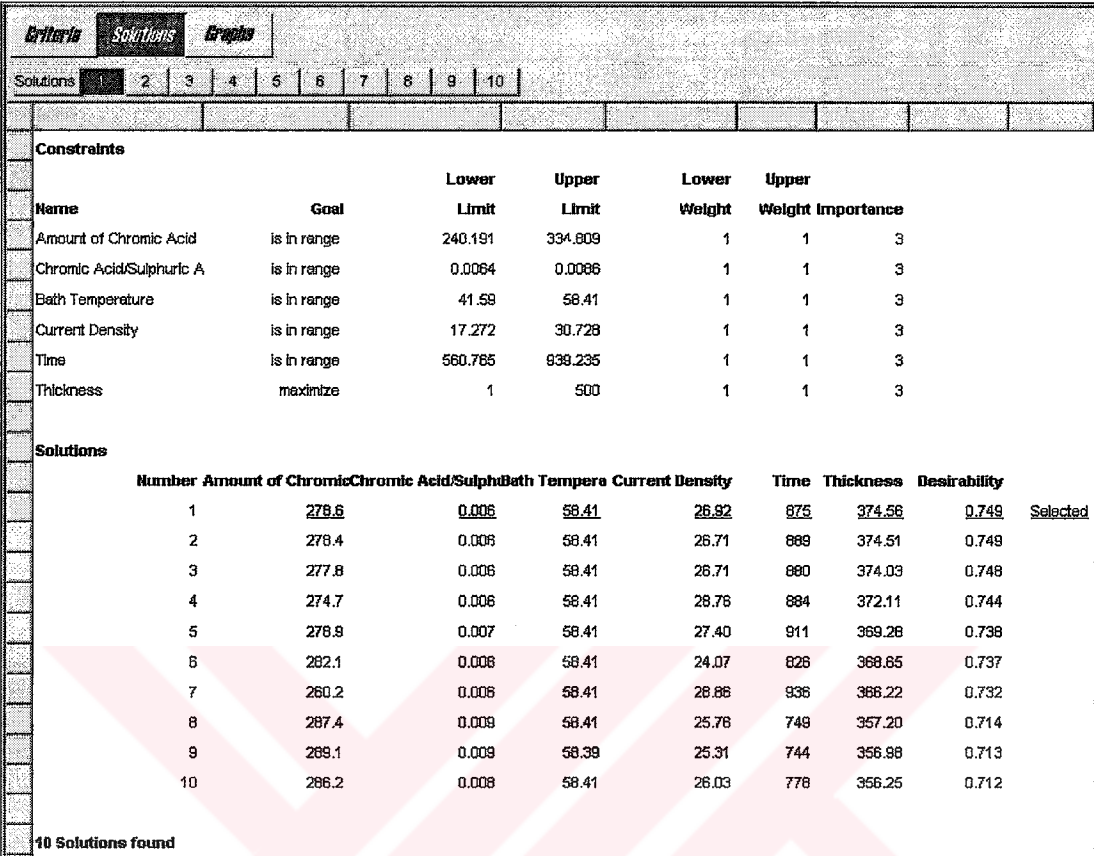


Figure 4.16. Numerical Optimization Reports for Plating Thickness

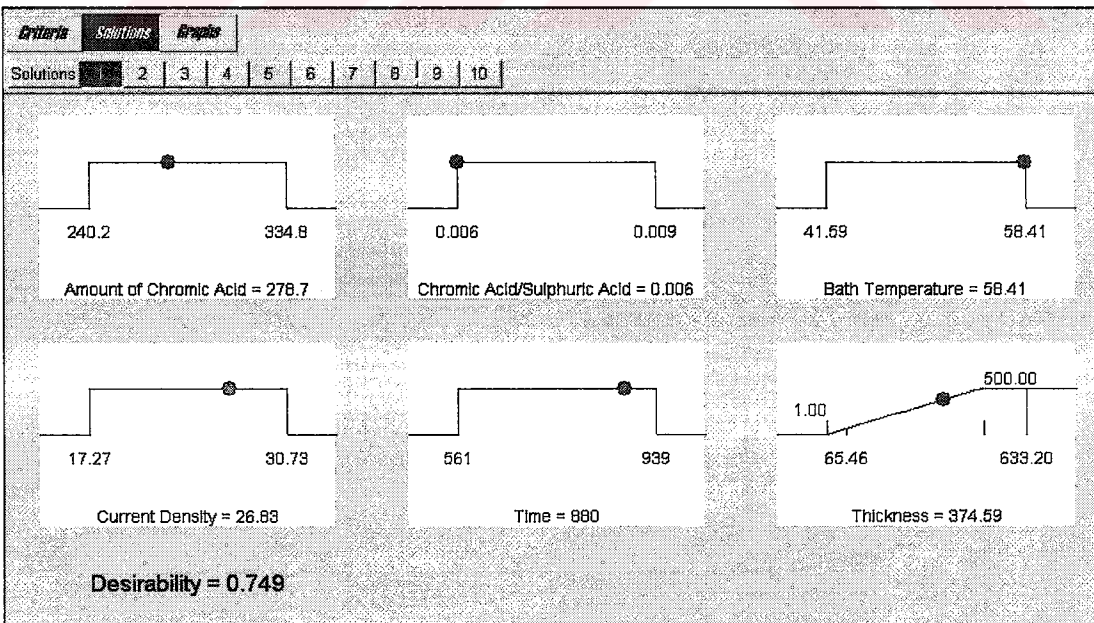


Figure 4.17. Ramps Report on Numerical Optimization of Plating Thickness

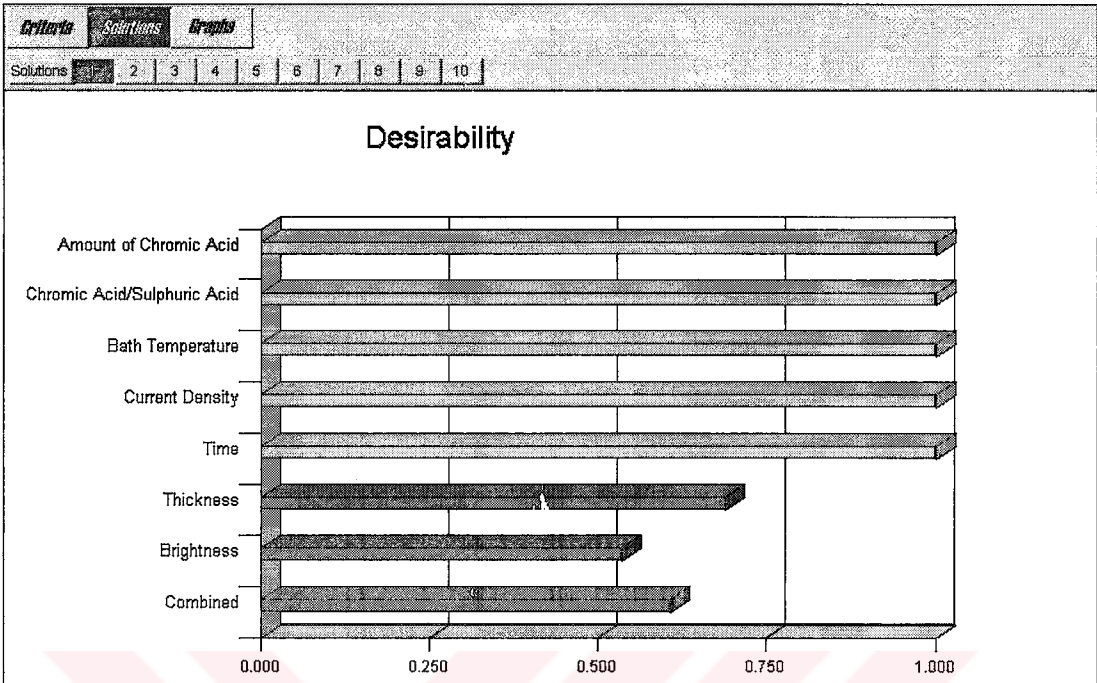


Figure 4.18. Desirability Histogram of Responses

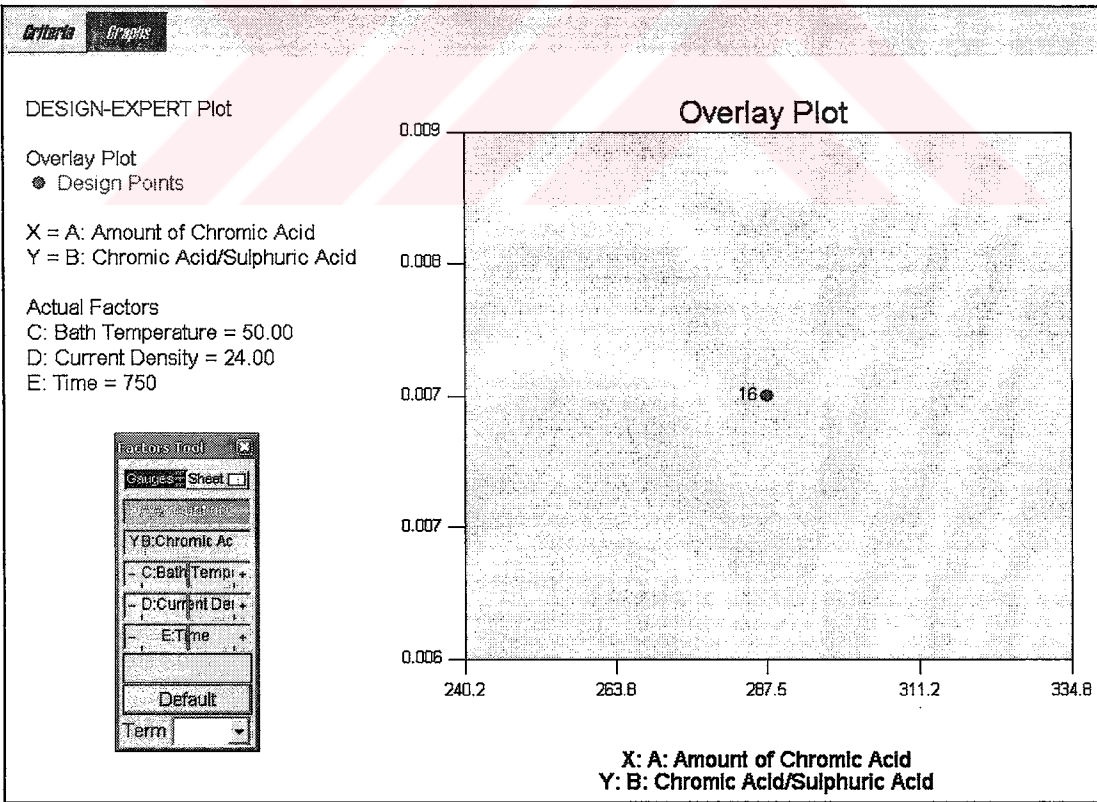


Figure 4.19. Overlay Plot of Factors

4.3. Effect of Process Parameters on the Brightness of Chromium Plating

The most desirable properties of the chromium as a metal coating are its inherent protective and decorative characteristics. Decorative chromium plating plays an important role in base metal protection. For decorative chromium plating, the most important property is the perfect brightness of the deposit. In the early days of chromium plating, since it was not practical to polish the chromium deposit after plating owing to the absence of a suitable polishing medium, the direct production of a bright coating from the bath was an essential pre-requisite for the practical application of the process. The deposit's high reflectivity is retained in service because of chromium's excellent tarnish, corrosion, wear, and scratch resistance. As it is mentioned in the previous section for the measurement of the brightness of the plating, reflectivity of the coating was measured and compared since reflectivity of the coating is directly proportional with the brightness of coating.

4.3.1. Amount of Chromic Acid

As it is shown in Figure 4.20, with increasing amount of chromic acid, the brightness of the chromium plating increases linearly. It can therefore be seen in Figures 4.21, 4.22 that the ratio of chromic acid to sulphuric acid and bath temperature interact with the amount of chromic acid. However current density and plating time exhibit no significant effect to the effect of amount chromic acid.

The brightness of chromium plating depends on the crystal orientation and crystal size of the deposits. For the brightest plating, nearly perfect crystal orientation and fine crystal sizes are desired. And it is known that, by increasing the amount of chromic acid coating thickness decreases and grain sizes become fine. Thus, the brightness (reflectivity) of chromium plating increases with increasing chromic acid concentration.

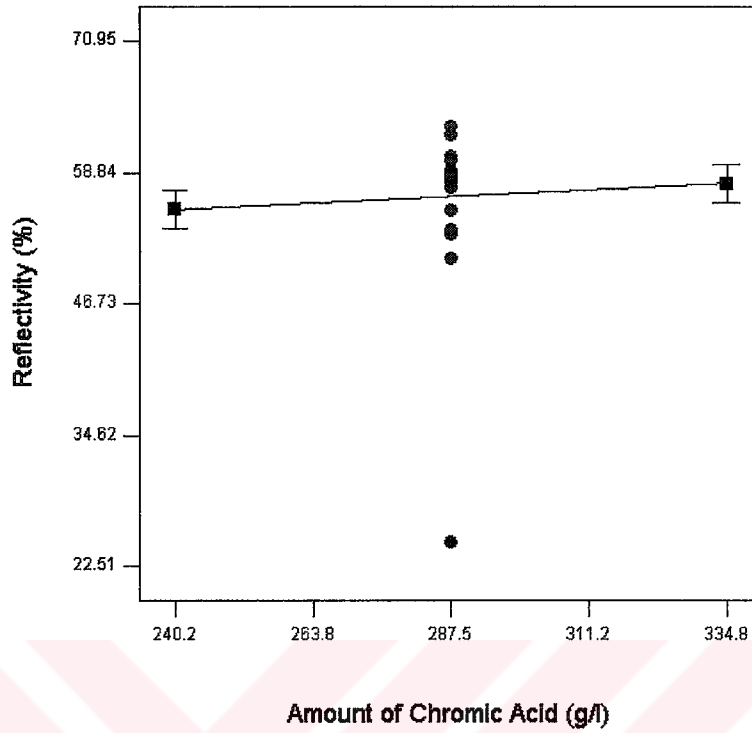


Figure 4.20. The Effect of Amount of Chromic Acid (CrO_3) on Brightness

Figure 4.21 indicates that while ratio of chromic acid to sulphuric acid is 0.006, increasing the amount of chromic acid causes a linear increase in brightness, however while ratio of chromic acid to sulphuric acid increased to 0.009, increasing the amount of chromic acid causes a linear decrease in brightness. The intersection point of the two curves in this figure can be reached when the amount of chromic acid is approximately at 315 g/l. Therefore, for higher brightness, higher ratio of chromic acid to sulphuric acid up to 315 g/l chromic acid should be selected and beyond this point lower ratio of chromic acid to sulphuric acid should be selected. As shown in Figure 4.22, change in bath temperature changed the relation between amount of chromic acid and coating brightness. At 42 °C bath temperature, coating brightness increases linearly with increasing amount of chromic acid, however, when bath temperature increased to 58 °C, brightness slightly decreases with increasing amount of chromic acid. The intersection point in this figure can be reached when amount of chromic acid is approximately 385 g/l. Therefore, up to 385 g/l chromic acid, higher temperature and beyond this point lower temperature should be selected for the brightest coating.

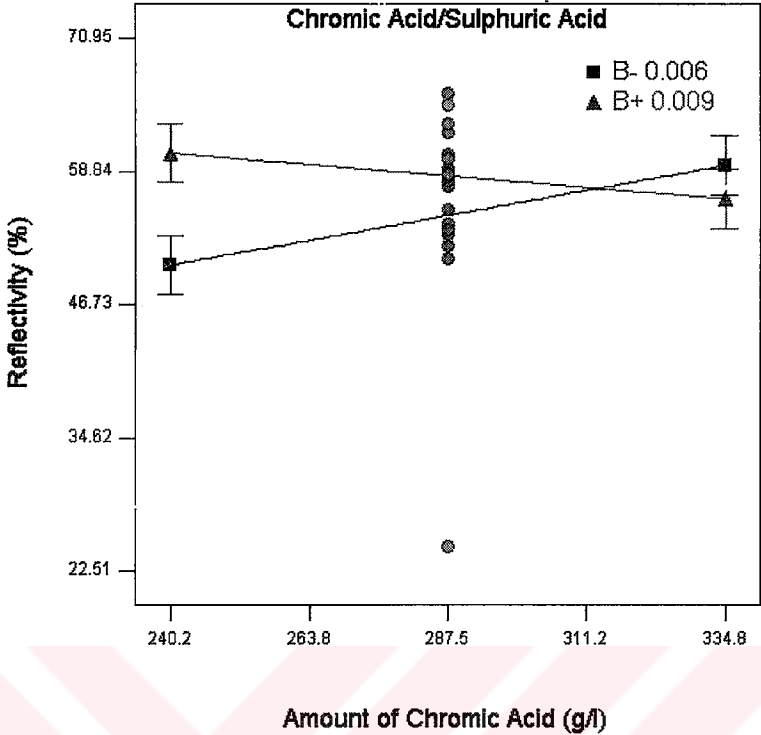


Figure 4.21. Interaction between Amount of Chromic Acid and Chromic Acid/Sulphuric Acid Ratio and their Effects to the Coating Brightness

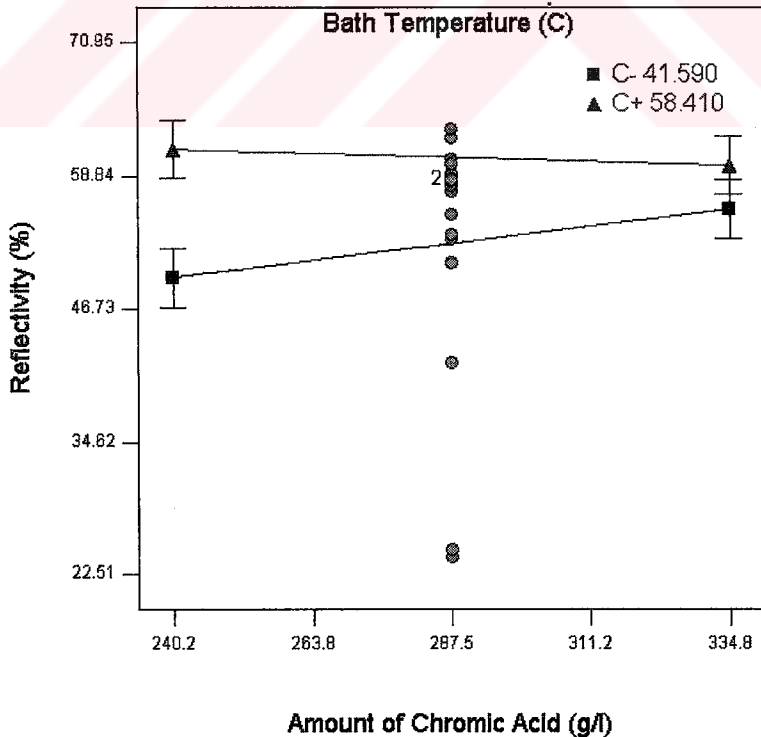


Figure 4.22. Interaction between Amount of Chromic Acid and Bath Temperature and their Effects to the Coating Brightness

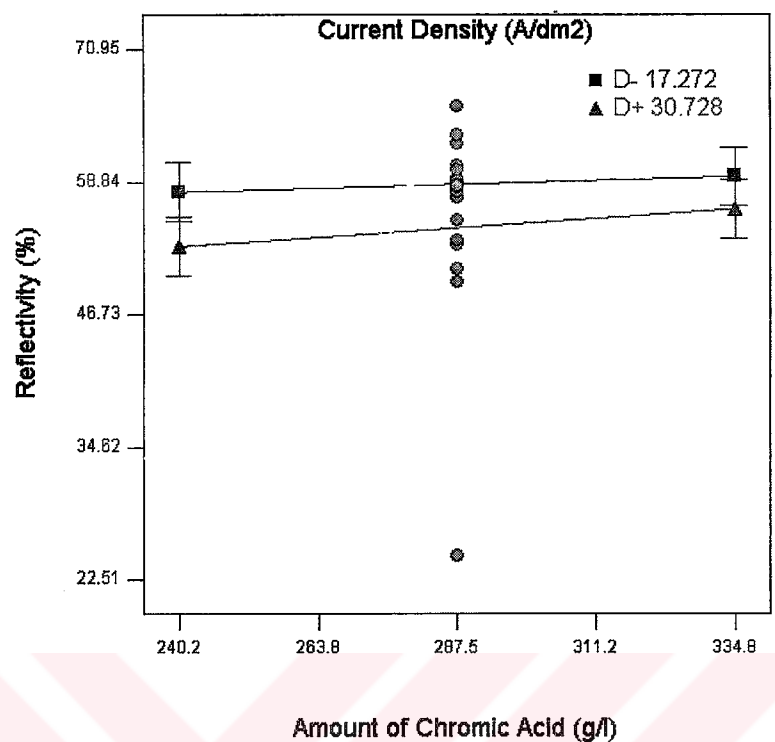


Figure 4.23. Interaction between Amount of Chromic Acid and Current Density and their Effects to the Coating Brightness

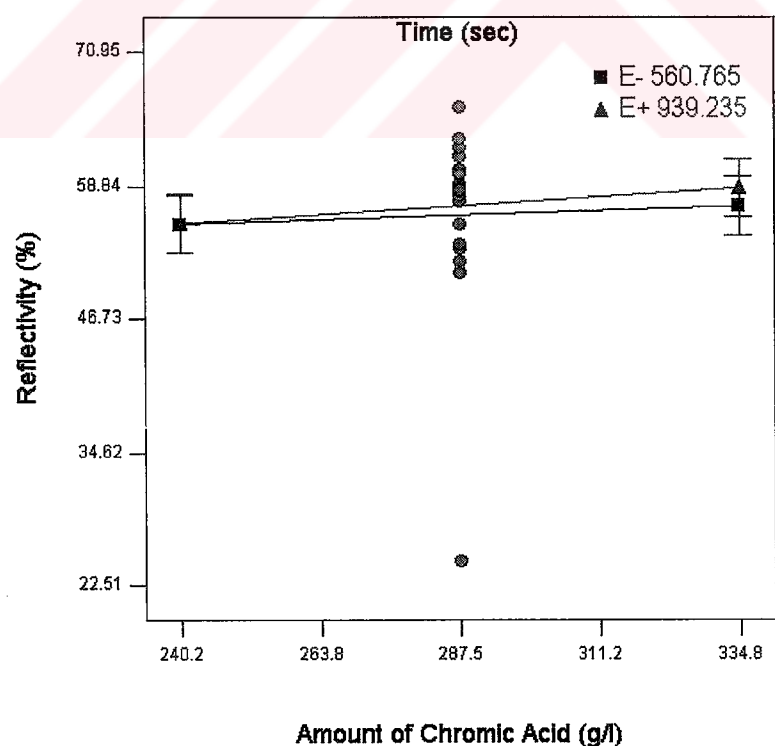


Figure 4.24. Interaction between Amount of Chromic Acid and Plating Time and their Effects to the Coating Brightness

The curves obtained in Figures 4.23 and 4.24 are parallel to each other. This indicates that plating time and current density were not changed the relation between brightness and amount of chromic acid. Hence, there is no interaction between these parameters. In order to provide a certain amount of brightness, the current density should be increased or plating time should be decreased, when amount of chromic acid is increased

4.3.2. Ratio of Chromic Acid to Sulphuric Acid

Figure 4.25 indicates that, increasing the ratio of chromic acid to sulphuric acid causes a linear increase on the coating brightness, slightly. According to the interaction graphs shown in Figures 4.26, 4.27, and 4.28, bath temperature, current density and plating time were not changed the relation between ratio of chromic acid to sulphuric acid and the coating brightness. Hence, there is no interaction between these parameters. In order to provide a certain amount of brightness, the bath temperature should be decreased, current density should be increased or plating time should be decreased, when amount of chromic acid is increased.

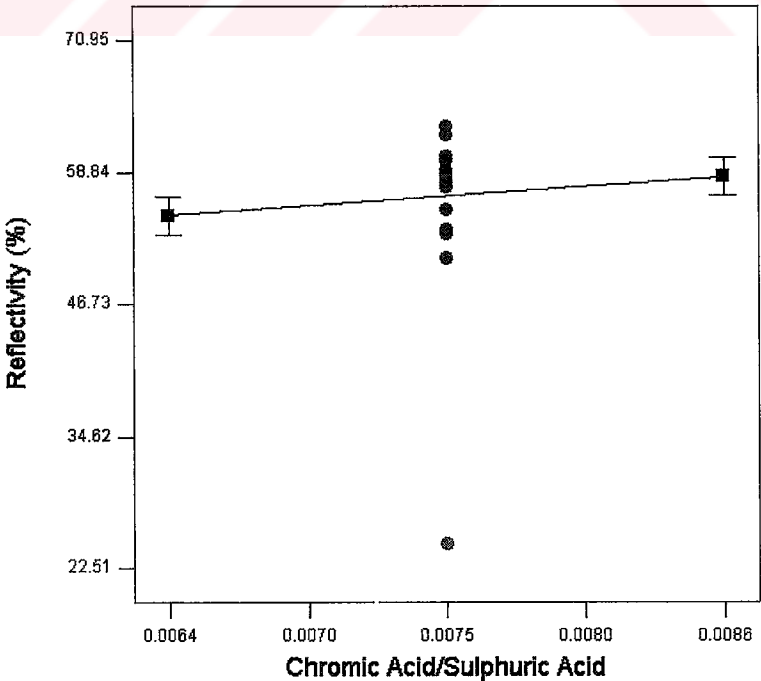


Figure 4.25. The Effect of Chromic Acid/Sulphuric Acid Ratio on Brightness

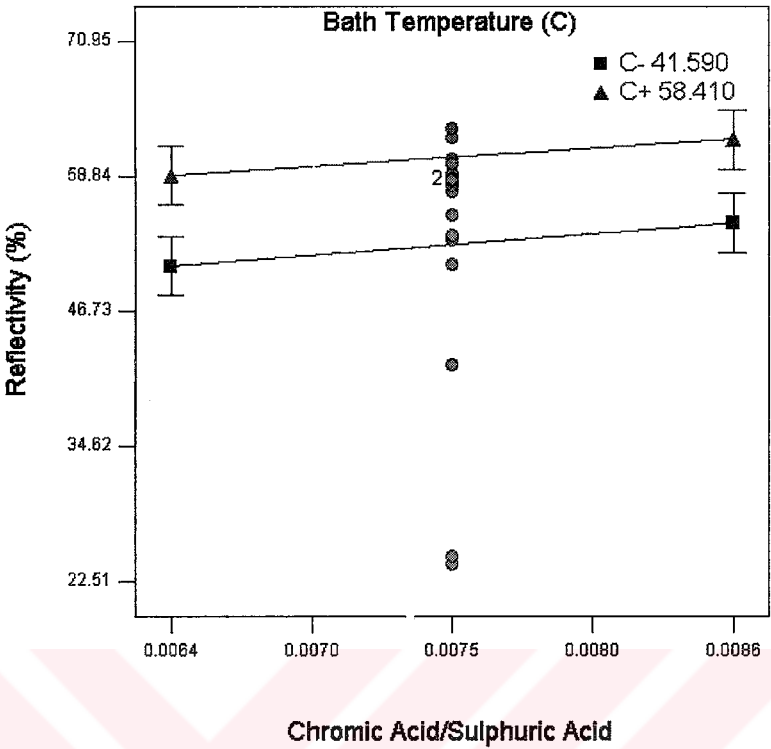


Figure 4.26. Interaction between Ratio of Chromic Acid to Sulphuric Acid and Bath Temperature and their Effects to the Coating Brightness

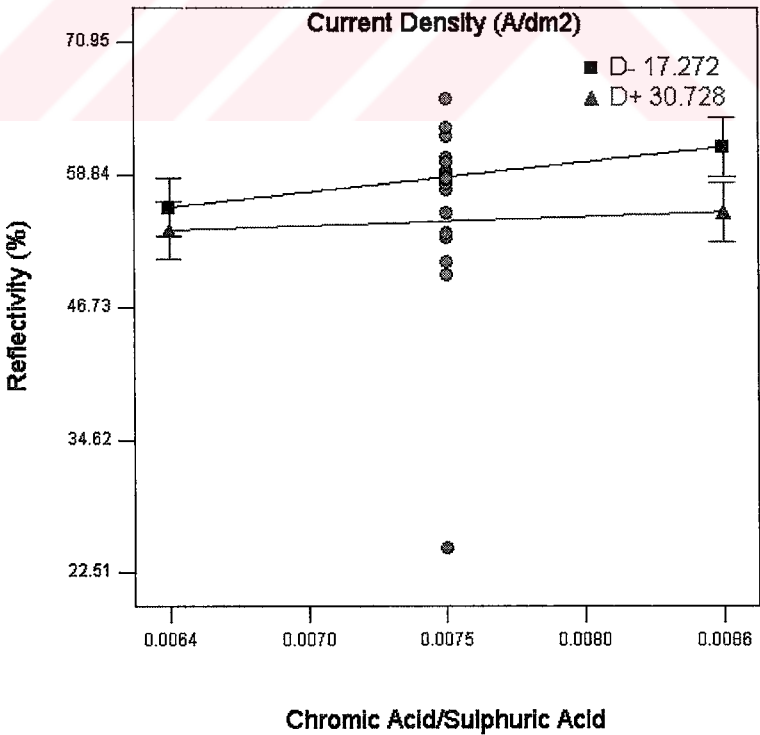


Figure 4.27. Interaction between Ratio of Chromic Acid to Sulphuric Acid and Current Density and their Effects to the Coating Brightness

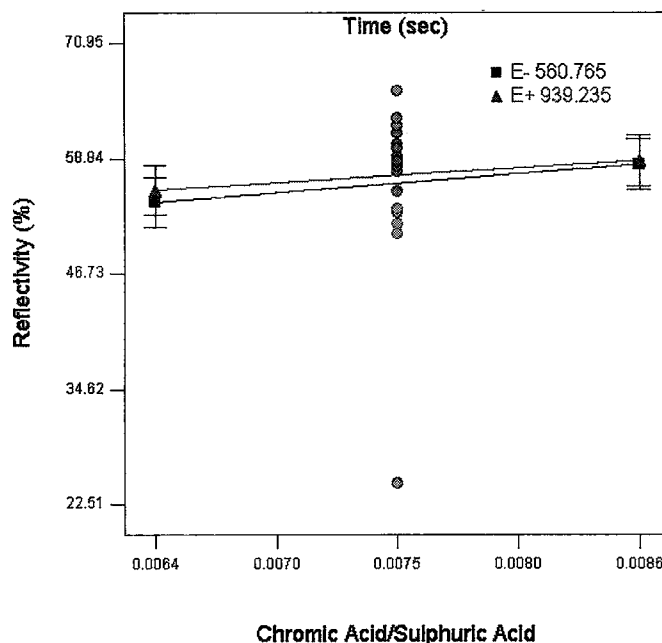


Figure 4.28. Interaction between Ratio of Chromic Acid to Sulphuric Acid and Plating Time and their Effects to the Coating Brightness

4.3.3. Bath Temperature

The effect of bath temperature on the coating brightness is shown in Figure 4.29. The results indicate that the brightness increases linearly with increasing bath temperature. Because the existence of cracks and scratches depends on the bath temperature. As the deposition temperature raised the deposits contain fewer cracks and scratches since deposits produced at high temperature are relatively stress-free. Thus, the brightness (reflectivity) of the coating increases with high temperature.

Interaction graphs shown in Figures 4.30 and 4.31, indicate that current density and plating time were not changed the relation between bath temperature and the brightness. It has been concluded that there is no interaction between these parameters. One of the following processes can be done, to provide a certain amount of brightness, when bath temperature is increased,

- Current density should be increased,
- Plating time should be decreased,
- Ratio of chromic acid to sulphuric acid should be decreased
- Amount of chromic acid should be decreased

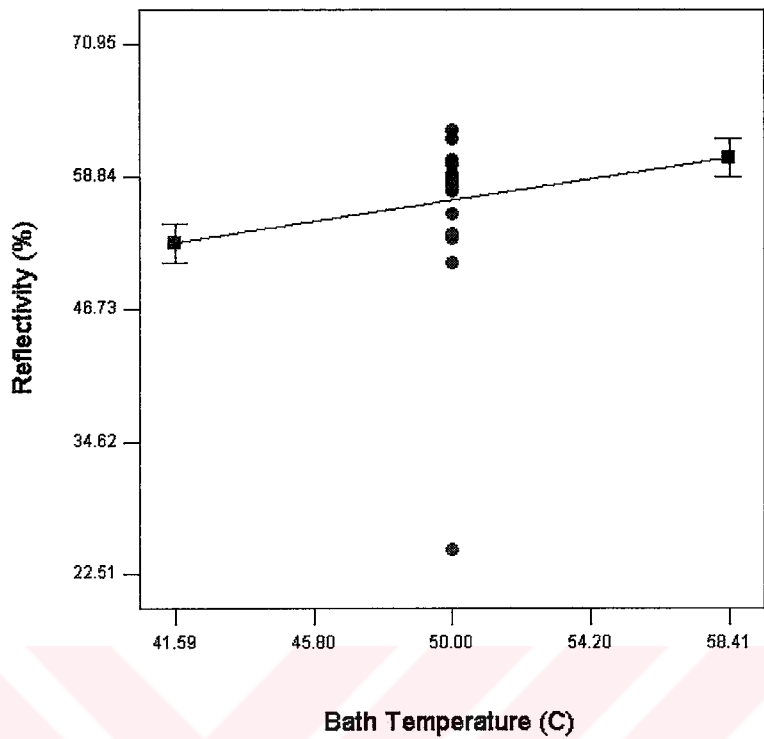


Figure 4.29. The Effect of Bath Temperature on Brightness

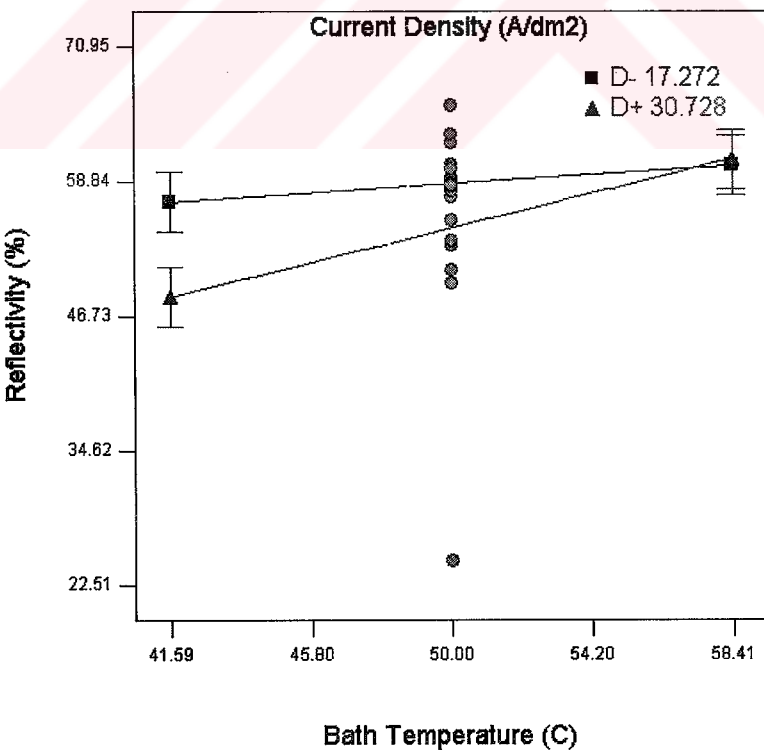


Figure 4.30. Interaction between Bath Temperature and Current Density and their Effects to the Coating Brightness

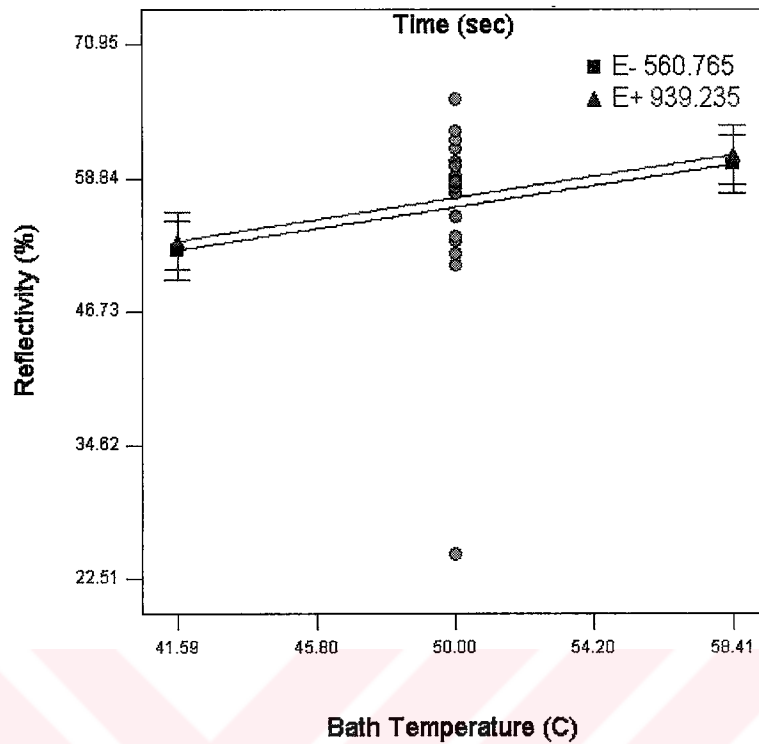


Figure 4.31. Interaction between Bath Temperature and Plating Time and their Effects to the Coating Brightness

4.3.4. Current Density

The influence of current density on the brightness is shown in Figure 4.32. According to the figure, brightness of the chromium plating decreases linearly with increasing current density. This is due to high current density forms rough and nodular deposits and leads to fully matt deposits (Weiner, 1980)

Interaction graph shown in Figure 4.33 indicates that there is no interaction between plating time and current density since two curves in the figure are parallel. It can be concluded from interaction graphs that, one of the following processes can be done to provide a certain amount of brightness, when current density is increased,

- Plating time should be increased
- Amount of chromic acid should be increased
- Ratio of chromic acid to sulphuric acid should be increased
- Bath temperature should be increased

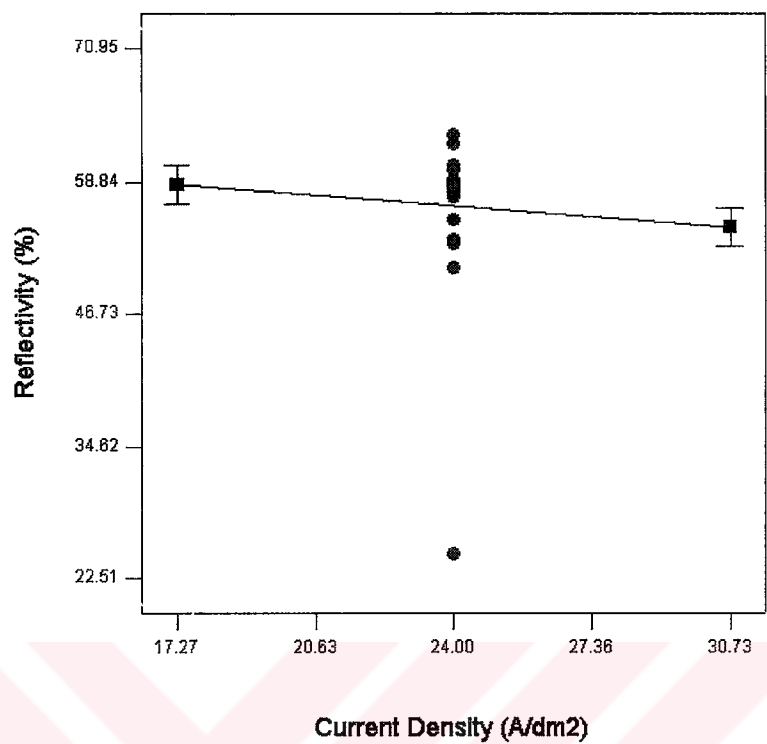


Figure 4.32. The Effect of Current Density on Brightness

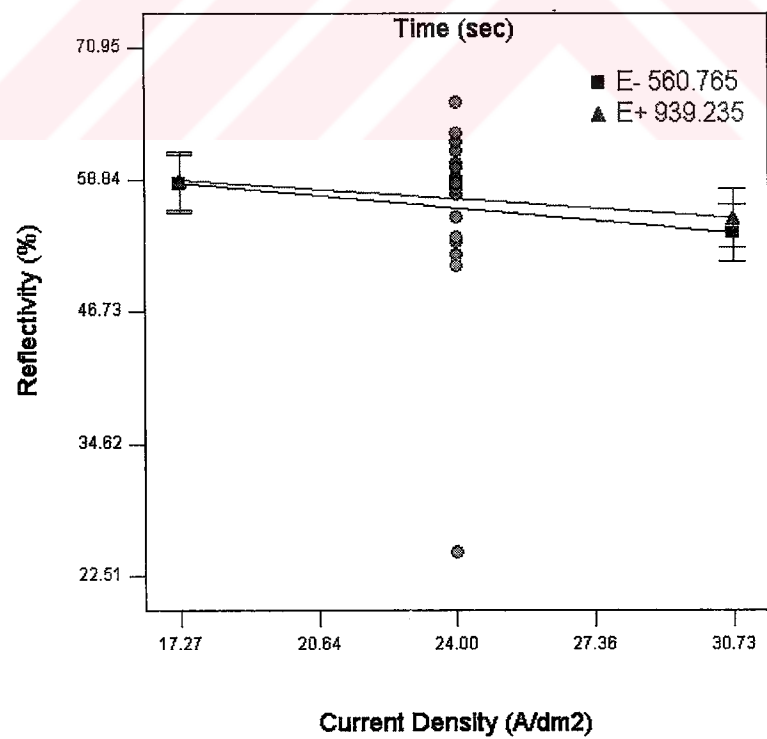


Figure 4.33. Interaction between Current Density and Plating Time and their Effects to the Coating Brightness

4.3.5. Plating Time

The variation of the brightness with plating time is shown in Figure 4.34. According to the figure, brightness of the chromium plating increases slightly with increasing plating time.

Interaction graphs between plating time and other process parameters are given in Figures 4.24, 4.28, 4.31 and 4.33. It can be concluded from interaction graphs that, one of the following processes can be done to provide a certain amount of brightness, when plating time is increased,

- Amount of chromic acid should be decreased
- Ratio of chromic acid to sulphuric acid should be decreased
- Bath temperature should be decreased,
- Current density should be increased

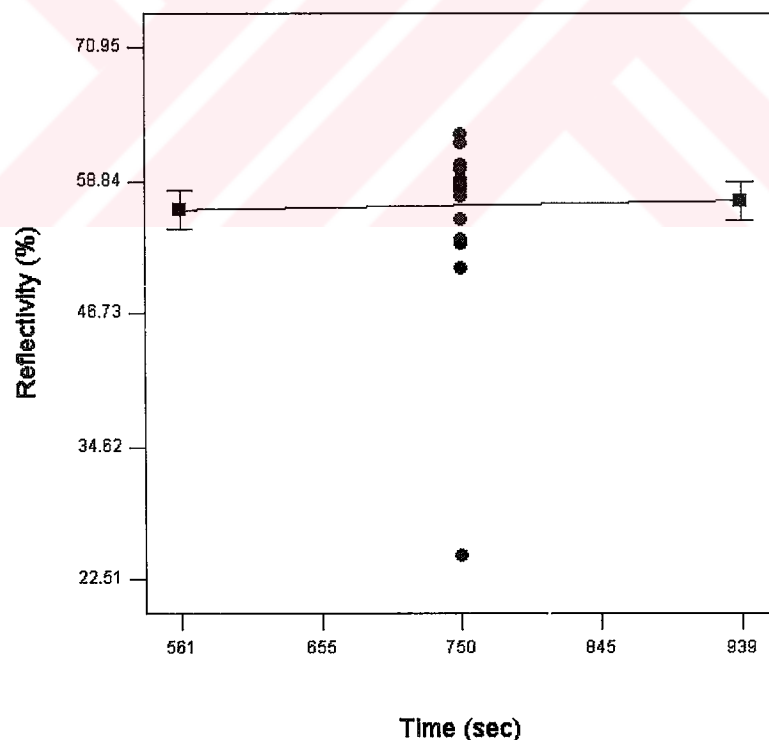


Figure 4.34. The Effect of Plating Time on Brightness

4.4. Optimum Values of Process Parameters for Brightest Plating

According to the optimization calculations, 10 possible solutions were found for the optimum chromium plating brightness. The values of process parameters, their corresponding brightness and desirability values are given in Figure 4.35.

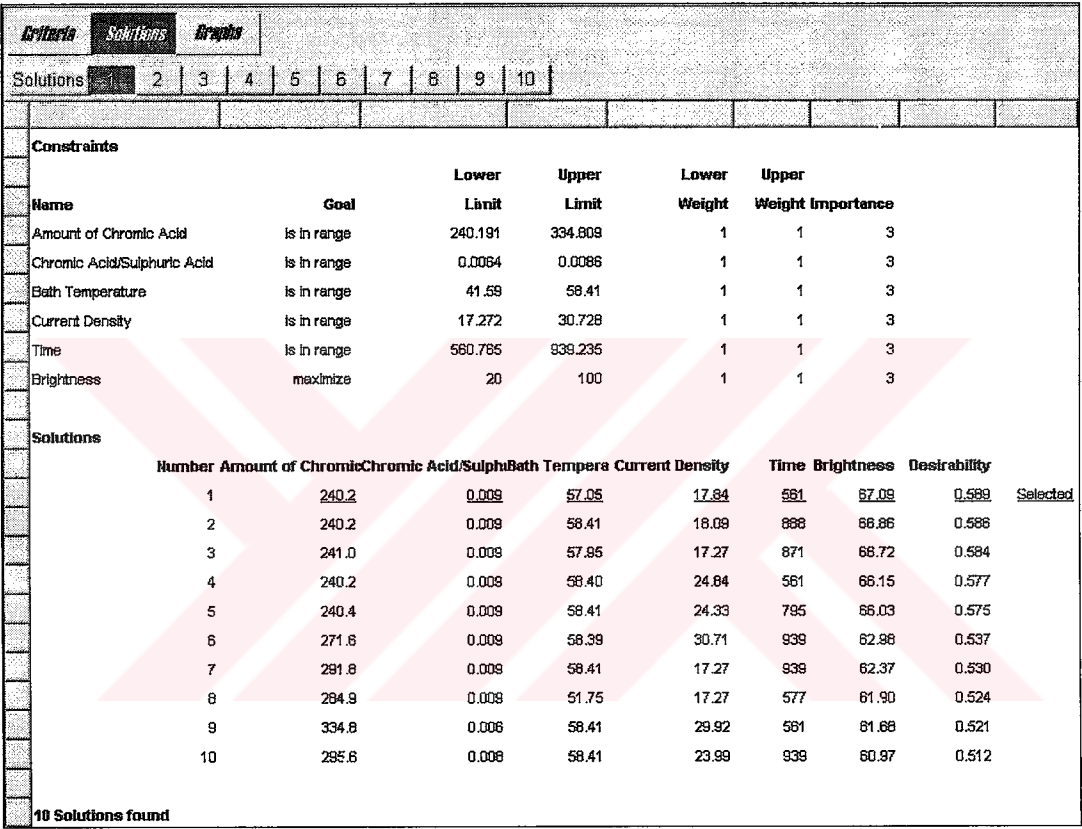


Figure 4.35. Numerical Optimization Reports for Plating Brightness

One of the solutions given in Figure 4.35 can be used to obtain optimum plating brightness. Thus, the optimum chromium plating conditions, which produce the brightest coatings, are given in Table 4.2. Also, the ramps report of the optimum solution is given in Figure 4.36.

Table 4.2 Optimum Plating Conditions for Brightest Plating

Amount of Chromic Acid (g/l)	CrO ₃ /H ₂ SO ₄	Bath Temperature (°C)	Current Density (A/dm ²)	Plating Time (sec)
240.2	0.009	57	17.8	561

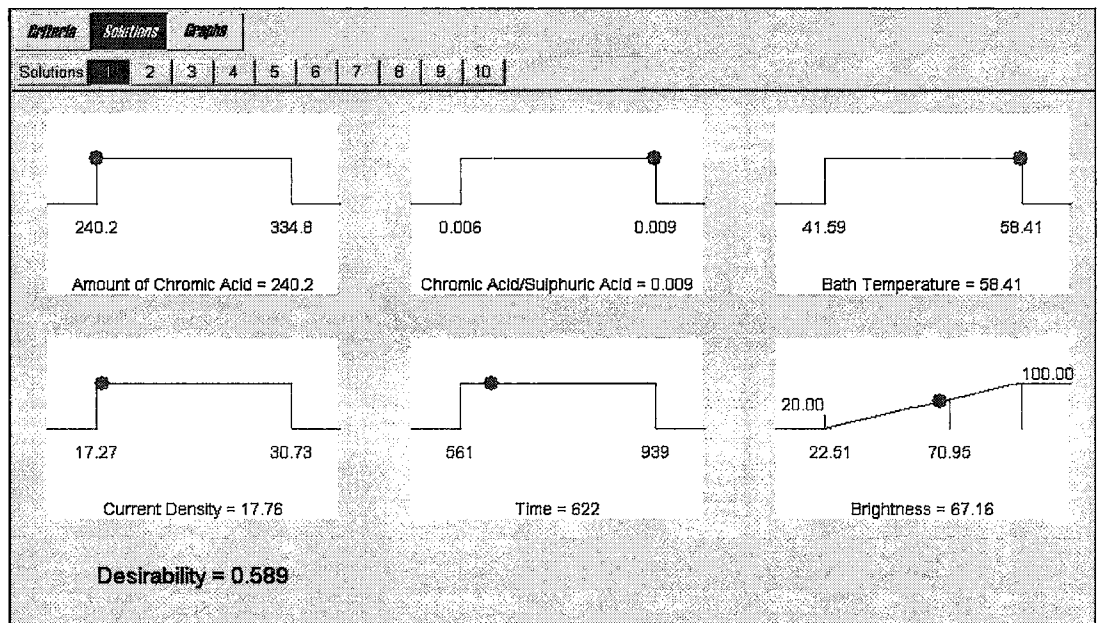


Figure 4.36. Ramps Report on Numerical Optimization of Plating Brightness

Criteria		Solutions		Graphs							
Solutions		1	2	3	4	5	6	7	8	9	10
Constraints											
Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance					
Amount of Chromic Acid	Is in range	240.191	334.609	1	1	3					
Chromic Acid/Sulphuric Acid	Is in range	0.0064	0.0086	1	1	3					
Bath Temperature	Is in range	41.59	58.41	1	1	3					
Current Density	Is in range	17.272	30.728	1	1	3					
Time	Is in range	560.765	939.235	1	1	3					
Thickness	maximize	1	500	1	1	3					
Brightness	maximize	20	100	1	1	3					
Solutions											
Number	Amount of Chromic	Chromic Acid/Sulphuric	Bath Temperature	Current Density	Time	Thickness	Brightness	Desirability			
1	264.1	0.009	58.40	25.71	726	349.36	63.66	0.619			
2	264.1	0.009	58.41	25.73	728	349.36	63.65	0.619			
3	266.8	0.009	58.41	26.20	770	350.46	63.62	0.618			
4	273.8	0.009	58.41	25.73	749	354.37	63.09	0.618			
5	262.7	0.009	58.41	24.43	684	345.18	64.18	0.617			
6	272.0	0.009	58.41	26.71	790	352.35	63.16	0.616			
7	279.7	0.008	58.41	28.26	939	371.86	59.96	0.609			
8	259.2	0.008	58.41	27.43	703	344.13	62.91	0.607			
9	269.5	0.007	58.41	27.21	672	361.65	60.69	0.606			
10	240.4	0.009	49.11	22.17	561	321.13	61.13	0.574			
10 Solutions found											

Figure 4.37. Numerical Optimization Reports for Plating Brightness and Thickness

4.5. Optimum Values of Process Parameters for Thickest and Brightest Plating

For some industrial applications, it may be possible for an electroplater or user to need chromium plating, which has the highest corrosion and wear resistance with the best decorative appearance. This time, both the brightness and thickness of chromium plating should be optimized. Figure 4.37 indicates the optimum values of process parameters, which provide the possible thickest and brightest coating. Thus, the optimum chromium plating conditions, which produce the possible thickest and brightest coatings, are given in Table 4.3. Also, the ramps report of the optimum solution is given in Figure 4.38.

Table 4.3. Optimum Plating Conditions for Possible Brightest and Thickest Plating

Amount of Chromic Acid (g/l)	CrO ₃ /H ₂ SO ₄	Bath Temperature (°C)	Current Density (A/dm ²)	Plating Time (sec)
264.1	0.009	58	25.7	726

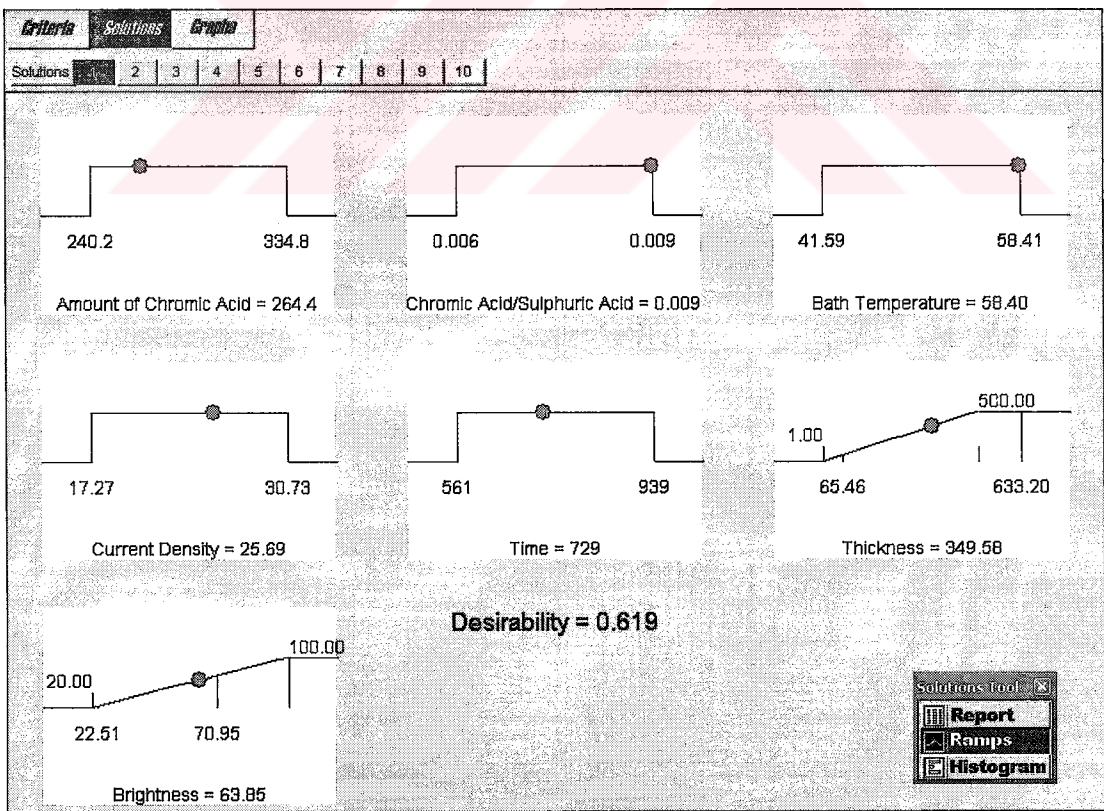


Figure 4.38. Ramps Report on Numerical Optimization of First Solution

5. CONCLUSION AND FUTURE STUDIES

5.1. Conclusion

The aim of this study was to investigate the effect of main parameters such as amount of chromic acid, ratio of chromic acid to sulphuric acid, bath temperature, current density and plating time on the thickness and brightness of chromium plating.

In this study, a small modern chromium electroplating plant was built as an experimental setup and MS58 brass alloy materials were chromium coated under different values of amount of chromic acid, ratio of chromic acid to sulphuric acid, bath temperature, current density and plating time, during experiments. The results of this study can be summarized as follows:

- It has been observed that the concentration of the bath and the dirtiness of the anodes' surfaces because of the lead chromate coating cause change in thickness and brightness of chromium plating despite other process parameters constant. It was reported that formation of lead chromate on the surface of the anodes during chromium plating changes the thickness of the chromium plating (Aydonat, 2002).
- The thickness of the chromium plating strongly depends on the amount of chromic acid, bath temperature, current density and plating time.
- Thickness of chromium plating increases up to a certain amount of chromic acid (approximately 275 g/l) then the thickness of chromium deposit was decreased after 275 g/l while the amount of chromic acid was increased. Also, it was observed that the variation of thickness between 265 g/l and 285 g/l was so small.
- An increase in the ratio of chromic acid to sulphuric acid results in a slight decrease in the coating thickness. The minimum thickness is reached when the ratio of chromic acid to sulphuric acid is approximately 0.0075. The thickness of the coating increases slightly with the further increasing in the ratio of chromic acid to sulphuric acid. Thus, it is concluded that changing the ratio of chromic acid to sulphuric acid

between 0.005 (1/200) and 0.010 (1/100) has no significant effect on the coating thickness. The addition of sulphuric acid (catalyst) to the plating bath provides higher penetration rate of deposits on the surface of the substrate and prevents the burning of coating during electroplating. No metallic coatings can be obtained without using catalyst in chromium plating process.

- Investigations showed that there is an interaction between plating time and ratio of chromic acid to sulphuric acid.
- It was observed that bath temperature has a strong effect on the thickness of chromium plating. The thickness of chromium plating increases with increasing bath temperature. It is not the case as indicated in the investigation of Wang Deqing et al., (2004). Since it is known that in chemical processes, increasing temperature accelerates the reaction and increases conductivity, the result obtained in this study is more realistic.
- Increase in plating time changes the relation between bath temperature and coating thickness. Therefore, there is an interaction between plating time and bath temperature.
- By increasing current density, the thickness of coating increases first, and reaches a maximum value while current density is between 24 A/dm^2 and 25 A/dm^2 and beyond this point, the thickness of chromium deposit decreases. This is the case as indicated by Wang Deqing et al., (2004). According to the investigations of Wang Deqing et al., the thickest coating can be obtained at a current density of 29 A/dm^2 . In this study, however the optimum current density value which gives the thickest coating has been found in between $24\text{-}25 \text{ A/dm}^2$.
- Investigations indicated that the thickness of the chromium plating increased up to a certain value of plating time (approximately 730 sec), however the thickness of chromium deposit beyond this point, the thickness of chromium deposit decreases while plating time increases. This is not the case as indicated by Wang Deqing et al., that the thickness of the chromium plating increases while plating time increases.

- It was observed that the brightness of the chromium plating increases linearly while amount of chromic acid increases.
- Variation in ratio of chromic acid to sulphuric acid and bath temperature change the relation between bath temperature and the brightness of chromium plating.
- Increasing the ratio of chromic acid to sulphuric acid causes a linear increase on the coating brightness, slightly.
- It is concluded that, bath temperature has a strong effect to the brightness of chromium plating. Brightness of the chromium plating increases linearly with increasing bath temperature.
- Investigations showed that the brightness of chromium plating decreases linearly with increasing current density.
- It is investigated that, the brightness of chromium plating increases slightly with increasing plating time.
- It is concluded that the optimum chromium plating conditions, which produce the thickest coatings are at 278.6 g/l of chromic acid, 0.006 ratio of chromic acid to sulphuric acid, 58 °C bath temperature, 26.9 A/dm² current density and 875 sec plating time.
- The optimum chromium plating conditions, which produce the brightest coatings are at 240.2 g/l of chromic acid, 0.009 ratio of chromic acid to sulphuric acid, 57 °C bath temperature, 17.8 A/dm² current density and 561 sec plating time.
- The optimum chromium plating conditions, which produce the possible thickest and brightest coatings are at 264.1 g/l of chromic acid, 0.009 ratio of chromic acid to sulphuric acid, 58 °C bath temperature, 25.7 A/dm² current density and 726 sec plating time.

5.2. Future Studies

In the future studies, this study can be developed by performing the considerations given below:

- The effect of process parameters on the hardness, corrosion resistance and wear resistance of chromium coating can be investigated.
- The substrate materials, with different chemical compositions, can be treated to investigate the effect of chemical composition.
- Instead of sulphuric acid, fluoride containing bath can be prepared and effect of fluoride can be investigated.
- Instead of Brass alloy, other materials such as steel or aluminium can be used as substrate material.
- Instead of direct current, pulsed current can be applied; hence differences between direct current and pulsed current can be investigated.
- Effect of nickel plating can be investigated.
- By coating copper under nickel layer, effect of copper coating to chromium coating can be studied.

REFERENCES

- ANANDAN C., WILLIAM GRIPS V.K., RAJAM K.S., JAYARAM V., and BERA PARTHASARATHI, 2002, "Investigation of Surface Composition of Electrodeposited Black Chrome Coatings by X-ray Photoelectron Spectroscopy", *Applied Surface Science*, Vol. 191, 254-260.
- ASM HANDBOOK, "Materials Selection and Design", Volume 20.
- AYDONAT HAKKI, 2002, "Galvano Teknikte Krom Kaplama", Alfa Basım Yayım Dağıtım Ltd. Şti.
- BERGENSTOF NIELSEN C., 1998, "On Texture Formation of Chromium Electrodeposits", *Surface and Coatings Technology*.
- BRANDES E.A., WHITTAKER J.A., 1967, "Ductile Electrodeposited Chromium Tubing and Other Shapes", *British Patent*, 1,081, 137.
- BRENNER A., BURKHEAD P., JENNINGS C.W., 1947, "Physical Properties of Electrodeposited Chromium", *Proceedings American Electroplaters' Soc.*, Vol. 34, 32-73.
- CARTER V.E., 1977, "Metallic Coatings for Corrosion Control", *Newnes-Butterworths*.
- CHIU L.H., YANG C.F., HSIEH W.C., and CHENG A.S., 2002, "Effect of Contact Pressure on Wear Resistance of AISI H13 Tool Steels with Chromium Nitride and Hard Chromium Coatings", *Surface and Coatings Technology*, Vol. 154, 282-288.
- CHEN Y.T., LIM B.H., LIM C.S., CHONG K.K., and TAN B.K., 2003, "High Precision ($1 \text{ part in } 10^4$) reflectivity measurement for the study of reflective materials used in solar collectors", *Solar Energy Materials and Solar Cells*, Vol. 80, 305-314.
- COBO E.O., SUÁREZ BALDO R.A., and BESSONE J.B., 1999, "Corrosion of Chromium Plated Rotor in Drilling Fluid", *Surface and Coatings Technology*, Vol. 122, 39-43.

- COTE PAUL J., and RICKARD CHRISTOPHER, 2000, "Gas-Metal Reaction Products in the Erosion of Chromium-Plated Gun Bores", *Wear*, Vol. 241, 17-25.
- CYMBALISTE M., 1938, "The Structure and Hardness of Electrolytic Chromium", *Trans. Electrochemical Society*, Vol. 53, 353.
- DENNIS J.K., and SUCH T.E., 1993, "Nickel and Chromium Plating", Third Edition, Woodead Publishing Limited.
- DEQING WANG, RIYUAN SHI, and TANGSHAN KOU, 2004, "Composite Plating of Hard Chromium on Aluminum Substrates", *Surface and Coatings Technology*. Vol. 184, 15-21.
- DIAZ ALBERTO GARCIA and PHILLIPS DON T., 1995, "Principles of Experimental Design and Analysis", Chapman and Hall.
- DUBPERNELL GEORGE, 1977, "Electrodeposition of Chromium from Chromic Acid Solutions", Pergamon Press.
- EILENDER W., AREND H., and SCHMIDTMANN E., 1948, "The Influence of Heat-Treatment on the Hardness and Gas Content of Hard Chromium Layers", *MetallOberflaeche*, Vol. 7, 143-145.
- FEDRIZZI L., ROSSI S., BELLEI F., and DEFLORIAN F., 2002, "Wear-Corrosion Mechanism of Hard Chromium Coatings", *Wear*, Vol. 253, 173-1181.
- HOSDOWICH J. M., 1949, "Scratch Hardness and Abrasion Hardness of Electrodeposited Chromium", *Proceedings American Electroplaters' Soc.*, Vol. 36, 103-125.
- HUME-ROTHERY W., and WYLLIE M.R.J., 1944, "The Structure of Electrodeposited Chromium", *Proc. Roy. Soc.*, A182, 415.
- LU GUOJIN, T. ADA EARL, and ZANGARI GIOVANNI, 2004, "Investigation of the Effect of Chromate Conversion Coatings on the Corrosion Resistance of Ni-based Alloys", *Electrochimica Acta*, Vol. 49, 1461-1473.
- LUNARSKA ELLINA, NIKIFOROW K., WIERZCHOŃ T., and ULBIN-POKORSKA I., 2001, "Effect of Plasma Nitriding on Hydrogen Behavior in Electroplated Chromium Coating", *Surface and Coatings Technology*, Vol. 145, 139-145.

- MAREK T., SÜVEGH K., VÉRTES A., EL-SHARIF M., McDOUGALL J. And CHISOLM C.U., 2000, "Defect Structure of Electrodeposited Chromium Layers", *Radiation Physics and Chemistry*, Vol. 58, 693-696.
- MONTGOMERY DOUGLES C., 1991, "Design and Analysis of Experiments", Third Edition, John Wiley and Sons
- OLIVARES J.A., RODRIGUEZ R.F., and REYES J.A., 2003, "Ray Tracing and Reflectivity measurements in nematic hybrid cells", *Optics Communications*, Vol. 221, 223-239.
- PALIK EDWARD D., 1991, "Handbook of Optical Constants of Solids-II", Academic Press Inc.
- PEPCHUK P.A., 1963, "A Comparative Study of Chromium Plating Baths Used for the Reforming of Automobile and Tractor Parts", *Zap. Leningr. Sel'skokhoz Inst.*, Vol. 93, 92-109.
- PICAS J.A., FORN A., IGARTUA A., and MENDOZA G., 2003, "Mechanical and Tribological Properties of High Velocity Oxy-Fuel Thermal Sprayed Nanocrystalline CrC-NiCr Coatings", *Surface and Coatings Technology*, Vol. 174-175, 1095-1100.
- PINA J., DIAS A., FRANÇOIS M., and LEBRUN J.L., 1997, "Residual Stresses and Crystallographic Texture in Hard-Chromium Electroplated Coatings", *Surface and Coatings Technology*, Vol. 96, 148-162.
- PLETCHER DEREK, and WALSH FRANK C., 1990, "Industrial Electrochemistry", Second Edition, Chapman and Hall.
- RICHARDS EDWARD S., 1950, "Chromium Plating", Third Edition, Charles Grifen and Company Limited.
- SAHRAOUI TAHAR, FENINECHE NOUR-EDDINE, MONTAVON GHISLAIN, and CODDET CHRISTIAN, 2003, "Structure and Wear Behaviour of HVOF Sprayed Cr₃C₂-NiCr and WC-Co Coatings", *Materials and Design*, Vol. 24, 309-313.
- SAMSONOV G.V., 1971, "Protective Coatings on Metals", Volume 3, Consultants Bureau.

- SHYAM BAHADUR, 1996, "Effect of Surface Coatings and Treatments on Wear", ASTM Publication.
- SIMÃO J., and ASPINWALL D.K., 1999, "Hard Chromium Plating of EDT Mill Work Rolls", *Journal of Materials Processing Technology*, Vol. 92-93, 281-287.
- SNYDER DONALD L., 1996, "Decorative Chromium Plating", Atotech USA Inc.
- SOLODKOVA L.N., and KUDRYAVTSEV V.N., 2004, "Corrosion-Protective Properties of Chromium Coatings in Marine and Coal-Mine Conditions", *Galvanotechnik*, Vol. 5, 1150-1154.
- STOCKEMER J., WINAND R., and VANDEN BRANDE P., 1999, "Comparison of Wear and Corrosion Behaviors of Cr and CrN Sputtered Coatings", *Surface and Coatings Technology*, Vol. 115, 230-233.
- SULLY A.H., and BRANDES E.A., 1967, "Chromium", Second Edition, New York Plenum Press.
- SURVILIENĖ S., ORLOVSKAJA L., BIKULCIUS G., and BIALLOZOR S., 2001, "Effect of MoO₂ and TiO₂ on Electrodeposition and Properties of Chromium Coating", *Surface and Coatings Technology*, Vol. 137, 230-234.
- TURNER T.A., 1998, "Canmaking: The Technology of Metal Protection and Decoration", Blackie Academic and Professional.
- UDY M.J., 1956, "Chromium", Second Edition, New York: Reinhold Publishing Corporation.
- WAHL H., GEBAUER K., 1951, "Wear Testing of Hard Chromium Coating", *Metaux (Corrosion-Ind)*, Vol. 26, 29-46.
- WEEKS M.E., 1956, "Discovery of Elements", 6th Edition, Easton, Pa.: Journal of Chemical Education.
- WEINER ROBERT, and WALMSLEY ADRIAN, 1980, "Chromium Plating", Finishing Publications Ltd.
- YIN K.M., and WANG C.M., 1999, "A Study on the Deposit Uniformity of Hard Chromium Plating on the Interior of Small Diameter Tubes", *Surface and Coatings Technology*, Vol. 114, 213-223.

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