

**KAUNAS UNIVERSITY OF TECHNOLOGY
MECHANICAL ENGINEERING AND DESIGN FACULTY**

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CHROME PLATING ON ABS PLASTICS

Final project for Bachelor/Master degree

Supervisor

Assoc. Prof. Dr. Regita Bendikiene

KAUNAS, 2015

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MECHANICAL ENGINEERING AND DESIGN FACULTY

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Final project for Master degree
Master in Mechanical Engineering (621H30001)

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**MASTER STUDIES FINAL PROJECT TASK ASSIGNMENT
Study programme MECHANICAL ENGINEERING**

The final project of Master studies to gain the master qualification degree, is research or applied type project, for completion and defence of which 30 credits are assigned. The final project of the student must demonstrate the deepened and enlarged knowledge acquired in the main studies, also gained skills to formulate and solve an actual problem having limited and (or) contradictory information, independently conduct scientific or applied analysis and properly interpret data. By completing and defending the final project Master studies student must demonstrate the creativity, ability to apply fundamental knowledge, understanding of social and commercial environment, Legal Acts and financial possibilities, show the information search skills, ability to carry out the qualified analysis, use numerical methods, applied software, common information technologies and correct language, ability to formulate proper conclusions.

1. Title of the Project

Chrome plating on ABS Plastics

Approved by the Dean 2015 y. May m.11 d. Order No. ST17-F-11-2

2. Aim of the project

The main aim of the project is to investigate the process of the chrome plating on the ABS plastic and to improve the quality of the product after it has been plated. The factors of plating on plastics is drawn and the consideration to attain good quality is recommended.

3. Structure of the project

Introduction, chrome plating process and material used in chromeplating plating on plastics, abs plastics, chrome plating, Injection Molding, Project Description, Problem Identification, Complication on the chrome plating on ABS plastics, Operating Environment, Part Preparation, Quality of the Molded part, Property of the suggested material, Numerical simulation of injection molding process, Results, Conclusion, Recommendation, References.

4. Requirements and conditions

To prepare final project according to KTU regulation and requirements.

5. This task assignment is an integral part of the final project

6. Project submission deadline: 2015 June 1st.

Given to the student

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SUMMARY

Plating on plastics is mainly used technology that provides decorative and functional finishes in the plastics. Chrome plating on plastic parts is widely used for decorative purposes. The application where the chrome plating are automobile industry, home appliance, electrical devices. The chrome plating have their own set of process steps to be carried out and some defects related to it. The main aim of the projects are Chrome plating process had been investigation had been done and the problems are identified. And according to problems identified some consideration are have been made. The solution is drawn by the considerations and the recommendation are given. This work also reviews the optimization of the parameters to obtain the best quality in the chrome plating of the ABS plastic. The main defect which have been identified is in-mold stress which have been produced during the molding of the part. In this work the material used is POLYLAC PA 272 of ABS plastics. By optimizing the parameters like cooling time, mold temperature and pressure hold time. The software used for analyzing and optimizing the parameters like cooling time, mould temperature and hold time is Solidworks plastics 2014. And it is identified that according to the process parameters of industrial reference, by changing the parameters like the mold temperature, cooling time, hold time will impacts the in the in-mold stress.

Key words – Chrome plating, ABS plastics, Optimization.

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Santrauka

Plastikų dengimas – tai technologija, kuri naudojama siekiant gauti dekoratyvias ir funkcines dangas. Plastikų chromavimas plačiai naudojamos dekoratyviniais tikslais. Chromavimas naudojamas automobilių pramonėje, dengiant buitines paskirties ir elektros prietaisų dalis. Chromavimo procesą sudaro seka tam tikrų veiksmų ir procesų, tačiau operacijos metu atsirandanta nemažai defektų. Pagrindinis šio projekto tikslas išanalizuoti chromavimo procesą, įvardinti problemas atsirandančias proceso metu. Identifikavus problemas rasti teisingus sprendimus. Darbe pasiūlyti chromavimo proceso tobulinimo sprendimai. Šiame darbe taip pat optimizuojami chromavimo parametrai siekiant pagaminti kokybišką produktą. Pagrindiniai defektai atsirandantys liejimo slegiant proceso metu – tai skyros paviršiaus žymė. POLYLAC PA 272 ABS plastikas buvo parinktas įgyvendinti projekto tikslus. Buvo optimizuojami šie parametrai: aušinimo laikas, formos temperatūra ir iūlaikymo laikas. Optimizavimas buvo atliekamas Solidworks programiniu paketu.

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Introduction

The chrome plating of ABS plastics is depositing a coat of chromium to the ABS plastics by means of electro deposition process. The main principle of this process is to impart the physical and chemical properties of the chromium on the surface of the ABS plastic. The main property of the chromium as a metal coating on the ABS plastic is to attain two purposes such as decorative and functional plating's.

In recent days chrome plated ABS plastics are have been used in various areas because of its light weight, corrosive resistant's, desired bright, smooth, reflective surface finish and many other properties which have been fulfilled by the replacement of the metal component.

The main applications of chrome plated electro plastics are shown below,

1. Automobile spares
2. House hold things
3. Electrical appliances.

The quality of the chrme plating is most important in the decorative chrome plating process. In this work it is mainly concentrated on the chromplating on ABS plastics. The chrome plating had been studied in this work and some recomendation have been given. The most case the quality had been affected by the quality of the molded part. The defect which have been caused in the molded part are in-mould residual stress, cracks, etc,. The material which have been used is POLYLAC PA 272 from the CHIMEI CORPORATION. The processing parameters of the ABS plastics on the injection moulding line affects the quality of the product after it have been chrome plated. In industries the workers have been setting some of the parameters to reduce those stress to attain the expected quality. Because of this the 40% of the moulded products have been rejected and this can be controlled by optimizing some of the parameters of the processing condition. In this work the parameters have been analyzed using solidworks 2014 and then optimizing the parameters which can produce less stress in the moulded part.

The main aim of the project is to investigate the process of the chrome plating on the ABS plastic and to improve the quality of the product after it has been plated. The factors of plating on plastics is drawn and the consederation to attain good quality is recommended. **The tasks** were raised to reach main aim to are,

- The important problem in the chrome plating have been identified.
- The problems are further investigated to draw the consideration thing to be followed.

- And to design and analysis the plastic part to find the amount of in-mold residual stress acting on it and optimize the parameters to reduce it.
- Solution are deduced from careful comparisons of different stages and other parameters.
- And the best consideration for the chrome plating on ABS plastic is recommended.

1. Chrome Plating Process and Material Used in Chrome Plating

1.1 Plating on Plastics

The plating of non-conductors has been achieved for many years. In the early 1960s' due to technological advances in chemical processing techniques, plating on plastics began on a commercial level. Industries that utilize plated plastics include the automotive, plumbing, appliance and electronics [1].

Metallization on plastics is normally undertaken for either decorative or functional purposes. Through metallization, the specific properties of plastics, such as light weight, design flexibility and low cost of manufacturing, are enhanced by the addition of properties usually associated with metals. These include reflectivity, abrasion resistance, electrical conductivity and a variety of decorative effects. The metallisation on non-conducting is carried out by means of vacuum metallization or vapor deposition, and plating [2].

Vacuum Metallization

It is the physical process rather than chemical process for depositing of metal coating on the surface of the prepared component. By using this process we can obtain up to $1-4 \times 10^{-6}$ in metal thickness on the surface [3]. It is a functional coating that exhibits a metallic luster but a low electric conductivity. This coating can be applied in notebook or tablet computers and cellular phones to provide a pleasant esthetic appearance with no interference to the radio-frequency signals sent and received by these devices [4].

Plating

Plating can be sub-divided into electroless plating and electroplating [2].

Electroless plating - Electroless process is an autocatalytic method in which the reduction of the metallic ions in the solution and the film deposition can be carried out through the oxidation of a chemical compound present in the solution itself, i.e., reducing agent, which supplies an internal current [5].

Electroplating – It is a chemical process of depositing a metal on the plastic. The principle used is to electrically conduct metal atoms such as copper, nickel and chrome off anodes which have been placed in the plating bath and then on to the plastic parts. The plastic part act as a cathode by means of preplating (i.e. electroless plating). When the current is applied the metal ions from the solution gets plated on the plastic parts [6].

1.1.1 Materials used for Plating

There are many metal materials which have been used for plating on plastic. According to their uses they have been used. For example chromium is used because it creates a non-corrosive layer on the surface and also it can be replaced some of metal components in automobile spares. Commonly Deposited Materials [6], [7].

- Chromium
- Gold
- Silver
- Copper
- Nickel
- Tin
- Solder (tin-lead alloy)
- Brass
- Cadmium
- Palladium
- Zinc

1.1.2 Applications

Almost all the plated plastics is for decorative finishes and only a small part is for engineering purposes [8]. The engineering plastics have vast applications in electronic products. Therefore, the metallized plastic materials have been applied in the aerospace, aviation, petrochemical, electronic and electric, automobile, plumbing parts and mechanical sectors as well as in the production of daily commodities [9, 10]. Almost 90% of plated plastic are have been used in the automobile industry and the remaining have been used in the electrical and plumbing works [8].

1.1.3 Decorative Plating

Decorative plating of a plastic have been impacting the physical and chemical properties of the part directly [11]. They have been used mainly because of some unique merits such as light weight, electric insulation, corrosion resistance, heat insulation and sound insulation [12] and it has been used for long time and their commercial importance is increasing, particularly concerning high quality

products [13]. The deposit's high reflectivity is retained in service because of chromium's excellent lubricity and resistance to tarnish, corrosion, wear and scratches [14].

1.2ABS Plastics

Acrylonitrile-butadiene-styrene (ABS) is one of the most important synthetic engineering resins, due to excellent properties on impact resistance, heat resistance, and chemical resistance along with characteristics of easy to fabricate, stable in finished size and good surface glossiness. ABS has achieved wide applications in machinery, vehicles and electric products now a day [15]. It consists of an amorphous phase of styrene–acrylonitrile copolymer (SAN) and a polybutadiene (PB) rubber phase. ABS is widely used in electrical and electronic equipments, in the automotive industry, telecommunication instruments, and other commodities [16, 17]. ABS (acrylonitrile-butadiene-styrene) is an engineering thermoplastic composed of an elastomer (butadiene) dispersed as a grafted particulate phase in a thermoplastic matrix of styrene and acrylonitrile copolymer referred as SAN [18]. ABS is the most usually plated plastic because of its excellent toughness, good dimensional stability, good process ability, chemical resistance and cheapness [19,20]. However, its application is limited because it is non-conducting and easily fretted. Metallized ABS can be widely used in many fields since its outstanding properties of engineering plastic and metal. For many years, activation process for metallization of nonconducting parts has attracted increasing attention [21-24].

ABS is a well-known terpolymer over the past decades. It has been used as a homopolymer or matrix of the composite materials. The tribological properties of ABS have been in studies over the years, whereas neat ABS has its limitations in tribology due to high friction coefficient and wear rate [25]. Metallized ABS with both outstanding properties of engineering plastic and metal can be used widely in electronic industry, petrolic industry and national defense field [25]. An attractive property of ABS is its processing temperature of around 200 °C which allows for compounding with wood particulates without thermally degrading the wood [26].

1.2.1 Properties of ABS Plastics

Brennan et al. studied the effects of the recycling and blending of ABS and high impact polystyrene on the mechanical properties. They found that changes in glass-transition temperature, tensile strength, and tensile modulus in reprocessed ABS were negligible, but strain to break and impact strength were considerably reduced [29]. Boldizar and Möller studied the properties of ABS subjected to a series of seven combined cycles of extrusion and ageing in air at an elevated temperature. They observed large changes in the tensile and flow properties. Moreover, they reported that from the

second to the sixth cycle, the elongation at break decreased markedly and attributed this result to the physical ageing of the SAN phase and to thermo-oxidative ageing of the polybutadiene phase [30].

High level of strength, rigidity, toughness and impact strength of ABS has led to its good mechanical properties. Its low shrinkage has made it to be used for producing parts with high accuracy and products of exceptional dimensional stability. Shrinkage is an unwanted phenomenon in injection moulding process which leads to changes in dimension and low part quality [31].

Table1.1 Properties of ABS material [32]

MATERIAL PROPERTIES	ABS
Tensile strength – yield (psi)	5300-6500
Flexural strength – yield (psi)	9400-11000
Modulus of elasticity (psi)	3.40e+0.5 to 3.77e+0.5
CTE (ppm/°C)	100-140
Deflection temperature at 0.46 MPA (°C)	90
Deflection temperature at 1.8 MPA (°C)	85
Max. continuous service temperature (°C)	85
Thermal conductivity (W/m-K)	0.14-0-30
Specific heat (J/g.°C)	1.2-1.4

Physical Properties

Impact Properties

The izod impact strength values (thickness of 3.175 mm) of commercial ABS products range from 75 J/m (1.2 ft-lb/in.) to 640 J/m (12 ft-lb/in.) [33]. The major factors for the impact strength of ABS include rubber matrix adhesions, rubber particle size and size distribution, rubber level, crosslink density of rubber particles, matrix molecular weight, matrix composition, glass transition temperature of the rubber, test temperature, strain rate and orientation. To achieve reasonable impact strength, the rubber matrix adhesion needs to be sufficiently high to transfer stress from the matrix to the rubber [34]. Good adhesion between rubber and matrix is achieved by the presence of an optimized graft structure and graft level. The ABS polymers with small rubber particles (about 0.1 µm in diameter) tend to have shear deformation rather than initiate crazes. The shear deformation is promoted by rubber particle cavitation, which becomes the major toughening mechanism [35]. On the other hand, ABS with large particles (about 0.5 µm size) favored crazing.

Tensile Properties

The tensile modulus, yield strength, tensile strength at break, elongation at break of commercial ABS products are in the ranges of 0.9-2.9 GPa, 18-51 MPa, 17-55 MPa, 1.5-100%, respectively (Modern plastic encyclopedia, 1993). A typical ABS yields at a strain equal to about 2.5-3.5%. Yield stress and modulus increases with higher strain rate and lower temperature and elongation at break decreases. The yield stress of ABS was found to increase linearly with the logarithm of the strain rate [36].

Thermal Properties

Heat distortion, softening, and glass transition temperature can be measured by using number of methods and the most common method used for heat distortion measurements of ABS is ASTM D-648 and ISO 75. The deformation temperature of sample to 0.25 mm can be said as heat distortion temperature under three point bending when heated at 2°C/min. It is satisfactory measure of ABS ability of withstanding deformation [38].

Flammability

Flammability is a critical measure in ABS applications where exposure to possible ignition sources is a concern. Adding halogen containing additives during compounding the improved flame resistance in ABS can be achieved. Non-halogen containing flame retardants can also be used that are less detrimental to the atmospheric ozone [42].

Electrical Properties

Electrical properties of ABS are fairly constant over a wide range of frequencies and are unaffected by changes in temperature and humidity level. Electrical property values for ABS polymers are: dielectric constant 2.4-5.0 over frequency range of 60-10⁴ Hz, dielectric strength 200-140 V/cm⁻¹ (360-508 V/mil), arc resistance 50-85 sec [37]. ABS is good insulators.

Chemical Resistance

The strong polarity of acrylonitrile results in the excellent chemical resistance properties of ABS and it can retain its mechanical properties at high acrylonitrile levels in extremely aggressive environments, including polar solvents. ABS can be used as a barrier for oxygen and carbon dioxide at very high acrylonitrile levels. The key component of ABS chemical resistance is the combination of resistance to solvent penetration and higher crack surface energy after solvent exposure [41].

Gloss and Molded Gloss Stability

The key factor to the ABS gloss is rubber particle size and it is found that the logarithm of gloss decreases linearly with particle size. Gloss is affected by many factors, especially during molding

and the parameters that increase the gloss are high mold surface temperature, fast injection speed, and high injection pressure [39]. Under long residence time and high melt temperature, the gloss of ABS is decreased by rubber particle agglomeration [40].

1.2.2 Why ABS material have been used

The morphology of the ABS polymer defines holes or micro pores in the plastic layer that are formed in the etch and become filled with metal in the process sequence (figure 1.1,1.2) [27]. ABS is most commonly used for chrome plating plastic applications due to the ease to plate and provide smooth and consistent plated plastic surface finish [28]. And due to its properties.

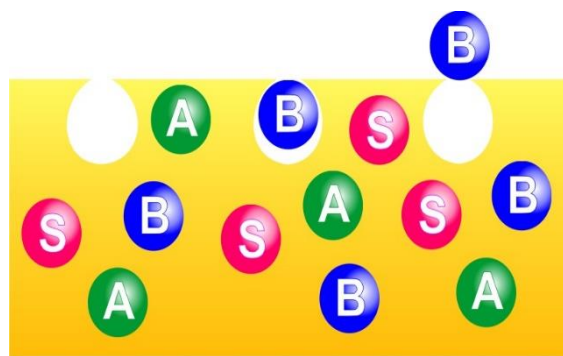


Figure 1.1 - During etching [43]

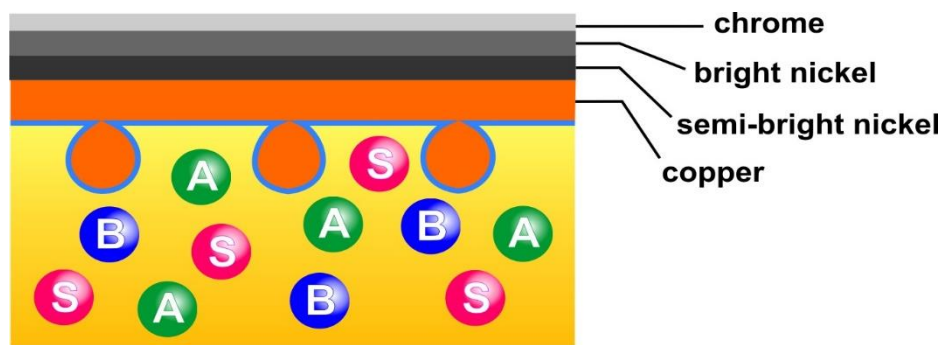


Figure 1.2 - After the coating [43]

1.3 Chrome plating

Chrome plating, is a plating of chrome over under plated layers of copper or nickel for decorative purposes or directly on the base metal for engineering purposes. Chrome plate may be either shiny or dull and often tends to highlight imperfections in the base metal. Decorative chrome is normally applied over copper and nickel (normally >0.0002 in. copper and >0.0003 in. nickel) as a very thin coating (typically 0.000050 in.). Hard chrome is applied for wear resistance, or to restore an old worn part to its original dimensions. It is generally applied directly onto the base metal [45].

1.3.1 Process

It is the process of electrically depositing the layer of on to hte surface of the workpiece . the workpiece to be plated is made as cathode in an electroyte bath containing a metal ion M^{n+} .



The M^{n+} may be a simple aquo ion such as hydrated Cu^{2+} or it may be metal complex such as $[Au(CN)_2]^{-}$. the preffered anode reaction is the disolution of the same metal to its precursor in solution (figure 1.3) [44].

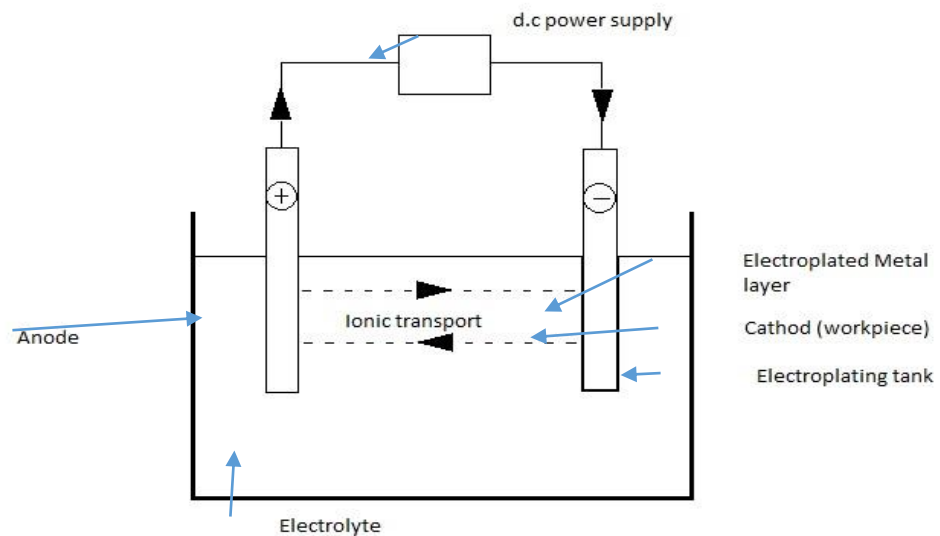
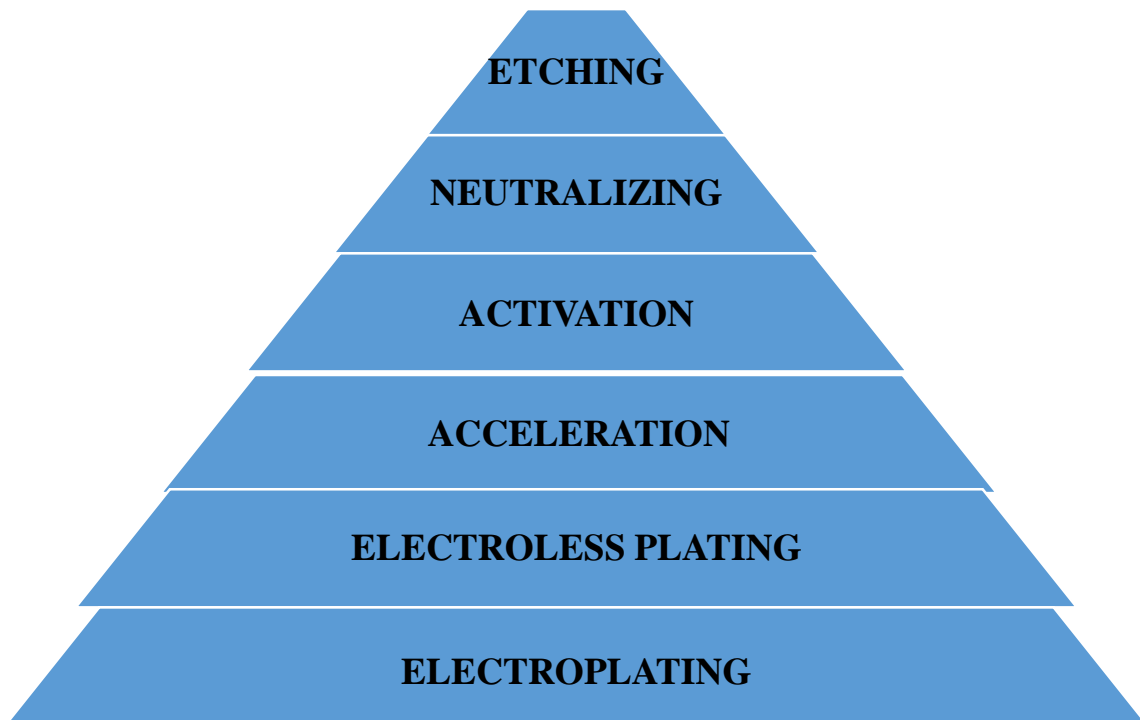


Figure 1.3 - Electroplating process [44]

1.3.2 Steps to be performed before Chrome Plating

Main steps to be carryout in conventional chrome plating process (figure 1.4)

Few steps have to be done before the part is been going under electroplating and the have been explained below[47-53]



1.4-Flow of conventional electroplating process [51]

Before the etching process the part must be cleaned from foreign material, dust and oil. At the each stages the part must be rinsed with hot or cold water.

Etching

It is the bath consist of highly concentrated acid solution of chrome and sufuric acid. The bath usually operate at the temperature between 50 °C and 70 °C. It should be carried out around 1-10 min. A water-soluble organic solvent and solvated hydroxyl ions to etch the surface of the part to improve adhesion of a metal coating with the part.

Neutralizing

After etching, the parts are thoroughly rinsed in water and then put into a neutralizer. These are materials such as sodium bisulfite or any of the proprietary products available that are designed to eliminate excess etchant from the parts and racks, usually by chemical reduction. . It should be carried out around 1-10 min

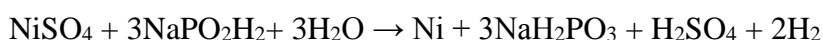
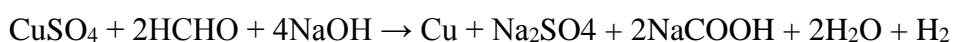
Activation

This step is used to activate the part using activation bath. In general, this activation is done by seeding the surface with a catalytically active metal, usually from palladium and tin salts. The parts are then plated with electroless nickel or copper. . It should be carried out around 3-5 min

Acceleration

After activation, the part undergoes with the activation step.

The accelerator bath is typically mixture of organic / mineral acid solution. It should be carried out around 3-5min. The function of this bath is to remove the excess tin ions from around the palladium nuclei which have been deposited in the part to promote quicker reaction initiation in the following electroless deposition step.



Electroless plating

The purpose of this step is to make the part electrically conductive to electroplating. In this process the part may be coated by Copper or Nickel by chemical dipping process. The Nickel or Copper is applied over the activated palladium layer. In which the chromium can be easily electroplated on the surface of the part. It should be carried out around 30-50 min. The Bright Acid Copper has two main functions in the plating on plastic line. These two functions are ductility/elasticity and leveling. The leveling aspect of the bath is much less important than the other.

Electroplating

Electro plating is the final stage in the chrome plating process. In this stage the chromium is coated on the part which have been plated in the electroless plating. . It should be carried out around 3-5 min. the hexavalent chromium is the source chromium and with one or more catalyst is used in this case. Most common catalyst is sulfate. And the mixed catalyst is used in some special properties.

1.3.3 Recent trends in chrome plating

In this new trends in this they have been changed the process to direct electroplating the part. Due to toxic element present in the acids which may affect the human beings who have been working with those process. So they have introduced the chromium-free etchant solution which can be worked in the room temperature. And they have been used palladium free activators have been also introduced. The word direct plating means that the part has been directly electroplated that the electroless plating have been removed from the process, had said by Ijeri, V., Shah, K., & Bane, S [59]. Due to toxic element present in hexavalent chromium present the chromic acid they have been introduced trivalent chromium to eliminate some of the problems associated with hexavalent chromium chemistry: high toxicity, low current efficiency, poor metal distribution, lack of coverage around holes, burns in high-current-density areas, and "whitewash" [53].

1.3.4 Electroplating techniques

According to the size and geometry of the components to be plated and the plating process have been used. And the plating process are [54-56],

Mass plating

This type of process have been used in coating of a small work pieces in large quantities. Such has bolt, screw, nut etc,. In this case it is not suitable for preventing scratches and enlargements. And the most widely used mass plating system is barrel plating.

Rack plating

Some of the work piece cannot be coated my the mass plating because of its size, shape and their special features in those cases this type have been used. In this case the work piece have been mounted on the racks for electroplating. This process is some time known as batch plating.

Continuous plating

The plating of metal strips, wire and tube is carried out in so called continuous plating. In this type the items to be plated movies continuously past either one row or between two rows of anodes at a substantial. Amajor advantage in this process lines arises in the case of plated metal strip, resulting in savings in the use of raw material and energy.

In-line plating

A recent development shows that integration of the plating and finishing process into the main production line. It brings the benefits of reduce the use of ecofriendly materials.by this poccus the consumption of chemicals are also have been reduced.

1.3.5 Monitors and controls

The quality is depend on the maintaining the concentration of the main constituents with in the specified limits (such as controlling pH, temperature and current density and maintains the purity of the electrolyte. And the other important things to eliminate the coating defects is properly preparing the parts. A skilled and knowledgeable operator can maintain a reasonable plating quality with little supporting equipment. However, trends to more automation to reduce costs with higher processing speeds, application of plating to higher value products, and assurance of quality plating make it necessary to utilize many monitoring and control facilities [57].

Process monitoring

Electroplating process conditions to be monitored and controlled in a typical line may include [68]:

1. Solution level,
2. Solution temperature,

3. Solution flow and agitation,
4. Solution chemistry
 - Metal concentration(s)
 - pH
 - Specific gravity
 - Additive concentration(s)
 - Impurity levels
5. Current at each electrochemical step,
6. Charge passed,
7. Cell voltages,
8. Line speed,
9. Blow-off air pressure,
10. Exhaust vacuum

Monitoring and control of finished products

There are at least as many ways to measure the results of a plating process as there are products produced using plating processes. Ultimately, the monitoring of a product produced using a plating process or of the film plated should be done based on an understanding of the properties of the deposit that are important to that product. And some of the things to be monitored and they are [57],

Thickness,
Colour,
Brightness,
Roughness,
Grain size,
Hardness,
Surface and Compositional Analysis.

Bath constituent concentration monitoring and replenishment

It is the most important thing to be monitored in this process to attain a very good quality products. The composition of electroplating solutions has changed very little in recent years with the exception of high-speed plating where higher metal content and special additives are used and new solutions designed to be more compatible with health and environmental requirements. Plating solution chemistry is usually monitored off-line by taking a solution sample and performing an analysis at the machine or in a chemical analysis laboratory. Metal ion concentration, supporting electrolytes,

additives, and pH are most often monitored. Metal ion concentrations are measured by colorimetry, polarography, or ion-selective electrodes. Automated versions of these methods have been developed for on-line analysis of many metals including nickel, copper, lead–tin, tin–silver, and gold [59], [60].

Safety and control measures

Storage and handling

Hazardous chemicals must be stored appropriately. This involves using the correct container, isolation of incompatible chemicals, the use of flammable or specialised chemical cupboards, and the correct labelling of containers.

Health monitoring

Schedule 14 is a list of hazardous chemicals requiring health monitoring and their associated types of health monitoring. These chemicals include chromium, cadmium and arsenic which are commonly encountered during electroplating.

Health monitoring must also be provided for workers using hazardous chemicals not listed in Schedule 14 where there is a significant risk to the workers' health from exposure to the hazardous chemical and there are valid techniques to detect adverse health effects or a valid biological monitoring procedure is available.

Common hazardous chemicals used in electroplating and their related health effects and recommended tests for health monitoring.

Table 1.2 Common hazardous chemicals used in electroplating and their related health effects and recommended tests for health monitoring [59], [60].

Hazardous Substance	Health Risk	Health Monitoring
Chromium* compounds	Ulceration of nose/skin Skin sensitisation Occupational asthma Occupational cancer	Skin inspection Respiratory testing Blood tests
Nickel	Dermatitis Occupational cancer Occupational asthma	Skin inspection Respiratory testing Blood tests

Acids/Alkalis Degreasers/Cleaners	Dermatitis Burns and Ulceration Eye/nose/throat irritation	Skin inspection General health check
Trichloroethylene	Dermatitis Eye/skin irritation Occupational cancer	Skin inspection General health check
Cyanide solutions/sludge	Poisoning Dermatitis Headaches/Nausea/Dizziness	Skin inspection General health check
Cadmium* containing powders/solutions	Poisoning Respiratory effects Anaemia/Liver dysfunction	Respiratory testing Blood tests
Cadmium* oxide	Occupational cancer	Blood tests Respiratory testing
Platinum salts	Occupational asthma	Respiratory testing
Oxides of nitrogen	Respiratory effects	Respiratory testing
Copper compounds	Dermatitis Eye/skin irritation Gastrointestinal effects	Skin inspection General health check Blood tests
Arsenic*	Haemolytic action on blood	Peripheral nervous system testing Skin inspection Urinary inorganic arsenic

* Schedule 14 hazardous chemicals .

Further information on the selection and use of personal protective equipment is available in the following Australian Standards:

- AS/NZS 1715 Selection, use and maintenance of respiratory protective devices.
- AS/NZS 1716 Respiratory protective devices.
- AS/NZS 1337 Personal eye protection (Series).
- AS/NZS 2161 Occupational protective gloves (Series).

- AS/NZS 2210 Occupational protective footwear (Series).

Advantages

Some advantages of electroplating [61],[62],

- It has good thickness control.
- It achieves mirror like finishes.

Applications:

- Military weaponry
- Medical diagnostic instruments
- Tools and dies
- Aircraft components
- Machine components
- Electronics & computer devices
- Enclosures, chassis and heat sinks
- Mechanical assemblies.

1.4 Injection Moulding

Injection moulding is an ideal process which have been used in manufacturing plastic part with most precise dimensions, in this process hot polymer is melt forced into the cold empty cavity of desired shape and is then allowed to solidify inside the mold under a high holding pressure [63]. The injection molding machine have been shown in figure 1.5.

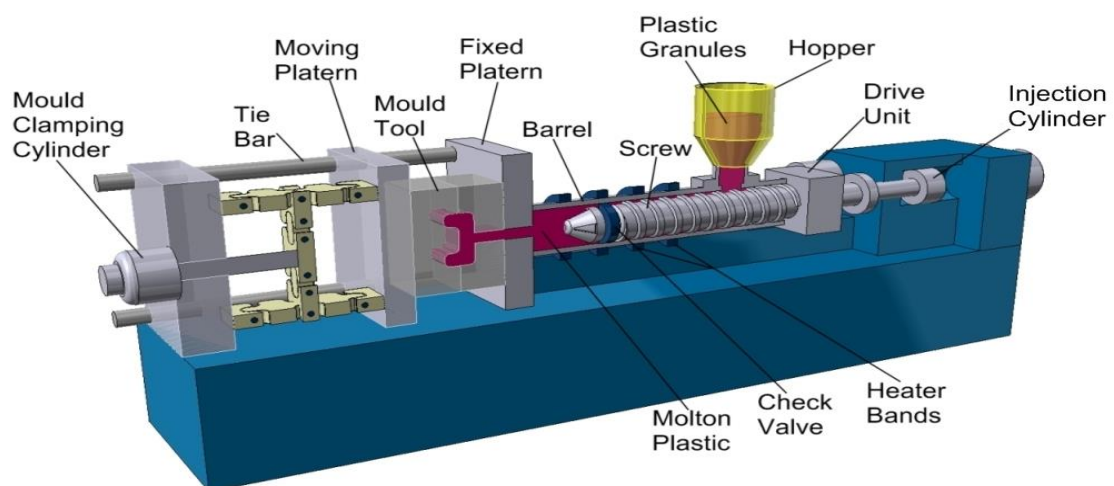


Figure 1.5-Injection molding machine [64]

The entire cycle is working under the three cycles and the stages are filling, packing and mold-opening (figure 1.6). Filling stage - In this stage the material have been melted at the specific temperature of the material and it have been field inside the cavity at a high pressure from the injection unit. Packing stage – it is the second cycle, in this cycle the molten material in the cavity is allowed to solidify at a high pressure to compensate for the anticipated shrinkage in the polymer. Mold- opening – it is the final stage of the process and in this stage the material have been fully cooled and the part is now ready to unpack from the cavity [65].

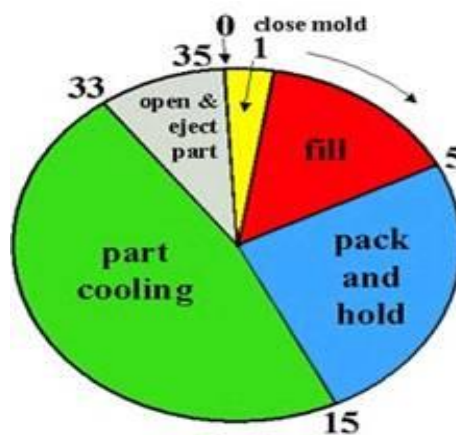


Figure 1.6 - Process cycle [66]

1.4.1 Molding Conditions

Molding condition plays a most important role in the plastic injection molding process. the good quality of the molded part including the strength, warpage and residual stress are have been depend on the conditions on which the part have been processed. And the molding condition's compromise's the most important parameters like melt temperature, mold temperature, fill time, pack time and packing pressure. The quality of the given molded part not only depends on the material property but also on the process parameters. By optimizing the parameters of the process we ca reduce the process time and also improve the quality of the product. The optimization can be done by trail-and-error method. But it can been seen that the trail-and-error method is costly and time consuming. There are common methods to optimize the parameters theoretical and they are non-gradient-based, gradient-based, and hybrid optimization techniques. The optimization can also been done on the basics of software (numerical simulation) [67].

2 PROJECT DESCRIPTION

2.1 Problem Identification

Effects of chromic acids

Effects in humans

Chromium (Cr) is ubiquitous in nature. Chromium exists mostly in two valence states in nature: hexavalent chromium [chromium (VI)] and trivalent chromium [chromium (III)]. The hexavalent form is 500 times more toxic than the trivalent. Due to the high toxic effects of Cr on human health. Chromium (VI) is commonly used in industrial chrome plating, and is a proven toxin, mutagen and carcinogen. Chromium speciation has attracted a great deal of attention because of the differential toxicity of its stable species. Cr(III) cannot usually cross cell membranes and its toxicity is considered to be relatively low and , whereas Cr(VI) is transported through anion channels as chromate (CrO_4^{2-}), and its reduction by different intracellular components (such as glutathione, acrobate, tocopherols and different enzyme cofactors) generates stable Cr(III) or unstable Cr(IV) and Cr(V) intermediates, which induces oxidative stress, DNA damage, apoptotic cell death and altered gene expression[68],[69],[70].[71].

Chromium (VI) has been recognized as a highly toxic elemental species on the basis of experimental and epidemiological evidence, and has been classified as a class I human carcinogen by the International Agency for Research on Cancer (IARC). Few studies have used the comet assay to determine chromium (VI)-induced damage to DNA. Cr (VI) exposure mainly occurs as a result of inhalation. A significant increase in the comet tail moment, which is indicative of genotoxicity, was found in isolated human peripheral blood lymphocytes and in gastric mucosa cells after in vitro exposure to chromium [72].

Epidemiological studies have indicated that chromium (Cr) is an important cause of human nasal and lung cancer, and studies have also revealed that chromium is mutagenic in bacteria and yeast [73].

The genotoxic effects of Cr have been reported. Elevated levels of sister-chromatid exchanges (SCEs) were observed in workers exposed to Cr compound in electroplating factories. Chromosomal aberrations (CAs) were found in studies of exposed workers. Chromium is also reported to cause skin dermatitis, nasal membrane, inflammation, ulceration and liver damage. When adsorbed into the body, it severely irritates gastrointestinal tract, leading to circulatory shock and renal damage. Cr (VI) compounds causes DNA strand breaks and cross-links in vivo and in cultured cells. The clastogenic and mutagenic effects of the ip-treated Cr (VI) compound in mice were reported, which showed a significant increase in the peripheral blood micro nucleated reticulocyte count [74].

Effects in drinking water

Water pollution by heavy metals is an important economic and environmental issue in numerous parts of the world. Among these heavy metals, chromium (Cr) is a common contaminant in surface water and groundwater resulting from electroplating. . Such a surface treatment is performed in baths composed of chromic acid (180–350 g/l), sulphuric acid (1.8–3.5 g/l) and water. It can contain chromium at concentrations ranging from tenths to hundreds of mg/l. The US EPA requires 0.05 and 0.1 mg/L of Cr (VI) in drinking water and inland surface waters, respectively. By contrast, Cr (III) toxicity is negligible because it often forms insoluble hydroxides at circum-neutral pH [75],[76].

Trivalent chromium, Cr (III), is considered to be a trace element that is essential for the functioning of living organisms; but at high concentration, it can be dangerous to health as it can coordinate with organic compounds which in turn leads to inhibition of some metallo-enzyme systems. Hexavalent chromium (strong oxidizing agent) which is primarily present in the form of chromate (CrO_4^{2-}) in alkaline and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) in acidic environment poses significantly higher levels of toxicity than the other valence states [77].

Quality of the molded material

The quality of the part have been plays an important role in the quality of the chrome plated plastics. The defects which have been appeared in the moled part will direstly reflect on the chrome plated part. The main defect which have bben mostly affect the quality of the chrome palted ABS plastic is in-mold stress. During the part have been molded som stress will form due to temperature and cooling of the mold. It is ABSorbed that due to stress occured the chrome plating will not been properly done on the material. Very high stress will even tends to crack an failure of the part[78].

2.2Complications on the Chrome Plating on ABS Plastics

The complications in chrome plating on ABS plastic can be taken into account by considering some conditions. The conditions taken into consideration are Quality of molded part, material preparation, Operating environment, Cost, and Scrap wastes. The chrome plating on ABS have been used in almost all the industrial based applications. The chrome plating had been used in two main important features like decorative and functional applications. The chrome plating on ABS is simply explained as the plating of chrome over a under plated layer of nickel and copper on the surface of the base metal. The effect of chrome plating had been based on the microstructure or deposition of material layer on to the surface of the substrate by means of chemical process.

Operating environment it is also be considered in the chrome plating conditions. The chrome which had been using in the chrome plating process consist of hazard's element like trivalent chromium and hexavalent chromium which may cause effects to the workers who have been working in the line. And while disposing the waste of the chrome wastes after the process which may cause effects to the environments.

The quality of the molded part is the most important consideration of the decorative chrome plated product because it creates cracks, burnt mark, void spaces which results in the failure of products.

Material preparation consist of different stages of process and Reduction of scraps is to be consider in the chrome plating process, the waste had been large in the industry because due to the some of the defects caused from the operating line and the quality of the molded part. the scrap is almost calculate as 40% of the finished part as been marked as a scrap because of its perfection.

2.2.1 Operating Environment

The operating environments conditions is where the production are had been going on (i.e.) where the plastic part is going under different chemical process steps at various chemical solution and hot water at various temperature. Chemical which are used in this process are chromic and sulfuric acid, palladium and tin solution, copper sulfate, nickel sulfate. And in this operating conditions.

Effects of chromic acid is widely known phenomenon. The hazards element in the chromic acid is affects the workers who have been working in the plating line the continuous work in the chromic acid environment will tends to death in the worker.

In the different stages of the material different acids have been used. And the most important acid which should take consider is etching stage which have been more hazard's chemical is used that is chromic acid, which cases affects in environments and as well as the workers who works in it. And palladium solution which used in conventional process had become very costly know days. Which makes rise in the cost of chrome plating product.

Alternatives for the etching solution

The normal process which is going under the etching process. The ABS plastic which have to be plated will have acrylonitrile-styrene matrix with butadiene rubber uniformly distributed on the surface the material. During the etching process the chromic acid react with the material and the butadiene is etched out from the material (figure2.1) leaving the microscopic holes which have been used as bonding area for activating and electroless deposit of material. The etching solutions normally

used are made from mixtures of chromic acid and sulfuric acid. Typically they contain 375-425 g/L CrO_3 and 180-220 mL/L H_2SO_4 and are operated at 50-65°C [49].

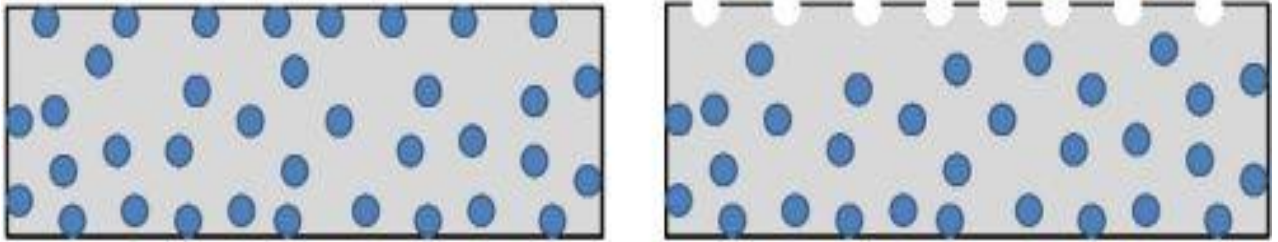


Figure 2.1-Left- Butadiene rubber in the ABS plastic Right- etched ABS plastic surface [49]

In the present case the etching on the ABS material have been performed by dipping of part into a mixed solution of 1:4 hydrogen peroxide and sulfuric acid at a room temperature. It have been tested fo rdifferent timings. And the micro structure of the result have been explain as shown in figure2.2.a-2.2.e. That the etching time effects the surface morphology of the part. The coarseness on the surface of the material have been getting increased when the etching time had been increasing [9].

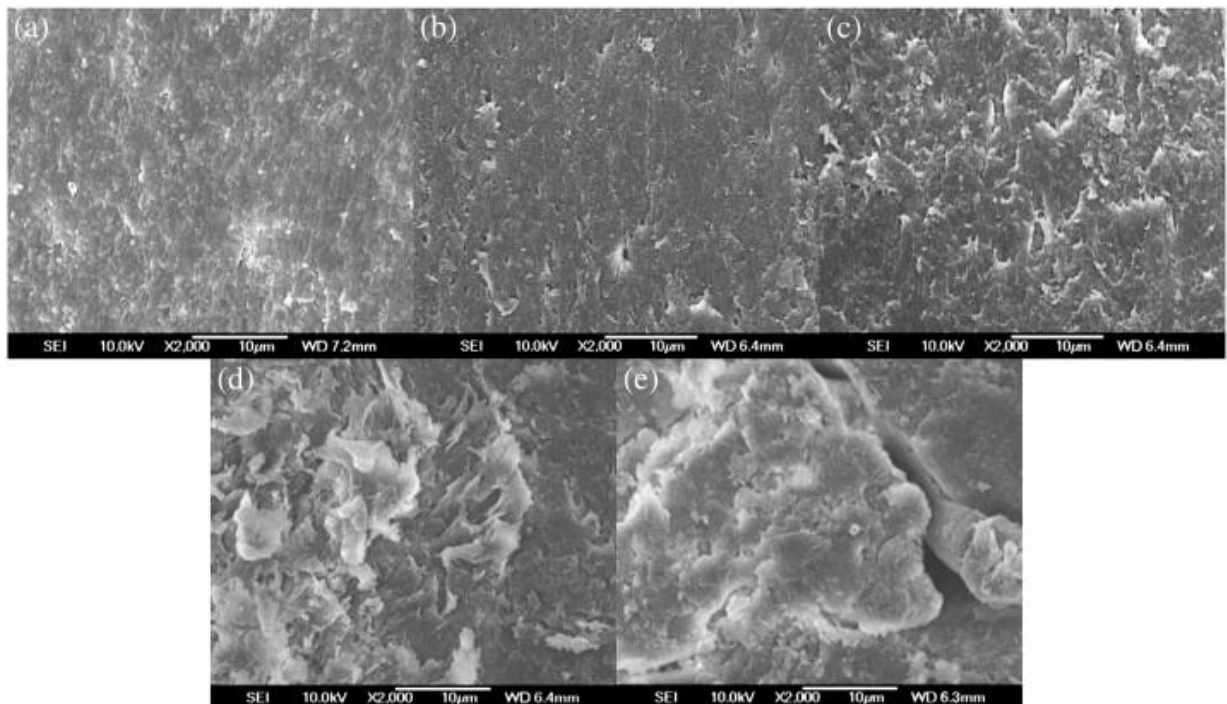


Figure 2.2-ABS material with different etching times a)0 min (unetched), b)5 min, c)7 min d) 9 min, e) 11min [9].

The effects of etching time on the ABS morphology were studied, and the best time have been selected for most optimal procedure, the 5 min have been selected, whereas the the increase in etching time may destroy the ABS polymer matrix.

Alternative for activation solution

Activation is the step which have been activates the surface of the material, in this step the catalyst metal site on the surface to initiate the oxidation of the reducing agent in the electroless plating step. It is the most pivotal step in the chrome plating process because it have been directly effects on the quality of the chrome plating. The conventional method of activation method of sensitizing, the method of dipping the part into the stannous chloride-palladium chloride bath to employ catalyst on the surface of the part. But it involves some problem which have some highly toxic Sn. If the activation is not done properly on the surface of the part it will result in the improper coating on the material. In the SEM photograph shown in the figure 2.3 The grains of Pd clusters having average size of 0.5–1.0 μm were fine and uniform, which were well-suited for catalysis to initiate the electroless plating [79].

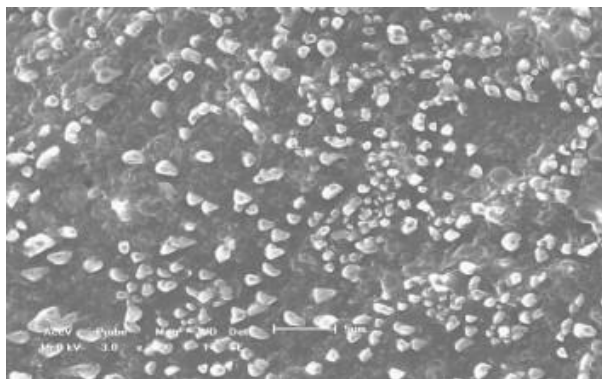


Figure 2.3- SEM photograph of ABS with noble activation of palladium [79].

After the previous method of etching the ABS part then the part should be dipped into the solution which consist of 1% of acetic acid and 15g/L CTS for 5 min at the room temperature and then it have been dried at 60 °C for 15 min ant the material have been changed from ABS to ABS-CTS (Figure3.4.a) . The ABS-CTS substrate were dipped into another solution called nickel sulfate solution at 40 °C foe 10 min. after rinsing the substrate were dipped into the another solution of potassium borohydride at 40 °C for 5 min of reduction. And then the substrate is then converted into ABS-CTS-Ni [9] and it have been tested on different timings (Figure 2.4.b - 2.4.e).

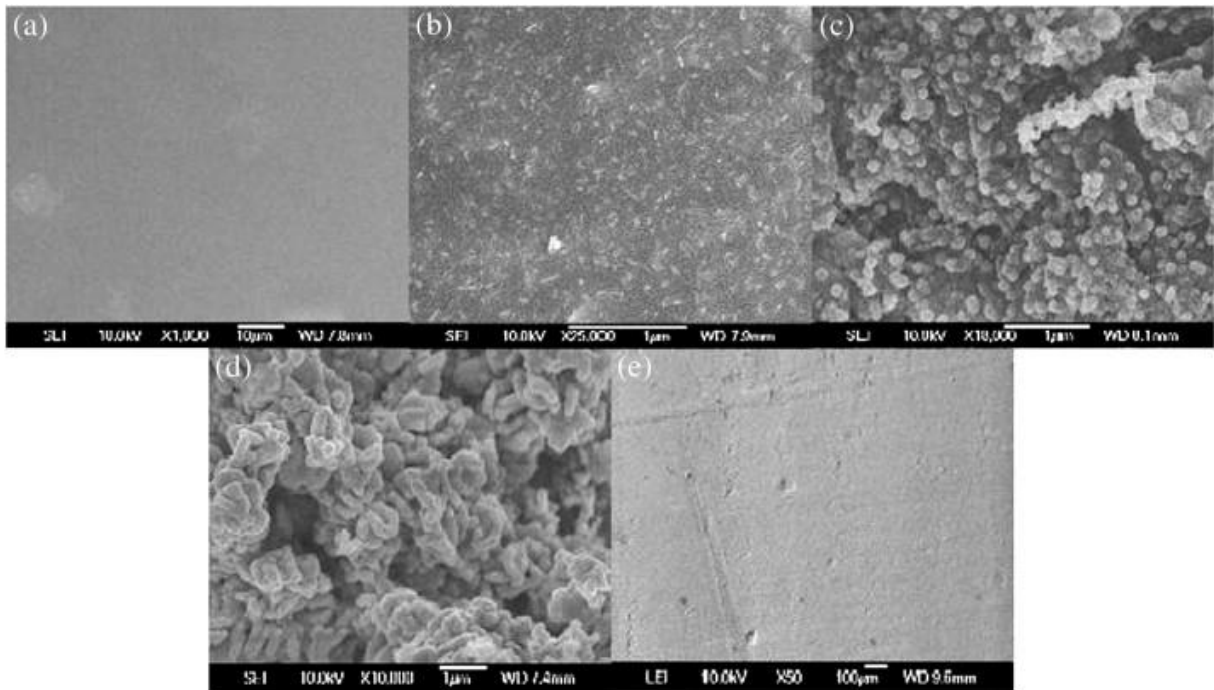


Figure 2.4-SEM photographs of surfaces of (a) ABS-CTS and (b) ABS-CTS-Ni and (c) Ni deposition at 2 min and (d) Ni deposition at 5 min and (e) Ni deposition at 30 min [9].

2.2.2 Part preparation

The material preparation may consist of many steps which will attain the chrome on the plastics

The conventional material preparation of the ABS plastics have been followed by the different steps which have been shown on the figure.

- The molded part should be cleaned with the alkaline solution to remove uncontaminated foreign materials and to remove grease and oil from the surface of the body.
- And followed by the cleaning It have been undergoes etching process. Which will create a microscopic hole which removes the butadiene rubber from the matrix of the ABS material.
- And followed by the etching the pat have been undergoes activation process which have been activating the bonding between the electroless plating and the material.
- And the acceleration process have been under gone to improve the activation of the palladium ions in the process.
- And the continued to the acceleration it have been under goes electroless plating to the material, which have been divide into two stage coating of copper and nickel to the surface of the part.
 - Before electroless plating the part have been rinsed with the chemical nickel bath to stat the electroless process.
 - And the first stage in the electroless plating is coating of thin layer of copper to the surface of the part to activate the part from non-conducting to conducting material.

- Second stage is coating of the nickel to increase the bright ness of the coating layer using nickel bath.
- And before the electroplating have been done to the part the material have been treated with solution which consist of copper to increase the addiction the chrome to the surface.
- And the final step is electroplating, in this stage the part which have been pretreated according to the above steps have been plated have been plated with the chromium.

This are the steps which have been followed in the conventional process and there are some draw back which had been identified in this steps and those are shown in figure 2.5 ,

1. The cost of the process is very high
2. The time taken to complete the process have been also high

And in case to reduce this new techniques have been consider and they have been developed and the steps in the convention process have been reduced.

The steps which have been developed have been show in the figure below

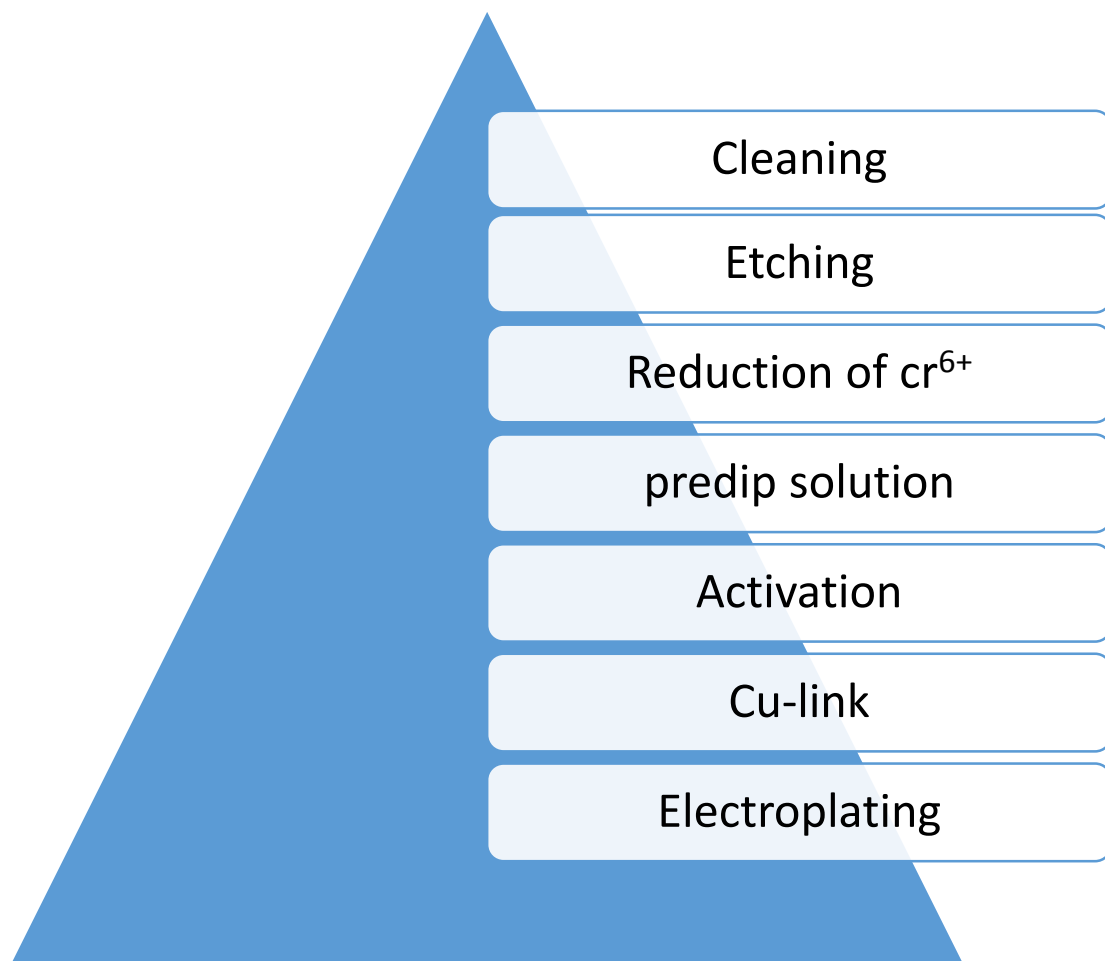


Figure 2.5 - Direct plating process

The greater challenge in the today's plating process is to reduce the steps in the electroplating process to introduce the new process techniques that should satisfy the conventional process of coating innovative material to the plastics. Therefore the innovative steps to be taken into account. The challenges had to be made in the plating process apart from the steps in the conventional process the implementing the new process method to plate on plastics [50].

The futuron technique or direct metallization of plastic have been developed by the Autotech. The first time they have been allowed to plate the plastic by direct metallization techniques. The main benefit of the futuron technique over the conventional technique is to reduce the unwanted steps. In the futuron technique the electroless plating process have been unnecessary. They have been introduced some change in the plating process, which have been reduced the steps in the electroplating of plastics in this case the next steps have been introduced instead of electroless they have been introduced the new step after the activation process, the new step is after the completion of activation step they have been introduces the copper link to the surface of the material which in case converts the material from non-conducting material to the conducting material. In this step the copper have been coated as thick coat on the surface which acts as the base for the electroplating process [50].

2.3 Quality of the Molded Part

The quality of the molded part will also plays a most important role in the quality of the chrome plated part. The defects like cracks, weld line and stress in the part will show directly in the finished part. The molded part which have to be under go some tests to reject the part before it goes to the electroplating line. The some of the test have been listed below.

2.3.1 Defects

Visual test

In this test the visual defects like short shot, thick weld lines and any cracks have been easily identified by the visually by looking at the part.

Blister

It is defect which have been appeared in the chrome plated part. The blister have been appeared as a scratch mark on the part which have been shown in figure 2.6. And the optical micro graph have been shown in the figure2.7. It have been formed due to the contaminants left over from the plastic molding processes were apparently not efficiently removed before the plating process [84].

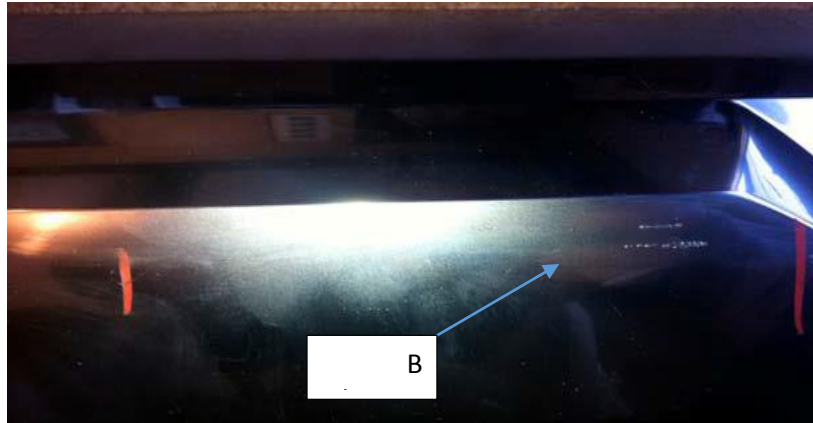


Figure 2.6-Blister in chrome plated part [84].

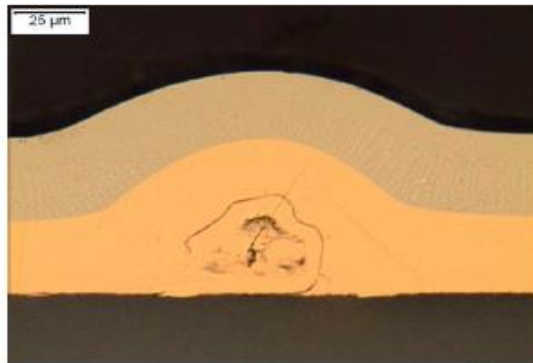


Figure 2.7-Optical micrograph of chrome plated part shown blister [84].

Acid testing of the specimen

After the part have been molded the stress and strain has been induced in the part, but to a certain extent the stress and strain is allowed. If the stress is more than the allowable the part may not be properly plated. In case of very high stress the part may tend to crack during the plating process. The stress that have been induced during the molding can be identified using the Acetic acid testing process which have been explained below. After the part have been molded the part must be immersed into the Acetic Acid solution for about 1-2 min and after that the part have been rinsed with the cold water and kept it aside for the part to dry then the White marks and lines will start to appear as internal stresses on the surface of the part (Figure 2.8) .



Figure 2.8 – Specimen before and after acid testing

The most important thing which have to see in the molded part is residual stress which have been induced in the part during the molding part will be affected. The part while it has been under goes a process in the chrome plating line due to the.

After the injection molding process the part which comes out of the molding machine has internal stress. Due to the internal stress present in the part, the material has defects. This defects is not visible until the chrome plating has been done on the part. When the part is subjected to chrome plating after cooling to room temperature releases internal stress because of the higher temperature of the coating solution. The internal stress causes the plated part to create void spaces and cracking [figure 2.9]. Cracking is particularly likely with chromium coatings because chromium has relatively low ductility at room temperature compared with many other metals [80].



Figure 2.9-Causes for the residual stress in the molded part

During the injection molding process, the polymer undergoes mechanical and thermal influences in the fluid, rubbery and glassy state. Due to this state which will induce residual stress and strain into to the final product, resulting in part defects like warpage, molecular orientation, or birefringence. The residual stress can be divided into flow induced stress and thermal induced stress. It's know that the flow induce stress is magnitude smaller than the thermal induced stress [81].

Flow induced stress -The flow induced stress is occurred due to the visco-elastic flow of the melt during the filling and the post filling stages of the process. The polymer near the cavity surfaces starts to freeze immediately after it comes in contact with the cavity surface. This stress corresponds with the orientation of the macromolecules [82]. Thermal residual stress – This stress caused due to the shrinkage during the cooling both inside the mold and demolding. Thermally induced stresses develop principally during the cooling stage of an injection molded part, mainly as a consequence of its low thermal conductivity and the difference in temperature between the molten resin and the mold. An uneven temperature field exists, with a hot and fluid core at the center and frozen layers next to the mold walls. This temperature field causes the material to cool from above to below the glass transition temperature at different times. And due to this stress it results in the warpage and may induce environmental stress cracking [83]. Due to this stress affects which may directly affects the chrome plating which may result in the improper coating of the chrome to the part or cracks may occur after the chrome plating process have been done.

How to reduce internal stress.

The internal stress can be reduced by two ways first way is to optimize some of the parameters of the process parameters. The parameters like melt temperature, mold temperature, cooling time, packing time, holding pressure [82]. The second method is to pretreating the part, (i.e.) before the part have been chrome plated the part must be pre heated around 120 to 150 F for 30 min which will reduce some amount of stress that have been induced in the part [80].

2.4 Properties of the Suggested Material

Table2.1 Properties of the requested material

Material properties	Values
Specific gravity	1.05
Density	1.04 g/cm ³
Melt Mass-Flow Rate (MFR) (230°C/3.8 kg)	6.6 g/10 min
Melt Mass-Flow Rate (MFR) (220°C/10.0 kg)	22 g/10 min
Moulding Shrinkage - Flow (0.126 in)	4.0E-3 to 6.0E-3 in/in
Drying Temperature	180 to 200v°F
Drying Time	2.0 to 4.0 hr
Drying Time, Maximum	8.0 hr
Suggested Max Moisture	0.020
Suggested Shot Size	50 to 70
Rear Temperature	420 to 445°F
Middle Temperature	450 to 470°F
Front Temperature	480 to 515°F
Nozzle Temperature	490 to 535°F
Processing (Melt) Temp	490 to 535°F
Mould Temperature	100 to 180°F
Back Pressure	50.0 to 100 psi
Screw Speed	30 to 60 rpm

2.5 Numerical simulation of injection molding process

2.5.1 Modelling

The part which have to be molded is have been first designed in the solidworks 2015 as shown in the Figure 2.10 and the material used is POLYLAC PA727 and the properties of the material have been explained in the table

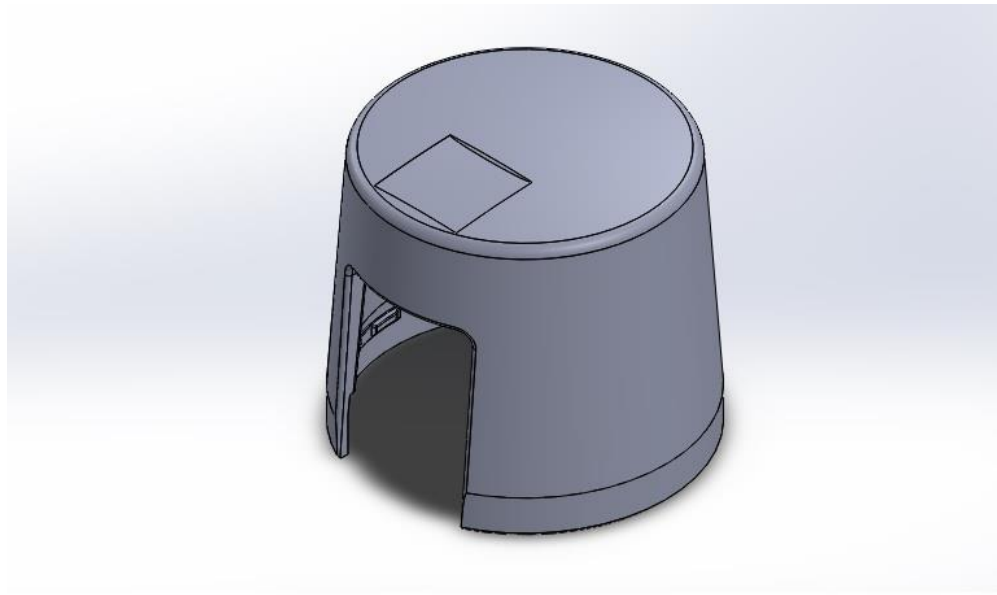


Figure 2.10 - Plastic part

The simulation have been done in the as sequence explained, at first the design which have been shown in the above figure have been done by using the software solidworks plastic 2014. And then the results from the molded part have been exported to the simulation in solidworks and the nonlinear analysis have been done and the results have been discussed below in the results.

The most important parameters such as melt temperature, mold temperature, cooling time and packing pressure and packing time are some of the most significant parameters affecting the residual stress based on previous researchers. And the fixed parameters which have been used most industrial for post filling simulation have been shown in the table and the processing post filling parameters have been also shown in the table. After the simulation the results have indicate that the residual stress acts.

2.5.2 Flow simulation

Table 2.2 Fixed parameters

Parameters	Value
Melt temperature	240°C
Mould temperature	60°C
Fill time	1s
Pressure hold time	15s
Cool time	25s
Packing pressure	80%
Ejecting temperature	90°C

In flow simulation using the above parameters the flow of the plastic had been done and the flow process had been done in the solidworks plastic software and shown in figure 2.11.

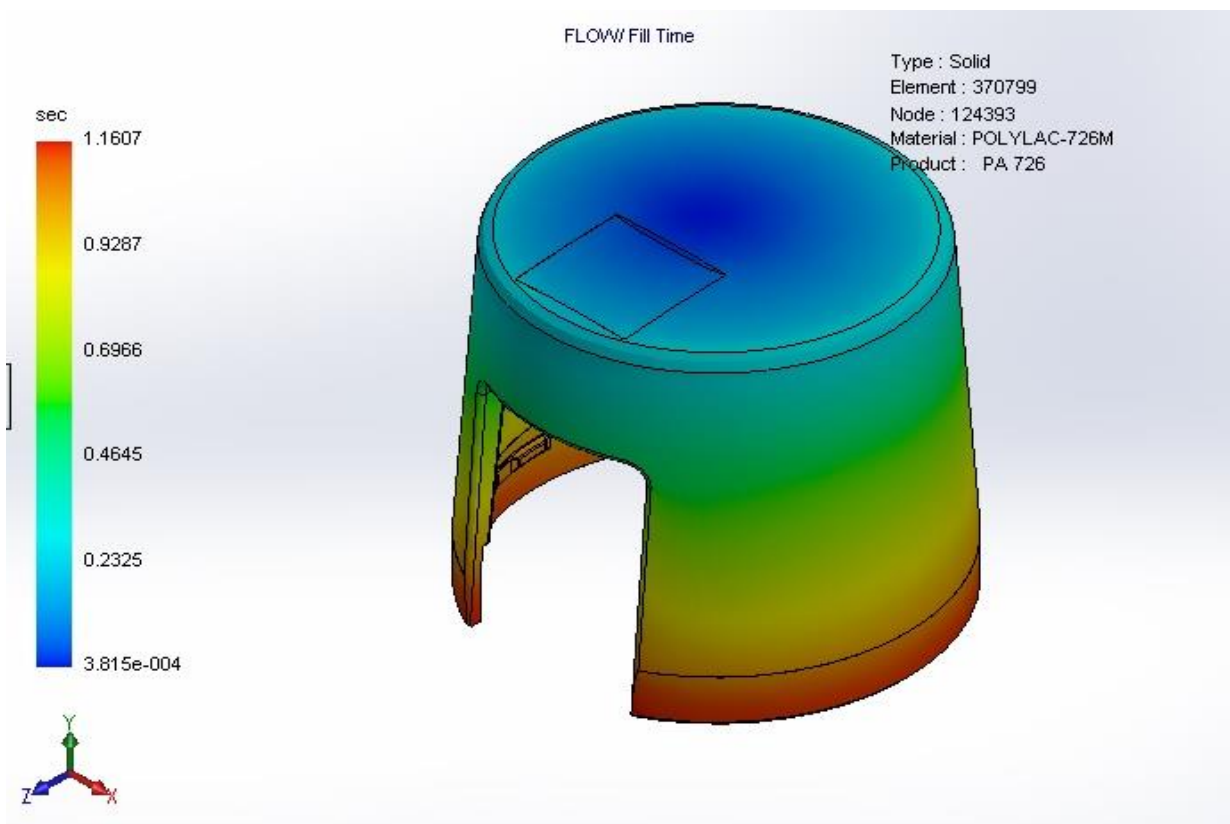


Figure 2.11-Flow simulation

2.5.3 Non-linear analysis

The non-linear analysis had been made on the solidworks by importing the values of the in-mold residual stress from the solidworks plastics to the solidworks simulation and the simulation had done according to the different cases and the stress strain values have been shown below

Case I:

In first case the parameters which have been selected according the the table 2.2 which have been used according to the industrial reference. The max stress and strain attain in this case are $4.811e+007 \text{ N/m}^2$ and $1.321e-002 \text{ m}$ shown in the figure 2.12, 2.13.

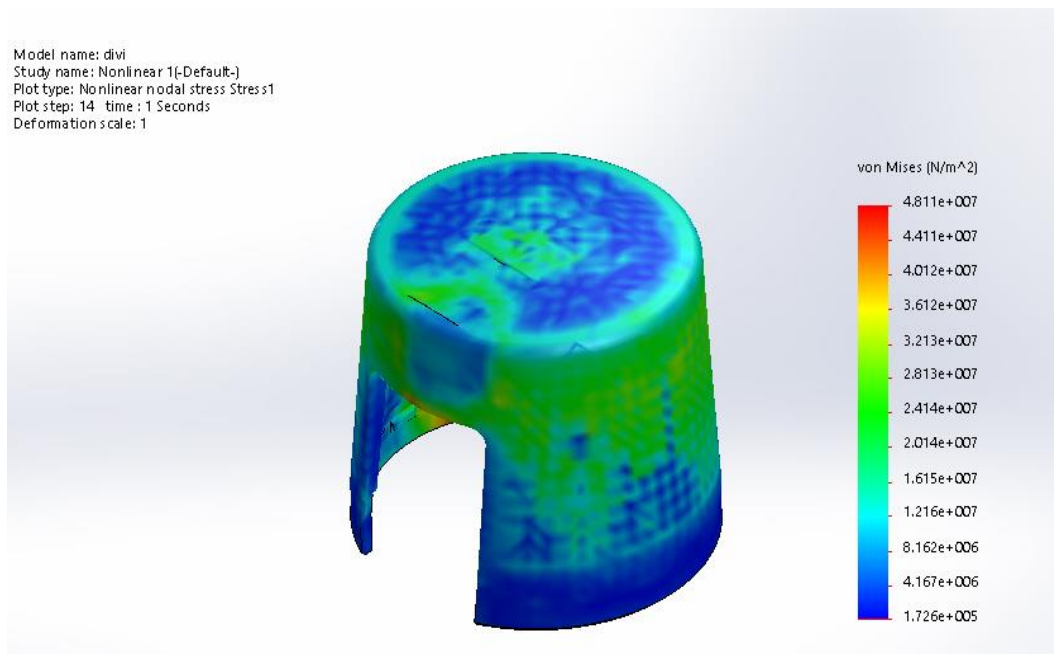


Figure 2.12-Non-linear stress

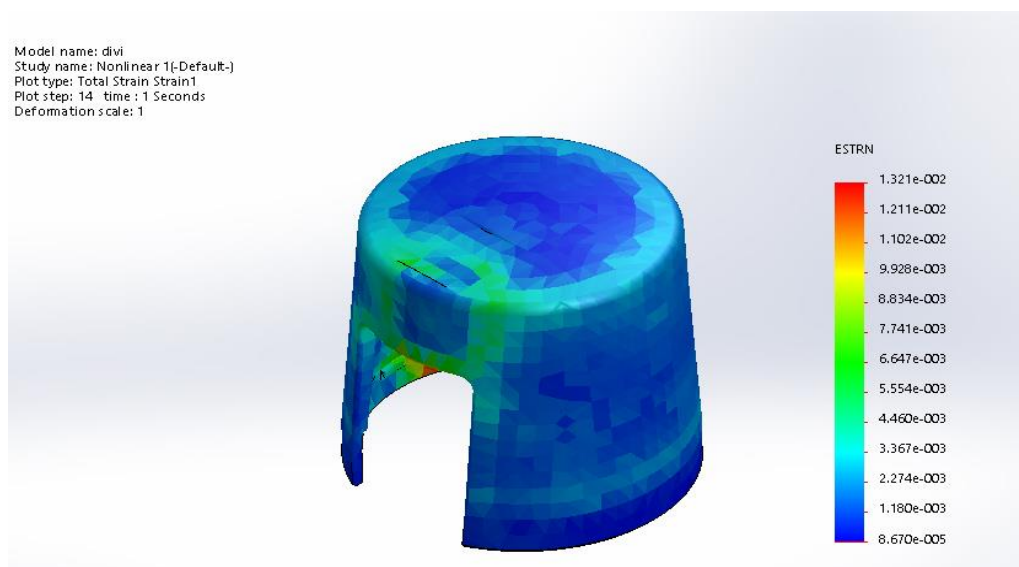


Figure 2.13-Non-linear strain

Case-2

In this case the process parameters used are mold temperature 60°C and the pack time have been increased. (i.e.) the pressure hold time has 20sec and the cooling time as 30sec. In this case the stress and strain attain are 1.826e+007 N/m² and 3.534e-003m as show in figure 2.14, 2.15.

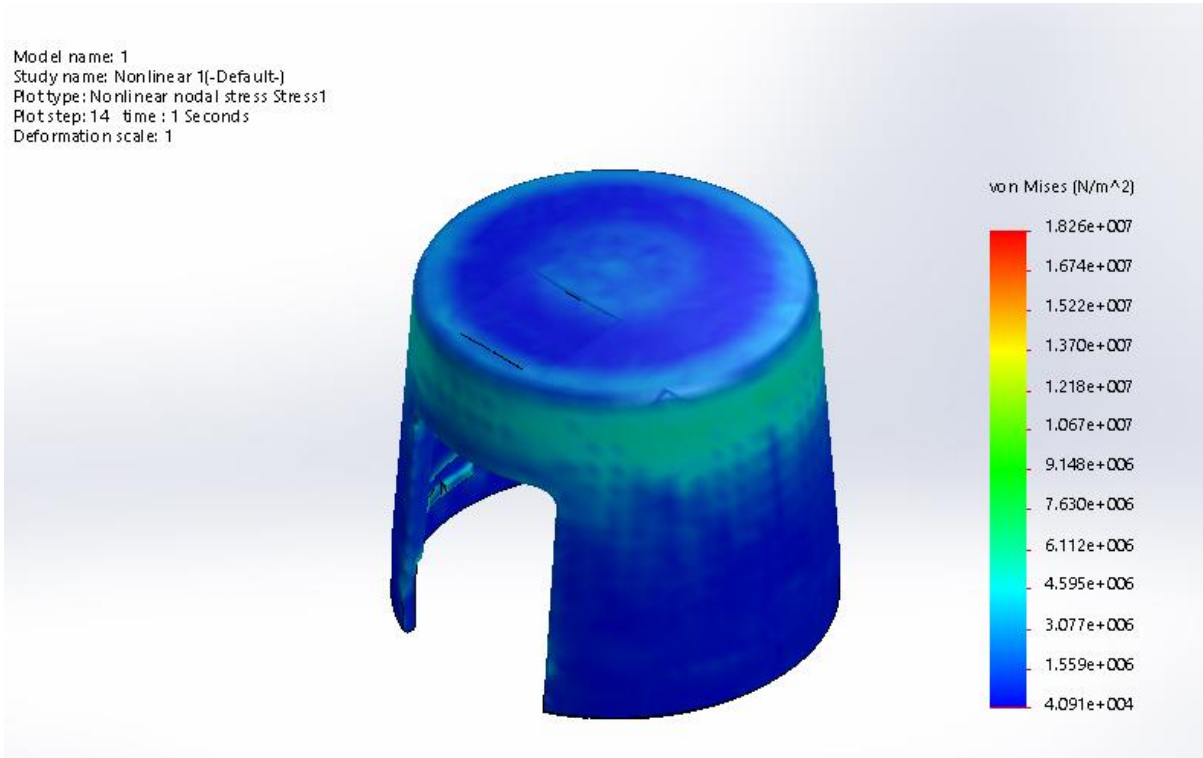


Figure 2.14-Non-linear stress

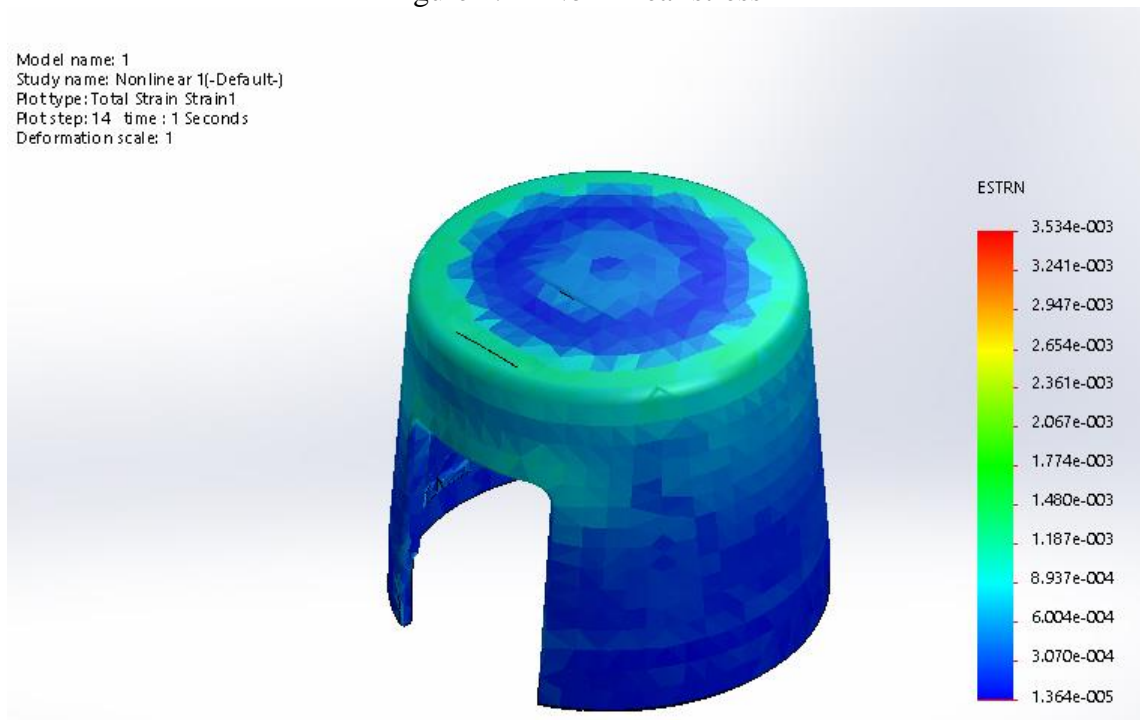


Figure 2.15-Non-linear strain

Case-3

In this case the process parameters used are mold temperature 70°C and the packin time have been same as case 1.the stresss and strain value attained are 1.578e+007 N/m² and 3.514e-003m as shown in the figure 2.16, 2.17.

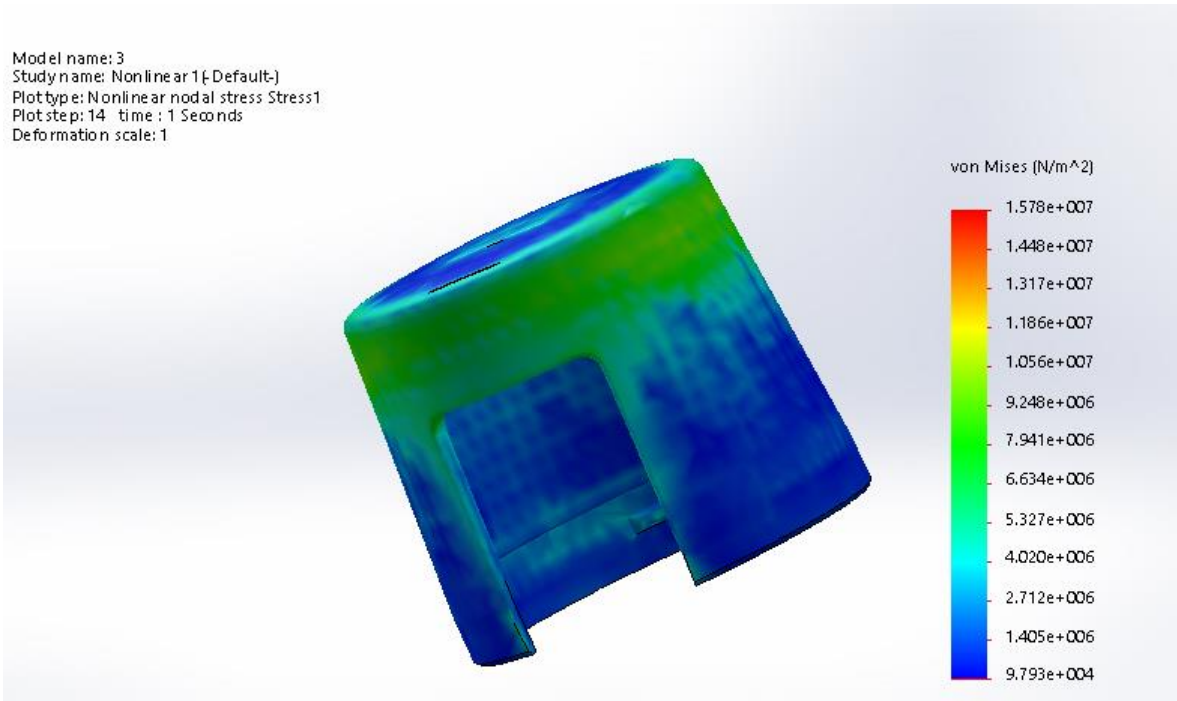


Figure 2.16- Non-linear stress

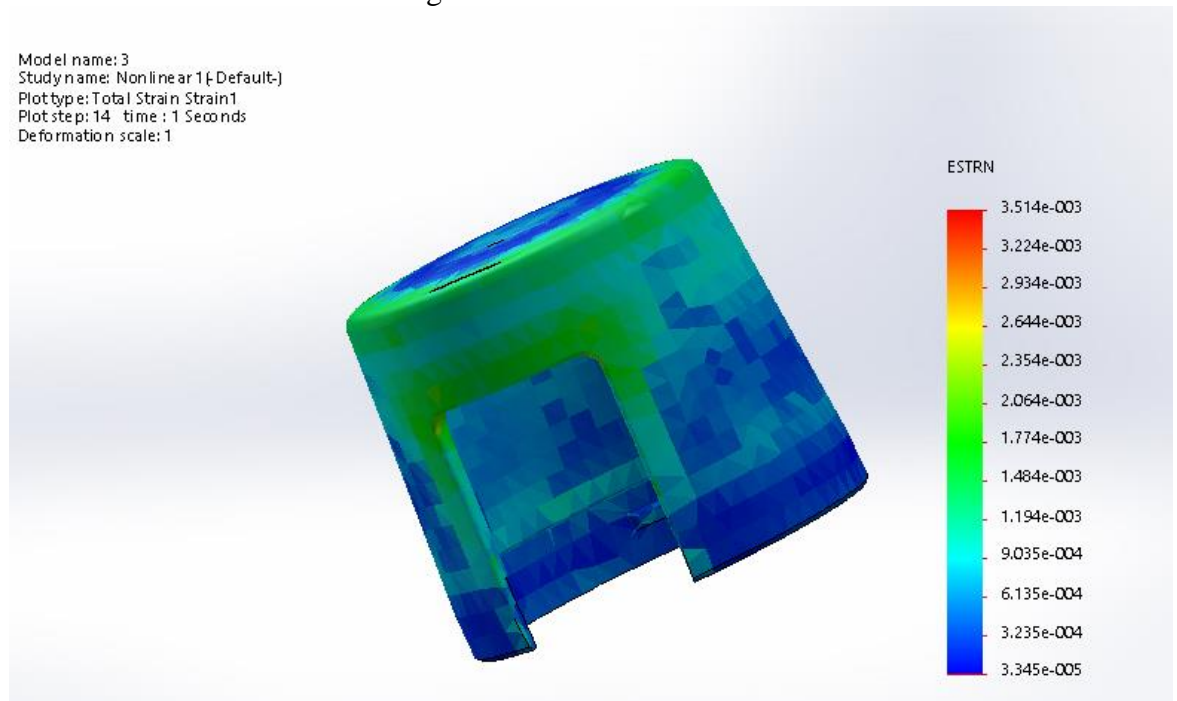


Figure 2.17-Non-linear strain

Case-4

In this case both the mold temperature and the pack timing had been changed and the results are shown in figure 2.18,2.19. the mold temperature 50, the pack timing is pressure hold time 20sec and cooling time is 30sec and maximum stress and strain are $1.839\text{e}+007 \text{ N/m}^2$ and $3.607\text{e}-003\text{m}$.

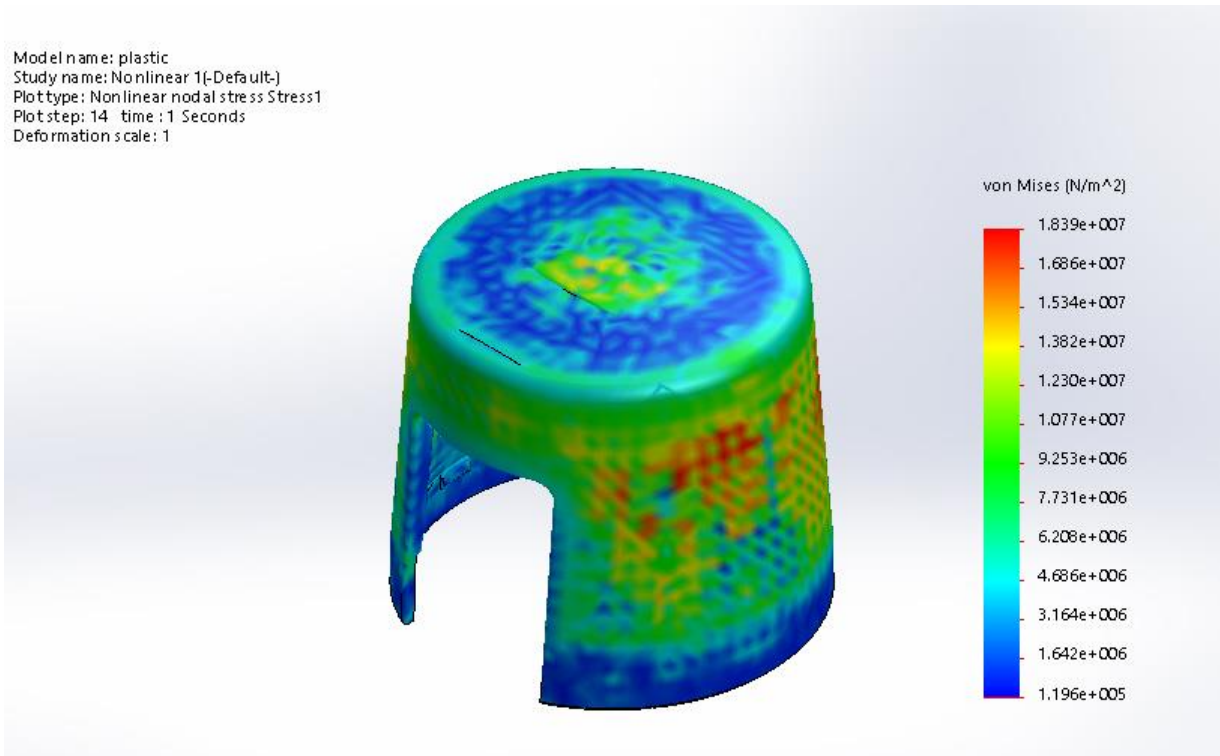


Figure 2.18- Non-linear stress

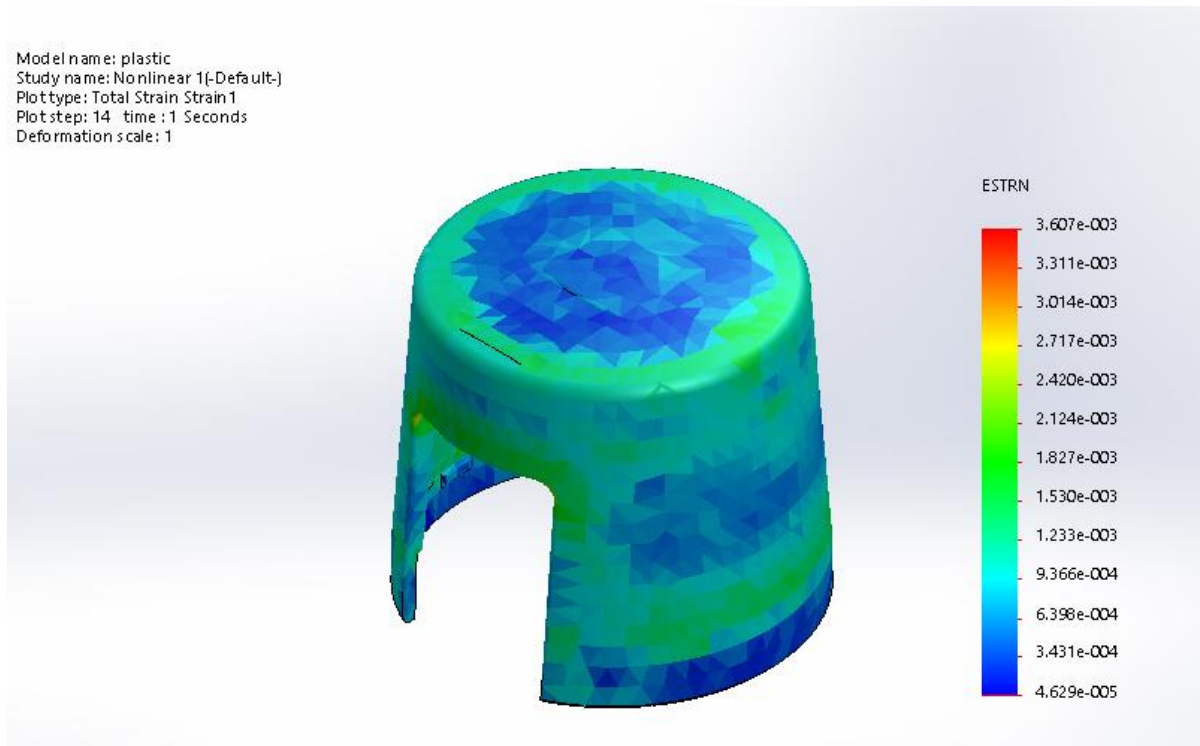


Figure 2.19- Non-linear strain

3. Results

From the four case it is prved that the mold temperature and the pack timing haveen been most influenced in the stress and strain occured in the molded part after it have been molded. It is clear that the stress and strain which had been form as a major deffect in the chrome platin git can been reduced by using the process parameters use to mold the part. And the figure 2.19 had shows the amount of stress and strain of the four cases. And the correct process parametrs should be used to mold the part.

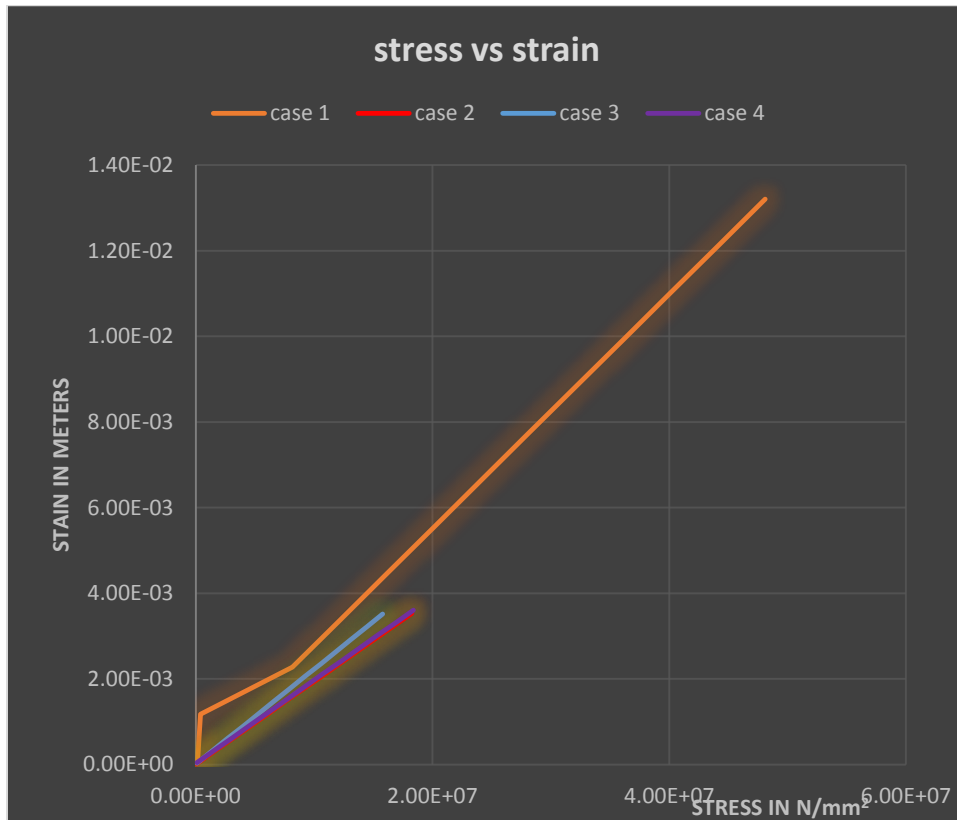


Figure 2.20 stress and strain occurred in four cases.

Conclusion

The plating on plastics which have placed most important role in the modern life and the chrome plating process have been studied in detail and the following conclusion have been drawn. The common factors which affects the chrome plating on ABS plastics.

1. The etching solution reacts in the chrome plating process and removes the butadiene rubber have been removed from the surface of the part. Because of this removal of butadiene rubber porosity holes have been formed on the surface. The alternative etching solution have been studied.
2. Activation is the process in which the copper ions from the electroless plating process gets attracted to the holes in the surface.
3. Part preparation is decides how the quality of the electroplated product and the new optimised preparation steps have been studied.
4. And the part had been designed and it is analysed that the residual stress can be altered by making the changes in the process parameters and the simulation had been done and the result proves that the in-mold residual stress can be altered by changing the process parameters.

Recommendation

After taking the consideration of the quality of the product and studying the chrome plating process involved in detail and the following suggestions are recommended. To reduce the hazardous elements in etching and activation step is to be reduced, and the alternate solutions should be taken into account. It is known that the first reason for the quality of the chrome plated plastic will directly depend on the quality of the product after moulding. It is good to inspect the quality of the part before it undergoes the chrome plating process. It is best to reject the part if the defects are seen. And it is recommended that the mold temperature and the pack timing should be optimised to reduce the in-mold stress formed in the molded part

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