STUDY OF VARIABLES OF ANODIZING

A thesis submitted to the Department of Metallurgical Engineering, Bangladesh University of Engineering and Technology, Dhaka, in partial fulfilment of the requirements for the degree of Masters of Science in Engineering (Metallurgical).

Submitted by

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ABSTRACT

A laboratory model anodising unit has been set-up and used in the study on the effects of the variables like time, temperature and concentration of the electrolytic bath on weight gain, hardness, electrical resistance and structure of the anodized layers. The weight of the anodic coating on pure aluminium anodes in sulfuric acid electrolytes was found to increase with decreasing temperature and concentration of the electrolytes while the weight decreased as the temperature and concentration of electrolytes were raised. The weight gain due to sealing in deionized water increased as the temperature and immersion time were increased. Hardness and electrical resistance was found to increase with decreased electrolyte temperature and concentration.

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CHAPTER - ONE

1.0 INTRODUCTION

Anodizing is an electrolytic process in which a metal is made the anode in a suitable electrolyte so that when an electric current is passed through the electrolyte, the metal surface is converted to a form of its oxide that has decorative, protective, or other desirable properties. The electrolyte provides oxygen ions that react with metal ions to form the oxide, and hydrogen is released at the metal or carbon cathode. Depending upon the solvent action of the selected electrolyte on the anodic oxide, the operating conditions employed, and voltage/current relationships, the metal anode continues to be consumed and converted to an oxide coating which progresses inward. The last formed oxide is adjacent to the metal-coating interface.

Anodizing differs from electroplating in two significant respects. In electroplating, the work is made the cathode, and metallic coatings are deposited on the work. In aundizing, the work is made the anode, and its surface is converted to a form of its oxide that is integral with the metal substrate. Anodizing processes have been developed for many metals. However, those used with aluminum are of the greatest commercial significance. Magnesium is anodized for improved resistance to corrosion and abrasion by procedures similar to those used with aluminum.

Other metals including copper, zinc, cadmium, silver, and steel usually are anodized to achieve decorative effects which often are fugitive unless they are protected by an organic overcoating. The basic reaction in all anodizing processes is the conversion of the metal surface to its oxide while the part is made the anode in a electrolytic cell.

1.1 Reasons for anodizing are:

1. **Increase corrosion resistance.** Aluminium oxide is corrosion resistant and impervious to atmospheric and salt water attack. The anodic coating protects the underlying metal by serving as a barrier to the corrodents. The amorphous aluminium oxide produced by anodizing is sealed by treating in acidified hot water.

2. **Increase paint adhesion.** The tightly adhering anodic coating offers a chemically active surface for most paint systems. Anodic films produced in sulfuric acid baths are colorless and offer a base for subsequent clear finishing systems. Aluminium-base materials that are painted for service in severe corrosive environments are anodized before being painted.

3. **Permit subsequent plating.** The inherent porosity of the anodic film enhances electroplating. Usually, a phosphoric acid bath is used for anodizing prior to plating.

4. **Improve decorative appearance.** All anodic coatings are lustrous and have relatively good abrasion resistance. Therefore, these coatings are used as the final finishing treatment when the natural appearance of the aluminium is desired or when a mechanically induced pattern is to be preserved. The degree of luster of anodic coating depends on the condition of the basis metal before anodizing. Dull etching decreases luster; bright etching, chemical or electrolytic brightening, and buffing increase luster, either diffuse or specular. Most of the aluminium used in architectural applications is anodized.

5. **Provide electrical insulation.** Aluminium oxide is a dielectric. The breakdown voltage of the anodic film varies from a few volts to several thousand volts, depending on the alloy and on the nature and thickness of the film.

6. **Permit application of photographic and lithographic emulsions.** The porosity of the anodic film offers a mechanical means of holding the emulsion.

7. **Increase emissivity.** Anodic films more than 8×10^{-9} mm thick increase the emissivity of the aluminium. When dyed black, the film has excellent heat absorption up to 232_C.

8. **Increase abrasion resistance.** The hard anodizing processes produce coatings from 1×10^{-3} to more than 4 mils thick. These coatings, with the inherent hardness of aluminium oxide, are thick enough for use in applications involving rotating parts where abrasion resistance is required. (Although all anodic films are harder than the substrate material, the coatings produced by chromic acid and some sulfuric acid baths are too thin or too soft to meet the requirements for abrasion resistance.

9. **Permit detection of surface flaw.** A chromic acid anodizing solution can be used as an inspection medium for the detection of fine surface cracks. When a part containing a surface flaw is removed from the anodizing bath, then washed and dried quickly, chromic acid entrapped in the flaw seeps out and stains the anodized coating in the area adjacent to the flaw.

1.2 Theory of Anodic Oxide Formation

The mechanism of anodic oxidation is complex, and till today some aspects are not completely understood. In accordance with Faraday's law, I gram equivalent of pure aluminium (8.9938g) reacts electrochemically when 96,500 columb of electricity is passed through the aluminium anode. However, not all of this aluminium appears as aluminium oxide in the coating. A significant ratio can be calculated between the weight of coating and the metallic aluminium or aluminium alloy removed. If all the aluminium were converted to oxide, this " coating ratio" would be 1.89

($Al_2O_3/2Al$). With the porous and adsorbent type of coating this ratio is significantly lower, seldom exceeding about 1.60. The coating ratio is lowered significantly by an increase in the sulfuric acid content or the temperature of the electrolyte. The ratio is also lower with aluminium alloys than with the pure metal. A lowering of the coating ratio indicates, in general, an increasse in porosity and decrease in abrasion resistance. It is known, moreover, that the coating is not all aluminium oxide, but contains chemically bonded and adsorbed substances such as sulfate and water from the electrolyte.

Theories of the structure of the overall film depend upon certain experimental observations:

a. Thick stable oxide films can only be formed in certain electrolytes. No such films form in acetic, nitric or hydrochloric acid and it is probable that incorporation of the acid radical is important in maintaining stability.
b. The total film porosity represents about 45% of the superficial film volume.
c. The initial film is dense but becomes less dense as the film growth proceeds.
d. Initially the film thickness increase by the theoretical amount, but falls off with time as the current efficiency decreases and the voltage increases.

Initially oxidation consists of dissolution of aluminium, but when a critical current density is attained the anode layer becomes saturated with Al^{3+} ions and a thin film of basic hydrated oxide forms. This raises the potential, whereupon evolved oxygen oxidizes the whole surface and dehydration may be attributed to the heating effects which causes cracking to occur. Once cracks form, internal oxidation can take place and film growth takes place at the internal interface. Therefore at the thin film stage internal oxidation takes place with some external dissolution, but as the film grows thicker pores develop and the external dissolution ceases.

The growing anodic film is therefore seen in two layers (Fig. 1): the inner barrier layer is a compact film of Al_2O_3 growing by diffusion of Al outwards and O inwards remaining relatively constant in thickness (0.025 μm), while the outer porous hydrated oxide film grows up to the finished thickness of 1-200 μm.

The barrier layer appears to form first and porosity develops as dissolution commences (the barrier layer must be resistive and must generate heat as current is passed). Electron microscopy[1] has shown that the film grows with an hexagonal cellular pattern, each cell containing a pore. As the voltage of anodizing increases so the cell size increases and the overall pore density decreases. The initiation of pores is still a matter of debate but is believed to be related in some way to the existence of barrier layer growth faults.

1.3 Development of Protective Oxidation on Aluminium

In the metal industry today aluminium occupies an increasingly large and important position. Owing its employment first and foremost to its lightness, systematic researches have shown this metal to have a remarkable range of properties which make it suitable, and indeed render it preferable, for a multitude of applications. Although pure aluminium is soft, when alloyed with suitable elements such as copper, magnesium, silicon, and manganese--it competes successfully in respect of strength and hardness with structural steel. For this reason aluminium has in recent decades been widely employed as a constructional material for vehicle and aircraft, for chemical plants and containers and in the field of architecture. Its electrical conductivity and the remarkable resistance of many of the alloy groups to atmospheric influences has enabled it to replace copper for overhead transmission lines in numerous areas of the globe. Its nonmagnetic properties, combined with good workability, have made the metal an outstanding material for the construction of an extremely wide range of apparatus, plant components, structural part, and useful objects of many types.

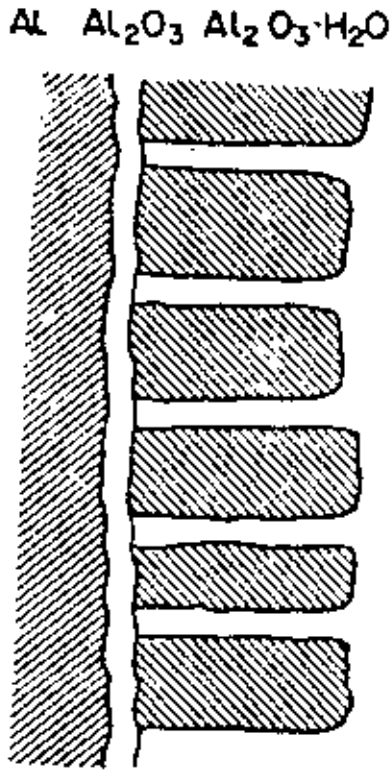


Fig. - 1

Aluminium and most of its alloys exhibit a high chemical resistance due to the fact that, as a result of its affinity for oxygen, aluminium forms, when exposed to air, a thin protective oxide film. This reaction occurs instantaneously and all over the surface and aluminium is in consequence always covered by a natural oxide film which, initially is very thin and steadily grows in thickness until at the end of some months it reaches its normal ultimate thickness which may reach 0.05 microns. This thin natural oxide film, which consist of some 20-30 molecular layer, is capable of protecting the underlying metal against the widest imaginable range of external corrosive influence which would otherwise attack and disintegrate the aluminium. Any mechanical damage to this oxide film is selfhealing, because immediate re-oxidation occurs.

This natural oxide is integrally attached to the aluminium and is effectively free from pores. As a result, the oxide film is very hard and strong mechanically and is resistant both to water and normal atmosphere, but the protection it offers is inadequate if other agencies are present to start corrosive attack on the metal. For this reason precesses were sought to reinforce the natural oxide film on aluminium and thereby endow the metal with an even greater resistance to corrosion.

It has long been known[3] that aluminium used as an anode combines with the electrolytically produced oxygen to form aluminium oxide on the surface of the metal. This phenomenon is utilized in rectifiers since the oxide film possesses the so-called " valve action ", that is to say that it allows an electric current to pass only in one direction. In the early part of this century' and more particularly between the two world wars, processes were developed for the artificial thickening or creation of the oxide film on aluminium and aluminium alloys- processes as significant for the commercial development of aluminium as was the discovery of Duralumin, the first age-hardenable aluminium alloy. It is possible in this way to build up much thicker layers which offer greatly improved protection than can be derived from simple oxidation in air. The processes for the artificial production of oxide films fall into two main groups:

(1) the purely chemical processes, which do not depend upon the use of electric current; and

(2) the electrolytic oxidation or anodizing processes, which depend upon the use of electric current.

The purely chemical processes depend upon the action of hot aqueous solutions on the metal. By reason of their simplicity they have deservedly attained some importance, but in general, they only allow the formation of rather thin, soft films,whilst the processes of the second group, the so-called anodic oxidation processes can be made to produce hard films 20 microns or more thick. In practice, therefore, application of the chemical processes is restricted to such special cases as the oxidation of interior surfaces of tubes or plant, of large containers and of surfaces which are exposed to only mild chemical attack, and to applications where they are used for the preparation of the surface of aluminium as a basis for subsequent painting or lacquering.

The most important protective surface-treatment processes fall into the category of anodic oxidation, since the films produced by anodizing not only give excellent corrosion-resistance to aluminium and to the majority of aluminium alloys, but they also enhance the appearance of the metal and make it possible to give aluminium any desired color. These facts have opened up a new and important range of applications for aluminium as a material and have added to the possibilities of employing the metal in certain technical applications.

Many processes have been commercially developed and are in use on a large scale. A brief description of these processes and of the plant required for their operation is given in the following chapters, since it is known that many aluminium-fabricating works require their own anodizing plant and also that those plants which operate independently play an important and interesting part in the technological development of the metal and are steadily increasing in number.

1.4 Field of Application

The surface treatment of aluminium represents the final phase of its fabrication. It is the process which gives the metal its finished appearance. Apart from considerations of increasing the corrosion-resistance of the material, the final appearance must also be taken into consideration when selecting the method of surface treatment. If the aluminium is required for constructional components or plant and apparatus into which no special aesthetic considerations enter, then the process to be employed will be decided purely upon the relevant properties required from the protective film -- such as its density, thickness, hardness or abrasion-resistance--but if, on the contrary, the aluminium is required for articles or components whose appearance is important it will be necessary to take this factor into account and to select appropriately both the anodizing process to be employed and the material to be treated.

The chemical oxidation processes are used now-a-days in cases where the corrosion-resistance is not required to meet exacting claims and where the aesthetic appearance is of limited importance. Such processes are suitable, as has been mentioned, particularly for the treatment of the interior surface of the cube and piping system, etc. and also in conjunction with suitable additional processes, such as painting or lacquering or coating with resins.

Mass-produced cheap articles are often chemically oxidized because this is an inexpensive method of depositing an artificial colored oxide film.

The processes in use at the present time can be applied to the oxidation of large surfaces, e.g. roof surfaces or coverings of large containers or holders of not very corrosive substances and, again in these cases, as a basis for the later application of paint and lacquer or artificial resin coatings.

In general, it may be said that chemical protective oxidation is used where bare aluminium is not suitable and where the cost, the requirements, or the nature of the object would prohibit anodic oxidation. Anodic oxidation, with its thick film, must, however, be used where a high degree of corrosion-resistance is called for. If the appearance is not of interest-- as for example, in the anodizing of industrial components--the relatively cheap and economic sulfuric acid processes are used.

1.5 Scope of This Work

Engineering applications of anodized components are increasing day by day e.g. in military, aircraft, door fittings, window frames, vehicle, chemical plant and in shipbuilding. The films produced by anozing enhance the appearance of the metal and make it possible to give aluminium any desired colour. For that reasons, systematic research have been carried out to have a remarkable range of properties such as corrosion resistance, electrical insulation, abrasion resistance.

Normally, anodic oxidation is extensively used for the production of protective and decorative films on aluminium and aluminium alloys using various types of bath e.g. sulfuric acid bath chromic acid bath. This investigation aims to study the effect of different parameters such as temperature, time, concentration of electrolyte on anodizing and to understand the effect of these parameters on the structure and properties of the anodised layers weight gain, hardness, microstructure corrosion resistance, electrical resistance, abrasion resistance of anodized layer has been studied. The microstructure could not be throughly studied due to the lack of an electron microscope. Since no equipments for anodizing was available considerable period of time was spent in the design and fabrication of a laboratory model anodising unit. Considerable time was also required for the trial operation.

CHAPTER - TWO

2.0 SURFACE PREPARATION

2.1 Introduction

A chemically clean surface is a basic requirement for successful anodizing. In selecting a metal cleaning process, the following factors among others, must be considered.

(a) the identification and characterization of the soil to be removed,

(b) identification of the substrate to be cleaned and the importance of the condition of the surface and structure to the ultimate use of the part

(c) degree of cleanness required

(d) capabilities of the available facilities,

(e) impact of the process on the environment,

(f) overall cost of the process and

(g) subsequent operations to be applied.

Normally the following steps are utilized in surface preparation.

2.2 Polishing and Buffing.

Both polishing and buffing are carried out by bringing the work into contact with wheels revolving at fairly high speeds. The main difference between the two operations lies in the construction of the wheels and the abrasives used in connection with them. Polishing may also be carried out on endless belts coated with abrasives; the choice between belts and wheels is determined by the configuration of the parts and the degree of automation appropriate to the operation--in effect and the total costs. Both polishing and buffing, are relatively labor intensive, and skilled polishers are becoming scarce. Belt polishing is somewhat less demanding of skilled labor than wheel polishing.

2.2.1 Polishing

Polishing wheels are usually of muslin, canvas, felt, or leather, Construction of the wheels can be varied to make available wheels of varying flexibility, best adapted to the shape and surface condition of the object to be finished. The hardest wheels are made of individual disks of canvas cemented together. On the other hand, the softest are composed of muslin disks sewn together. Intermediate grade consist of wheels formed from sewed section on muslin disks either glued or cemented together.

The abrasives required for polishing are fastened to the surface of the wheel by an adhesive, usually hide glue or silicate cements. The glue must be of high grade, and strict precautions are required to prevent bacterial degradation of the adhesive Wheels are "Set up "in series of individual operations including melting the glue, adding the abrasive, coating the wheel, and setting the glue. Silicate cements have the advantage of requiring fewer precautions and of being applicable at room temperature, without he need for special equipment.

2.2.2 Buffing

Buffing may be used for the production of several types of finishes: stain, preliminary smoothing, cut-and-color for smoothness and some luster, and color buffing for producing high gloss or mirror finishes.

Buffing wheels are usually of muslin, of various constructions: sewed, pocketed, or folded, etc. Buffing wheels in general are more flexible than polishing wheels. Grades of muslin are specified by thread count : the denser the thread the less flexible the wheel and the harder the surface to be buffed.

Abrasives for buffing are commonly applied in the form of a greaseless compound formed into a bar which combines the binder (glue) and the abrasive. Many grades are available, depending on the metal to be buffed, the amount of metal to be removed, and the finish desired. Wheel speeds in general are somewhat lower than for polishing, in the range of 25 to 30 m/s.

2.3 Alkaline Cleaning.

It is the most widely used method for cleaning aluminium and aluminium alloys. This method is easy to apply in production, and equipment costs are low.

Aluminium is readily attacked by alkaline solutions. Most solutions are maintained at a pH between 9 and 11 and they are often inhibited to some degree, to minimize or prevent attack on the metal. The most frequently used cleaner is the mildly inhibited type.

Cleaners of either the etching or the nonetching type have some ability to emulsify vegetable and animal oils or greases, but no mineral oils or greases. Therefore, they can sometimes remove fresh buffing compounds.

The nonetching types of cleaners may be classified as silicated and nonsilicated cleaners. The silicated cleaners are based on aqueous solutions of sodium carbonate, trisodium phosphate, or other alkalis, to which small amounts of sodium silicate are added to inhibit cleaning.

Compositions and operating conditions of common alkaline cleaners are given in Table-1

Table-1

Etching Cleaners

1.	Sodinum hydroxide	18.88 to 63 gm
	Sodium phosphate	0.6 to 3 gm
	water	1 litre
	Tempatature of bath	60 to 82°C
	Immersion time	30 Sec to 10 min.
2	Sodium hydroxide	1.56 to 4.67 gm
	Sodium phosphate	6.22 to 50 gm
	Sodium carbonate	6.22 to 50 gm
	water	1 litre
	Temperature of bath	60 to 82°C
	Immersion time	2 to 5 min.

Noneteching Cleaners

1.	Sodium pyrophosphote + Sodium	
	metasibbicate toal of	12.47 to 62 gm.
	water	1 litre
	Temperature of bath	60 to 71°C
	Immersion time	2 to 5 min.
2.	Trisodium phosphate + sodium	
	metasilicate	12.47 to 62.3 gm
	water	1 litre
	Temperature of bath	60 to 71°C
	Immersion time	2 to 5 min.
3.	Sodium carbonate	5 to 15 gm
	trisodium phosphate	5 gm
	water	1 litre
	Temperature of bath	79 to 96°C
	Immersion time	2 to 5 min.
4.	Sodium carbonate	10 to 40 gm
	sodium silicate	5 to 10 gm.
	water	1 litre
	Temperature of bath	60 to 71°C
	Immersion time	2 to 5 min.
5.	sodium carbonate	3 to 6 gm
	Sodium metasilicate	3 to 6 gm
	water	1 litre
	Temperature of bath	60 to 71°C
	Immersion time	2 to 5 min.

2.4 Acid Cleaning

Acid cleaners may be used alone or in conjunction with other acid, alkaline, or solvent cleaning systems. Vapor degreasing and alkaline cleaning may be required for the removal of heavy oils and grease from workpieces before they are immersed in an acid bath. One of the main functions of an acid cleaner is the removal of surface oxides prior to anodizing.

A mixture of chromic and sulfuric acids is commonly used to remove surface oxides, burn-in oil, or other films, such as the iridescent or colored films formed during heat treating. This acid mixture cleans and imparts a slightly etched appearance to the surface, preparing it for anodizing.

Aluminum parts should be insulated from ferrous metal baskets or supports when immersed in acid cleaning solutions, because contact of these two metals can produce a galvanic action that causes corrosion. Materials such as vinyl plastisols, epoxy, polyethylene and polypropylene may be used for insulation. When practical, baskets or rods should be of the same material as the workpieces.

2.5. Chemical Brightening

It smooths and brightens aluminum products by making use of the solution potential of the aluminum surface in the various baths employed and of the local differences in potential on the aluminum surface.

In general, chemical brightening baths are concentrated or dilute acid solutions containing oxidizing agents. The acids commonly used are sulfuric, hydrochloric, nitric, phosphoric, acetic and, to a lesser extent, chromic and hydrofluoric. Ammonium bifluoride is used when it is desirable to avoid the hazards that attend the use of hydrofluoric acid. Oxalic and citric acids may be used as alternates for acetic acid. Fluoboric and fluosilic acids may be used as alternates for hydrofluoric

acid. Nitric and chromic acids and, less often, ferric sulfate and hydrogen peroxide are used when oxidizing conditions are required. The following types of bath is utilized in chemical brightening.

2.5.1 Phosphoric-Nitric Acid Baths

Among the various types of concentrated baths, the phosphoric-nitric acid baths are the most widely used in the United States. Compositions and operating conditions for two commercial baths of this type are given in Table-2.

Table-2

1.	Chromic acid	37.42 to 74.83 gm
	Sulfuric acid (66_ Be)	1.2 to 1.5 pt
	Water	1 litre
	Temperature of bath	43.33 to 82.22 ^{O}C
	Immersion time	Up to 2o min
2.	Nitric acid (42_ Be)	4 to 6 pt
	Hydrofluoric acie (48%)	88.75 to 710 cc
	water	1 litre
	Temperature of bath	Room temperature
	Immersion time	1 to 5 min.
3	Sulfuric acid (66_ Be)	0.8 pt.
	Hydrofluoric acid (48%)	88.75 CC
	Chromic acid	31.18 gm
	water	1 litre
	Temperature of bath	65.55 to 71 ^{O}C
	Immersion	2 to 5 min.
4.	Nitric acid (42_C Be)	0.3 to 1 pt
	Sodium sulfate(hydrate)	50 to 100 gm
	water	1 litre
	Temperature of bath	77 to 79.44 ^{O}C
	Immersion time	4 to 8 min.
5	Phosphoric acid	266 CC
	chromic acid	17.15 gm
	water	1 litre
	Temperature of bath	43 to 65 ^{O}C
	Immersion time	1 to 5 min.

2.5.2 Phosphoric and Phosphoric-Sulfuric Acid Baths.

Concentrated solutions of phosphoric acid at operating temperatures above 175 ^{0}C were the first baths employed for brightening aluminum. A more effective bath, which combines some smoothing or " polishing" with brightening action, is one containing (by volume) 75% phosphoric acid and 25% sulfuric acid. This bath, which is operated at 90 to 230^{0}C. produces a diffuse but bright finish.

A white film of phosphate salts remains on the metal after treatment in either of these bath under some conditions of composition and bath temperature. The film must be removed, and this can be accomplished with a hot (60 to 70^{0}C) aqueous solution of chromic and sulfuric acids. The composition of this acid solution is not critical, and may range, by weight, from 2 to 4% CrO_3 and 10 to 15% H_2SO_4.

2.6 Electro-brightening Processes

There exists no agreed definition of the term "electrobrightening", but it can be defined as: "a process in which an increase in reflectivity of a metal object is produced, by passage of a current, when that object is made the anode in a bath containing a suitable electrolyte and having conditions adjusted to the range in which brightening is produced. It does not produce any appreciable degree of smoothing, as can be obtained from processes usually known as " electropolishing". An obvious corollary is that the object must be highly finished by mechanical polishing before treatment.

2.6.1 The Brytal Process

This was developed[8] by N.D. Pullen, of the British Aluminium Co. Ltd. and patented in 1934 (Table -3). The metal is allowed to etch for 15-30 seconds prior to switching on the current, the duration being largely dependent upon the purity of the metal and increasing with it. After this treatment a thin " smudge" film is present on the surface of the brightened article. A sulfuric acid solution or a nitric acid solution will remove this smudge.

This process is the most widely used electro- brightening treatment in this country, having the merit that relatively simple equipment is required and the tank need only be of mild steel. Its disadvantage is that it requires a relatively high operating temperature, which can present difficulty in a large tank. due to local temperature differences. Further, care has to be taken in positioning the article in relation to the cathodes and the surface of the electrolyte, owing to the danger of streaking of the metal surface from gas bubbles. Auxiliary cathodes and rotation of the work in the bath may also be necessary with round recessed articles. A high standard of preparation is necessary, and white patches due to overheating of the metal surface in polishing may be revealed after brightening. Compositions and operating conditions of this bath is given in Table-3.

2.6.2 The Alzak Process

This was developed[8] by R. B. Masson, of the Aluminium Company of American, almost simultaneously with Brytal.

Owing to the corrosive nature of the solution, it is necessary to use a stainless- steel or rubber-lined tank. The acid is rather more expensive than the cheap alkaline materials used for Brytal. Its limitations are similar to those of Brytal, except that it operates at a lower temperature which is not difficult to maintain. The fact that it has not been widely used in Great Britain is probably due to the association of Braytal with the British Aluminium Co. Ltd. Who for some years was the sole producer of anodizing quality material. Compositions and operating conditions of this bath is given Table-4.

Table-3

Sodium carbonate	150 gm
Sodium phosphate	50 gm
Water	1 litre
Current	27-32 mA/sq cm.
Voltage	10-14 volt
Temperature	75-85^{o}C
Immersion time	5-8 min.

Smut removal

Sulfuric acid	10% (vol)
or nitric acid	10 to 15% (vol)
Temperature of bath	21 to 27^{o}C
Immersion time	15 to 30 sec.

Table-4

Fluoboric acid	2.5% (by weight)
Temperature of bath	30^{o}C
Current density	10.76 to 21.53 mA/sq.cm
Voltage	15 to 30 V
Immersion time	5 to 10 min.
Agitation	None

Smut Removal

Phosphoric acid	1.0% (wt)
Chromic acid	0.5% (wt)
Temperature of bath	88 to 99 ^{o}C
Immersion time	30 Sec.

3.0 THE THREE PRINCIPAL TYPES OF ANODIZING PROCESSES

(a) chromic, in which the active agent is chromic acid

(b) sulfuric, in which the active agent is sulfuric and

(c) hard patented processes that use sulfuric and oxalic acids as the active agents. Other processes, used less frequently and for special purposes. employ sulfuric-oxalic, phosphoric, oxalic, boric solutions.

3.1 Chromic Acid Process

The sequence of operations employed in this process depends on the type of sample, composition of sample and the principal objective for anodizing.

Chromic acid anodizing solutions contain from 3 to 10% chromic acid ($C_{r2}0_3$) by weight. A solution is made up by filling the tank about half full of water, dissolving the acid in the tank, water is added to adjust to the desired operating level. Temperature of the bath is normally mainmained at 40°C.

A chromic acid anodizing solution should not be used unless:

1. The pH is between o.5 and 1.0
2. The concentration of cholorides (as NaCl) is less than 0.02%.
3. The concentration of sulfates (as H_2SO_4) is less than 0.05%
4. The total chromic acid content, as determined by pH and Baume reading, is less than 10%.

When the anodizing process is started, the voltage is controlled so that it will increase from 0 to 40 volts within 5 to 8 min. The voltage is regulated to produce a current density of not less then 1 mA/sq cm, and anodizing is continued for the specified time period (usually, 30 to 40 min). At the end of the cycle the current is gradually reduced to zero, and the part is removed from the bath within 15 sec and rinsed.

3.2 Sulfuric Acid Process

The basic operations for this process are the same as for the chromic acid process. Parts or assemblies that contain joints or recesses that could entrap the electrolyte should not be anodized in the sulfuric acid bath. The concentration of sulfuric acid (sp gr, 1.84) in the anodizing solution is 12 to 20% by weight.

A sulfuric acid anodizing solution should not be used unless:

1. The concentration of cholorides (as NaCl) is less than 0.02%.
2. Aluminum concentration is less than 20 g per liter.
3. Sulfuric acid content is between 165 and 200 g per liter.

At the start of the anodizing operation, the voltage is adjusted to produce a current density of 12.91 mA/sq cm. The voltage will increase slightly as the aluminum content of the bath increases. When a current density of 12.91 mA per sq cm. is attained, the specified process is continued until the specified weight of coating is produced, after which the flow of current is stopped and the parts are withdrawn immediately from the solution and rinsed.

3.3 Hard Anodizing

The primary differences between the sulfuric acid and hard anodizing processes are the operating temperature and the current density at which anodizing is accomplished. Hard anodizing produces a considerably heavier coating than conventional anodizing for a given length of time. The hard anodizing process employs a sulfuric acid bath containing 10 to 15% acid by wight, with or without additions. The operating temperature of the bath ranges from 5 to 10°C ,and current density is between 21.53 and 38.74 mA/sq cm. Higher temperatures cause the formation of soft and more porous outer layers of the anodic coating. This change in coating characteristics reduces wear resistance significantly and tends to limit coating thickness. Excessive operating temperatures result in dissolution of coating and can burn and damage the work.

Proprietary processes also are common of these processes uses a solution containing 99.78 to 103.96 gm of sulfuric acid and 9.98 to 17.46 gm of oxalic acid ($H_2C_2O_4$) per liter of water. This solution is operated at 10°C and a current density of 27 to 39 mA/cm^2 (voltage is increased gradually from zero to between 40 and 60 volts); treatment time is 25 min per mil of coating thickness.

3.4 Specinl Anodizing Processes

Table-5 gives the operating conditions for three anodizing baths that are used to produce an anodic coating with a hardness and porosity suitable for electroplating, or to produce anodic coatings of hardness or thickness intermediate to those obtainable from chromic acid, sulfuric acid and hard anodizing baths.

Table-5. Compositions and Operating Conditions of Solution for Special Anodizing processes.

Type of solution	Composition (by weight)	Current density, mA/sq.cm.	Solution temperature ^{o}C	Treatment time, minutes
Sulfuric-Oxalic	H_2SO_4, 15 to 20% + $H_2C_2O_4$, 5%	13	30-35	30
Oxalic	$H_2C_2O_4$, 3%	13	22-30	15-60
Phosphoric	H_3PO_4, 20 to 60% (vol.)	3.22-13	25-35	5-15

3.5 Process Limitations

Composition of the aluminum alloy, surface finish, prior processing, temper or heat treatment, and the use of inserts influence the quality of anodic coatings. The limitations imposed by each of these variables on the various anodizing processes are indicated below.

3.5.1 Alloy Composition

The chromic acid process should not be used to anodize aluminum casting alloys containing more that 5% Cu or more than 7.5% total alloying elements because of excessive pitting, commonly refered to as burning, may result. The sulfuric acid process can be used for any of the commercially available alloys, whereas the hard anodizing process is usually limited to alloys containing less than 3% Cu and 7% Si.

Two or more different alloys can be anodized at the same time in the same bath if the anodizing voltage requirements are identical. This condition is more critical for the sulfuric acid process than for the chromic acid process.

3.5.2 Surface Finish.

Anodic films accentuate any irregularities present in the original surface. However, surface irregularities are emphasized more by the chromic acid bath than by the sulfuric acid bath.

Sheet materials should be rolled from homogenized ingots from which surface oxides are removed prior to rolling. Clad sheet should be handled to prevent mechanical abrasion or exposure of the core material. Anodizing magnifies scratches and if the core material is exposed it will anodize with a color different from that of the cladding.

Anodizing grade must be specified for extruded products so that mill operation are controlled to minimize longitudinal die marks and other surface blemishes.

Surface irregularities must be removed from forging, and the surfaces of the forging must be cleaned by a process that removes trapped and burned-in die lubricants. Special attention is required when polishing the flash line, if this area is to appear similar to other areas of the forging after anodizing.

Castings can be anodized provided their composition is within the process limits described above under "Alloy Composition". From the standpoint of uniform appearance, however, anodizing usually is undesirable for castings, because of their nonuniform composition and their porosity. Improved results often can be obtained by soaking castings in boiling water after cleaning and before anodizing. This treatment, however, merely attempts to fill surface voids with water, so that voids do not entrap anodizing solution.

Usually, permanent mold castings have the best appearance after anodizings, then die castings, and finally sand castings. Permanent mold castings should be specified if an anodic coating of uniform appearance is required. Anodizing usually reveals the metal flowlines inherent in the die-casting process, and this condition is objectionable if uniform appearance is desired. In general, Solution heat treatment prior to anodizing is benificial for producing the most uniform and bright anodized finish obtainable on castings Regardless of the product form, rough finishing should be avoided when maximum corrosion resistance or uniformity of appearance of the anodic coating is desired. Rough surfaces, such as those prodnced by sawing, sand blasting and shearing . are difficult to anodize and should be strongly etched prior to anodizing to assure even minimal results.

The machined areas of castings or forging may have an appearance different from that of the unmachined surfaces.

3.5.3 Prior Processing

Because of their effect on surface finish, welding, brazing and soldering affect the appearance of the anodic coating, for the reasons above. In addition, the compositions of solders usually are not amenable to anodizing.

Spot, ultrasonic pressure or other types of welding processes where there is no introduction of foreign metal, fluxes or other contaminants do not affect the appearance of the anodic coating.

3.5.4 Temper or Heat Treatment

Differences in temper of non-heat-treatable alloys have no marked effect on the uniform appearance of the anodic coating. The microstructural location of the alloying elements in heat treatable alloys affects the appearance of anodic coatings. Alloying elements in solution have little effect., but the

effect is greater when the elements are precipitated from solid solution. The annealed condition should be avoided when maximum clarity of the anodic film is desired.

3.5.5 Inserts or Attachments.

Inserts or attachments made of metals other than aluminum must be masked off, both electrically and chemically, to prevent burning and corrosion in surrounding areas. The masking must completely seal the flaying surface between the insert and parent metal, to prevent adsorption of solution, which may result in corrosion and staining. Therefore, it is desirable to install inserts after anodizing.

4.0 ANODIZING EQUIPMENT AND PROCESS CONTROL

4.1 Chromic Acid Anodizing.

Mild steel tanks are satisfactory for chromic acid baths. It is common practice to line up to half of the tank with an insulating material, such as glass, to limit the cathode area with respect to the expected anode area (a 1 to-1 ratio is normal). In nonconducting tanks, suitable cathode area is provided by the immersion of individual lead cathodes; however, these require the installation of additional busbars to the tanks for suspension of individual cathodes.

Provision must be made for heating the anodizing solution from 32 to 35 ^{o}C. Electric or steam immersion heaters are satisfactory for this purpose. Electric heaters are preferred, because they are easy to operate and do not contaminate the bath.

The anodizing process generates heat; therefore, agitation is required to prevent overheating of the bath and especially of the electrolyte immediately adjacent to the aluminum parts being anodized. Exhaust facilities must be adequate to trap the effluent fumes of chromic acid and steam.

4.2 Sulfuric Acid Anodizing

Tanks for sulfuric acid anodizing may be made of mild steel lined throughout with plasticize polyvinyl chloride and coated on the outside with corrosion resistant synthetic-rubber paint. (Other suitable materials for tank linings are lead, rubber and acidproof brick). Tanks made of special sulfuric-acid-resistant stainless steel (containing copper and molybdenum), or made entirely of an organic material also may be used. The tank should have controls for maintaining temperature at between 20 and 30^{o}C. Requirements for agitation and ventilation are the same as for chromic acid solutions.

The surface of the floor under the tank should be acid resistant. The bottom of the tank should be about 6 inch above the floor on acid- resistant and moisture- repellent supports.

A separate heat exchanger and acid make-up tank should be provided for sulfuric acid anodizing installations. This tank should be made of lead-lined steel. Lead is preferred over plastic for the lining because lead withstands the heat generated when sulfuric acid is added. Polyvinyl chloride pipes are recommended for air agitation of the solution and for the acid-return lines between the two tanks. Cooling coils should be made of chemical lead or antimonial lead pipe.

4.3 Hard Anodizing

Most of the hard anodizing formulations are variations of the sulfuric acid bath. The requirements for hard anodizing tanks are substantially the same as those for sulfuric acid anodizing tanks, except that cooling, rather than heating, maintains the operating temperature at 5 to 10 ^{O}C.

4.4 Temperature-control equipment

For all anodizing, processes must regulate the over all operating temperature of the bath and maintain the proper temperature of the bath and the proper temperature at the interface of the work suface and electrolyte.

The operating temperature for most anodizing baths is controlled within $1^{O}C$. This degree of control makes it necessary for the temperature-sensing mechanism and heat lag of the heating units to be balanced.

When electric immersion heaters are used, it is common practice to have high and low heat selection so that the bath can be heated rapidly to the operating temperature and then controlled

more accurately on the low heat setting. Standard thermistor thermostats are used for sensing the temperature within the bath and activating the heating elements.

In steam heated systems, it is advantageous to have a throttling valve to prevent overheating. An intermediate heat exchanger is employed in some installations to prevent contamination of the electrolyte and the steam system by a broken steam line within the anodizing bath.

4.5 Agitation

Agitation may be accomplished by stirring with electrically driven impellers, by recirculation through externally located pumps, or by air. In some installations the anode busbars are oscillated horizontally, thus imparting a stirring action to the work.

The two primary requirements of an agitation system are that it is adequate and that it does not introduce foreign materials into the solution. With air agitation, filters must be used in the line to keep oil and dirt out of the solution.

4.6 Power requirements for the principal anodizing processes

Direct current is required for all processes, Some hard anodizing procedures also required a superimposed alternating current. At present, most power sources for anodizing employ selenium or silicon rectifiers. Compared to motor generators, the selenium rectifiers have greater reliability, are lower in initial cost and maintenance cost, and have satisfactory service life.

Voltage drop between the rectifier and the work must be held to a minimum. This is accomplished by using adequate busbars or power-transmission cables.

Automatic equipment to program the current during the entire cycle is preferred. Manual controls can be used. but necessitate frequent adjustments of voltage. The presence of recording voltmeter in the circuit insures that the time-voltage program specified for the particular installation is being adhered to by operating personnel. Current recording devices also are advantageous.

4.7 Masking

When selective anodizing is required, masking is necessary for areas to be kept free of the anodic coating Masking during anodizing may be required also for post-anodizing operations such as welding, for making an electrical connection to the basis metal, or for producing multicolor effects with dye coloring techniques.

Masking materials usually consist of pressure-sensitive tapes and stop-off lacquers. The tapes may have a metal on vinyl (or other plastic) backing. Stop-off lacquers provide satisfactory masking, but some types are difficult to remove. For effective masking when either type of materials is employed, work surfaces should have a high degree of cleanness.

4.8 Racks for Anodizing

Anodizing racks or fixtures should be designed for efficiency in loading and unloading of workpieces. Important features that must be included in every properly designed rack are as follows:

4.8.1 Current carrying capacity

The rack must be large enough to carry the correct amount of current to each part attached to the rack. If the rack is too slender for the number of parts that are attached to the rack, the anodic coating will be of inadequate thickness, or it will be burned or soft as a result of overheating.

4.8.2. Positioning of parts

The rack should enable proper positioning of the parts to permit good drainage, minimum gassing effect and air entrapment, and good current distribution.

4.8.3. Service life

The rack must have adequate strength and sufficient resistance to corrosion and heat, to withstand the environment of each phase of the anodizing cycle.

The use of bolt and screw contacts, rather than spring or tension contacts is a feature of racks designed for anodizing with the semihard-coat color processes. These processes require high current densities and accurate positioning of work pieces in the tank. Bolted contacts are used also on racks for conventional hard anodizing. However, bolting requires more loading and unloading time than tension contacts.

4.9 Materials for Racks

Aluminum and commercially pure titanium are the materials most commonly used for anodizing racks. copper, brass, phosphor bronze, and steel (including stainless steel) can be used for their current-carrying ability, spring-tension properties, or strength, but these materials must be

insulated form the electrolyte by the application of a rack coating compound. Aluminum alloys used for racks should contain not more than 5% Cu and 7% Si.

Racks made of aluminum have the disadvantage of being anodized with the parts. The anodic coating must be removed from the rack, or at least from contacts, before the rack can be reused, A 5% solution of sodium hydroxide at 35 to 65°C, or an aqueous solution of chromic and phosphoric acids (30 gm of C_rO_3 and 30 ml of H_3PO_4 per litre of water) at 75 to 85°C, can be used to strip the film from the rack. The chromic-phosphoric acid solution does not continue to attack the aluminum rack after the anodic film is removed.

On many racks, aluminum is used for splines, and other large members, and titanium for the contact tips. The tips may be replaceable or nonreplaceable. Although replaceable titanium tips offer versatility in racking, the aluminum portions of the rack must be protected with an insulating coating. However, if the anodizing electrolyte penetrates the coating, the aluminum portion of the rack may become anodized and thus become electrically insulated from the replaceable titanium contact. A more satisfactory rack design employs nonreplaceable titanium contacts on aluminium splines that are coated with a protective coating. Titanium contacts that are welded to replaceable titanium crossbars offer a solution to many racking problems created by the variety of parts to be anodized. These crossbar members can be rapidly connected to the spline. Titanium should not be used in solutions containing hydrofluoric acid.

Plastisol (unplasticized polyvinyl chloride) is used as a protective coating for anodizing racks. This material has good resistance to chemical attack by the solutions in the normal anodizing cycle; however, it should not be used continuously in a vapor degreasing operation. Furthermore, if the coating becomes loose and entraps processing solution, the solution may bleed out and drip on the workpieces, causing staining or spotting.

5.0 Coloring and Sealing of Anodized Coating

5.1 Coloring Anodic Coating

In addition to so-called integral-color anodic coatings, where the color results from the metallurgical characteristics of the aluminum alloy are specially developed anodizing procedures, most aluminum alloys can be anodized in general purpose electrolytes and subsequently colored. Porous-type anodic coatings can be colored with organic dyes, certain inorganic pigments, and electrolytically deposited metals.

5.1.1 Organic dyes

The actual process of dyeing the aluminum oxide film is very simple. A water solution of 0.025 to 1.0% of organic dyestuff at a temperature of 65°C composes the dyebath. The aluminum, previously anodized is simply immersed in this bath for a short period of time usually ten minutes. The work is then sealed and is resistant to further dyeing or staining.

Rinsing after anodizing, followed by immediate dyeing, is of prime importance, Since some dyes will not dye aluminum in the presence of sulfate ion, poor rinsing can cause streaks and discolorations. Even in the case of dyes not affected by sulfates, any carry over of acid causes a lowering of the pH of the dyebath which means shade variations in succeeding batches of work. In the design of parts to be color anodized, care must be taken to avoid the use of closed heads or seams which are impossible to rinse. In the case of parts containing recesses which are difficult to rinse, a neutralizing bath of sodium bicarbonate is of value. In working with coated racks, care must be taken that the rack coating does not separate, thereby forming pockets that can entrap sulfuric acid, later allowing it to seep out into the dyebath. Work must not be allowed to stand in the rinse tanks between anodizing and dyeing, but should be dyed immediately, following a

thorough rinsing. For most effective rinsing three tanks should be used. In this way the final tank will remain relatively free of acid.

5.1.2 Electrolytic Deposition

After anodizing in sulfuric acid, metals can be electrolytically deposited in the oxide pores to achieve shades of gray, bronze, gold, black, and red, Proprietary processes have been developed based on coloring electrolytes containing nickel, cobalt, tin, selenium, tellurium, vanadium, cadmium, copper, iron, magnesium, lead, and calcium although those employing nickel, tin or cobalt are of greatest commercial significance. Essentially, the technology of electrolytically depositing metal into the oxide coating can be likened to electroplating. Many colored anodic coating of this type have good resistance to hear and fading and have been exploited primary for architectural applications

5.2.0 Sealing Anodic Coatings

The utility and performance of anodic coatings on aluminum often depend upon the type and quality of post anodizing treatment employed. The term sealing generally denotes a treatment which renders the coating nonabsorptive or introduces into the coating a material that enhances or modifies the characteristics of the anodic coating. Sealing usually involves subjecting the anodic coating to a hot aqneous environment which causes hydration of the coating. With certain aqueous solutions, components of the sealant are absorbed by the coating. Other solutions permit precipitation of materials into the coating by hydrolysis of specific metal compound.

The process of sealing involves a dissolution of oxide and repreciption of voluminous hydroxide inside the pore. Prolonged sealiug causes aging and densification of the precipitate.

Some aqueous sealants contain metal salts, the oxide or hydroxide of which may be coprecipited with the aluminum hydroxide. With such sealants, benefits results from this reaction as well as from the hydration. Sodium dichromate sealants are useful because they combine the attributes of hydration with the corrosion inhibiting characteristics of chromate ions.

The resistance of anodic coatings to staining and corrosion depends upon the absorptivity of the coating. Therefore, sealing treatments usually are employed immediately after anodizing. Improperly sealed coatings can account for pitting attack, color change, and mottling. Highest dielectric values also require sealing of the coating.

Choice of sealant depends upon the kind of environment to which the anodic coating will be subjected and any special performance requirements. Also to be considered are any postsealing surface treatments, e.g.. painting or adhesive objectives, and it is practical to employ a dual sealing treatment in order to capitalize on the peculiar advantages of each.

5.3 Water

The most widely used sealant employs water, although only high-quality water is effective. Distilled or deionized boiling water--low in solid and free of phosphates, silicates, fluorides, and chlorides--is required. Mixed-bed ion-exchange systems or a two -column type charged with a strong-base anion and a strong acid cation exchange resin are satisfactory for furnishing sealing water. In some finishing lines, continuous ion exchange of the sealing water is used to remove deleterious ions dragged in by rack or anodized items.

The presence of trace amounts of phosphates and silicates significantly retards hydration of the coating. Chlorides and fluorides also will prevent adequate sealing and even cause pitting attack of the anodic coating.

Sealing temperature is important and should be 98-100^{O}C; lower temperatures require much longer sealing times. The time required for formation of boehmite approaches infinity at temperatures below about 65^{O}C.

To preclude undue attack of the coating and to permit proper hydration, the sealing water should be maintained at a pH of 5.5 to 6.5. Buffers, such as sodium acetate, are sometimes used to facilitate pH control.

Sealing time should not be shorter than 10 minutes for thin (2.5 _m) oxite film and can be as long as 60 min for thicker (25 _m) coating. Extension of sealing time ensures more complete hydration, but longer times do not entirely compensate for poor control of other sealing variables, such as temperature, pH, and water purity.

Surfactants and dispersing agents may be added to the water to minimize the formation of a powdery smudge on the work. Care must be exercised that they are of the type that does not adversely affect the adhesion of paints or other applied coatings used subsequently. Phosphates also are effective for mininizing smudge, but they retard hydration significantly.

A variation of water sealing is steam sealing. The prime advantage of this technique is that contaminant-free moisture is ensured. The major disadvantage is that equipment costs are much higher than for tank sealing using boiling water. Compared with conventional water- sealing methods, equivalent sealing is claimed to be faster with steam, the sealing rate increasing with increasing steam temperature.

5.3.3 Vapor Techniques

Anodic coatings may be impregnated with certain organic materials in the vapor phase. The sealing materials is placed in a closed container with the anodic coating and heated to temperatures ranging from 93 to 260_. In the case of certain resin-forming substances the monomer is vaporized, adsorbed by the coating, and polymerized, thus forming a solid resin in the pores.

Wax like materials can also be applied by vapor phase treatments, Stearic acid carbowax and paraffin are examples of materials which can be vaporized. When such materials condense, the pores of the anodic coating are plugged with the solid materials. Vapor sealing is not important commercially, primarily because of the rather cumbersome procedures involved. Its prime utility would be for applications where aqueous sealing systems or hydrated anodic coatings might be undesirable.

EXPERIMENTAL

6.0 Introduction

Two general types of anodic coatings on aluminium and aluminium alloys are produced, decorative and hardcoating. The present study has been carried out on hard anodic coating which are specified for engineering purposes. They are produced with lower solvent action of the electrolyte on the sample. The following is a general description of the processing steps utilised for producing hard anodic coating on aluminium.

6.1 Raw Materials

Commercially pure aluminium collected from the local market was used in this investigation.

6.2 Preparation of Specimen for Anodizing

The specimens used in these experiment were sheared from sheets to dimensions 30mm x 20mm x 2.5mm. The specimens were then polished and buffed by bringing the work in contact with wheels of different size revolving at 1400 and 2800 rpm. During polishing and buffing proprietory chemical compound called lusture and hyfin were used successively to bring brightness upon the specimens. Polishing and buffing wheel were bonded with abrassive of different mesh number (90, 180, 270) by glue. For each sample, three to four polishing wheels having different mesh number abrassive and one to two cloth buffing wheels were used. At the begining of polishing operation, course grain abrassive bonded wheels were used and towards the end of polishing operation fine grain abrassive bonded wheels were used. During buffing soft cloth wheel was used. After buffing the samples were electro-polished in a solution whose compositions and operating conditions have been given in Table 3. Then the samples were washed thoroughly in

running water and final washing was done in distilled water from where the specimens were dipped in concentrated nitric acid to remove smut and rinsed in distilled water and was dried by using a hot air blower.

6.3 Anodizing Set-up

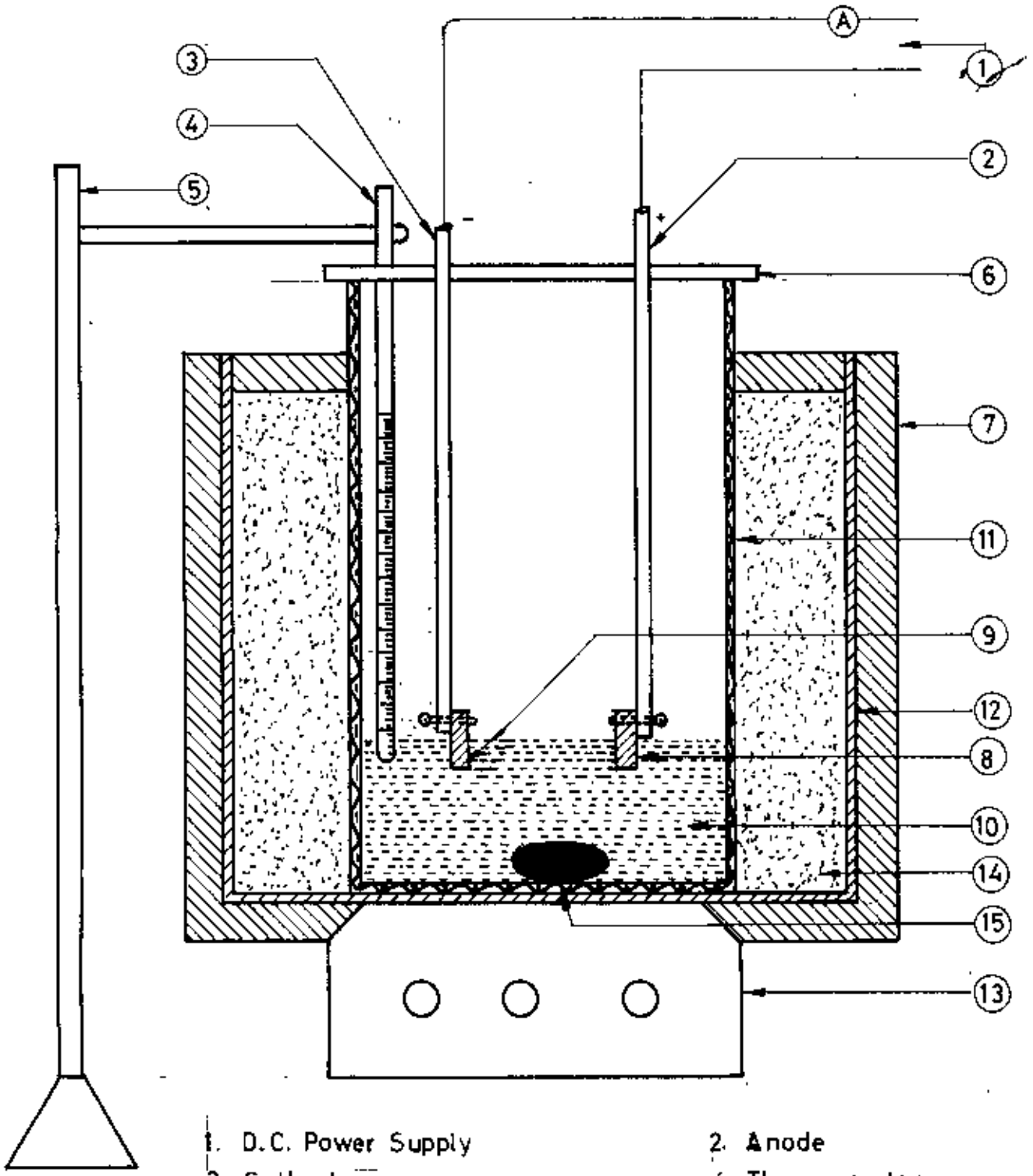
Anodizing was carried out in a laboratory type anodizing set-up consisting of a breaker, a DC power supply, a thermometer, a magnetic stirrer, a container made of plastic sheet covered with polistyrene foam, a burette stand and perspex holder.

The breaker was placed within the polistyrene container which was filled with ice and water to reduce the temperature of the electrolyte. To maintain constant temperature the quantity of ice in the container was varied manually. The container was placed upon a magnetic stirrer so as to be able to agitate the electrolyte automatically. Anode and cathode were connected to D.C. power supply via a miliammeter through a perspex holder. The X-section of the set-up has been shown in fig. 1.

6.4 Anodizing Operation

To prepare the anodizing solution the beaker was filled to approximately two-thirds of its marking point with clean deionized water and the necessary volume of sulfuric acid was added very slowly while the solution was agitated. After the addition of acid, the solution was diluted with water to the working level.

All the accessories were then set-up and the power supply of magnetic stirrer was switched on to homogenise the temperature of the bath. Required amount of ice was supplied into container to get the desired temperature. The prepared samples were then weighted carefully in a digital balance (precision _ 0.1mg) and connected as the anode side and a stainless steel block as the cathode. A



1. D.C. Power Supply
2. Anode
3. Cathode
4. Thermometer
5. Stand
6. Perspex holder
7. Plasticized foam
8. Job
9. Stainless steel cathode
10. Electrolyte
11. Beaker
12. Plastic sheet container
13. Magnetic Stirrer
14. Cold water
15. Magnet

FIG. 2 ANODIZING UNIT

milliameterto measure specified current was also placed in the circuit. The power supply was then switched on and the voltage was gradually increased to get the required current. At the end of anodizing for a predetermined time period e.g. 20, 40, 60 min etc. at desired temperature, the power supply was switched off and the workpiece was taken out. The same procedure was followed for anodizing at different time, temperature and electrolyte concentration.

6.4.1 Rinsing

After anodizing the specimens were thoroughly swilled in clean cold water to remove surplus electrolyte. After swilling the specimens were dried and stored in a desicator for further investigation.

6.4.2 Sealing

After swilling some of the samples were transferred without delay to deionized water heated to a constant temperature of 98^{0}C. The specimens were kept immersed in the hot water bath for two hours. At the end of this time period the specimen was withdrawn, dried and stored in a desicator for further investigation.

6.4.3 Dying and Sealing

After anodizing and thorough cold-water rinsing some of the specimens were immersed in a heated (65^{0}C) aqueous solution containing 2 g per litre of proprietory pigment to perform dying. Immersion time was 10 mins. After dying, parts were rinsed in cold water and sealed by immersing the sample in heated (98^{0}C) deionized water for 2 hours. At the end of this period the samples were withdrawn and stored in a desiccator. It is to be noted that in the present study only two specimens were dyed and sealed only to exhibit the colour of anodizing.

6.4.4 Operating Conditions

The applied voltage was adjusted to produce a current density of 12.91 mA/sq cm. Same current density was used for all the samples anodized. The electrolyte concentration was set at 5%, 10%, 15%, 20% and 25% sulfuric acid (by wt). Temperature of the bath was $5^{o}C$, $10^{o}C$, $15^{o}C$, $20^{o}C$ and $25^{o}C$. Anodizing time was 20, 40, 60 and 80 minutes. The solution was agitated to homogenous temperature by using magnetic stirrer and to maintain the temperature of the bath ice was supplied to the water outside of the beaker.

6.5 Methods of Investigation

6.5.1 Introduction

For the determination of chemical, physical or mechanical properties of anodized layer several test like magnetic method, eddy current, weight gain measurements, X-ray diffraction, hardness measurement, resistance measurement, metallography, Beta Back scatter, salt spray etc. are made in the course of fundamental research[10] or for control purposes in development or production. But in the present study only the following testing methods have been investigated (because only these facilities were available).

6.5.2 Weight Gain Measurement

After anodizing the increasing weight of the samples was determined by weighing the samples in a digital balance (precision 0.1mg).

6.5.3. Microhardness Measurement

Microhardness values were determined by using Shimadzu Microhardness Tester (Model 80380) Microhardness measurements were carried out using a 50 g load for 5 s. on polished pure aluminium specimen. Microhardness of different anodized samples were also measured by using 50 g load for 5 s.

6.5.4 Resistance Measurement

Resistance developed in anodized samples were determined in the High Voltage Laboratory, in the Department of Electrical & Electronic Engineering, BUET with the help of a voltmeter placed parallel and an ammeter placed in series in the circuit. A 2-kiloohm resistance was also placed in series in the circuit. (Fig. 2) Resistance developed in the anodized samples were calculated by using Ohm's law.

6.5.5 Metallography

The anodized specimens were then cut-off at right angles to the anodized surface and one piece was then mounted in thermosetting resin in such a way that only the transverse section was revealed. The specimens were then prepared for microscopic examination by using standard techniques to observe the microstructure of anodized layer.

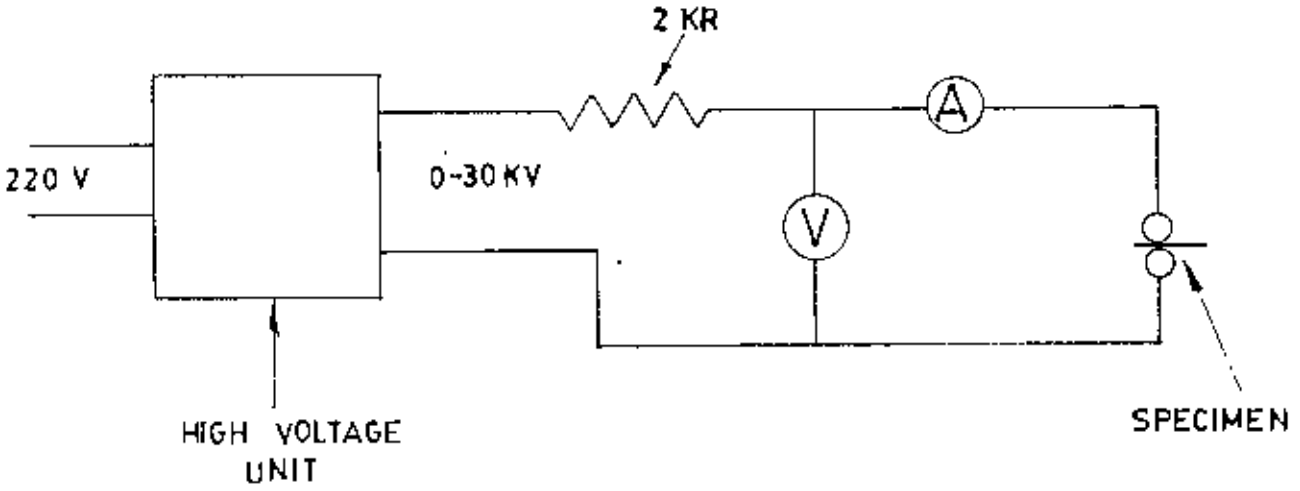


FIG.-3 CIRCUIT DIAGRAM.

7. RESULTS AND DISCUSSIONS

7.1. Introduction

In the present investigation of anodizing of aluminium has been carried out in sulfuric acid electrolyte at different concentrations, for different time and at different temperatures. The results of these experiments have been analyzed in terms of weight gain, microstructure, surface hardness and resistance developed.

7.2 Weight Gain

In weight gain determination three parameters were studied keeping two parameters constant and changing one parameter. Three parameters are as follows.

7.2.1 Effect of Time

In each of the following cases the pieces were anodized for 20, 40, 60 and 80 minutes and the weight gain was determined.

1. At a constant temperature of 25°C and a constant electrolyte concentration of 10% H_2SO_4 (by weight).
2. At constant temperature 20°C and a constant electrolyte concentration of 10% H_2SO_4 (by weight).
3. At constant temperature 20°C and a constant electrolyte concentration of 15%, H_2SO_4 (by weight).

Figs. 4, 5 and 6 are the graphical representation of the results of weight gain measured with respect to time in the cases of 1, 2 and 3 (mentioned above) successively. From these figures it may be observed that the weight of the anodized layer increases with respect to time. It is also observed that initial weight gain is more and at the end of a certain period rate of weight gain decreases. This is because at the starting period the whole surface of the aluminium sample is available for anodizing. As a result the rate of formation of aluminium oxide is more than at the end of certain period when the formation of anodized layer takes place by diffusion of aluminium and oxygen outwards and inward respectively.

Fig. 7 shows that the weight gain at $20^{o}C$ is more than the weight gain at $25^{o}C$, at a constant electrolyte concentration of 10% sulfuric acid (by wt). This is because at higher temperatures the rate of dissolution of anodized layer is more as compared to the rate at lower temperature. As a result at higher temperatures rate of formation of anodized layer is reduced.

The weight gain with respect to time is more at 10% sulfuric acid electrolyte concentration than weight gain at 15% sulfuric acid electrolyte concentrations (Fig. 8). This is because like higher temperatures, the rate of dissolution of the anodized layer is higher at higher electrylyte concentrations.

7.2.2 Effect of Temperature

The specimens anodized at temperatures of $5^{o}C$, $10^{o}C$, $15^{o}C$, $20^{o}C$ and $25^{o}C$ were studied to determine weight gain at a constant time of 40 min and a electrolyte concentration of 10% H_2SO_4 (by weight). The results are given in Fig. 9. From Fig. 9 it may be observed that before sealing, weight gain decreases with an increase in temperature and the weight gradually becomes approximately constant. But after sealing weight increases continuously with increasing temperature. This is because anodized layer formed at higher temperature goes into solution

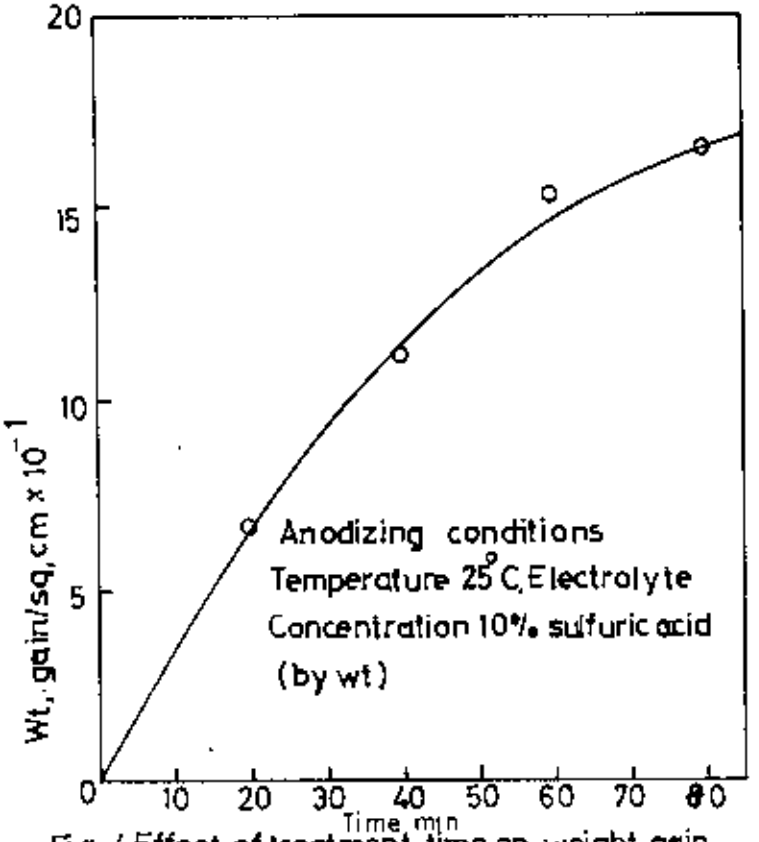


Fig 4,Effect of treatment time on weight gain

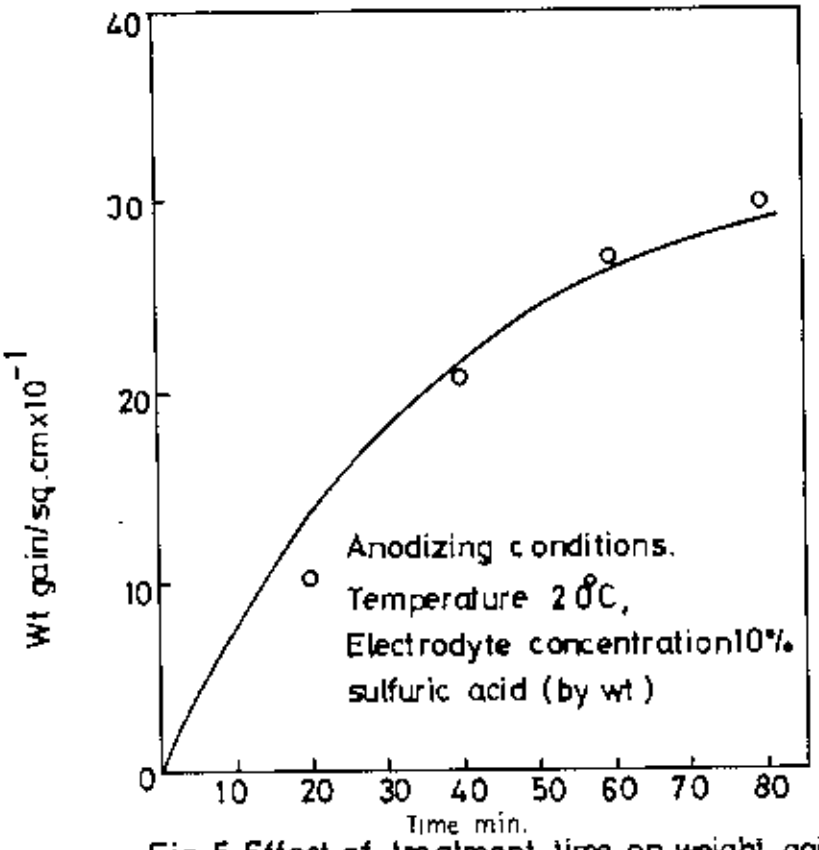


Fig. 5 Effect of treatment time on weight gain

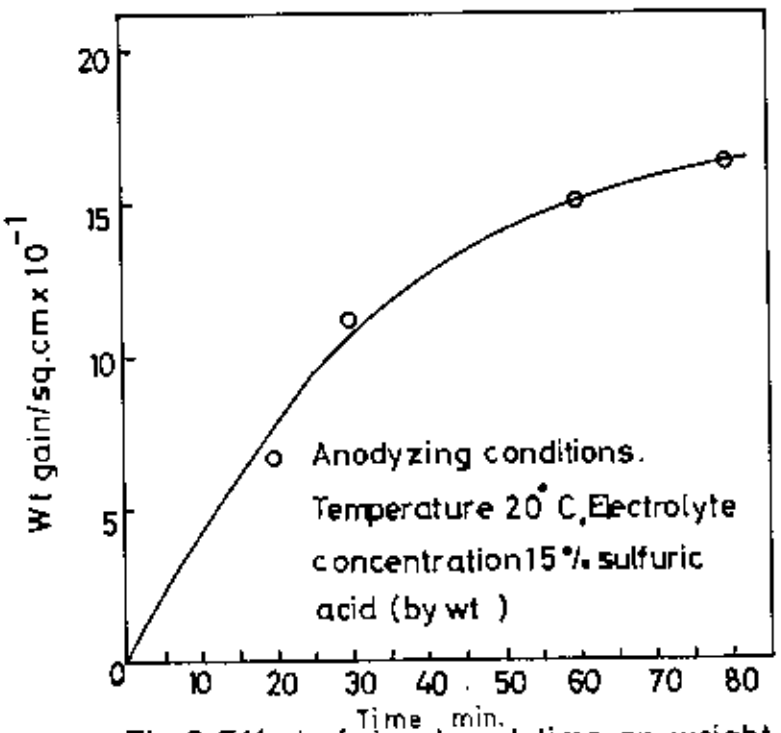


Fig.6. Effect of treatment time on weight gain

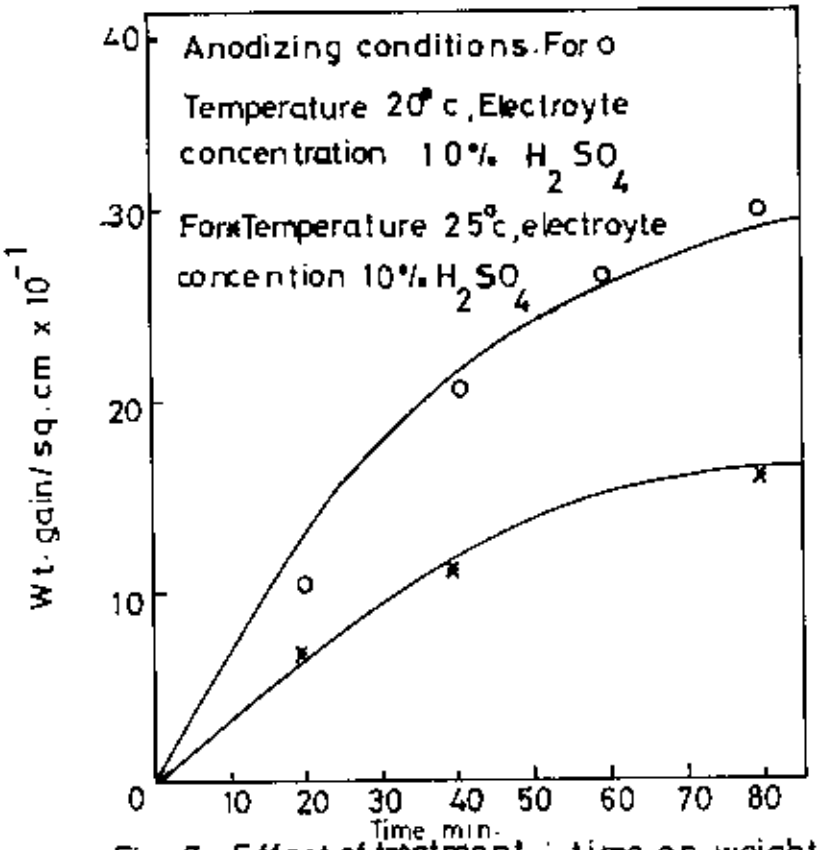
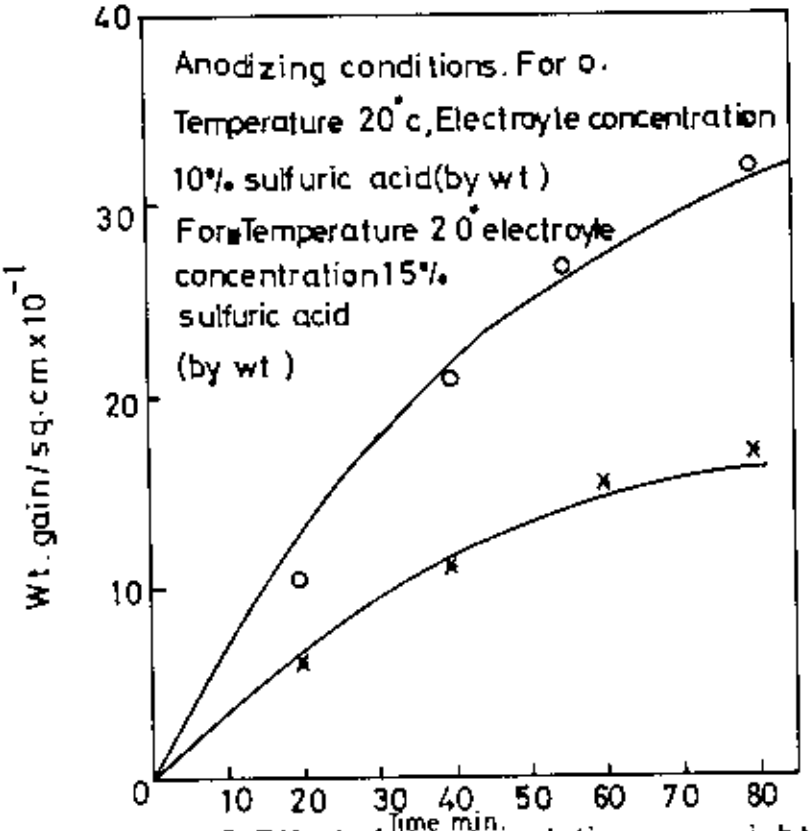


Fig. 7 Effect of treatment time on weight gain



Fig·8·Effect of treatment time on weight gain

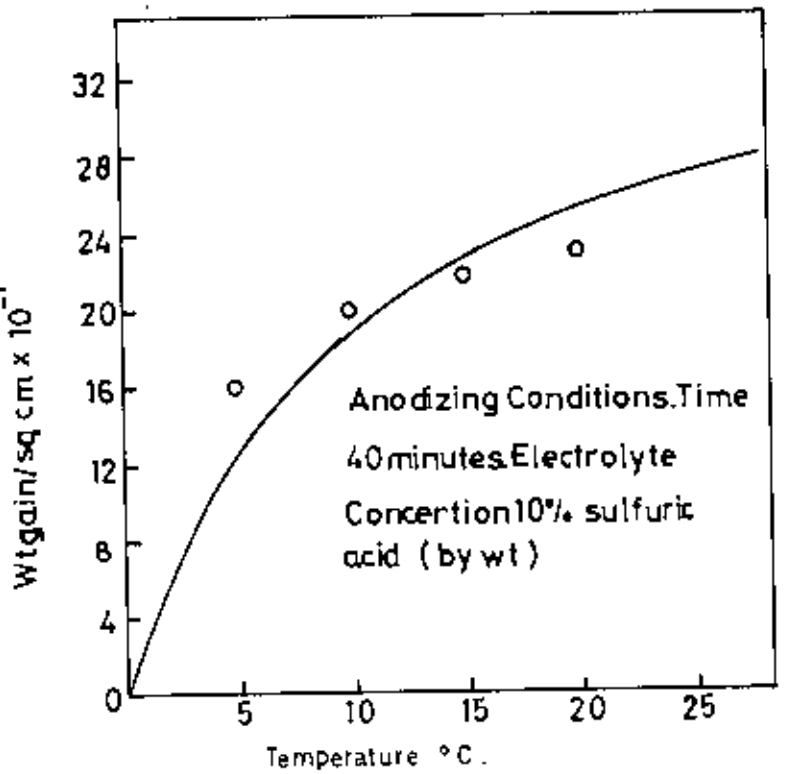


Fig-9 Effect of temperature on weight gain

quickly at higher temperature than at lower temperature. So the trend of the curve is down-ward. On the other hand, the size of the pores formed in the anodized layer increases with increasing temperature. During the sealing operation pores formed in the anodized layer is precipitated with passive bohmite ($Al_2O_3.H_2O$) in the pores and effectively seals and passivates them. For this reason in the case of sealing, with increasing temperature weight gain increases. But at lower temperature the size of pores are small. So after sealing weight gain is less compared to higher temperature anodizing.

7.2.3 Effect of Electrolyte Concentration

Effect of anodizing at electrolyte concentrations of 5%, 10%, 15%, 20% and 25% H_2SO_4 (by weight) were investigated at a constant temperature of 20°C and for a time of 40 minutes to determine the weight gain. Results obtained are graphically represented in Fig. 10. From Fig. 10 it may be observed that at lower electrolyte concentration the weight gain is more and at higher temperature weight gain is less. This is because the rate of dissolution of the anodized layer increases with increasing electrolyte concentration and vise versa.

7.3 Hardness Measurement

Hardness values obtained on samples anodized at 10% H_2SO_4 (by weight) electrolyte concentration for a period of 40 minutes at different temperature has been represented graphically in Fig. 11. From Fig. 11 it may be observed that hardness on samples anodized at lower temperature is more than on those anodized at higher temperatures. At lower temperature grain size of the anodized layer is small. As a result grain compactness is more and nonporous oxide layer is produced and due to this the hardness increases. But at higher temperatures grain size of anodized layer is more and more porous layers are produced. After sealing, these layers are converted into passive boehmite ($Al_2O_3.H_2O$) which is less hard than nonporous layers. So the hardness of the

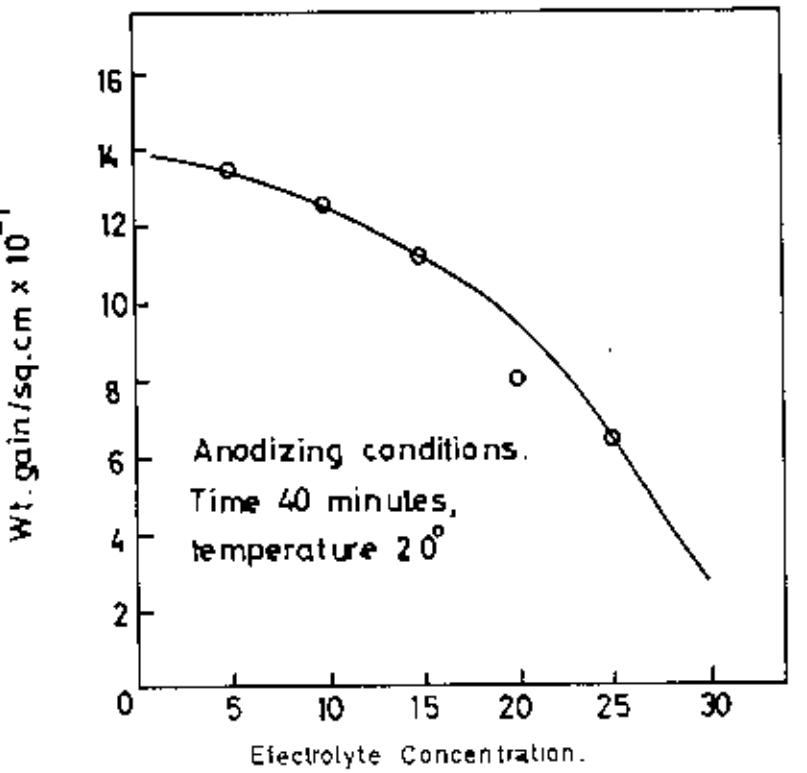


Fig.10 Effect of electrolyte concentration on weight gain.

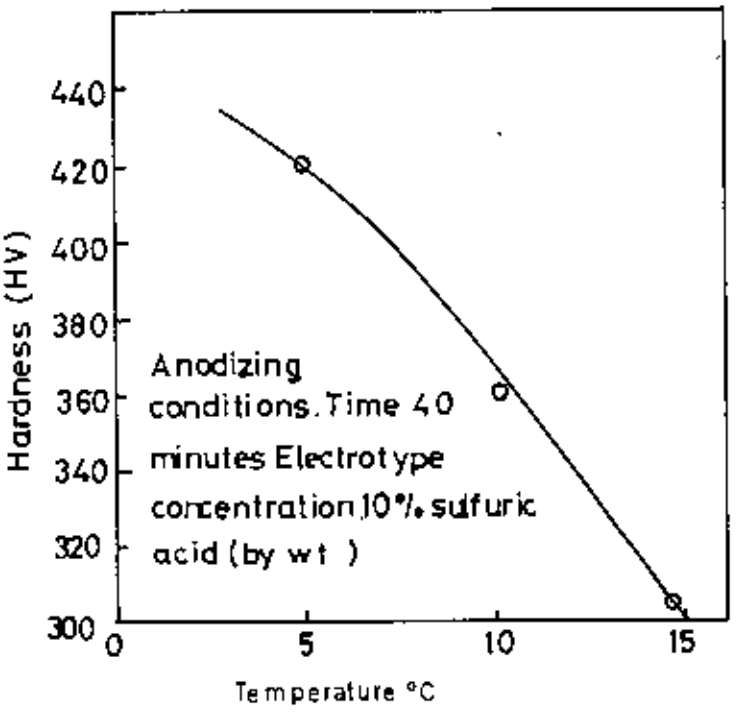


Fig.11-Effect of treatment tempera ture on surface hardness of unanodized sample

anodized layer formed by anodizing at higher temperatures is less as compared to the anodized layer formed at lower temperatures.

7.4 Resistance Measurement

The results of resistance measurements on samples anodized at 5^0, 10^0, 15^0 and 20^0C at a electrolyte concentration of 10% H_2SO_4 (by weight) and for a period of 40 minutes have been graphically represented in Fig. 12. From this figure it may be observed that resistance developed on samples anodized at lower temperature is more and the resistance developed at higher temperature is less. This is because at lower temperature the rate of attack of the oxide layer by the electrolyte is less leading to the formation of a nonporous oxide layer whose resistance is more. On the other hand, the rate of attack of the oxide layer increases with increasing temperature and a porous oxide layer is produced whose resistance is less. It is known that aluminium oxide layer acts as an insulator. Hence the nonporous oxide layer produced at lower temperature is a good insulator and this formation of nonporous films have led to a wide application in the industrial field of electrolytic capacitors and rectifiers.

7.5 Microstructure

Microstructure of anodized layers formed during anodizing at 5^0C in 10% H_2SO_4 (by weight) electrolyte for a period of 40 minutes has been shown in Fig. 13(a). From this figure it may be observed that the anodized layer is very thin and nonporous and size of the grain is also very fine. At lower temperatures dissolution rate of aluminium oxide is very slow and diffusion rate of aluminium and oxygen is also slow. As a result, the anodized layer produced during anodizing under these conditions is nonporous and thin.

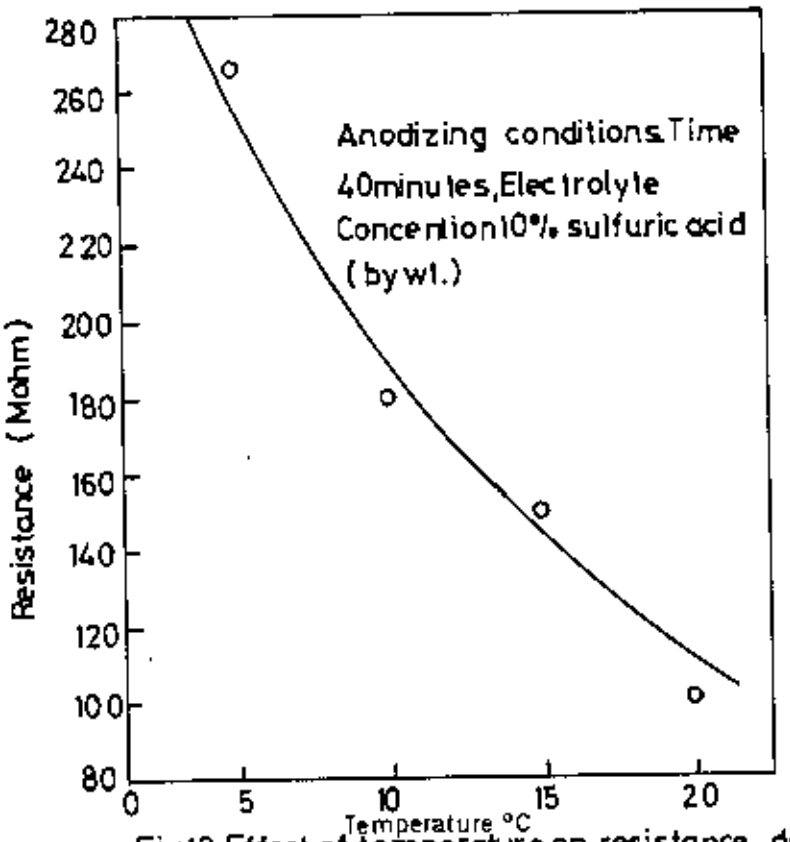


Fig.12. Effect of temperature on resistance developed

Microstructure of anodized layers formed during anodizing at 15°C using in 10% H_2SO_4 (by weight) electrolyte for a period of 40 minutes has been shown in Fig. 13(b). From this figure it may be observed that the anodized layer is thin and it contains a nonporous oxide layer adjacent to the sample surface and a porous oxide layer at the outer part of the sample. Because at this mentioned temperature at the end of certain interval dissolution takes place due to heat developed between oxide.

Microstructure obtained after anodizing at 20°C in 10% H_2SO_4 (by weight) electrolyte for a period of 40 minutes has been shown in Fig. 13(c). It may be observed that it contains nonporous oxide layer adjacent of the sample surface and porous oxide layer at the outer part of the sample. Here the size of the porous grain is coarse. At higher temperature the diffusion rate increases and reason is same mentioned in 13(b) and the dissolution rate also increases due to heat generation between oxide layers. As a result the size of the pores produced increase which are hydrated to produce hydrated aluminium oxide ($Al_2O_3.H_2O$) during sealing.

Fig. 13(a)

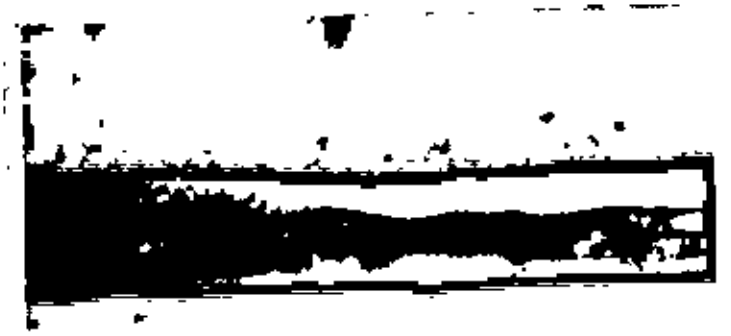


Fig. 13(b)

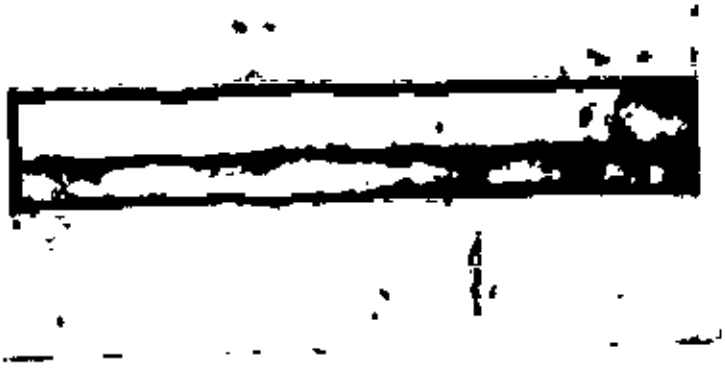


Fig. 13(c)

Microstructure of Anodized Layer at

13(a) temperature 5°C, Electrolyte Concentration 10% H_2SO_4 (by wt), time 40 minutes.
13(b) temperature 15°C, Electrolyte Concentration 10% H_2SO_4 (by wt), time 40 minutes.
13(c) temperature 20°C, Electrolyte Concentration 10% H_2SO_4 (by wt), time 40 minutes.

CONCLUSIONS

The following conclusions can be drawn fron the results of this study.

1. Coating thickness increases with the time of anodic oxidation upto a certain limit.

2. Coating thickness increases with decreasing temperature and concentration of the electrolyte.

3. More porous coating is produced with high temperature and concentrated electrolyte.

4. More abrasive layer is produced with dilute electrolyte and lower temperature and longer time of treatment.

5. Sealing time decrease with increase sealant temperature.

6. Impervious layer is produced with sealing at longer time.

SUGGESTION FOR FUTURE WORKS

Electrolytes most commonly used in applying anodic coatings include sulfuric acid, chromic acid, oxalic acid and mixtures of sulfuric and oxalic acids. These electrolytes are most commonly used for aluminium and magnesium and their alloys. There are many factors which include solution concentration, solution temperature, time, applied current density, material compositions affect anodizing. Anodic coating on aluminium in sulfuric acid electropyte at varying temperature, time and acid concentrations have only been studied in this case. Studies on aluminium and magensium alloys can be undertaken to investigate the effects of factors mentioned above. Effect of alloying elements and coatings on properties such as fatigue, corrosion resistance, electrical resistance, abrasion resistance and subsequent plating can be studied. Finally, an overall comparative study among the processes and factors can be studied.

APPENDICES

Table-6: Wt. gain as a function of time at temperature 25°C and electrolyte concentration 10% sulfuric acid by weight.

Sample No.	wt of sample before anodizing gm	wt of sample after anodizing gm	Difference in wt. mg	wt gain/sq. cm mg x 10^{-1}	Time, min.
1	12.52471	12.53311	8.40	6.70	20
2	11.94562	11.95962	14.00	11.16	40
3	12.45861	12.47761	19.00	15.15	60
4	12.45769	12.47819	20.50	16.35	80

Table-7: Wt. Gain as a Function of Time at Temperature 20°C and Electrolyte Concentration 10% Sulfuric Acid (by Volume).

Sample No.	wt of samle before anodizing gm	wt of sample after anodizing gm	Difference in wt mg	wt gain/sq. cm mg x 10^{1}	Time min.
1	12.63367	12.64217	8.50	6.78	20
2	12.63467	12.65187	17.20	13.71	40
3	12.58346	12.60986	26.40	21.05	60
4	12.71125	12.74755	36.30	28.95	80

Table-8: Wt. Gain is a Function of Time at temperature 20°C and Electrolyte Concentration 15% Sulfuric Acid (wt.)

Sample No.	wt of sample before anodizing gm	wt of sample after anodizing gm	Difference in wt mg	Wt. gain/cm^2 mg x 10^{-1}	Time min.
1	12.79842	12.80562	7.2	5.75	20
2	12.89472	12.90672	12	9.56	40
3	12.68978	12.70898	19 2	12.2	60
4	12.69875	12.72425	25.5	13.16	80

Table-9: Wt. Gain/Loss is a Function of Temperature at Time 40 Minutes and Electrolyte Concentration 10% Sulfuric Acid (by wt) at Time 40 Minutes.

Sample No.	wt of sample before anodizing gm	wt of sample after anodizing but before sealing gm	Difference wt in before sealing mg	Wt. of gain/cm² mg x 10^{-1}	Wt. of sample after sealing gm	wt of sample after sealing	Wt. gain/cm² mg x 10^{-1}	Temperature °C
1	12.89421	12.91521	21	16	12.91721	23	16	5
2	12.74734	12.76734	20	15	12.77234	25	20	10
3	13.75912	13.77812	19	13.5	13.78712	28	22	15
4	12.63467	12.65187	17	12.4	12.66467	30	23	20
5	11.94562	11.95962	14	10.20	11.99062	35	27	25

Table-11: Hardness is a Inverse Function of Temperature at Electrolyte Concentration 10% H_2SO_4 (by wt) and Time 40 Minutes.

Sample No.	Diagonal distance on unanodized aluminium surface µm	Diagonal distance on anodizing surface µm	Hardness of unanodized aluminium surface HV	Hardness of anodized aluminium surface HV	Temperature °C
1	49	12.3		613.0	5
2	49	12.8	77.23	566.0	10
3	49	14.5		441.0	15

Table-12: Resistance is a Inverse Function of Temperature at Electrolyte concentration (10% H_2SO_4) and Time (40 min.)

Sample No.	Temperature °C	Resistance MΩ
1	5	266
2	10	180
3	15	150
4	20	100

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