

Electrochemical Technology in Pollution Control

Dr. J. R. Mudakavi

Department of Chemical Engineering

Indian Institute of Science, Bangalore

Lecture – 28

Electroplating 1

Greetings to you, we will continue our discussion on the Electrochemical Technology for Pollution Monitoring. And, now I would like to concentrate on Electroplating Wastes, but before starting the electroplating wastes, I would like to talk to you about electroplating, because the electroplating is that branch of sort of chemical technology you can say, it has got chemistry in that, it has got a engineering in that, it has got metallurgy and several other aspects of there involved in electroplating.

So, electroplating wastes in general constitute one of the biggest challenges to our society nowadays, but without electroplating it is almost impossible to survive. So, electroplating basically involves the modification of the surface properties of the metals and plastics also nowadays. In electroplating apart from plastics, we also work on metals such as aluminum, there that those processes are known as aluminum anodization, and sometimes we work on processes called as passivation, and then electro deposition all are related to electrochemical technology only.

But, there will be some slight amount of differences in the procedure, for getting the good quality finish, for functional as well as aesthetic purposes of the metal components, quite often we require bearings and we require nice looking machinery, nice looking metals, nice looking cars, nice looking scooters etcetera. All of them require certain amount of metal finishing or surface finishing as it is called quite often we want specific properties for the metals to function metal parts. And, those properties are imparted using metal plating, that is the electroplating electro deposition all those processes.

So, let us learn a little bit about electroplating afterwards I will talk to you about electro chemical wastes, which can how it can be handled and all those things we can learn.

(Refer Slide Time: 03:37).

Metal finishing comprises of five General categories: electroplating (electrodeposition, electroless deposition and mechanical methods), anodizing and nonmetallic coatings.

These are ancillary industries to all the other processes which include mechanical and chemical cleaning, process control, plant engineering, safety and waste treatment.

So, let us start our today's lecture with electroplating. What is the electroplating? Electroplating is a metal finishing operation and metal finishing comprises of 5 general categories, they include electroplating. There are three considerations here, electro deposition, electro less deposition and mechanical methods.

Then, two non-processes, two related processes, that is anodizing and non-metallic coatings. Usually, we expect electroplating to comprise all other processes, where electricity is used to modify the surface properties of all the metals. So, basically these are all ancillary industries to all other processes and other industries. For example, if you want to make a reactor in a chemical engineering industry the reactor should have certain properties is not it.

The properties what we expect from a reactor in a chemical engineering is we want it to be non-corrosive, it should not break down during the operation, it must withstand higher

pressure, higher temperature etcetera. Sometimes, we use metal earth moving equipment's at that time the desirable properties of the machinery would be strength of the tools.

So, we want hard chromium coating at that time or steel. Even in steels there are several thousand varieties of steel, which are nothing, but alloys and stainless steel is one of them, normal steel is another of them, and what we use for our railway trains wheels and the girders, bridges, they all have different specifications of mechanical strength, which cannot be imparted directly from the alloy combinations. Sometimes, the properties need to be exactly on the surface of the property. So, that specific functions can be handled.

For example, in 99 percent of the proper cases, we want most of the metals to be non-corrosive. Sometimes, we want finish which is very smooth and reflective. Sometimes, we do not want reflective coatings. So, like that there are different kinds of requirements on different metals, gold and silver are extensively used for ornamental coatings. So, you make any coating any jewelry with brass or copper or silver and then coat them with gold that would be wonderful this thing.

Nowadays, such things are available in the market 1 gram gold and other ornaments they are available very cheap not so, costly like original gold and it will serve the purpose for the time being and requirements are enormous. So, sometimes we want the metals to perform in harsh conditions such as sea water and ships, under sea water under sea water it must be functioning without corrosion and other related properties.

So, electro finishing is a sort of ancillary industry to all other industries most of them anyway, which include mechanical and chemical cleaning process control sometimes and then plant engineering, that is involved. And, associated with the metal finishing because it requires some certain amount of electricity and other things, there requirement is safety aspects need to be looked into. And, the waste treatment that is associated with most of the electrochemical properties, industries, properties processes and all those things are involved.

(Refer Slide Time: 08:55)

Quite often metals are unsuitable for a variety of applications in the form in which they are produced. Steels, raw aluminum or copper, are susceptible to corrosion or breakage or mechanical and chemical deformation. In order to convert them into specific components for long term usage with enhanced characteristics metal finishing is required.

So, quite often metals are unsuitable for a variety of applications in the form in which they are produced. For example, copper when it is produced it is known as blister copper, that is done by Bessemer process and that cannot be used as such, because it will have blisters all around the in the metal just like moon surface. So, not possible to use them directly, steels there are different kinds of steels that are produced I have already talked a little about it.

Then, raw aluminum we cannot use, because raw aluminum is very soft and raw copper they are all susceptible to corrosion, or they can break on mechanical and chemical deformation. It is quite often they do not have the strength, desired strength.

So, under mechanical pressure or chemical attack many metals do not survive the requirements and sometimes they dissolve, sometimes they corrode, sometimes there will be attack on the metal leading to formation of holes. And, there will be leakage and several other

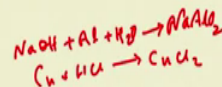
related properties are associated with pure metals. Obviously, we cannot use pure metals for many of the applications straightaway anyway. So, in order to convert them into specific components for long term usage that is with enhanced characteristics we need the metal finishing.

(Refer Slide Time: 10:55)

Metal preparation

Before metal finishing, the metal parts must be cleaned of the soils and contaminants. Cleaning is critical. Cleaning affects adhesion, appearance, composition and corrosion resistance of the final deposit. Each basis metal requires a somewhat different pretreatment. For example Al cannot be cleaned with the same solution that is useful for steel and vice versa. Alloys present difficulties because cleaning solutions may attack alloying non-uniformly.

Example: Zn-Al alloys cannot be cleaned with single solution. while Al is cleaned zinc is dissolved.



So, before metal finishing, the metal must be metal parts must be cleaned of the soils and contaminants. Normally, there will be lot of time gap between a metal production and the subsequent usage. Suppose a metal is produced today it may be required for use after three months.

So, till the 3 months what you will do with the metal that is produced. You have to store it somewhere, how do you store it? The moment you store it in the atmosphere metal will start getting attacked by oxygen corrosion will start. Sometimes, there will be soil contamination

soil will be adhering to the metal when it is during storage, sometimes it may be contaminated. So, many things can happen before a metal is taken up for producing a component.

So, during that time metal is subject to lot of mechanical and chemical stresses. And, therefore, they become dirty, they become soiled, so to take care of these things before we make a metal part out of a metal, a cleaning process is required. So, all the soils and contaminants must be removed, from the metal surface and cleaning normally affects the adhesion, appearance, composition and corrosion resistance of the final deposit.

Because, cleaning has to be proper otherwise there will be always certain amount of the properties of the soiling will get carried into the final finish. So, each basis metal, basic metal requires a somewhat different treatment, we cannot have a uniform pretreatment for all the metals, that is not possible. For example, aluminium, what happens to aluminium? Aluminium cannot be cleaned with the same solution, that is useful for steel and vice versa, many of the metals we clean with sodium hydroxide.

Now, aluminium cannot be cleaned with sodium hydroxide at all. Because, sodium hydroxide will dissolve aluminium very simple reaction $\text{NaOH} + \text{Al}$ will give you NaAlO_2 . So, that will go into solution. So, it is a fairly simple I can write here $\text{NaOH} + \text{Al} + \text{H}_2\text{O}$ can go to NaAlO_2 . So, if you store aluminium or if you clean aluminium with sodium hydroxide, you will lose aluminium. Same thing is true with silver with steels, iron, copper. Copper, if I clean it with hydrochloric acid, then what happens, copper chloride will form and it will dissolve the copper.

So, steel for example, steel can be cleaned with a little with alumina with hydrochloric acid, iron can be cleaned, but all the metals cannot be cleaned with sodium hydroxide, they cannot be cleaned with hydrochloric acid etcetera etcetera. Some metals are attacked by the alkali; some metals are attacked by the acids. So, in such cases it is very difficult to adopt a universal method for cleaning all the metals.

Alloys present special difficulties because cleaning solutions may attack the alloying compounds non-uniformly. For example, you can alloys are what are alloys basically? Alloys are mixtures of metals, melted together and formed a cast into different types of shapes. So, just like zinc aluminum alloys, I have if I have zinc and aluminum. They cannot be cleaned with a single solution at all why, I cannot clean it with alkali because aluminium will react with alkali giving NaAlO_2 .

I cannot clean the alloy with acid also because acid will react with the zinc present in the zinc aluminium alloy. So, aluminium is cleaned and zinc will dissolve. So, the alloying properties will be lost. Same thing is true with most of the alloys, for example, aluminium magnesium same way, same problem, al mag your mag wheels you must have heard, for most of the car tyres the support metal is mag wheel, magnesium, aluminium, caster material, that holds the tyre together that cannot be cleaned using a single solution.

Same thing all because the same problem alloys cannot be cleaned, because the one while one metal may be clean the other metal may be dissolving. It is a very common problem with most of the cleaning processes. So, we also add to the cleaning solution something known as inhibitors. Inhibitors are extend the concentration of the acids and alkalis or make them in effect make them ineffective for attacking, for the attacking reaction.

(Refer Slide Time: 17:55)

Electroplating process

electroplating is a process in which metal ions migrate from positive to negative electrode. an electric current passing through the solution causes objects at the cathode to be coated by the metal in solution. the size, shape and weight of the objects being plated determine the quality of plating

So, after the we discuss that after our discussion, we can talk about electroplating processes. So, what is electroplating? Electroplating is a process in which metal ions migrate from positive to negative electrode. This we have already seen number of times while I have been teaching you electrochemistry. So, cations will go towards cathode, anions will go towards the anode. So, how does it happen? Because, we pass the electric current in a solution containing the electrolyte that material, which is to be deposited.

So, I need a cathode I need a anode. So, most of the time cathode is the material, which needs to be electro chemically treated. Surface modification and electroplating processes, in most of them the object to be cleaned is a cathode not the anode ok. So, the size, shape and weight of the objects being plated determine the quality of plating is not it. So, the cathode should be the same material that you wish to plate.

So, every time sometimes you may wish to plate a rod, sometimes you may wish to plate a surface, a circular piece, sometimes you may wish to plate a statue of a god with gold. So, the whole gods statue of should be made a cathode. So, that on the cathode god will be statue god will be coated with gold, the statue will be coated with the gold. So, the objects being plated the size shape and weight of the objects being plated determine the quality of plating.

Sometimes what happens now? Basically, we want to take a metal plate, which is very straight forward, which is a squarish material, then plating is very easy because I needed a need one more anode in between it can the ions can go and coat uniformly all over the cathode. Suppose, it is a statue, then statue will have hands, face, nose, eyes everywhere. So, it is not a single planar material that is to be coated. So, plating quality has to be different for statues compared to normal sym square plates, or circular plates, or rods etcetera.

(Refer Slide Time: 21:15)

Electroplating is done to protect, beautify, insulate or increase the corrosion resistance, conductivity, solderability etc. plating is carried out on iron or copper alloys, brass etc.

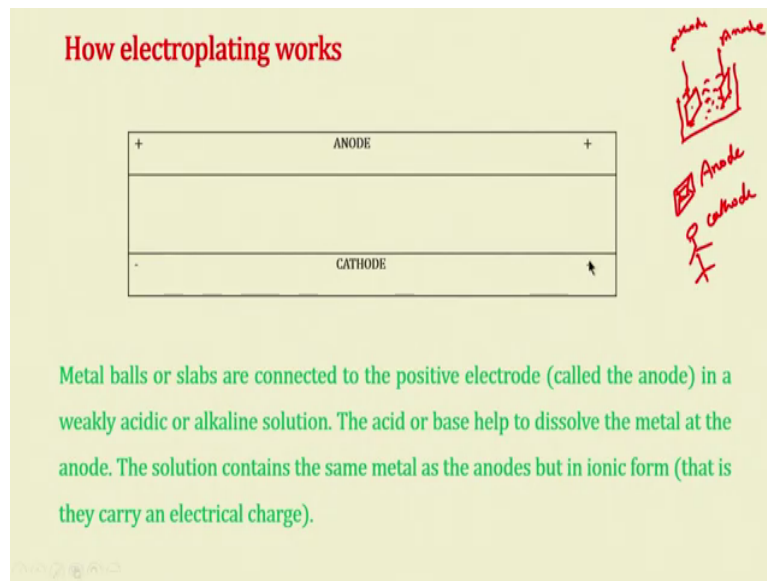
Cu, Ni, Cr, Zn etc provide mechanical protection. Cd and Zn provide sacrificial protection.

So, this is what I have been concentrating on. So, I tell the people that electroplating is basically done to protect to beautify, to insulate, or increase the corrosion resistance, I can increase the conductivity, make a substance which is non-conductive, into a conductive material, I can increase the solderability of the material etcetera.

So, electroplating is done for various purposes and plating is carried out on iron, copper, alloys, brass, aluminum, silver, titanium many other materials. What are the materials to be coated with what we want to coat on the base plate. Let us call the material to be coated as the base metal and the what we want to coat is the another material, that is we can coat materials with copper, I can coat with nickel, I can coat with chromium, zinc and many other metals I can coat.

I can coat titanium, cobalt, etcetera to give specific mechanical properties. And, they provide mechanical protection. To the base metal, we always talk of base metals and coating material. Cadmium and zinc, they provide sacrificial protection; that means, they may get damaged during the operation, but the basic baseplate will remain unharmed, unaffected. So, that is also one of the objectives of electroplating.

(Refer Slide Time: 23:14)



So, this is how the electroplating works? I have put a very simple schematic diagram. Here, I have put on the top one anode that is positively charged and that is the that takes the anions, and here I have put the cathode in between the 2, I have an electrolyte. I can use metal balls or slabs of metals, they I connect them to the positive electrode, that is called as anode. And, in a weakly or acidic solution I can put the anode dip the anode and acid or base can help to dissolve the metal at the anode, and the solution contains the same metal as the anode, but in ionic form that is they carry they are able to carry the electrical charge.

The basic electroplating process is essentially same, I have a bath, I put a anode; I put a cathode ok. And, then this is cathode this is anode and I dip them both in solutions, and anode can be in the form of a base plate, something like this, this is the anode and this could be our cathode, object to be plated, it can be anything ok. I am just I have just drawn a simple picture

of a man statue manikin. So, the anode can be a slab like this, or it can be a ball, or it can be anything.

(Refer Slide Time: 25:50)

As an electrical current passes through the solution, these ions migrate towards the negative electrode (called the cathode) where the object to be plated is attached. The ions gain an electron at the cathode, which causes the object to attract a coating of the metal in the solution. This coating builds one atom at a time in accordance with Faraday's law which states that 1 Faraday (96500 coulombs) of electricity will deposit 1 gram Equivalent weight of any metal. The current passing through the solution is measured in Amperes ($1\text{ A} = 1\text{ coulomb per second}$).

And, an electrical current I passed through the electrolyte, these ions migrate towards the negative electrode, where the object is to be plated the ions gain an electron at the anode, which is causing the object to attract a coating of the metal ions gain in electron at the cathode. This coating builds one atom at a time in accordance with Faraday's law, which states that one Faraday of electricity will deposit 1 gram equivalent of any metal the any metal means the metal which we want to coat.

The current passing through the solution is measured in amperes; we have covered most of it earlier in our introductory lecture and in the electroplating procedures. So, I am not going to delve into those aspects, but this is only for the sake of brevity what is the electroplating.

(Refer Slide Time: 26:53)

Brass plating

Brass is an alloy of copper and zinc

Copper plating

Copper plating, exclusive of continuous strip plating and nickel, is the most common metal plated. It is a soft, red, ductile and solderable surface. It is not often used as a final plate, however, because it tarnishes easily.

So, the figure whatever you draw for electroplating is something like, what I have shown you for potentiometry try to remember two beakers, one electrode in each and the etcetera etcetera. Only difference is in electroplating there will be only one bath in which both the electrodes are placed, that is the only. In potentiometer and all if they are not in one bath, one beaker, we put a salt bridge.

Here, there are no salt bridges. Only one container in which a metal is dipped, one is cathode, another is anode and I passed the it contains electrolyte, I pass the current and all these Faraday's laws and other things are obtained. So, what I am going to tell you now is how to what are, what kind of things we plate brass plating. So, brass is nothing, but an alloy of copper and zinc. So, brass can be playing coated with gold let us say.

So, many of the temple temples will have gold plating in their top. So, Tirupati temple is coated with gold plates and it is not actually gold plate, it is a brass plate with coated with gold. So, similarly copper plating. Copper plating exclusive of continuous strip plating and nickel is the most common plated, common metal plated. It is a soft, red material, ductile, what I am talking about is the quality of the painting ok, coating.

So, the coated copper is a very soft, thin, metal, layer, it is reddish, it looks very beautiful, it is ductile and it provides a solderable surface. It is not often used as a final plate; however, because it tarnishes easily. You cannot keep a copper plated substance, they open to atmosphere, because any copper material will start looking dirty to look greenish it will look dark, patches everything it will start atmospheric oxygen, will sulfur sulfide, all those things will keep the electroplated copper they make them look dirty.

(Refer Slide Time: 30:02)

Copper maybe plated from a variety of baths beautiful depending on the final finish desired. probably the most common used is still the copper cyanide bath, which is used for both a finish coat and as an under plate or Strike, followed by another finish coating of copper or some other metal. For details on the chemistry of the many copper plating baths in current use, see the chapter entitled copper plating in this Guidebook.

So, but there are lot of copper coated, copper materials in the use in our day to day life. Sometimes copper may be plated from a variety of baths and beautiful depending on the my final finish desired. Probably the most common used material is still the copper cyanide bath, and which is used for a coat and as an under plate or strike, what is strike? A strike is that kind of material coating, where it is just dipped in dipped for a second and taken out.

So, there will be immediate coating of the copper a very thin layer, that is the that serves as the base plate and on that base plate again we coat nickel and other things to give adherence properties. So, the strike apart from the strike, it must be followed by another finish, the coating of copper or some other metal. For details on the for details of such processes the chemistry of the many copper plating baths, we have to see the chapter dealing with the copper plating in several books.

(Refer Slide Time: 31:24)

Among the most common copper plating specifications are Mil-C-14550 and GM 4252 M (Copper and tin plating), now superseded by ASTM B 734 and B 545. Typically, copper will be applied to 0.0001 to 0.0002 in. (2.5 to 5.0 micrometre) and finish coating for commercial copper plate will run 0.0002 to 0.0004 in. (5.0 to 10 micrometre). The upper limit of 0.0004 in. (10 micrometre) applies generally to externally threaded parts, but is common to most applications as well. some automotive applications require 0.0005 in. (12.5 micrometre) minimum.

I am not going into details among the about copper plating baths etcetera, because they are all specialized subjects, but you can imagine that whenever there is copper plating. Copper will keep on plating as long as the material looks beautiful. Once, it is function is removed what remains in the as an electrolyte will have base metal powder, it will have chemicals, it will have copper also. So, rinse water etcetera etcetera.

So, the quality of the uneconomical electrolyte produced, after the electroplating is over poses the challenge as an environmental waste material. So, coming back to our discussion among the most common copper plating specifications, these are copper technical specifications that mill C 14550 and GM 4252 that is for copper and tin plating.

Now, they are all superseded by standard American Standards, number these are the numbers books or instructions B 734 or B specifications you can say. And, typically copper will be applied from 0.0001 to 0.0002 inches that corresponds to approximately 2.5 to 5 microns micrometers. And, the finish coating for commercial copper plating will be approximately 002 to 0004 inches, in commercial copper plating's.

That corresponds to 5 to 10 micrometer that should be more than enough. The upper limit is 0.0004 that is 10 microliters. Suppose, I coat still more then what happens? I can always continue coating with copper more than 10 microns, 10 micrometer, it is not desirable, because the quality of the coating adherence will be will decrease, if I keep on coating it more and more.

So, generally to externally threaded parts and all 0004 inches point that is 10 microns is more than enough, but it is common to most applications as well. Any plating for that matter, it should not be very thick. Some automotive applications require 0.0005 inches or 12.5 microns minimum. They usually the metal part person who needs the metal parts, for his use he will specify what should be the thickness of the material.

(Refer Slide Time: 34:41)

Chromium plating

Chromium plating is applied as layer of Copper and Nickel for decorative purposes. chromium plating is more difficult to Run than many common metals, because of its very poor throwing power. Among the most common chromium plating specifications are ASTM B 456 (actually copper/ Nickel/ chromium) and Federal specification QQ-C-320.

So, continuing our discussion, let us talk about chromium plating, what is chromium plating? Chromium is a very shiny metal; you must have all seen chromium materials 99 percent of the shine comes from chromium coating, on all metals containing steels. So, you may have scissors, scissor is a chromium coated material. You may use shaving blade, which is looking very nice before you use, that is coated with chromium. There are earth digging equipment's, which contains the tools to dig the earth and they are all coated with chromium hard chromium plating.

So, chromium plating is applied as a layer of copper and nickel. First we coat it with copper and then a little copper will not have adhesive property enough to hold the chromium, then after copper we give a coating of nickel on copper. So, copper we call it as flash, copper flash and then we have nickel, on that nickel we coat the chromium.

So, chromium coating will be so always associated with copper or nickel as the base plate. And, to that base plate is our steel component, which is to be coated, because steel has got the strength to for many mechanical operations. So, coming back to this discussion, chromium plating is applied as a layer of copper and nickel for decorative purposes as well as functional properties.

So, chromium plating is more difficult there are many common metals, because of it is very poor throwing power. What is the throwing power? It is the power, it is the electrolyte we are talking about, in electrolyte the material which has to be removed from the electroplating solution on to the cathode, the rate of deposition, depends upon the throwing power of the electrolyte.

So, for zinc and all it is very easy to take out zinc from zinc chloride solution, zinc nitrate solution as electrolytes, but for chromium it is very difficult to take out chromium from chrome chromium solution, that is dichromate solutions. So, the throwing power is again a function of the chemical property of the solution. Among the most common chromium plating specifications, we have ASTM B 456, that corresponds to copper nickel and chromium and federal specification also is there, there are several other Indian standards as well.

(Refer Slide Time: 37:59)

Decorative chromium is normally applied over Copper and Nickel (normally greater than 0.0002 in. (5 micrometre) copper and greater than 0.0003 in. (7.5 micrometre) nickel) as a very thin coating typically 0.000050 in. (1.0 micrometre). The appearance of the final parts is usually determined by the under plate and is not the exclusive results of chromium plating.

So, decorative chromium again you may just imagine your knife or scissors or something like that, which looks very shiny. There they all look like you know stainless steel, what we use in our normal kitchen, but a decorative chromium is normally applied over copper and nickel, normally greater than 0.002 inches that is approximately 5 microns. And, copper has to be greater than 7.5 microns copper and greater than 0.0075 microns nickel in a way as a very thin coating of about 1 micron micrometer now.

And, the appearance of the final parts is usually determined by the under plate and it is not exclusive results of chromium plating. You do not have to remember all these numbers for if you are taking the course for examination. We will not expect you to remember these specifications, but it is for your convenience and for your knowledge, I am giving you this kind of information.

(Refer Slide Time: 39:24)

Hard chromium is applied for wear resistance or to restore an old worn parts to its original dimensions. It is generally applied directly onto the base metal. The appearance of hard chromium varies with the substrate onto which it is plated and can range from semibright to dull gray. A common chromium plating specification is AMS 2406. "Chromium- Hard deposit- On Ferrous Metal Parts," and QQ-C-320-"Chromium Plate" Class 2-Engineering, and ASTM B 177.

So, hard chromium is applied for wear resistance or to restore and old worn parts into, it is original dimensions. It is generally applied directly to the base material, iron or steel etcetera. The appearance of hard chromium varies with the substrate on which it is plated. Sometimes I use stainless steel, sometimes I use ordinary steel, sometimes I use simple metal, iron pieces etcetera. They also can be coated, I can use them on ball bearings, many of the applications are there and the appearance can change from semi bright, but material to matte finish and matte finish to dull gray also, if I keep on coating more and more the shine will go off.

So, it is always preferable to do the coating with the minimum quantity, if, you want a very good shine. If, you do not want a very good shine go for medium quality, that is extra deposition. Extra deposition also will give you strength as a for use subsequently. So, a common chromium plating specification is AM 2406. "Chromium-Hard deposit on Ferrous

Metals Parts”, that is the title and QQ-C-320” is another standard that is chromium plate plus 2-Engineering and ASTM B 7177 is another material.

So, whenever you want to coat anything, whenever you want to quote anything, what you should do is go to these specifications, ASTM or QQ-C-320 or a AMS 2406 and find out exactly, how they describe and what should be the quality of the chromium? And, they will also describe you what should be the electrode, what should be the anode, what should be the cathode?

What should be the electrolyte concentration, how long you have to run, what should be the concentration? When it is no more applicable and all those specifications will be built into the standards and you have to work on that. We will continue our discussion on electroplating for some more time before we move on to electroplating waste treatment.

Thank you very much.