

Electrochemical Technology in Pollution Control
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Lecture – 31
Electroplating 4

Greetings to you, we were discussing about the Electroplating operations and I was describing to you the electroplating equipment and I had told you that electroplating equipment becomes a very convenient tool for automatic automation.

So, I have told you that the articles to be plated are fixed on a cathode bar on which number of things can be hung. So, every piece acts as a cathode for collecting the electroplating material. So, there is a requirement of uniform current distribution all over the plating, all over the plating article. So, if there are more the plating will be convenient; if there are less part of the material will be lost and the efficiency will become less.

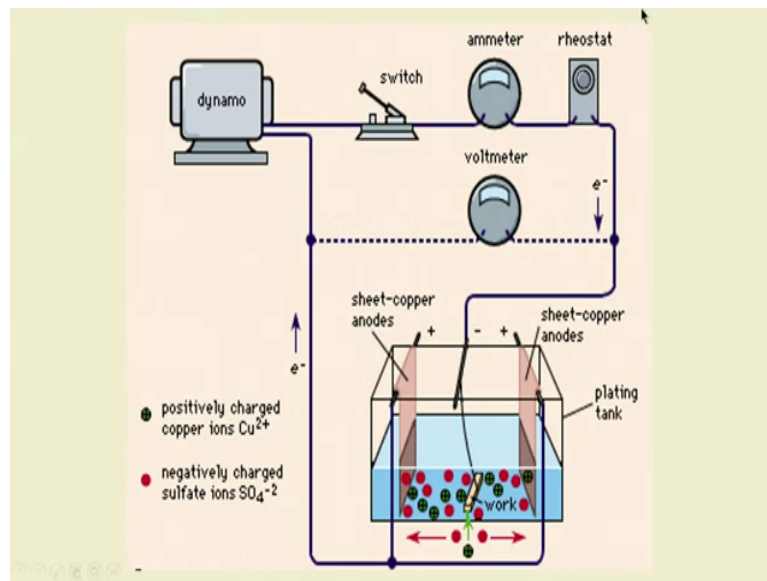
So, what we need is, we need to have the racks cathode racks must process the necessary current carrying capacity. They must possess the necessary current carrying capacity to enable uniform current distribution throughout the surface of the cathode article. So, a low-rpm motor drive you know the solution should be churning whenever we are electroplating, that helps in providing oscillatory motion to bring about cathode. It is not education; [Laughter] to bring about cathode cathodic action actually although. So, I will correct it here that is cathodic action.

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The racks must process the necessary current carrying capacity and enable uniform current distribution. A low-rpm drive motor helps in providing oscillating motion to bring about cathode ~~education~~^{action}. The plating bath can be heated with steam or cooled with water through coils or pipes. Immersion heaters or external heat exchangers may also be used for heating or cooling.

So, the plating bath can be heated with steam or cooled with water through coils or pipes and immersion heaters or external heat exchangers may also be used for electroplating heating, cooling and all those operations they can be automated.

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Now, this is a sort of figure for you to study the operation of an electroplating bath. Here I have a sheet copper anode ok and here I have sheet copper anode again and then this is the work to be plated with the copper solution; that means, I have one cathode and two anodes ok. Center one is cathode and this is anode so, that copper sulfate copper from the anode can dissolve and come over here and then get plated and then the article will be plated with copper.

So, this is known as plating tank, sheet copper anodes, sheet copper anode here and then this is the plating electrolyte and I have shown cations and anions here, a little bit plus and minus and the current will be carried like this and then it will be connected to a motor.

A same thing this is also sequentially connected. So, there is no problem with respect to this and then I have a switch to start the operation of electroplating on off. And the moment, I

have everything ready all the cathode I can instead of 1, I can put another 10 here on the cathode hanging like this, one here, one here, one here, one here like that and then I need an ammeter a rheostat to control the current and a voltmeter for maintaining.

So, this is basically an extension of the beaker operation what I had shown you during while I was teaching you the potentiometry. Only thing is here both the anode and cathode are in the same plating tank.

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In commercial electroplating applications, special attention is given to factors like cathode and anode current densities, cathode and anode current efficiencies, rate of deposition and throwing power. Current density is commonly accepted as amperes/sq. ft. of anode and cathode surface. the cathode current efficiency refers to the amount of metal plated to the amount that could theoretically be deposited by the same amount of current according to Faraday's law : 96500 coulombs could theoretically deposit 1 equivalent of the metal.

So, in commercial electroplating a special attention must be given to factors like cathode and anode current density, cathode and anode current efficiency, rates of deposition and throwing power. Throwing power I had already discussed with you, it depends upon the characteristics of the electrolyte.

So, it is very important for us to worry about to choose chemicals with good throwing power. Current density is commonly accepted as you can express also as amperes per square feet of the anode and cathode surface. The cathode current efficiency refers to the amount of metal plated to the amount that could be theoretically deposited by the same amount of current according to Faraday's law.

There is nothing new in electroplating because these [Laughter] according to Faraday's laws the things to be recorded the things to be plated essentially remain the same whether we like it or not and fundamentals have been established way back in 1700 1800 AD. So, there is nothing new, but only thing is automation improvements keep on happening in the field all the time, applications keep on growing. Therefore, there will be requirement of expressing all these things. For example, cathode current efficiency and all these things probably were not known around that time.

But in electroplating such expressions as amperes per square feet of anode, amperes per square feet of cathode and all these things assume importance in modern day science. So, anode current efficiency approximately again refers to the amount of metal dissolved at the anode.

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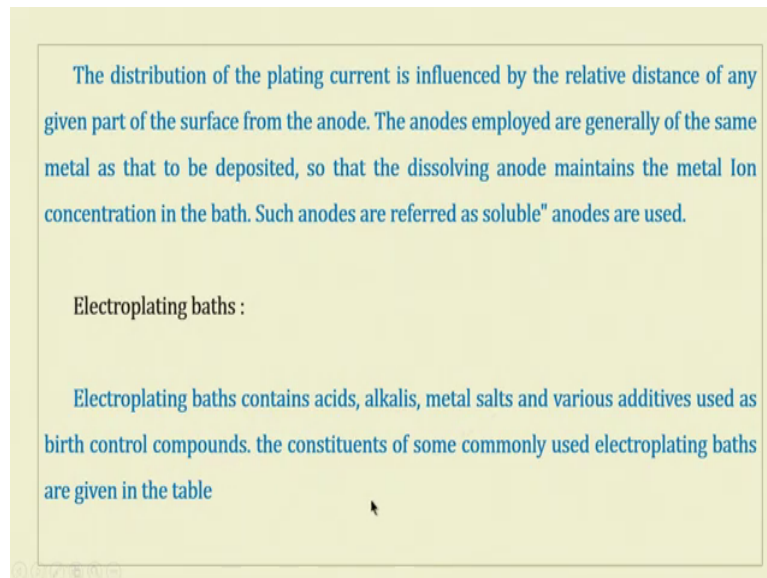
Anode current efficiency refers analogously to the amount of metal dissolved at the anode. The product of the cathode current density and efficiency gives the rate of deposition at the cathode. Throwing power refers to the uniformity of plate thickness that can be expected on a shaped article over the surface of which the current density will vary because of current distribution.

See for cathode it is the efficiency for deposition, for anode it is the efficiency that is removing from the anode that is metal loss weight loss. So, after particular metal weight loss, it will not be efficiently throwing out the chemical because anode has to dissolve and cathode it has to be deposited. Therefore, the requirement is same, but I can express it as either as anode or cathode. Sometimes I have an anode which is shaped look fantastically geometrically like a block, but cathode could be a statue; it may be an ornament what people wear here there.

And it may be your watch strap there that is to be coated with gold or silver or stainless steel like that that also is possible. So, the both anode efficiency and cathode efficiency can be expressed both mean the same. So, throwing power refers to the uniformity of the plate thickness that can be expected or that is happening. You can also calculate and how much has been plated on a shaped article over the surface and of which current density will vary because of the current distribution. This last sentence you please study more and there is nothing very

rocket science about it, but we are all we are talking about the throwing power anyway. So, it depends on the current density and the current distribution also.

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The distribution of the plating current is influenced by the relative distance of any given part of the surface from the anode. The anodes employed are generally of the same metal as that to be deposited, so that the dissolving anode maintains the metal ion concentration in the bath. Such anodes are referred as soluble" anodes are used.

Electroplating baths :

Electroplating baths contains acids, alkalis, metal salts and various additives used as birth control compounds. the constituents of some commonly used electroplating baths are given in the table

Ultimately whenever we talk of current distribution electroplating, we talk of current density and current distribution. So, the distribution of the plating current is influenced by the relative distance of any given part from their surface from the anode. Here you should imagine the if the ions have to travel for long distance, then the plating efficiency will be very less. So, the size of the plating bath should be optimum to get the beautiful current throwing power.

So, the anodes employed are generally same of the same metal because anode will dissolve maintaining the electrolyte concentration to get continuously good throwing power of the deposit. So, the dissolving anode maintains the metal ion concentration in the bath, such anodes are referred as soluble anodes. In electroplating baths if we want to discuss a little bit,

it must contain acids, metal salts and various other additives used for as bath control baths control compounds.

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| Electroplating process | Bath composition |
|------------------------|--|
| Copper cyanide | Copper cyanide, sodium cyanide, sodium carbonate, sodium hydroxide and Rochelle salt. |
| Gold cyanide | Metallic gold, sodium phosphate and potassium cyanide |
| Iron | Ferrous sulphate, ferrous chloride, ferrous fluoroborate, ammonium chloride, calcium chloride, sodium chloride and boric acid |
| Silver | Silver cyanide, potassium sodium cyanide, potassium sodium carbonate, potassium hydroxide, Potassium Nitrate and carbon disulphide |
| Chromium | Chromic acid and sulphuric acid. sometimes with fluoride catalyst |
| Cadmium cyanide | Cadmium cyanide, sodium cyanide, sodium hydroxide and cadmium oxide |
| Cadmium fluoroborate | Cadmium fluoroborate, fluoroboric acid, boric acid, ammonium fluoroborate and licorice |
| Zinc cyanide | Sodium cyanide, zinc oxide, sodium hydroxide and zinc cyanide |
| Acid- zinc | Zinc sulphate, ammonium chloride, Ammonium Sulphate or Sodium acetate and glucose or licorice |
| Tin- zinc alloy | Potassium stannate, zinc cyanide, potassium hydroxide and potassium cyanide |
| Copper- fluoroborate | Copper fluoroborate and fluoroboric acid |
| Acid - copper sulphate | Copper sulphate and sulphuric acid |
| Copper pyrophosphate | Copper pyrophosphate, potassium hydroxide and ammonia |
| Brass and bronze | Copper cyanide, zinc cyanide, sodium cyanide, sodium carbonate, ammonium and Rochelle salt |
| Acid -tin | Tin fluoroborate, fluoroboric acid, boric acid, stannous sulphate, sulfuric acid, cresol, sulphonic acid, Napthol and gelatin |
| Stannate tin | Sodium stannate, sodium hydroxide, Sodium acetate and hydrogen peroxide |
| Lead-tin | Lead fluoroborate, tin fluoroborate, boric acid, fluoroboric acid, fluor and hydroquinone |
| Nickel(watts) | Nickel sulphate, Nickel chloride, nickel fluoroborate, boric acid, phosphoric acid, |
| Nickel -acid fluoride | Nickel chloride, hydrofluoric acid, citric acid, sodium lauryl sulphate as wetting agent. |
| black Nickel | Nickel ammonium sulphate, Nickel sulphate, Ammonium Sulphate, zinc sulphate and sodium thiocyanat |
| Tin -Nickel alloy | Nickel chloride, stannous chloride, ammonium fluoride, ammonium bifluoride, sodium fluoride and hydrochloric acid |

So, the constituents of some commonly used the electroplating baths are given in the table here, copper cyanide. For copper electroplating process here we use copper cyanide, sodium cyanide, sodium carbonate, sodium hydroxide and Rochelle salt.

And gold cyanide we use metallic gold, sodium phosphate and potassium cyanide; cyanide is a required chemical. So, I always make a joke that without potassium cyanide and sodium cyanide so, much economical operations will never take place involving gold buying selling making and then stealing, [Laughter] robbery and then the transport you know and then so much technology in jewelry making. So, many thinks is sodium and potassium cyanides are

responsible because they are the chemicals which are used to which are used to produce gold and dissolve a gold, electroplate gold etcetera.

So, which cyanide if it goes in our body we die and without cyanide, we die economically. So, it is just a joke, but cyanide just to impress upon you the importance of cyanide. So, but we do not use cyanide in day to day a regular routine actions for example, in the case of iron who use ferrous chloride, ferrous fluoborate, ammonium chloride, calcium chloride, sodium chloride, boric acid etcetera; to maintain the. Here boric acid sodium chloride and other things, they have all maintained required to maintain a particular quality of the plating bath. So, that other plating conditions are fulfilled and we get a good coating.

Silver again we use cyanides, carbonates, hydroxides and carbon disulphides sometimes. Chromium we use chromic acid and sulphuric acid, sometimes fluoride as a catalyst. Cadmium cyanide, sodium cyanide, sodium hydroxide like that there are the I had explained to yesterday that there is a book on by the manufacturer of the electroplating chemicals that is known as handbook of electroplating by a Scanning and Mitra that is Indian version and that book describes to you all their kinds of bath what I am describing here. Even though this information I have not taken from that book, but it contains many other information that are required for electroplating.

So, acid copper sulphate we have used we use copper sulphate etcetera. Apart from these things, you can study this table and find out what are the different chemicals that go into and that gives you an idea of what the effluence also would be containing.

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Waste treatment Technologies

Some specific applications of waste treatment Technologies used for electroplating wastes are summarized in the table

| Waste treatment problem | Treatment technology |
|---|--|
| 1. Removal and/or recovery of dissolved salts | Hydroxide precipitation, sulphide precipitation, ion exchange, membrane filtration, insoluble starch xanthate, peat adsorption, carbon adsorption, electrolytic recovery, high pH precipitation (for Complex with metals) |
| 2. Removal of dissolved salts for reuse of water | Reverse osmosis |
| 3. Recovery of process baths | Electrodialysis |
| 4. Removal of Organics | Aerobic decomposition, carbon adsorption, resin adsorption |
| 5. Destruction of cyanides and cyanates | Electrochemical oxidation, oxidation by chlorine, oxidation by ozone, oxidation by Ozone with UV radiation, oxidation by hydrogen peroxide (for destruction of cyanides only) |
| 6. Suspended solids removal | Flotation, certification, ultrafiltration, sedimentation, diatomaceous Earth drying |
| 7. Sludge dewatering | Centrifugation, pressure filtration, diatomaceous Earth filtration, sludge bed drying, vacuum filtration |
| 8. Reduction of chromium (VI) (some metal finishing and cooling tower blowdowns) | Electrochemical reduction |
| 9. Concentrations and recovery of process chemicals | Evaporation |
| 10. Oil removal | Centrifugation, coalescing, flotation, skimming, ultrafiltration (oil breakdown can be accomplished by aerobic decomposition) |

So, waste treatment technology are important in all electroplating operations and here is a small list of waste treatment problems that is removal and recovery of dissolved salts, they are all resources. So, we cannot let them we should not let them out of the out of our sight into the environment, there they can play havoc.

So, the treatment technology for dissolved salts is precipitation, it can be hydroxide precipitation or it can be sulphide precipitation. I can remove the ions dissolved salts as ion exchange, membrane filtration, starch xanthate and then peat adsorption, carbon adsorption, electrolytic recovery high pH precipitation; many other complex technologies are available and they can be treated that way. So, removal of dissolved salts for reuse of water; if you want to reuse the water then reverse osmosis is the best technology. Even though lot of people say reverse osmosis generates concentrated wastes at the same time giving you very good quality

that is like a distilled water quality for reusing. Nearly 50 percent of the input water gets lost in reverse osmosis as waste which needs to be handled separately.

But nowadays there are membranes which can handle up to 85 to 95 percent 80 to 85 percent of the waste giving you 95 almost 90 percent recovery of water. Other things need to be of course, handled in a separate way that we also will discuss. There is one technology of reverse osmosis, I want to discuss with you in this course that is known as VSEP we will I have already I had already mentioned to you earlier, but it is a separate topic I have decided to include here. And then recovery of process baths, we can go for electro dialysis and process bath solvent solution can be reused for as a an electrolyte.

Removal of organics: Here I have to tell you that there are lot of materials which go into an electroplating bath. One is the acid treatment acid hydrogen embrittlement, I had already talked to you in my previous classes. Another is to get a smooth surface and to maintain high quantity of acids we do not want acids to be very dangerous. So, we had inhibitors to reduce the harshness of the acids, then we add brightness, then we want to improve the throwing power. So, the solution should be fair it should not be very viscous.

So, we add surfactants there are three kinds of surfactants anionic, cationic and nonionic. So, a good plating bath will have at least about 8 to 10 additional non-related compounds. So, such organic compounds are can be removed by aerobic decomposition carbon adsorption and resin adsorption.

So, suspended solids again we can go for flotation and then ultrafiltration, sedimentation, diatomaceous earth drying, pressure filtration and then sludge bed drying, vacuum filtration etcetera. Then reduction of chromium is a very important aspect of all electroplating wastes because 90 percent of the electroplating happens in with chromium. So, electrochemical reduction of chromium is a must because I have already told you that hexavalent chromium is used as an electrolyte and if it is thrown away as hexavalent chromium, the it will cause lot of problems.

The WHO limit for water hexavalent chromium drinking water is about 0.5 ppm and the concentrations that happen in bore wells in Pinya in Bangalore are of the order of about 160 ppm. It is like Fanta and gold spot. So, concentrations and recovery of process chemicals again we can use multiple effective operators to get rid of the salts and then oil removal of course, it is a very important because most of the metals are stored with a layer of oil. So, centrifugation, coalescing, flotation, skimming, ultrafiltration, oil breakdown for using aerobic decomposition; these are all quite possible in these are they not only possible, but they are probably a must for handling the electroplating waste.

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Applications of electroplating

1. Plating for decorative purposes

Chromium, nickel, silver, gold, copper, brass and rhodium are the most widely used metals for decorative plating. zinc, cadmium, tin, lead, Platinum And Palladium are also used for special decorative effects.

The base metals and alloys that are the most commonly subjected to electroplating are Steel, brass, copper, nickel, silver, white metal alloy of lead, zinc or tin base and Aluminium alloys.

Applications: Now I think I will complete my let my discussion with electroplating just by giving you a glimpse the applications and here I have recorded that chromium, nickel, silver, gold, brass etcetera they are the most widely used for metal decorative plating, base metals

and alloys are most usually are made of steel, brass, copper, nickel, silver, white metal alloy etcetera.

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The type of the plating required is determined on the basis of appearance desired, the intended use of the finished article and the nature of the base metal being plated. Chrome plating is most commonly used for decorative purposes because of its durability and resistance to chemical attack, abrasion and tarnish.

Electroplating is widely used in the manufacture of aircraft, automobiles, refrigerators, electrical appliances such as irons, fans, hot plates and toasters, builders hardware such as door knobs, locks, hinges and strike plates, jewelry, Radios, cameras, typewriters, watches, purses, umbrellas etc.

Then the type of plating required is determined on the basis of appearance desired and the intended use of the finished article and nature of the base metal being plated or base metal plated, chrome plating is mostly used for decorative purposes because of its durability and resistance to attack by acids, alkalis etcetera abrasion and tarnish.

Its electroplating is also widely used in the manufacture of aircraft, automobiles and then refrigerators electrical appliances such as irons, fans, hot plates, toasters, builders; hardware such as door knobs, locks, hinges strike plates many many things and it is too difficult to completely list the plating jobs.

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2. Plating for protection

Steel being the most commonly used construction material, is the most widely used basic material which must be protected from corrosion and chemical. the protective plates that are commonly used on steel are zinc, cadmium and Sn. these are applied on stamped, spun or cast articles at some stage in their manufacture. zinc plating is preferred in Industrial and rural atmosphere whereas plating is a better choice in seashore or salty atmospheres. tin does not provide the Galvanic protection offered by zinc and cadmium.

Sometimes we do objects for protection. Steel is the most commonly used construction material in all pillars and other things; they need to be coated because it will come in contact with the soil and cement and porous materials etcetera and that must be protected from corrosion and chemical.

Sometimes you must have heard of this TMT bars, you know a lot of advertisement keeps on coming on TVs and other things; all cinema actors usually end up giving you advertisements on TMT bars. They You know they are all rotated stainless steel rods not stainless steel rotated steel rods with very high strength. So, they are applied and spun or cast articles at some stage in their manufacture. Zinc plating is preferred in industrial and rural atmospheres. Whereas, plating is a better choice in seashore or salty atmospheres, tin does not provide the galvanic protection offered by zinc and cadmium.

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However, in case of food containers and food handling equipment, tin plating is preferred as it not only protects Steel but also does not contaminate the food. In applications where protection as well as decorative effects on Steel are needed, copper, Nickel and chromium plates are used. Copper and brass are generally plated with Ni and Cr. When metals are plated for protection against their environments, due consideration must be given to the Galvanic effects of the metal couple to avoid undesirable effects.

So, in case of food containers and food handling as far as possible, tin plating is preferred as it not only protects steel, but also does not contaminate the food. But in applications where protection as decorative effects on steel are needed normally copper, nickel, chromium plates are used plating basically coated articles. Copper and brass are generally plated with nickel and chromium.

When metals are created for protection against environment, due consideration must be given to galvanic effects of the metal couple to avoid undesirable effects that is why we use sacrificial anodes and cathodes wherever there is application.

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3. Plating for surface and engineering effects

Improved performance and service life of cast iron or Steel glass molds is achieved by the application of low concentration chromium plate. chromium plate on the important surfaces of molds for plastics improves the life of the mold and also the appearance of the molded product. chromium plate on the surface of dies for drawing or extruding copper, brass and steel brings about considerable reduction of the wear on the die and thus improve the appearance of the drawn metal.

Application means wherever there is chance for harsh environmental conditions openness. So, in plating surface engineering surface and engineering effects, we can increase the life of cast iron or steel and chromium plate on important surfaces or molds for plastics, improves the life of the mold and also appearance of the molded product that will appear smooth and very nice thing. Then extruding copper, brass and steel again we use chromium plating and considerable reduction of wear happens in ball bearings etcetera there not only alloys, but sometimes they are coated also.

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4. Electroforming

The radio, radar, aircraft, automobile, glass, Steel, rubber, printing and munition industries use several products made either partly or fully electroforming. this method helps in the manufacture of articles where other methods have been totally ineffective.

So, electro forming radio, radar, aircraft, automobiles, glass, steel, rubber, printing and munition industries they all use several products made either partly or fully electroformed chemicals metals. This method helps in the manufacture of articles where other methods have been totally ineffective.

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5. Plating on non - metallic materials

Non-metallics such as synthetic resins, cloth, paper, wood, porcelain, leather etc., are usually plated for decoration, preservation or to prepare light weight materials with metal surface characteristics, surface conductance and strength. non metallics are also plated in connection with electroforming and electroplating

And plating on nonmetallic now a days is gaining strength, lot of cars and other metal other materials do get painted with silver, aluminum and [Laughter] many other metals. 90 percent of the car applications what you see in your day to day life are decorative coatings. So, most of them are having base metals of plastic that is nylon, ABS and other kinds of plastics that are coated with metals to give you a shiny appearance and beautiful finish.

So, at this stage I would like to conclude my discussion on electroplating wherever possible I have tried to indicate the need for handling the electroplating waste and chemical aspect. So, we will look into the chemical aspects of electroplating waste, we will look into that later. And so, that brings us to the end of our discussion on electroplating.

So, we will continue our next class on batteries and why batteries is, because we need to understand the battery is some sort of an extension of electroplating operations and the

applications are myriad, then the requirement of batteries is so, enormous that it has grown into a its own specialized field, I want to give you a small account of batteries and battery technology in my next class.

Thank you very much.