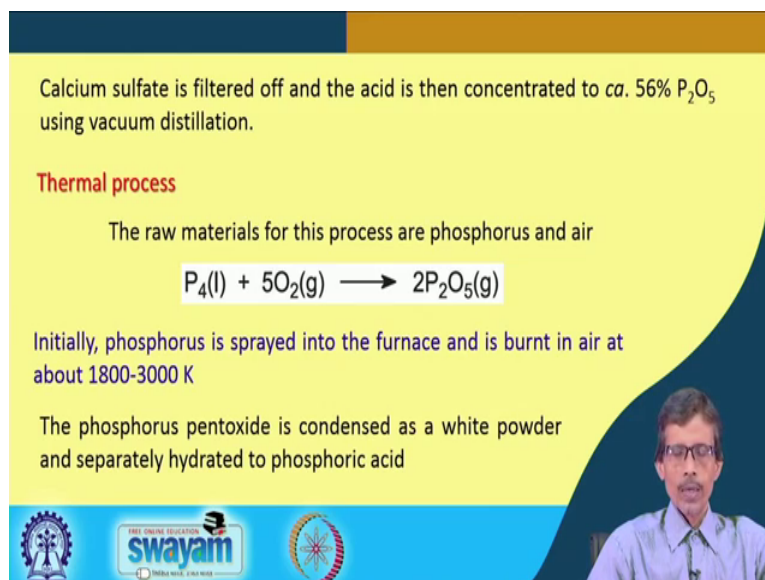


Industrial Inorganic Chemistry
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Lecture – 12
Phosphoric Acid Salts

So, welcome back, where we are talking about the production of calcium sulfate along with the production of your Phosphoric Acid. So, calcium sulfate we are getting from that particular reactor where we are handling the ore.

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Calcium sulfate is filtered off and the acid is then concentrated to ca. 56% P₂O₅ using vacuum distillation.

Thermal process

The raw materials for this process are phosphorus and air

$$\text{P}_4(\text{l}) + 5\text{O}_2(\text{g}) \longrightarrow 2\text{P}_2\text{O}_5(\text{g})$$

Initially, phosphorus is sprayed into the furnace and is burnt in air at about 1800-3000 K

The phosphorus pentoxide is condensed as a white powder and separately hydrated to phosphoric acid

The slide also features a small video inset of the lecturer in the bottom right corner and logos for IIT Kharagpur and Swayam in the bottom left corner.

So, it can be filtered off, so calcium sulfate is separated out and the acid is then concentrated to about 56 percent of the actual P₂O₅, what is known as the corresponding anhydride of your phosphoric acid.

So, concentration up to that point can be utilized using vacuum distillation. So, basically we have to remove this particular water molecules whatever there; such that we will get something as that particular phosphoric acid which is known in the market as the syrupy phosphoric acid or orthophosphoric acid or we consider it as the syrupy phosphoric acid as its corresponding form as the ortho.

So, orthophosphoric acid which is basically a very heavy one and we will highly concentrated one, and it can be considered as in terms of your P₂O₅ because the P₂O

5, which is also an anhydride form of your phosphoric acid and that will see also that how we can utilize this also is a very good desiccant this P_2O_5 whether we will be able to make P_2O_5 also from that phosphoric acid that will also be an interesting area to understand.

So, this concentrated phosphoric acid what we use, we can get up to 56 percent of this from the wet process. Then other process will be considering over here is your thermal process; that means, heating something which can be burnt away to give you the ultimately your phosphoric acid. So, thermal process as the name tells you that now we will be utilizing directly the phosphorus.

So, the wet process was giving us something, where we are utilizing your phosphate rock or apatite rock from the simple treatment of your sulfuric acid, but if we get the elemental phosphorus; that means, white phosphorus or red phosphorus from the phosphate rock, what we can do? We can use that particular elemental phosphorus for making pure quality of phosphoric acid, not directly from your phosphate ore or the apatite.

Now, we can neutralize via your elemental phosphorus. So, that particular industry will give us what we can give you that particular production of phosphorus from the rock sample. So, phosphorus will be there, it will have some utilizations are making phosphorus from the rock is also another industrial aspect. And along with that that particular phosphorus can be utilized for making phosphoric acid.

So, how we do that, simply we can go for burning phosphorus with a plenty of O_2 , what we are getting from AIR; such that as I just now told you that, we are in the process of making P_2O_5 , so in process of making this P_2O_5 , in terms of this P_2O_5 , if we can burn it will get the phosphorous pentoxide, which is a useful desiccant, still now we use it for the laboratory purposes, in the desiccators and all this which can very nicely absorb water molecules.

So, absorption of all these water molecules will be useful for getting this P_2O_5 as a useful desiccant. So, it is a very costly one also. So, if we burn it that P_4 , which is a one form is the solid form, but if we can take it in the liquid form, so this one form has been taken as the liquid form, with that oxygen of air we immediately get that phosphorous pentoxide as the gas.

And that phosphorus pentoxide in the gaseous form is the typical reaction the thermochemical reaction tells us because all the thermodynamic parameters we can calculate out the temperature required, the product conversion and all these things can be found out from these, but from the inorganic chemistry point of view, what we see now that the oxidation of these in excess air not giving us any other intermediate oxidation state of phosphorus because whenever we are talking about this phosphorus you should also be considered the corresponding oxidation state.

This is the highest possible oxidation state what will be achieving over here is your plus five oxidation states. So, that plus 5 oxidation state what we will be getting is for your P_2O_5 . So, that P_2O_5 can be now condensed from the gas as a solid one and that solid one is available in the market in the bottle form also is the white powder solid. So, that white powder solid, some industry is there is devoted in making this P_2O_5 and selling it to the market.

So, what we do? We have to have some furnace for making this oxidation process of elemental phosphorus. So, elemental phosphorus oxidation by O_2 of the air will give us the P_2O_5 and that phosphorus now, it can be liquid or it can be a powder also since we are talking in terms of a liquid form of that P_4 , it is sprayed into the furnace and burnt in air at a very high temperature in the range of 1800 to 3000 K, you see very high temperature is required for this particular conversion.

So, high temperature oxidation of phosphorus, basically give us phosphorus pentoxide. So, what will do now as I told you that this phosphorus pentoxide in a bottle form is as the laboratory reagent is available as a solid white powder. So, that solid white powder can be obtained from the gaseous form of this P_2O_5 and it can be condensed as a white powder and it can now go for the next step of reaction; that means how we make phosphoric acid from your phosphorus pentoxide. So, since it is an anhydride of phosphoric acid, so we have to hydrate it. So, that is why it is separately hydrated to phosphoric acid; that means, in a controlled manner if we add or if we spray water on P_2O_5 will get the phosphoric acid.

So, when we put in a laboratory, the typical phosphorus pentoxide in the desiccator to trap the extra water of some compound or some material; such that, we keep everything in a dry form because, some of the typical reactions also we can do over phosphorus

pentoxide; such that, water can be eliminated from the compound itself, some organic compound can be transformed. If we take out that water from that particular molecule to convert this some other form that a can be converted to b, but if we have some extra water molecule in some precipitate, suppose that you can have some ferric hydroxide precipitate, which has been filtered over a filter paper and we want to dry it up.

So, on the filter paper which is in the conical flask, so they keep that particular moist ferric hydroxide over filter paper within the desiccator and the desiccator is supported by at the bottom we can have calcium chloride, fused calcium chloride which is a moderately checking the atmosphere; that means, moisture free, but it is not so good to dry your ferric hydroxide in moist form which has been obtained by filtrations. For that purpose we you have to add and secondary desiccant which is your P_2O_5 . So, P_2O_5 will take the extra amount of water which has been trapped in your ferric hydroxide precipitate; such that, after 1 day or after 20 hours, we get that particular ferric hydroxide in the dried form; that means, the water free form.

And by that time, if you are a very good looker on the situation what is happening around you in the laboratory in the environment everywhere, you should be watchful all the time. If we look at the corresponding fate of the P_2O_5 because the P_2O_5 we have taken on a (Refer Time: 08:53) or watch glass, which is a white powder and immediately after putting that powder we keep it in the desiccators. And after that, after 1 day or 2 days, what we get? We get the dried compound in the desiccator which was there in a round bottom flasks, in a beaker or in a conical flask. We get that this one is getting mossman; that means, the moisture is passing from your ferric hydroxide precipitate to your P_2O_5 and that P_2O_5 is moisten basically, tracking that particular water and is giving us some glassy material some sticky glassy material.

So, as it is taking water it is quickly converting it to a corresponding version which we told you that is the syrupy one is there not a liquid one, is syrupy one is a very sticky 1. So, that sticky material is nothing, but your corresponding syrupy phosphoric acid, but still it can have the ability to trap further moisture because your all the P_2O_5 has not been converted, some amount some percentage of P_2O_5 can be converted to your phosphoric acid.

So, remaining one is within that particular sticky material. So, the passage of water or water abstracts and capacity of that particular material is decaying. So, it is very slow for the next step of water obstruction, but still it can take the water. Finally, it is basically a typically glassy material when all the phosphorus pentoxide has been converted to your phosphoric acid.

So, this is a very nice example laboratory example if you see only that how phosphorus pentoxide can be useful for the industrial purpose for making phosphoric acid.


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Phosphoric Acid Salts

Used in non-fertilizer applications.
Sodium mono-, di-, tri- and polyphosphates from phosphoric acid and sodium carbonate or sodium hydroxide

$\text{H}_3\text{PO}_4 + \text{NaOH} \longrightarrow \text{NaH}_2\text{PO}_4 + \text{H}_2\text{O}$ $\text{H}_3\text{PO}_4 + 2 \text{NaOH} \longrightarrow \text{Na}_2\text{HPO}_4 + 2 \text{H}_2\text{O}$ $\text{H}_3\text{PO}_4 + 3 \text{NaOH} \longrightarrow \text{Na}_3\text{PO}_4 + 3 \text{H}_2\text{O}$	$2 \text{NaH}_2\text{PO}_4 \xrightarrow{245^\circ\text{C}} \text{Na}_2\text{H}_2\text{P}_2\text{O}_7 + \text{H}_2\text{O}$ $2 \text{Na}_2\text{HPO}_4 \xrightarrow{300-400^\circ\text{C}} \text{Na}_4\text{P}_2\text{O}_7 + \text{H}_2\text{O}$
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Higher molecular weight sodium polyphosphates are utilized in the manufacture of **processed cheeses**, condensed milk and **frankfurters** and as **pigment suspension stabilizers** and in the tanning of leather.



So, we get this one and this particular phosphoric acid we can convert for some other phosphoric acid salts. So, what we see now that in all these cases we have that particular thing what we have produced so far is your H_3PO_4 . So, since it is acid, like that of your typical acid base reaction if it is reacting with one molecule of sodium hydroxide, so molar ratio of reaction is 1 is to 1; such that, this particular acid is a triprotic acid H_3PO_4 . So, one of the acidic proton we will be converted to your corresponding sodium salt; that means, $\text{O}^- \text{Na}$, OH will be converted to $\text{O}^- \text{Na}$.

So, if we convert only one of that will be getting NaH_2PO_4 , so mono sodium hydrogen phosphate will be getting. Why we are seeing all these things, why you are studying all these thing because, this can have now some non fertilizer application. So, far you have seen that phosphorus or phosphorus bit compounds can be useful for fertilizer applications, but this can be useful for some other non fertilizer application.

So, first thing what we can try is the corresponding sodium salt. We can have some other salts also like that of your ammonium salt, we can have the calcium salts also. So, large number of salts we can make because, the property wise all these salts are different depending upon your cationic form what you are getting from that particular phosphate salts.

So, what will be getting is the corresponding phosphoric acid salt. So, when the reaction is 1 is to 2, we get the corresponding di sodium hydrogen phosphate, when it is 1 is to 3, we get trisodium phosphate or typically is a simple sodium phosphate which is Na_3PO_4 , where all the 3 protons are phosphoric acid has been removed and we get a typical anionic form; that means, the phosphate ions present in that particular compound along with the sodium ion. So, we consider it as the sodium phosphate in your hand.

And now, what we can use these, why we are making these? We are making something which is different now, as will be getting something because if we have one phosphate in your hand and another phosphate in your hand, whether will be able to condense the, to get some diphosphate or we can go for far further to get make some triphosphate or some cyclic phosphates.

So, whether we will be able to get something like that of our silicate formation; that means, silicates we all know that the silicate can have the sudden type of silicate structures, what we get in our cement on the silicon material clay material and all these things for getting those structures.

So, silicate is tetrahedral SiO_4 ion we can have SiO_4 minus in phosphate is also a tetrahedral center and if that can be condensed to here for some other condensation reaction, the first one what we can get it is that since, this one from reaction of sodium hydroxide can also be substituted by sodium carbonate, where your product is also your carbon dioxide and that carbon dioxide formation is also there and that will be typically eliminated from the medium and that will also give rise to the corresponding sodium salt of these compounds.

So, heating this particular disodium salt, as well as the mono sodium salt, so so we are having 2 salts; 1 is the monosodium phosphate and another is that di sodium phosphate. And in one case, if we heat it to 245 degree centigrade, in another case if we heat beyond

that from 300 to 900; that means, about 500 degree centigrade, if we heat it, will also get 2 types of salts.

So, when it is mono sodium will be getting something $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ and when it is disodium will be getting $\text{Na}_4\text{P}_2\text{O}_7$, but the basic unit is all same; that means, we get a di phosphate unit. So, this di phosphate unit only difference is the corresponding protonation level on the oxygen atoms present with that particular network. In one case, we have still two hydrogen atoms attached to the oxygen of the phosphate groups di phosphate groups, but in the second case we do not have any such hydrogen atom attached to the phosphate group so that, I phosphate group.

So, these are the corresponding one for making these compounds. So, it is possible to make the diphosphates starting from your phosphoric acid. So, higher molecular weight sodium polyphosphates, we can consider because this is a basically a polymerization reaction through phosphor attachment of one phosphate to the other.

So, higher molecular weight sodium polyphosphates are utilized where we utilize because they have some very good application for this purpose, because the first thing we should ask all the time because it is a basically a application process because the industrial process we are talking about, why we should study this, why we should know the preparation process, because a preparative method and not only in the laboratory scale, but it is in the large scale, so industrial scale.

So industrial scale is also very important so that, industrial scale of production will tell us that this particular materials would be useful for some useful purpose. So, if we can have some process where the people are making the dairy industry, the agricultural industry they are making some processed cheeses. So, cheese making is a another industrial purpose. So, an industrial process, but that should be stored to increase the self life; such that we can have in the market for 1 month or 2 months in a packet form; in fact, form we can sell it.

So, you have to increase the self life; such that, it is not degrading, it is not decomposing, it is not decaying in time, because the milk products are always susceptible for bacterial infections or growth of the different bacteria in it and it is degrading very quickly even for simple lactobacillus production over there which basically decay all the milk, all the milk product.

So, these particular one can function as a stabilizer. So, this higher molecular, only the higher molecular weight species is not the only sodium salts; that means, the sodium hydrogen phosphate disodium hydrogen phosphate or only sodium phosphates are not useful you can go for the more complex one; that means, the bi tri etcetera. As a stabilizer for process cheeses, it can be a stabilizer or it can be a protector basically for condensed milk, the frankfurters from the name of the German Frankfurt city.

So, frankfurters is also some food material and as pigment suspensions stabilizers. In all these cases what we see is basically they are stabilizers, they are stabilizing that particular condition, that particular food material; that means, if we have a cheese, cheese is not getting degraded. If we have the condensed milk, condensed milk will remain as the condensed milk, it will not go for its fermentation or any other bacterial degradation.


So, it basically stabilizing so it is basically inhibit the bacterial growth, the degrading thing, then the decomposition of this material, that will resist that particular bacterial growth in the particular milk material. And sometimes this can also be utilized for tanning of leather because, we all know that the chromate tanning is also useful, the potassium dichromate or potassium chromate is useful for utilization of the particular process in the leather industry, which is standing of leather. Similarly, these pyrophosphates or the poly phosphates are also useful in the leather industry. So, the leather industry people are also utilizing a huge amount of this phosphoric acid salts.

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These acid salts are used in metal cleaning, for phosphatizing, in boiler water treatment and for buffer systems e.g. in the textile industry.

Disodium dihydrogen diphosphate is used as baking powder.

Industrially It is prepared in a two-step process by treating calcium phosphate with sodium bisulfate


$$\text{CaHPO}_4 + \text{NaHSO}_4 \rightarrow \text{NaH}_2\text{PO}_4 + \text{CaSO}_4$$

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So, how it looks like? One such example I am giving over here is your monosodium, once we call it monosodium phosphate or you can consider it as sodium dihydrogen phosphate or NaH_2PO_4 . How we make it industrially it is prepared in a 2 step process by treating calcium phosphate with sodium bisulfate.

So, is a typical process, where we are handling something instead of getting it as your corresponding sodium salt. Now we are handling something which is known as your calcium salt. So, since we are when we are using sodium we are getting a tri sodium salt, when you are handling calcium, you can use directly with calcium hydroxide or calcium oxide.

You can get it as CaHPO_4 , so it is calcium hydrogen phosphate. So, calcium hydrogen phosphate truly speaking, it is not calcium phosphate because, the other one which we have seen that the rock material is also known as calcium phosphate where no hydrogen is present. So, it is known as calcium hydrogen phosphate.

So, truly speaking, it is calcium hydrogen phosphate when react with another by sulfate salt, which is sodium by sulphate. So, it is biphosphate salt and another one is a bisulfate salt. So, reaction of bisulphate salt with the biphosphate salt giving you a sodium dihydrogen phosphate because the transfer of these hydrogen basically is taking place from this bisulphate to this biphosphate space; that means, this HPO_4^{2-} will have the greater affinity for proton abstraction from HSO_4^- .

This is the typical simple acid base reaction, what we can consider as if we have HSO_4^- in our hand and HPO_4^{2-} in our hand and we can ask this very simple question that where the hydrogen or the proton transfer can take place. So, which one is functioning as the acid and which one is functioning as the base.

So, one of the species will have the higher affinity for the proton that is why your HPO_4^{2-} is functioning as a base, that HPO_4^{2-} is abstracting the proton not from any other acid, but is taking that particular proton from a by salt which is your sodium bisulfate and it looks like this particular dihydrogen phosphate, sodium dihydrogen phosphate is the again another white, but is the granule as one white granules of this material.

So, why these acid materials we are studying, so is a very huge subject of study. So, we can consider it in a large amount and we will get a little bit we will see also for your ammonium salts, as well as some of the, what we have seen like that of your calcium salt. So, it can also further utilize because we have started our journey from your used as the fertilizer, then we are reaching over here for the leather industry.

Now, we are going to some metallurgical industry, which is for metal cleaning. The technique for that particular metal cleaning, that the surface cleaning metal surface cleaning is known as the phosphatizing. So, phosphatizing; that means, the very small layer or a very thin layer of the metallic surface can be utilized for making the phosphates and that phosphate, the metal phosphate can be removed from that particular surface; such that, you get a very clean material for electronic use or other views, where you use very clean and very neat metallic surface.

So, these salts are utilizing for phosphatizing the metallic surface. Then if we have some the boiler water treatment, so that boiler water treatment also that the water quality is also improved and for making some buffers because, as just now I told you that what type of salt you are using, whether it is a calcium salt or a sodium salt which is a typical sodium salt of phosphoric acid or a dihydrogen salt or a monohydrogen salt, will all will have a different PKA values because for 3 protons we can have three different PKA values.

And depending upon the PKA values and 3 different ranges basically, if we know the three different PKA values of the phosphoric acid, we now know that which salt we can

use to get a typical buffer at that particular pH. So, 3 PKA values will now control the corresponding buffer range for its buffering action for all these reactions. So, for a textile industry as for example, if we see for if you utilize it for textile industry and that particular textile industry, if it utilizing some particular buffer medium, so we have to choose that particular sodium salt which can give rise to the corresponding amount of pH of that particular buffer, which will be useful for your textile industry.

So, this particular one, as well as this one, the other one the disodium salt, so disodium dihydrogen diphosphate, so if we can have something; that means, Na_2H_2 and the phosphate diphosphate. So, this sort of very complex molecules we can have, but still it is a diphosphate material and that diphosphate material what we can get is that, it can also be utilized as a baking powder.

So, in the corresponding baking industries the baking industry can also utilize these as the corresponding salts. So, unlike our common table salt and all these things, so these are very useful salts starting from a leather industry to our food industry. So, food industry always will be very happy in making all these things, but the quality of these salts should be pretty high because it should be edible in nature and we utilize this for our eating purpose, we use this and we eat it with along with thus all this food material.

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In the second step, the resulting solution of monosodium phosphate is partially neutralized

$$\text{NaH}_2\text{PO}_4 + \text{NaOH} \rightarrow \text{Na}_2\text{HPO}_4 + \text{H}_2\text{O}$$

Orthophosphates, di- and monohydrogen phosphates

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So, this particular one once we have this; that means, one we get this as the sodium dihydrogen phosphate to make it disodium hydrogen phosphate this is; that means, you

can go for another level of deprotonation, so another level of deprotonation now what we can use that, the previously what we have seen, that we are going this particular form sodium hydrogen sulfate or sodium bisulfate, we are making we are not using any strong alkali like sodium hydroxide.

So, second step, so is as I told you that is a 2 step process for this 2 step process what we use this now in the for the second step; that means, for the getting this as from H_2PO_4 from H_2PO_4 , how we get HPO_4 , now you have to use some strong base. That strong base is nothing, but your sodium hydroxide. So, if we use the sodium hydroxide for this particular purpose, we can use get that particular NaHPO_4 .

So, all these things starting from something like your orthophosphoric acid, what do you see now that if, we completely remove all the protons from the orthophosphoric acid, we will end up with ortho phosphates like Na_3PO_4 , Na_3PO_4 is your example for your ortho phosphate. Then we can have di and monohydrogen phosphates; that means, we can have 2 hydrogens present in it that particular salt or 1 hydrogen present in that particular salt, is not only the nature of that particular salt, not only the amount of sodium present with that particular salt, but also the corresponding supply of the proton at a required required PKA value of the reaction medium which is also very important.

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The slide is titled "Ammonium phosphates" and features a yellow background with a blue header and footer. It contains two chemical reactions in a box:

$$\begin{aligned} \text{H}_3\text{PO}_4 + \text{NH}_3 &\longrightarrow \text{NH}_4\text{H}_2\text{PO}_4 \\ \text{H}_3\text{PO}_4 + 2\text{NH}_3 &\longrightarrow (\text{NH}_4)_2\text{HPO}_4 \end{aligned}$$

Below the reactions, a green box contains the text: "Used in fire protection e.g. as an additive in fire-extinguishing agents for fighting forest fires, as flame retardants in paper, textiles and poly(urethanes), in the prevention of afterglow in matches."

Below that, it states: "Tetrapotassium diphosphate - used in liquid cleaners due to its high solubility in water."

The footer includes the Swayam logo and a small video inset of a man in a light blue shirt and glasses.

So, what we get now that, if we just simply move quickly to some good example of ammonium phosphates, sodium phosphates we have seen because, the ammonium part

the ammonia NH_4^+ part is also very useful as we know like that of your ammonium nitrates ammonium part can be utilized very nicely for your fertilizer purpose to add some micro nutrients to your soil.

So, it is a very simple reaction now instead of giving sodium hydroxide or calcium oxide or calcium hydroxide, now you will use directly ammonia ion. So, ammonia will be added directly to give you the corresponding mono ammonium salt and the diammonium salt like that of your sodium. And they are very much useful, they can use for now fire retardant clothes that we are talking about now for fire protection that as additives in fire extinguishing agent for fighting forest fires; that means, when you have a huge fire and the huge amount of fire extinguisher are not working.

So, we all should know what is the corresponding mechanism for the different fire extinguisher; nowadays, because even the spraying carbon dioxide can function as a good fire extinguisher. Similarly large number of some is foam based some is the other type of base, but we should know also because even we also do not know, you only seen small fire in some building, in some library, in some school or colleges.

But we do not know how we have to tackle the corresponding fire in forest because, we do not have much in our country, but in some advanced countries like US and in all other cases they are there firefighting system is so equipped that this would fight the corresponding fire in the different forests because, then we all know that is where only few days back and you see that the California coast and all other things are there because their wind; wind is also very high speed they are moving. So, fire is moving one place to other and the whole forest is getting burnt away.

So, we should have some special technique for that particular one. So, in fighting the forest fires, we use this particular ammonium salts for that. Then fire retardant papers, which will not catch fire very quickly, then textiles and their polyesters. Then poly which polyesters some polyesters are your poly urethanes, so poly urethanes are there is one variety and sometimes to prevent the afterglow in matchsticks, when we burned the matchstick then sometimes we say that is we extinguishing the fire your matchstick is glowing.

So, to retard or to prevent that particular afterglow because that is dangerous because sometimes, we just extinguish the flame of the matchstick and we throw it away, but still

you have the afterglow on the matchstick. So, we have to use some material or some chemical for that chemical treatment of that particular purpose and that chemical treatment is nothing, but use of this particular simple ammonium phosphate salts.

And this ammonium phosphate salts, so this is not the end of all these things stories up here and one of them is therefore, is that also if we can able to make is that tetrapotassium diphosphate, which can be used as the liquid cleaners due to its high solubility in water.

Since it is a tetra potassium; that means, 4 potassium ions are there, no hydrogen nothing is there, so all the potassium can come out as the potassium ions from that particular salt and which can be very useful as because the phosphates will remain in the liquid medium, which can be very useful as a liquid cleaner. So, liquid cleaner or liquid cleanser which can use some other type of salts, so all these salts have very useful application for this particular phosphorus based compounds.

Thank you very much.