Chemical Technology
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Module - 8
Polymer
Lecture - 6
DMT and Terephtalic Acid, Polyester,
PET Resin, PTB Resin

We are discussing the module 8 of the organic chemical technology course, and in the lecture 5 we discussed about the nylon 6 and nylon 66 and the various raw material for the nylon 6 and nylon 66. But, so for the development of the synthetic fiber industry and the 2 textiles, which you can say and that was only major back to was with the coming of the polyester.

So, we will be discussing in case of this synthetic fiber industry that is the d m t terephthalic because these are the two important feed stock for this polyester. And then in brief we will be discussing about the PET resin and the PPT resin because, now the PET and the PPT that is being used in large scale and lot of the development is coming. Especially in the packaging industry use of the PET and PPT. So, for the DMT or the terephthalic acid is concerned it was starting in the DMT with the development of the various purification technologies, it was possible to shift from the DMT to terephthalic acid. And what we called it the purified terephthalic acid.

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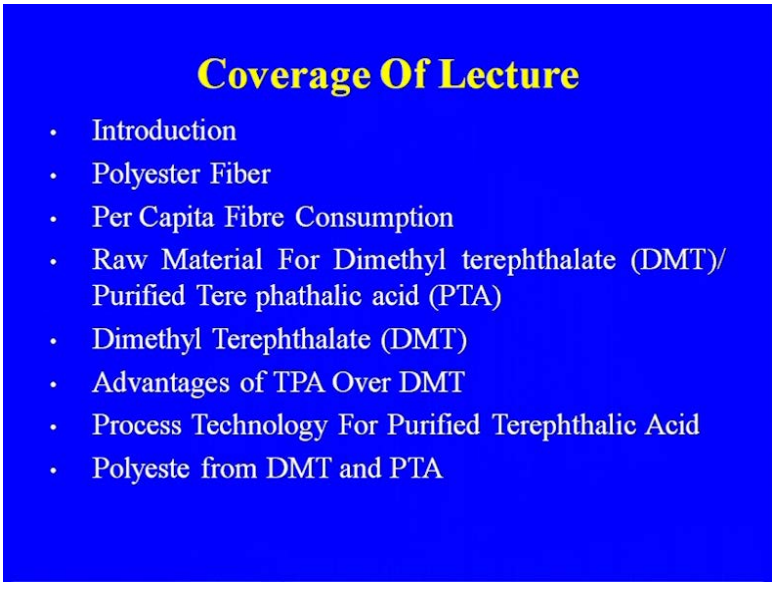

That is the raw material for the starting phase of the development of the polyester that was from the d m t and from it was shifting from the DMT and terephthalic. Because of the crystallization process or the sublimation process that was developed for the purification of the terephthalic acid. So, the coverage of the lecture will be introduction, polyester fiber importance about the polyester, fiber per capita consumption of the polyester, raw materials for the dimethyl terephthalate and purified terephthalate.

Then manufacture of dimethyl terephtalate, then the manufacture of the purified terephthalic acid. We will be discussing in detail advantage of the purified, some time both what we are using TPA terephthalic acid or PTA purified terephthalic acid what the advantage of what was the reason are because, now the most of the units of the polyester which are using the DMT in that has been either close or that has been shifted to the TPA as a raw material.

So process technology for the purified terephthalic acid, here we will be also discussing what the various routes are? Various routes are available for the purified but, two important processes which is available mobile process that is we are using one is based on the crystallization and the sublimation and there is for the only one is the crystallization. Another is the sublimation process for purification, then the polyester from the DMT and the PTA.

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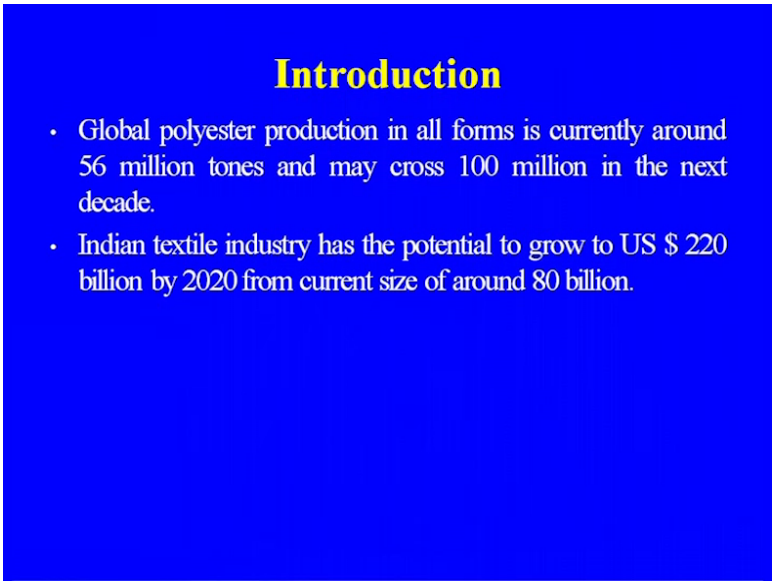

How we are making the polyester the same way as we discussed about the nylon six here also the process after the polymerization we are getting the polyester which may be either as a chips you can get or it will go to the your spinning process where the polyester fibers stables. Whatever and whichever the form that is required that you can produce and also in the last we will be discussing about the PT resin and DPT resin.

So, for the polyester is concern as I told you the one of the very important part of the synthetic fiber. Global polyester production in all forms is currently around fifty six million tones and may cross hundred million tons in the next decade, Indian textile industry has the potential to grow about two twenty billion u s dollar by two thousand twenty from the current size of eight eighty billion .

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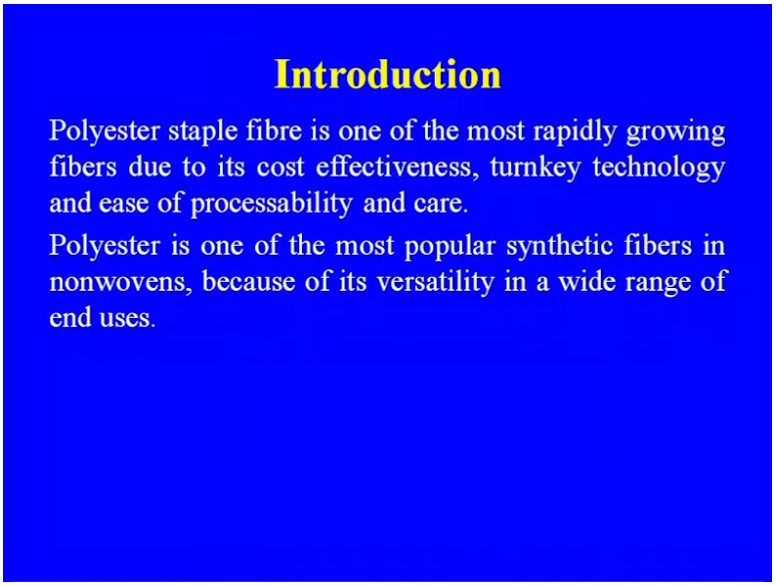

So, this was the how the growth reaches of the polyester. Now, let us discuss about the importance of the polyester fiber. Why we need the polyester and what was the actually the real development? Which has taking place in case of the synthetic fiber industry because of the coming of the polyester the various, actually the combination of the polyester with the cotton with the acrylic fiber that is there and this has reduced the cast considerable of the textile material. So, polyester staple fiber is one of the most rapidly growing fibers, due to its cost effectiveness turnkey technology and ease of the process ability and the care polyester is one of the most popular synthetic fiber in nonwovens because of its versatility in a wide range of end users.

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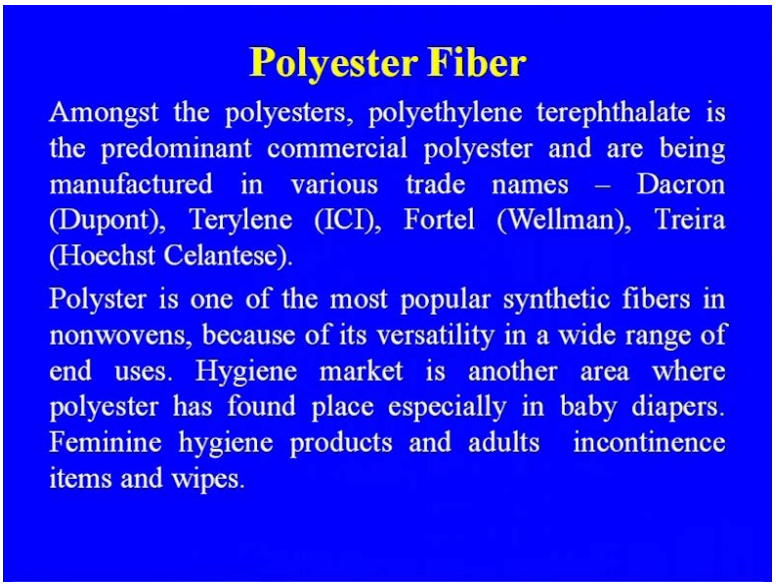

Amongst the polyester, polyethylene terephthalate is the predominant commercial polyester and are being manufactured in the various trade names means this is the p polyester means the that is the name of the Dacron terylene treria that is the Hoechst celantese. So, these are the treria that is another trade name for Terylene and Dacron. These are the two famous trade name one was because due point has been the pioneer in the manufacture of the synthetic fiber, whether it is in nylon six or polyester.

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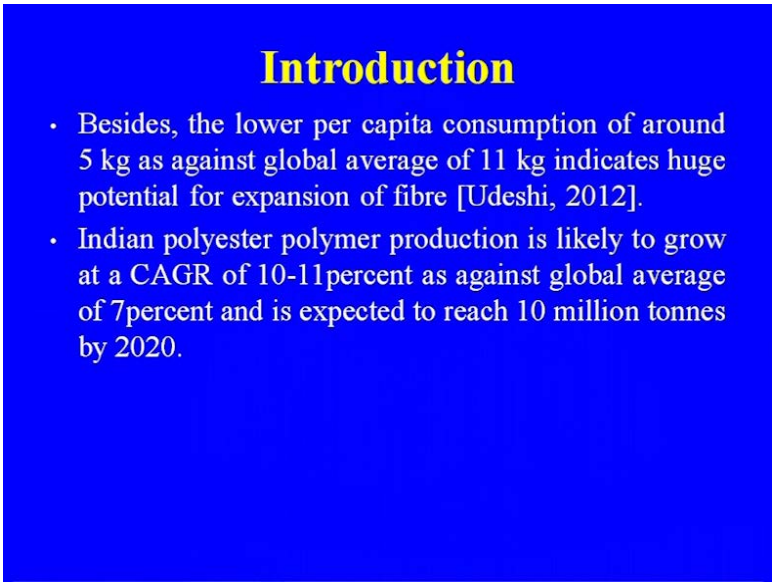

So, polyester is one of the most popular synthetic fibers in nonwovens because of its versatility in a wide range of end users. Hygiene market is another area where polyester is found an place especially in the baby diapers because now you see the use of the diapers that has increased like anything and so this is the another actually importance in case of the polyester fiber. Then the feminine hygiene products and adults incontinence items and wipes these are the other uses of the polyster.

Beside the lower per capita consumption of around five k g in India as against the global average of eleven k g, that indicates that there is huge potential for the expansion of the polyester industry in India. And this is the reason number of large units that has come which are making the polyester as well as the PET resin also, and then we are also having this export market for the polyester and especially the reliance they are supplying their polyester to other country. Also Indian polyester polymer production is likely to grow at the ten to eleven percent as against the global average of seven percent and is expected to reach ten million tons by two thousand twenty.

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Per Capita Fibre Consumption

Kg/per capita	2000	2011
North America	35	35
Latin America	7	8
West Erope	22	24
East Europe	6	12
Africa/M.east	3	4
China	10	20
India	4	5

This is the per capita consumption of the various fibers. Which we are seeing and our per capita consumption, that is low and so there is lot of the scope of the development of the synthetic fiber industry.

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World Consumption Of Non Woven Man-made Fibers (% Of Total)

Man-made Fibers	2000	2007
Polyester	22.5	23
Polyamides	1.5	1.5
Acrylic fibers	2.0	3.0
Polypropylene fibers	63.0	62.7
Viscose rayon	8.0	7.0
Other synthetic fibers	3.0	2.8
Total consumption, million tonnes	3.3	4.0

This is the percentage of polyester that we are making from the nonwoven manmade fibers. Woven it is more, it is the only in the nonwoven sector because the polypropylene is showing high figure but, polyester in the woven sector it is the maximum is of the polyester.

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Capacity and Production of Polyester in 2010-11

Polyester	Installed Capacity	Production	
	2010-11	2005-06	2010-11
Polyester Filament Yarn	1730	1015	1496
Polyester Staple Fibre	1266	623	1036
Polyester Staple Fibrefil	67	47	53

43 Capacity and production of Synthetic fibre in 2010-11, ('000 MT)

This is the capacity and production of the polyester in India and the polyester filament. Because we are having the different for yarn staple i staple fiberfill. So, the three category of the polyester that is available and this is the install capacity and this is the

production this is one seven three multiplied by one hundred one thousand tons this all figure multiplied by one thousand tones.

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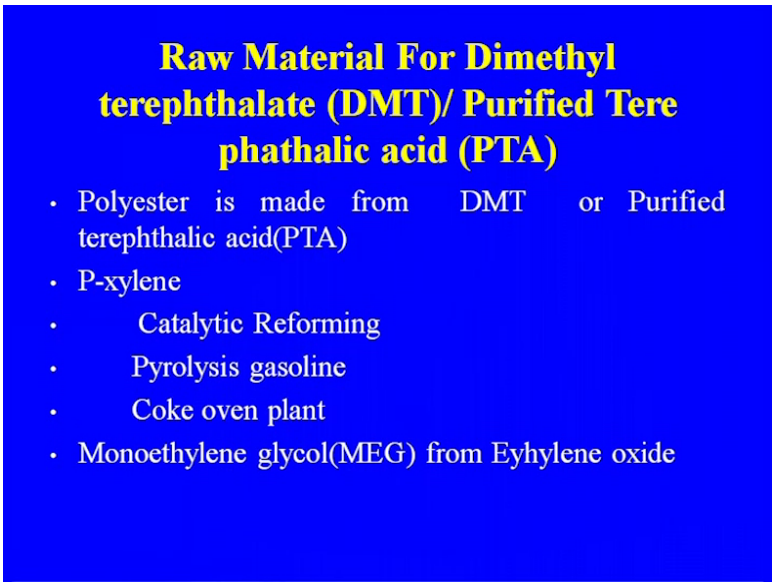

So, the raw martial for dimethyl terephthalate or the purified terephthalate PT or TP do not confuse with PT or TP both are the same but, DMT or the terephthalic raw material again the same for both. The polyester is made from the DMT or purified terephthalic acid after the polymerization of DMT or the purified terephthalic acid. Here actually the Para xylene that is the major raw material for making of the DMT or the terephthalic acid, this is the Para xylene which we are getting one of the major source that is the catalytic reforming another source may be the pyrolysis gasoline coke oven plant. Earlier before coming of the petro chemical complex heat for the coke oven plant that we were getting the aromatics although the yield of the Para xylene, that is much less in case of the coke oven plant.

Another important feed stock that; we need in case of the polyester manufacture. That is mono ethylene glycol and one of the biphotophitial which we are getting here. In case of the polyester manufacture in the DMT that is the methanol and this is the world capacity of the methanol. One source of the methanol that is also shown through the DMT routes because in the process we are getting the methanol. So, let us discuss about the dimethyl terephthalate and then I will discuss about the compare why shifting from the dimethly terephthalate to terephthalic acid is there.

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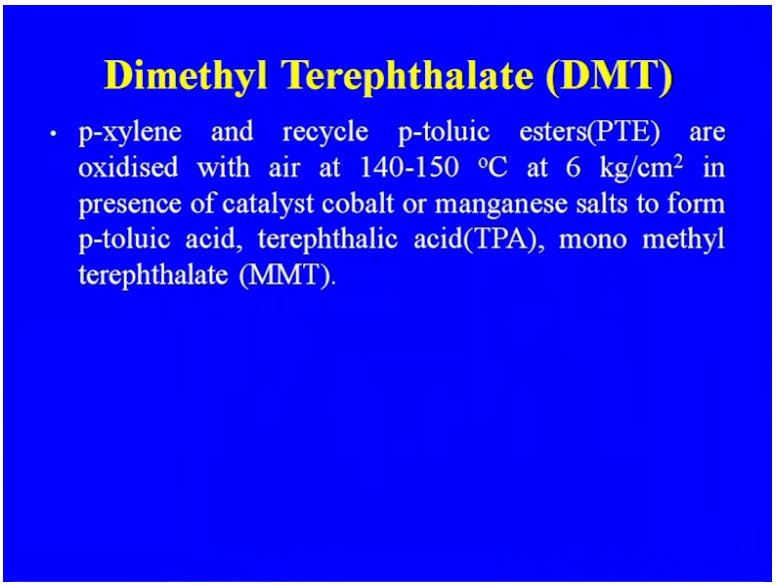

So, Para xylene and the recycle Para toluic because, Para toluic acid is formed in the process or oxide with air at one fifty to one fifty degree centigrade in the presence of the cobalt or manganese salt to form Para toluic acid, terephthalic acid and mono methyl terephthalate. This Para toluic acid which is the Para toluic that recycled in the system.

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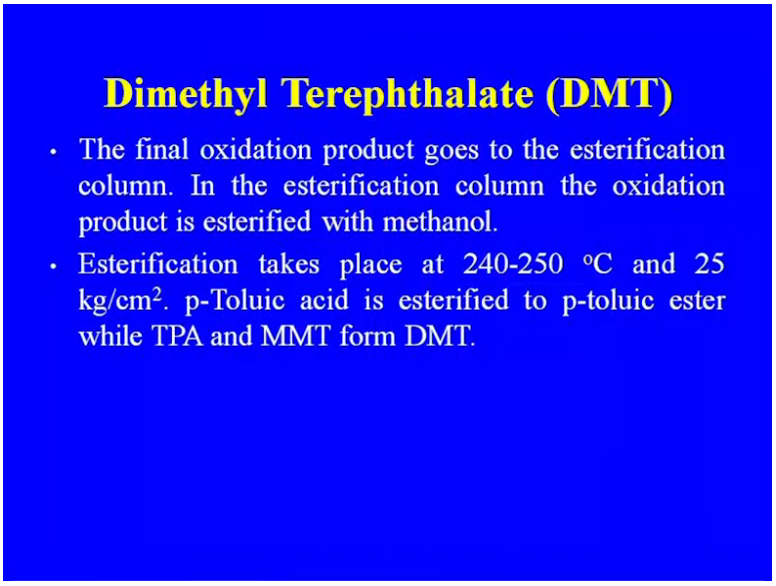

The final oxidation product goes to the esterification column. In the esterification column oxidation product is esterified with methanol. Esterification takes place at two forty to two fifty degree centigrade Para toluic acid is esterified to Para toluic ester while TPA

and MMT form, DMT that is dimethyl terephthalate and that is the crude terephthalic acid and this MMT that is making going for the DMT.

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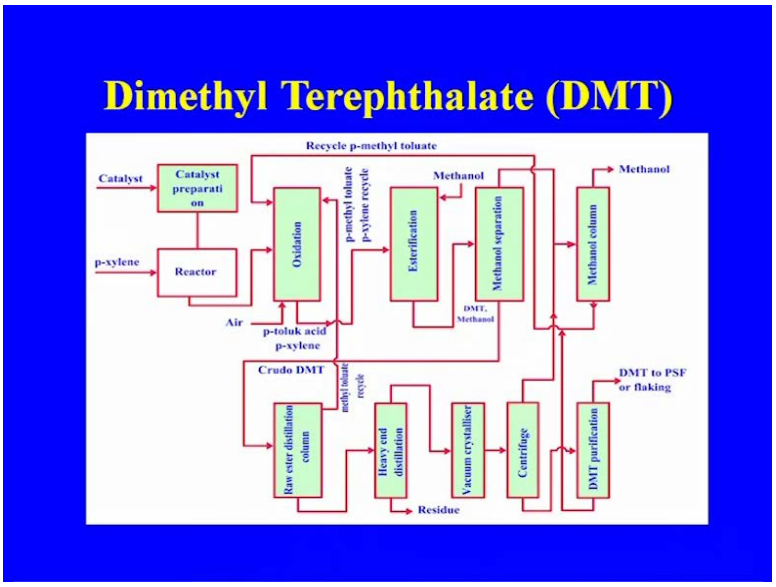

This is the process before going to the process for dimethyl terephthalate that is the Para xylene that is going to the catalyst preparation section. Then Para xylene that is going to the reaction section oxidation esterification where methanol and here as i told you during the process methanol again, it is been generated in the reaction and the final that the DMT that is going for the polyester plant for making of the polyester that is the polymerization of the d m t.

So, these are the series of distillation column where the separation that is taking place and the vacuum crystallizer is there, the centrifuge is there where the centrifugation is there and the recycle Para methyl toluate that is going again to oxidation term and finally, the DMT that is going to d m t purification section. So, this is the process which we are using here actually, these are the separation of the methanol that is taking place here and here the top product that is going to the methanol column.

Because this is light end that is going to the methanol column where the separation of the methanol that is taking place. Now, let us come to the terephthalic acid which I told you that all the polyester units we are using the DMT that has been either close or they have been shifted. They have shifted their raw material from DMT to terephthalic acid and so DMT was the traditional raw material for the manufacture. Even during the starting

when the polyester came into the market it was the Bombay dying which started manufacturing the DMT and the DMT to polyester.

But, after coming of the pathalgana plant of the reliance industry they started making this polyester from the terephthalic acid that was the actually the change over from the raw material and now this situation because they are making terephthalic acid in their hajara plant and so, the most of the market of the polyester that is from the terephthalic acid and another one of the big unit that has come that is the Indian

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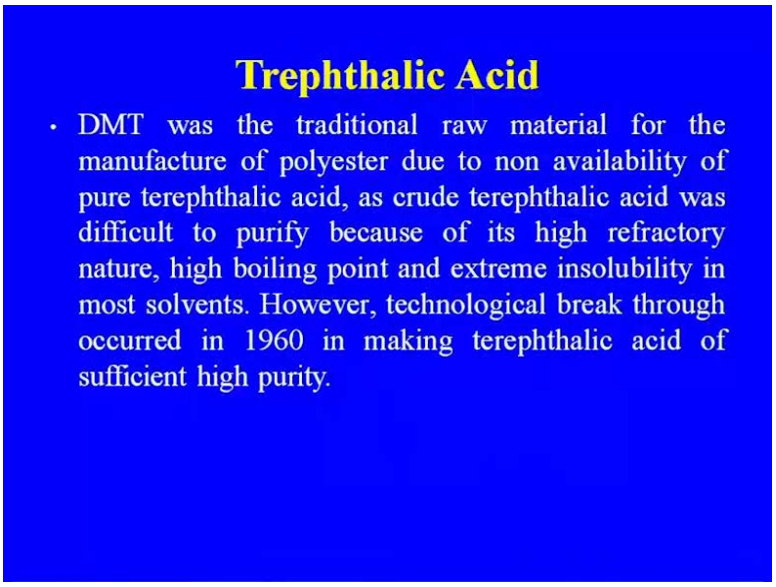

Panipat refinery, they have started their terephthalic acid plant which is again the Para xylene route. Para xylene to terephthalic acid they are making and that is one of another major development that took place in case of the terephthalic acid manufacture. So, the DMT which was the traditional raw material for the manufacture of polyester, due to non availability of pure terephthalic this was the problem during the initial stage of the polyester manufacture. When the DMT was used for making the polyester as crude terephthalic acid was difficult to purify because of the high refractory nature high boiling point and extreme insolubility in most solvents.

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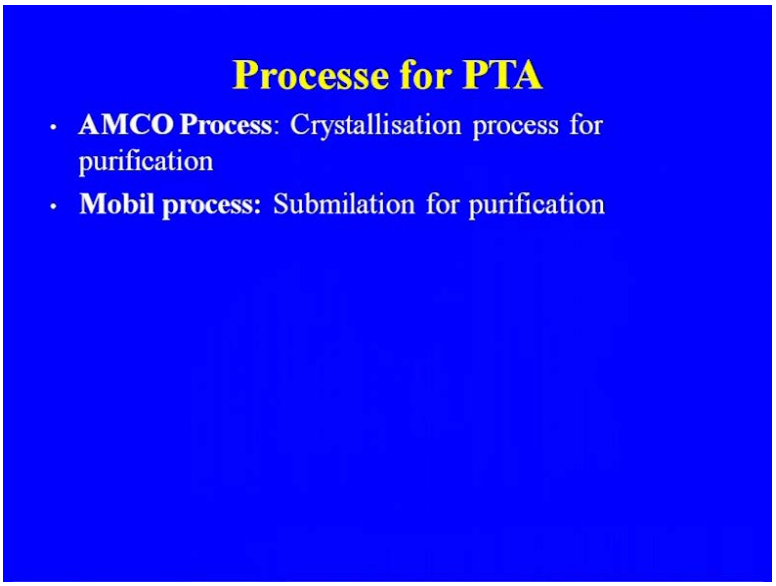

However, the technological breakthrough occurred in nineteen sixties in making the terephthalic acid of the sufficient high purity with the development of the separation. The purification process based on the crystallization and the sublimation these are the two processes by which we are making the purified terephthalic acid. One is the AMCO process where the crystallization process is used for purification, another is the mobile process where the sublimation is used for the purification of the terephthalic acid.

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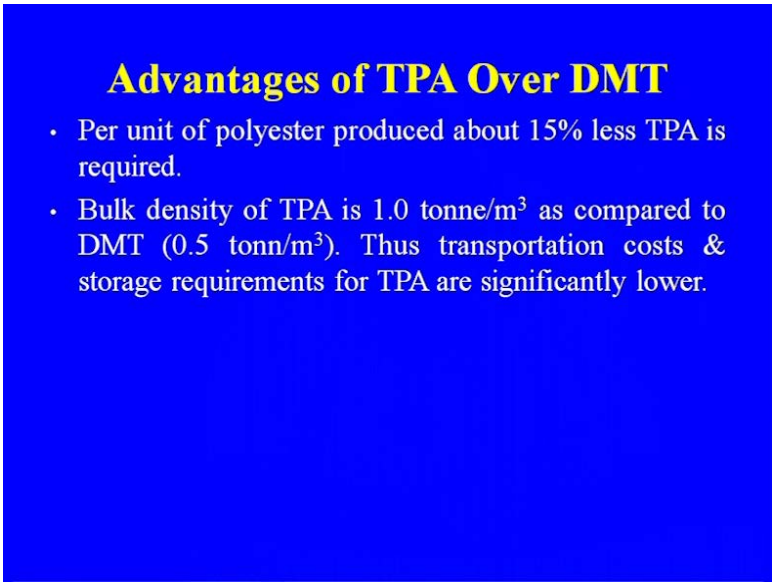

So, let us discuss why TP over DMT what was the need for shifting from TPA to DMT. per unit of the polyester produce about fifteen percent less TPA as required. If you compare with the DMT bulk density of TPA is one point zero as compared to DMT it is zero point five. Thus the transportation cost and storage required for TPA are significantly lower because of the higher bulk density in case of the terephthalic acid.

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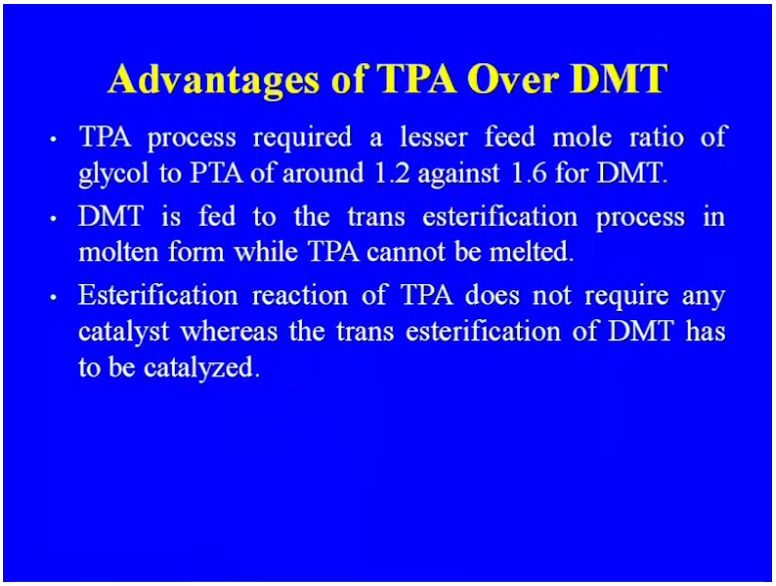

Another advantage TPA process required a lesser feed mole ratio of glycol to PTA because here in the process we need the ethylene mono ethylene glycol is around. This is the one point two against the one point six for DMT that is the mole ratio of the glycol to PGAPTA. Again we are using as I told you the PTA is term we are using for the purified terephthalic acid. DMT is fed to the transesterification process in molten form while the TPA cannot be melted. So, esterification reaction of the TPA does not require any catalyst where as the transesterification of DMT as to be catalyzed with

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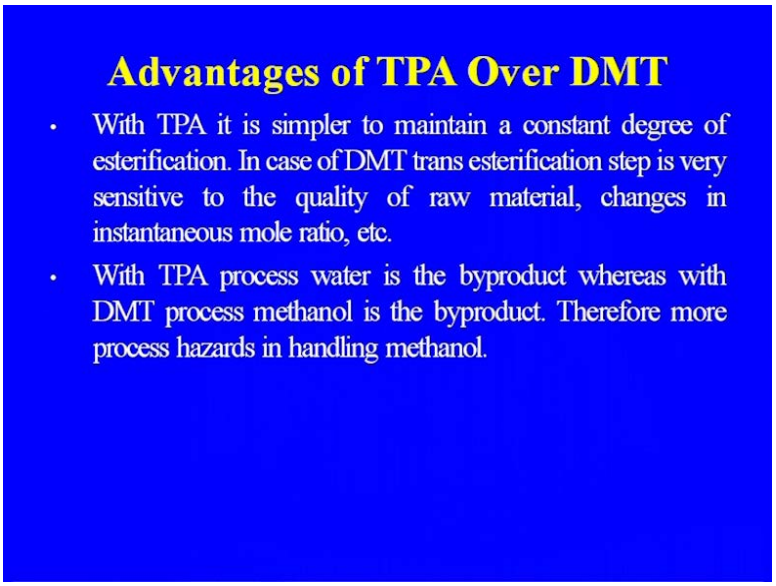

TPA it is simpler to maintain a constant degree of esterification. In case of a DMT transesterification step is very sensitive to the quality of the raw material, changes in the instantaneous mole ratio etcetera. So, this was the actually, the purity of the product that was also one of the reason of the shifting from DMT to TPA because the polyester which you are getting from the purified of the better quality than what we are getting from the DMT the TPA process water is byproduct where as with d m t process methanol is the byproduct. Therefore more process hazard in handling of the methanol. That is there in case of the TPMT process.

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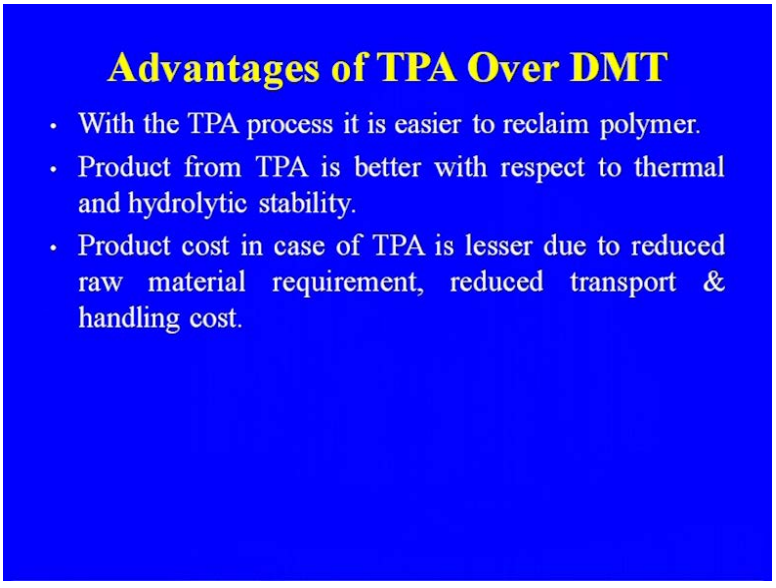

Another advantage that with the TPA process it is easier to reclaim the polymer, product from the TPA is better with respect to the thermal and hydrolytic stability, product cost in case of the TPA is lesser due to the reduced raw material requirement reduced transport and handling cost which I told you that the work density is less at the same time raw material requirement in case of the terephthalic case is less than fifteen percent less than this d m t.

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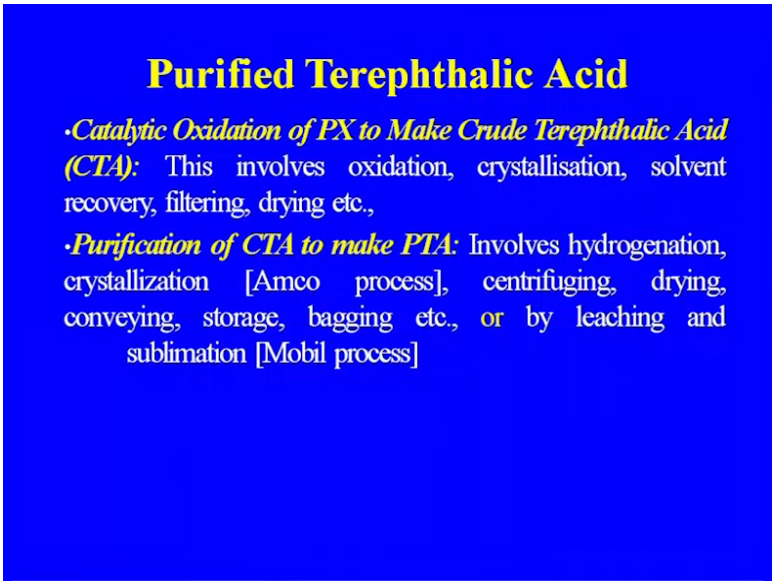

So, let us discuss what is the method that we are using so the purified terephthalic acid catalytic oxidation of Paraxylene to make crude terephthalic acid. This involves oxidation crystallization solvent recovery or filtering or drying purification of CTA to make PTA involves hydrogenation crystallization. That is in case of the AMCO process centrifuging drying conveying storage bagging or by leaching and sublimation that is in case of the mobile process. So, both these technologies are available and that is being used for the making of the purified terephthalic acid.

During the leaching because in the mobile process let, us discuss during leaching impurities like Paracarboxy benzaldehyde and cobalt catalyst are removed from the crude TPA. Crude TPA is further purified by sublimation.

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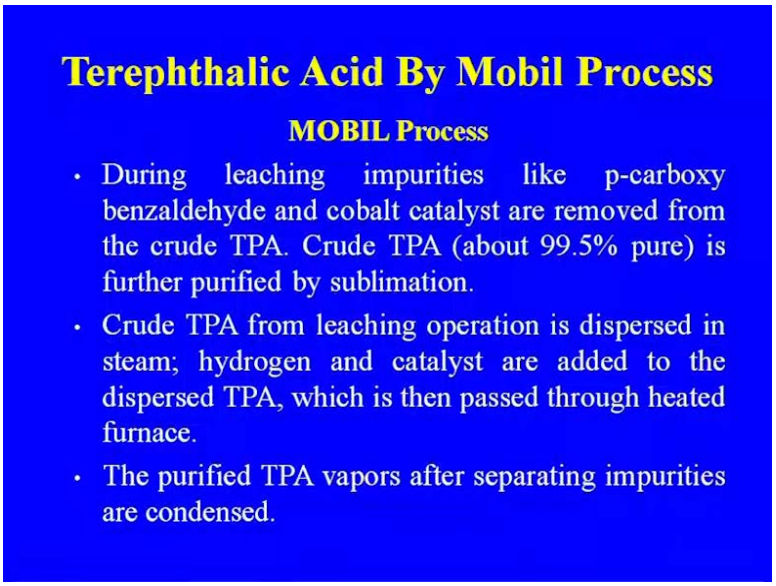

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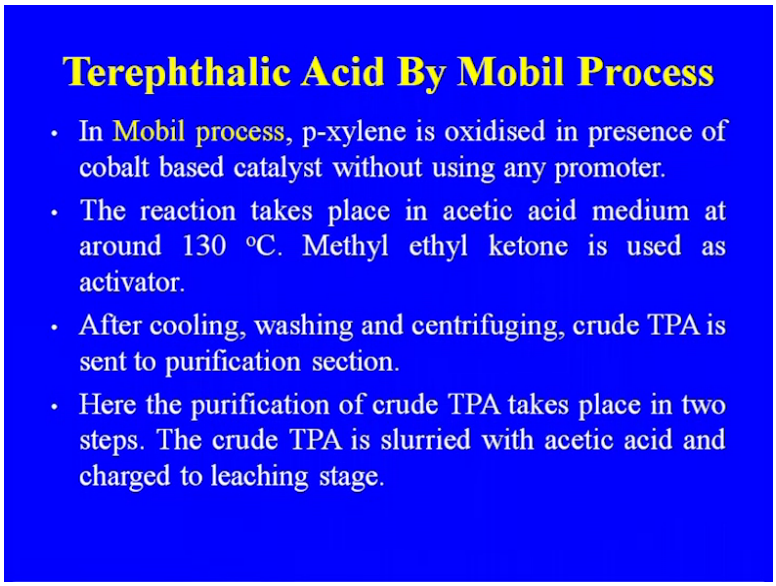

So, let us first discuss this mobile process the Para xylene is oxidized in the presence of the cobalt based catalyst without using any promoter. The reaction takes place in acetic acid media at around one thirty degree centigrade methyl ethyl ketone is used as activator after cooling, washing and centrifuging, crude TPA is sent to the purification section. Here the purification of the crude TPA takes place in two ways. The crude TPA is scurried with the acetic acid and charged to leaching stage.

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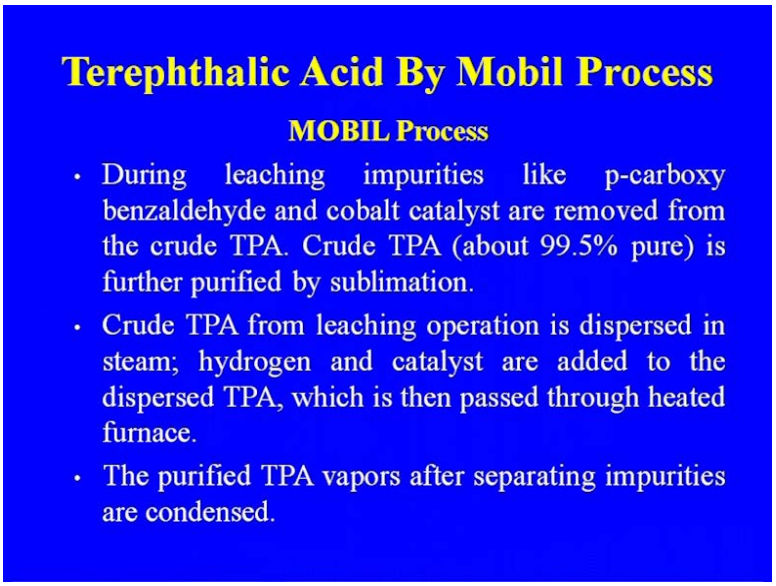

So, this was about during leaching impurities are removed crude TPA from leaching operation is dispersed in steam; hydrogen and catalyst are added to which is then passed through the heated furnace. The purified TPA vapors after separating the impurities are condensed.

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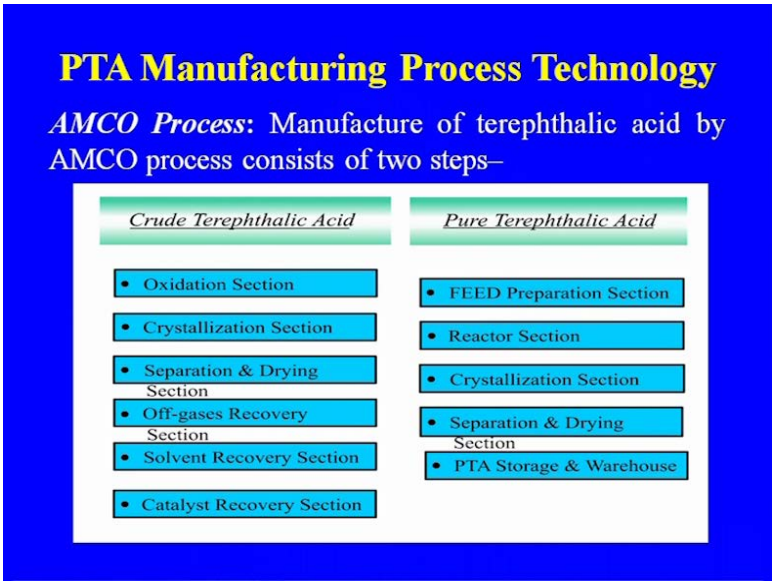

This is the AMCO process oxidation crystallization separation and drying, off gases recovery, solvent recovery, catalyst recovery and this is for purifying the feed

preparation reactor section, crystallization, separation, drying and the PTA storage. Here we don't have that sublimation process was there in the mobile process.

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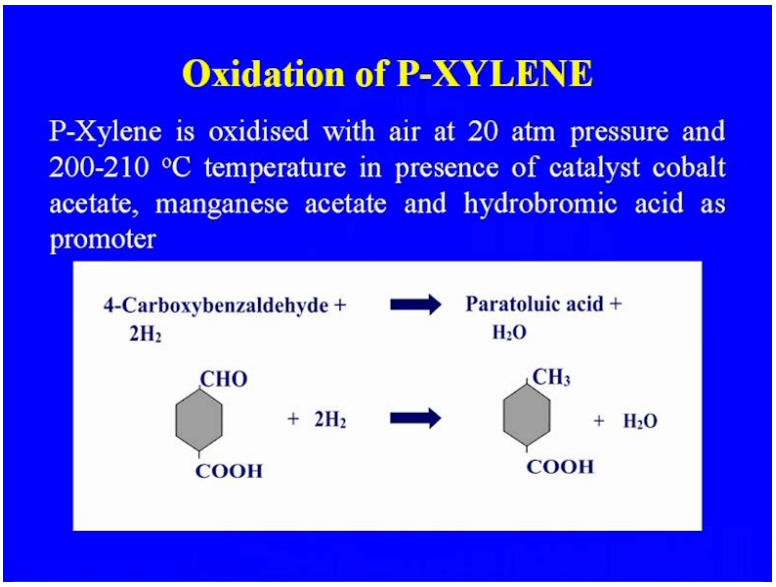

This is the reaction that is taking place in case of the Paraxylene. That is in the presence of air that is oxidized at this Para xylene is oxidized with air at twenty atmosphere pressure in presence of the catalyst cobalt acetate, manganese acetate and hydrobronic acid as a promoter.

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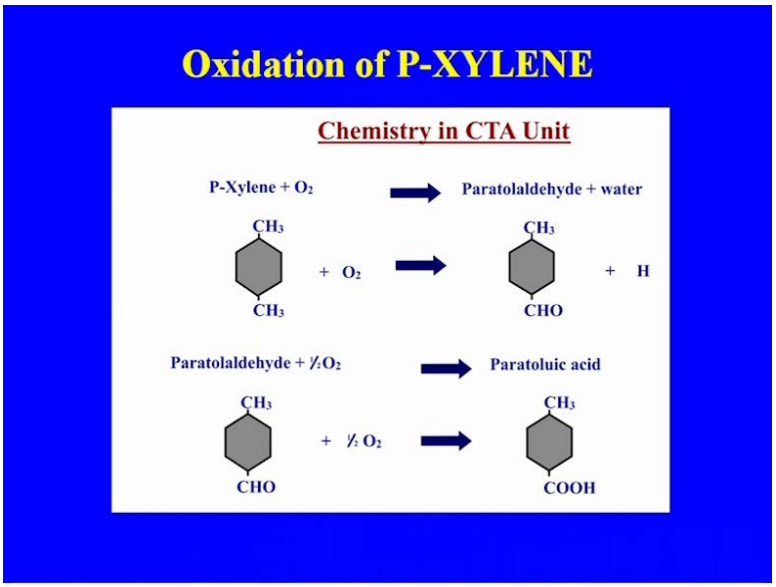

These are some of the reaction that is these are the reaction that is taking place in case of your. Actually, the hydrogenation part that was for the removal of the impurity that is here in this case this was for the removal of the impurity.

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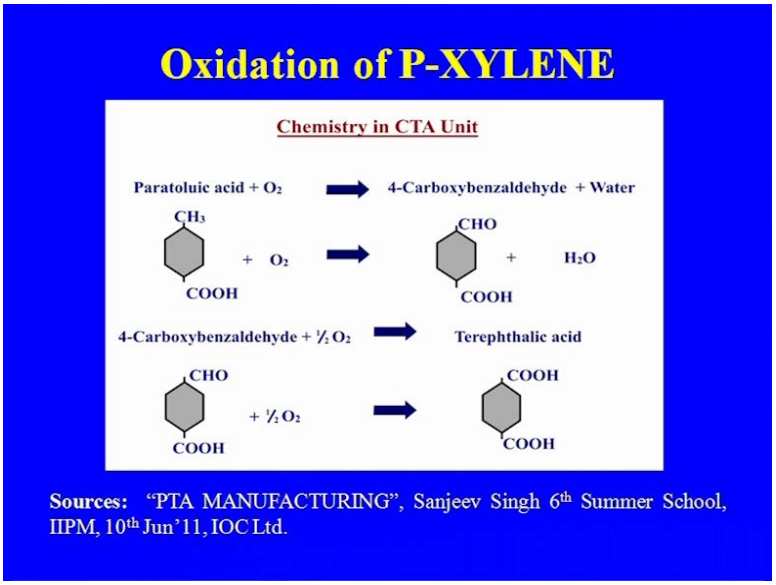

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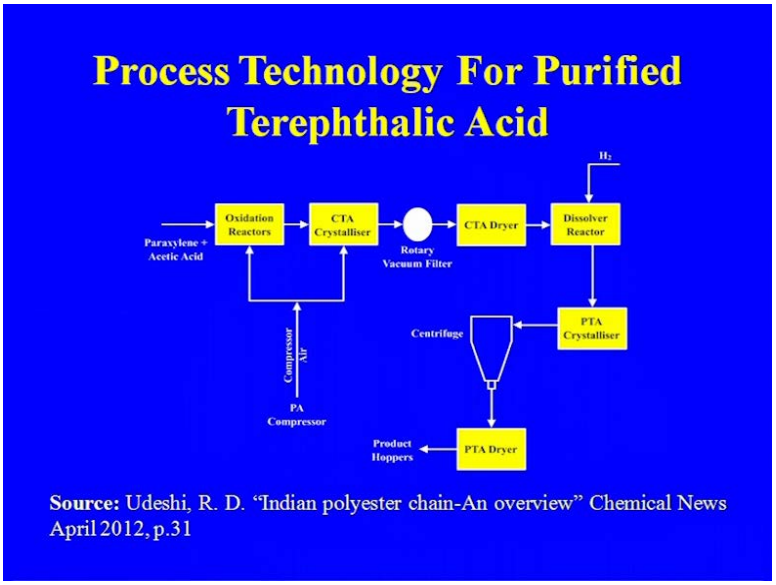

And chemistry in the case of the crude terephthalic acid this is the reaction that is taking place. Oxidation and then this is in case of the finally, the Paratoluic acid which is there that is because that is again changed to the four carboxybenzaldehyde plus oxygen and this is converted to terephthalic acid. And this terephthalic acid which you are getting is

the four carboxybenzaldehyde; this is the process that you are getting from the oxidation of Paratoluic acid to four carboxybenzaldehyde.

This is the process technology for purified terephthalic acid Para xylene preceding the oxidation reactor. Here actually one of the acetic acid that is used in during a process and so, this crystallizer rotary vacuum filter dry dissolver p t a crystallizer. Here actually, two stages of the crystallization that we are taking and finally, the PTA that we are getting here which may go on further for spinning.

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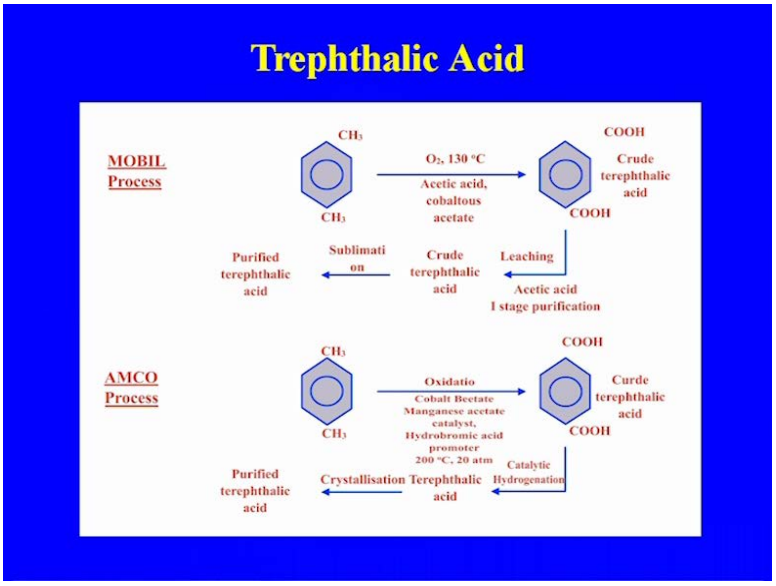

These are the various reaction that is taking place and as I told you the purification part of the crude. In case of the mobile process that is the sublimation, in case of the AMCO process the crude terephthalic acid through the crystallizer, that is going to the series of crystallizer and then the purification that is taking place. So, for the oxidation part is concerned that is not much different only in case of the impurities that has to be removed during the process and the care that has taken in case of the purified to get a pure terephthalic acid which was the problem in the initial stages of the DMT the polyester manufacture from DMTM?

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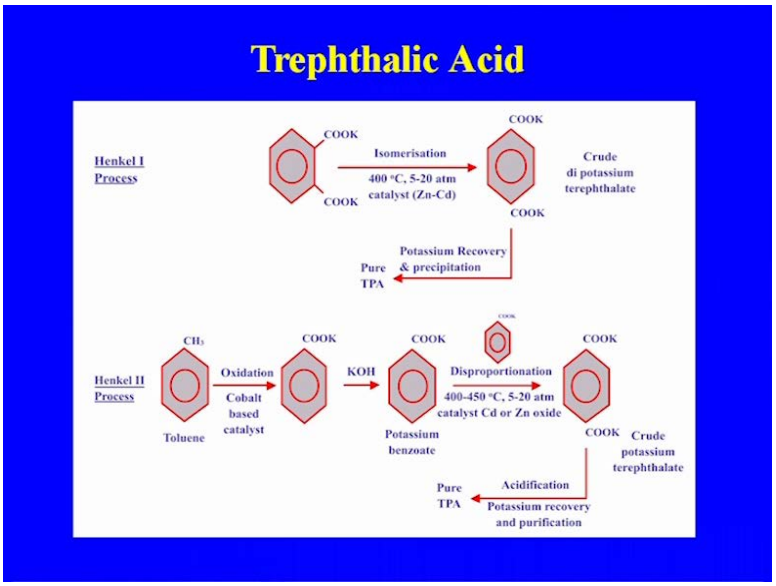

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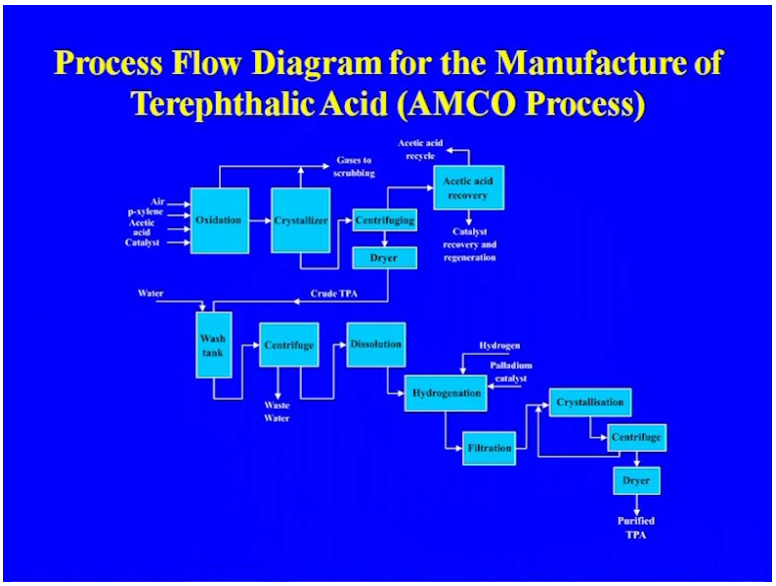

These are the two another process that has been developed. That is the Henkel process or the Henkel two processes, this is the AMCO process in more detail that as I told you we are having the oxidation crystallizer centrifuging. Then again wash tank centrifuging hydrogenation for removal of the impurities filtration. Again crystallization centrifuging and drying so, this part is for the removal of the impurities which is present there

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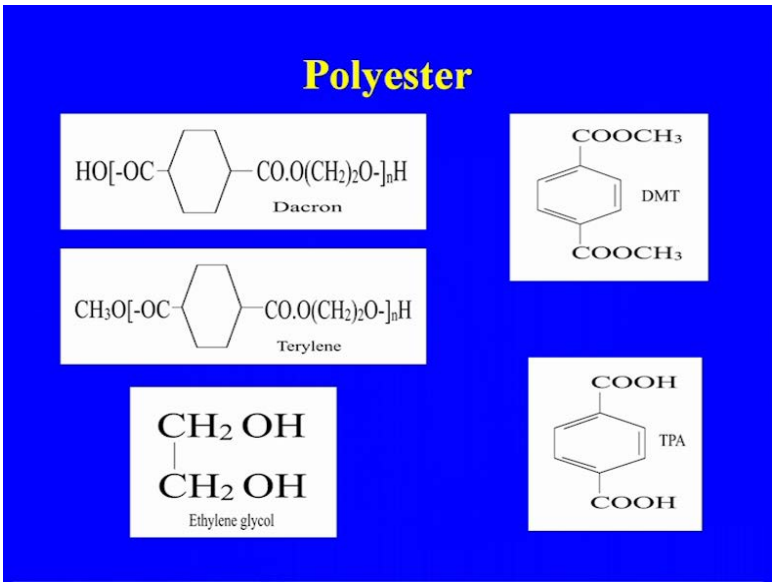

And this is for the separation from here it is going through for recovery of the acetic acid that you are getting again, that is present in the reaction

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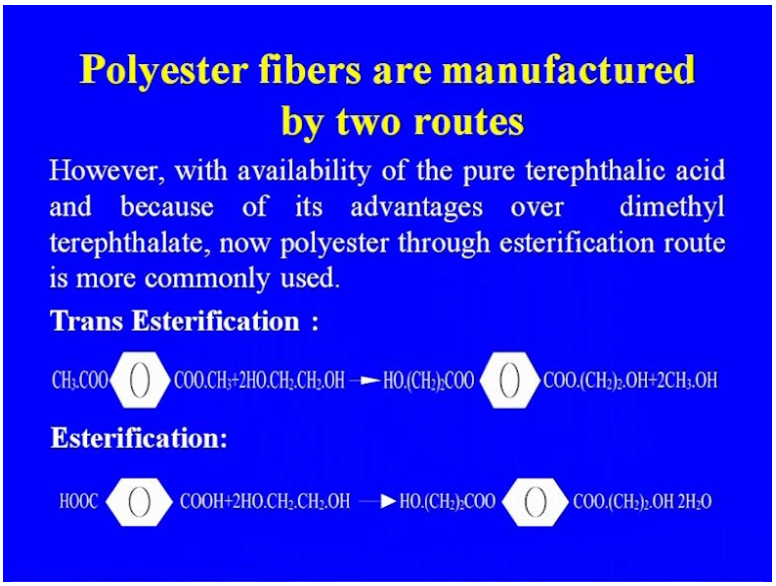

So, as I told you that we are having the two routes. One is this DMT route another is your terephthalic acid purified terephthalic acid route. So, the transesterification or the esterification reaction that is taking place. In one case that we are getting the methanol as a byproduct but, another case only the water is coming. So, this is the difference between

these two process apart from the purity handling of the DMT or the advantage of the raw material this is one of the another because this part.

But, so for the image is concerned in both the process that we are using only this, is the process hazard that is there in case of when you are going for the DMT root. Now, let us discuss the polyester process technology. What are the various steps involved in making of the polyester?

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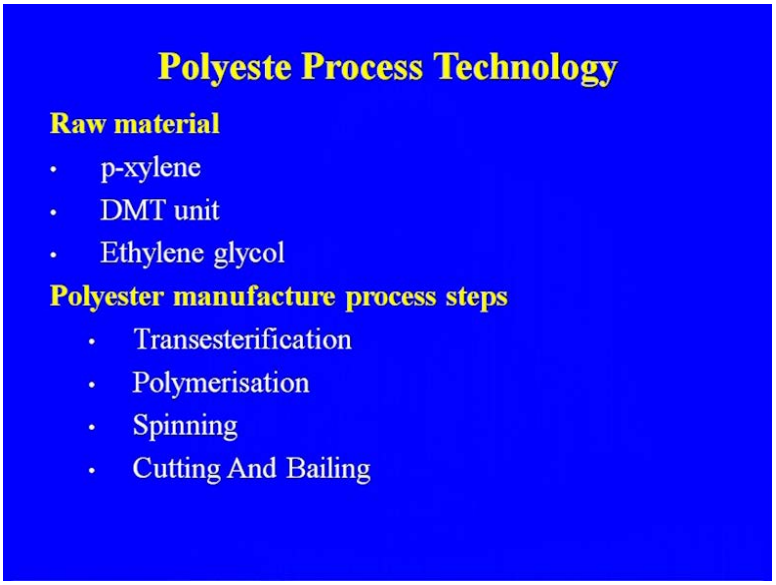

Here actually, the raw material as I told you that is Para xylene DMT or it may be PGA unit depending upon it. It may be DMT or PTA then the ethylene glycol polyester manufacture that from the PTA the transesterification.

Polymerization spinning cutting and bailing because here also the polyester which are melt. We are having is three types of the spinning process one is the melt spinning another is the dry spinning and third is the wet spinning. So, in the case of the nylon and polyester we are having the melt spinning. But, in case of the akalic fiber which will be discussed in the next lecture. What we are doing that or even in case of the viscous rayon we are having the wet spinning process where the resin regenerated.

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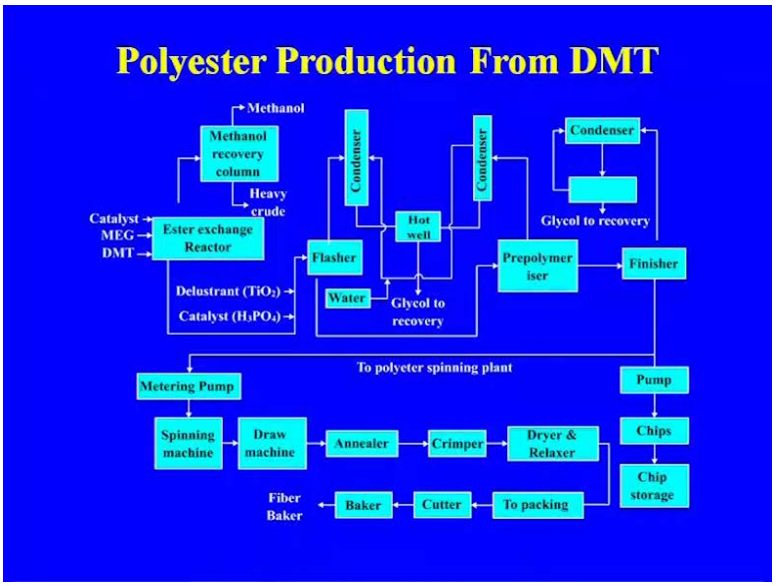

In the case of the viscous rayon and here also the regeneration of the fiber that is taking place in case of the akalic fiber. But, with the development of dry methyl formomide solvent now, the spinning of the akalic fiber that has been actually the process that has been more simplified. And so, we are using in case of the melt spinning it is melted and then it is passed to in case of this dry spinning.

It is dissolved in a solvent and then passed through and while coming with the hot air steam. That is the removal of the solvent that is taking place. So, here in case of the spinning process we are using the melt spinning. So, this is actually in case of the DMT route and here also your seeing that with the same chips. That is the chip storage to packaging or it will be the chips which you are getting after the polymerization the chips that will go for the metering spinning. Draw machine annacaler and the crimper and then the dryer and relaxer? So the process is same only here, reaction which i discussed earlier that slightly difference in the reaction is there and here you are getting methanol as a byproduct in the process

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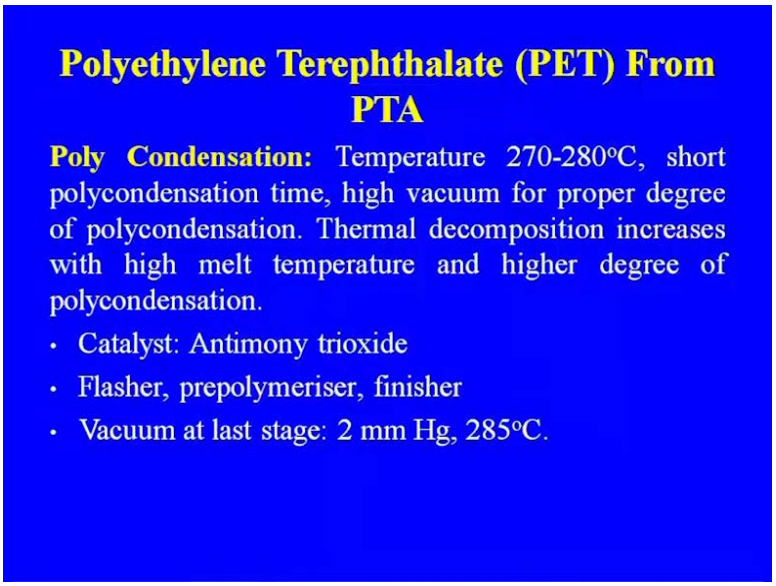

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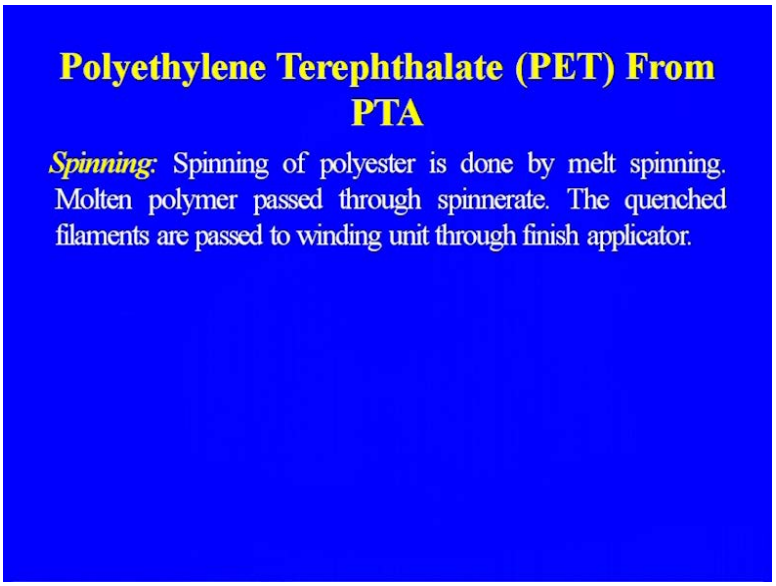

So, this is the polyester from the DMT route where methanol that you are getting as a byproduct. So, as I told you there are two steps involved one is the in case of the polyester that is one is the your poly condensation another is spinning process after the polymer which your are getting. So, there are the catalysts which are being used antimony trioxide flasher prepolymeriser finisher vacuum. This is the reaction this is operating condition that you are having the vacuum at the last stage. Two meter HG temperature is around two eighty five degree centigrade. Spinning of the polyester is done by melt spinning. Molten polymer passed through spinneret number of the

spinneret fine poles are through that spinneret that is the molten poly molten has been passed. The quenched filament, are passed to winding unit through finish applicator.

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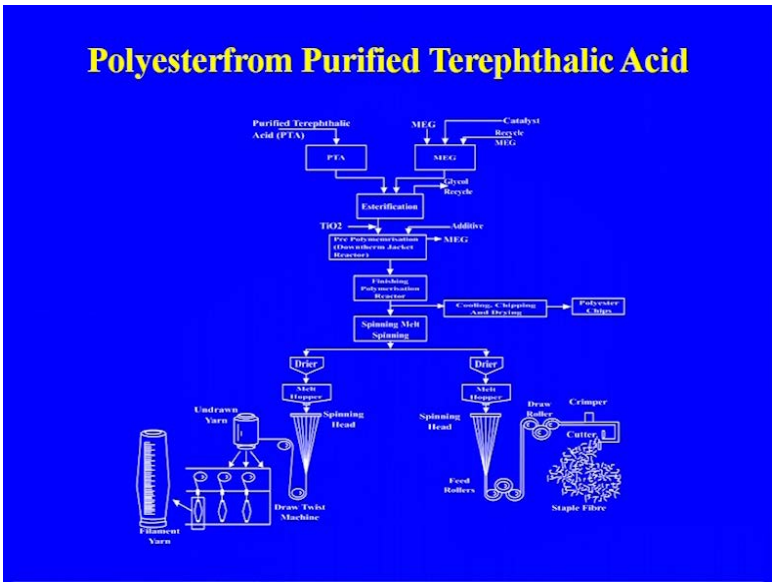

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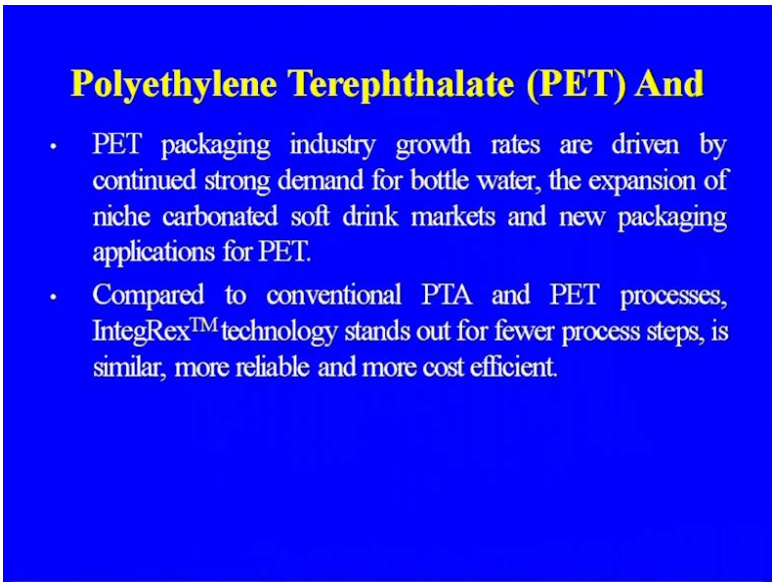

So, this is the process which already we discussed the two types of the fiber we are getting the stapled fiber or the yarn. That your continuous yarn that you are getting now discuss about the polyethylene resin. The PET resin packaging industry growth rates are driven by continued strong demand for bottle water mineral. Water that is one of the huge amounts of the bottle that you are using the PETT resin expansion of the new

carbonated soft drink because you see this soft drinks packaging. Also, we are using this PET resins and the new packaging application of the PET these are some of the driving force compare to the conventional PTA and PET process. This is the

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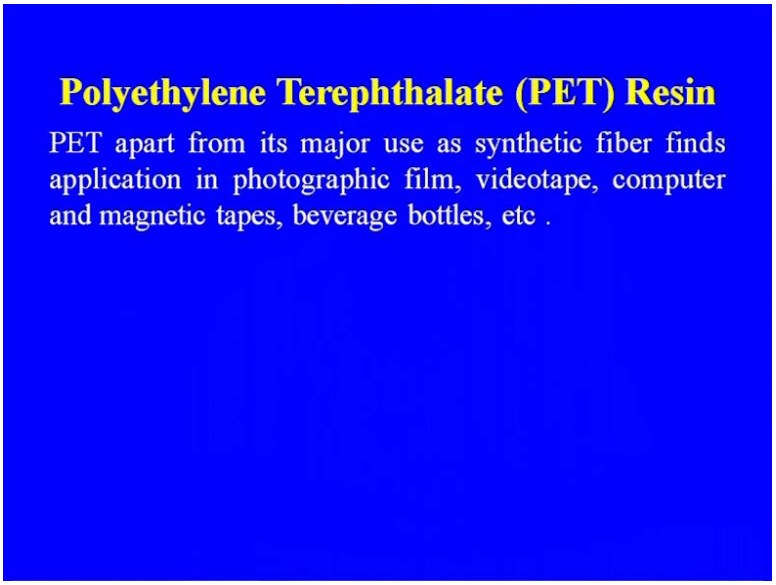

One of the technologies that has been developed that interrex. TM technology stands out for fewer process steps, Similar more reliable and more cost efficient. PET apart from its major use as synthetic fiber finds application in the photographic film videotape computer and magnetic tapes beverages bottles etcetera.

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This is you can say the PET resin and similar actually, the chips also we are getting in case of the polyester which is going for the textile industry. And these are the some of the application of the PET resin different packaging martial that we are using for the soft drinks this is made from the recycle feed because recycling pouf. The plastic that becomes very important also because the both recycling to the process it or by the destructive distillation the recovery of both the method that has been. Here the bottle that is in made with the only the recycle bottles.

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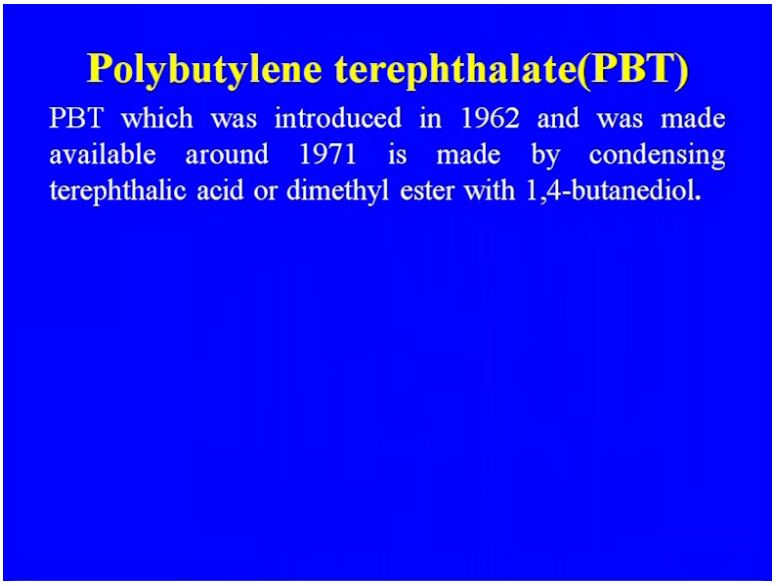

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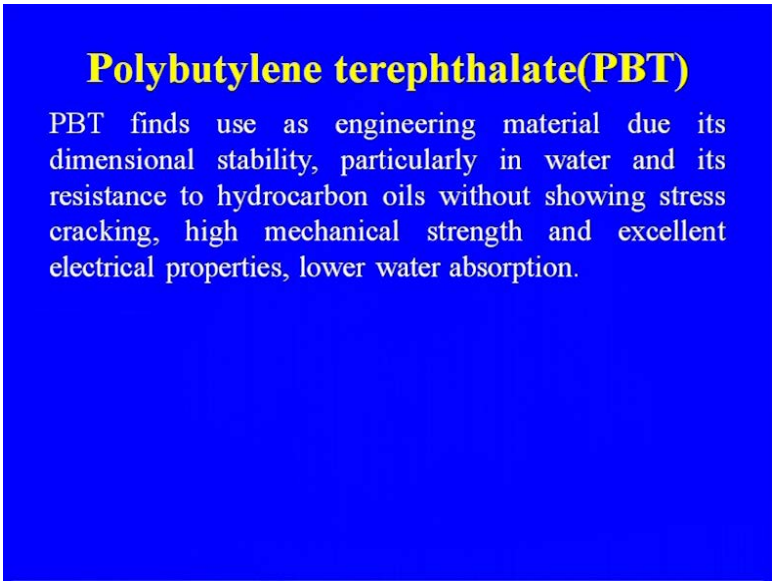

Another important development has been in case of the use of the terephthalic acid. Polybutylene terephthalate manufacture PBT which was introduced in nineteen sixty two and was made available around nineteen seventy one is made by condensing terephthalic acid or dimethyl ester with one four butanediol.

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Blends of PET and PBT are used in glass fibers reinforced grade.

PBT find application in pipe, pump hosing, impeller bearing brushing, gear wheels, and electrical parts such as connector and fuse cases, automotive parts and toothbrush bristles.

Because of thermoplastic nature both PET and PBT may be injection or extrusion molded.

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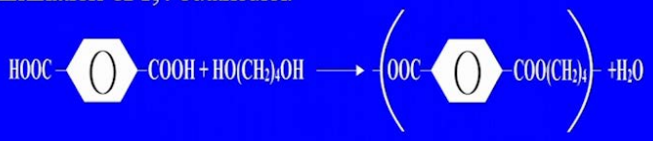
Polybutylene terephthalate(PBT)

Polybutene terephthalate is polymerised in two stages.

In first stage bis-hydroxy butyl terephthalate (Bis-HBT) is formed through trans-esterification of DMT with 1,4-butanediol.

In second stage Bis-HBT is polycondensed into PBT with elimination of 1,4-butanediol.



So, this is one of the major user of the PBT finds use as engineering material due to its dimensional stability, particularly in water and its resistance to hydrocarbon oils without

showing stress cracking, high mechanical strength and excellent electrical properties, lower water absorption.

So, these are some of the advantage of the PBT blends of the PET and PBT are used in glass fibers reinforced grade. PBT find application in pipe; pump hosing, impeller bearing brushing, gear wheels, and electrical parts, such as the connector and the fuse cases, automotive parts and toothbrush bristles. Because of the thermoplastic nature both PET and PBT may be process by injection or extrusion molded Terephthalic acid to DMT to terephthalic acid. And there driving force for the development of the polyester industry. That is because of the ability of feed stock. If you say the Para xylene from the catalytic reforming process are much important.

And this is the reason also like total cost of the polyester that is much less than synthetic fiber industry. And so, now the clothing purposes you are having the various combination of the polyester with viscous. And normally now we are called it the so that is also the blend of the viscous and this polyester other blending it may be blender with the akali fiber also and the this is the reason with the coming of the akalic fiber and the polyester there has been lot of the changes in the carpet industry in the curtains which you are getting different variety of the curtain with much-much lesser cost we are getting this material.

Otherwise cost of the curtain that is combine compare to the polyester that is very only problem in case of the polyester clothing that is not so comfortable because our so it is not very comfortable but, at least it is better than nylon but, if you compare with the viscous it much be some blender of the viscous and the polyester. So, that more comfort is there so, this was actually about the polyester industry and you see the number that has come and one of the major producer of the polyester that is reliance industry. And there are the major players in case of the textile industry also, because most of the polyester the unit which you based on the DMT as i told you earlier also that has been taken over by the reliance industry. It may be JCT or the Raymond fiber or it may be the Indian poly fiber, all that is unit now they are using terephthalic acid purified terephthalic acid.