Course Name: Combustion of Solid Fuels and Propellants
Professor Name: Dr. Srinibas Karmakar
Department Name: Aerospace Engineering
Institute Name: Indian Institute of technology-Kharagpur
Week: 02
Lecture: 11 Propellants Ingredients (contd.) and Classification of Solid Propellants

Welcome back. We are discussing about solid propellant ingredients in the context of solid propellants. So, so far we have talked about the different types of fuels used in solid propellants, different types of oxidizers like the inorganic oxidizers, the organic oxidizers like explosives. So, in terms of inorganic oxidizer oxidizers we have talked about the nitrate based oxidizer, perchlorate based oxidizers and there we have also talked about that the ammonium perchlorate is considered to be the workhorse oxidizers, because that is the most commonly used oxidizers in solid propellant rocket. And the due to the high performance this oxidizer is preferred, although there are some issues related to the products coming out from the this type of oxidizers for example, like chlorine substances, chlorine related compounds like HCL.

However, the ammonium perchlorate oxidizer is very common for solid propellants. Then we have said that since both the fuels and oxidizers are solid crystals or even solid particles, if we talk about the metal particles as fuels they are solid spherical particles whereas, the crystal oxidizers are solid crystals. So, we need to have some kind of a glue in order to hold them together. So, binder takes care of that by holding fuel particles and crystal crystalline oxidizers to form that matrix and to give the structural glue.

So, we have said that the various polymers are used as binders and they are mainly the polybutadiene and we have said that the modified ends of the poly butadiene molecules, we can have like hydroxyl terminated polybutadiene which is kind of a common binder used for solid propellant or it can have like carboxyl terminated. So, let us look at their formula very quickly and then we will move on to other ingredients alright. So, we have written that earlier that the very common binder is HTPB. So, we said that the it can have like polybutadiene. So, many of them are like in a group butadiene is in a group.

So, if the if the polybutadiene chain attached with some kind of a poly acrylonitrile group and acrylic acid group, they are going to form PBAN it is called poly butadiene acrylic acid acrylonitrile. So, the acrylonitrile group will be like you know CH 2 CH. Or it can have like acrylonitrile. So, carboxyl and nitrile groups get attached to the butadiene chain to form it is highly cross linked chain network. So, PBAN is kind of linear and cross chains and it gives lower tensile strength with smaller elongation.

There are modification of you know this carboxyl groups in PBAN and making them towards the end it gives the better mechanical properties. So, the modified version of the

polybutadiene is like carboxy terminated polybutadiene which is CTPB. So, this gives you know better mechanical property. Better mechanical property means it can give the good quality of the binder which can hold the the crystalline oxidizes and fuels better and it will going to give the improve the mechanical property of the grain as well. So, that is one of the common oxidizers which have been tried.

The other the most common one as I said is the HTPB and of course, PBAN is also the common one. So, HTPB is hydroxyl terminated polybutadiene. So, the polybutadiene chain will ends with hydroxyl radical. Now, this is you know widely used in the manufacture of manufacture of composite solid propellant. Now, the molecular mass is going to vary depending on the you know the how many chains are present there.

So, typical values of the molecular mass can be you know it can vary from like 30000 to even 1 lakh kg per kilo mole. So, that largely depend depending on the polymerization the degree of polymerization which is going to tell us that how much molecular weight is there. Of course, we in order to have like a higher molecule we need to have like a higher dense HTPB polymer in order to improve the volumetric loading of the composite propellant. And of course, we need to have like a better mechanical property of the grain as well, but the preferred choice of the polymeric fuel or polymeric binder is the HTPB. Other than that PBAN is also used as the binder for composite solid propellant, but of course, the high performance of the HTPB is preferred for wide application in composite solid propellants.

So, basically the role of the binder to give the structural glue of the fuel and structural glue for the propellant grain. Propellant grain means which containing the fuel metallic fuel as oxidized as particles the crystalline oxidizers for example, like ammonium perchlorate fuel as aluminum particles. So, the binder will give the structural glue to glue to hold those solid particles in the composite propellant matrix. Now, what are the other ingredients as we said that the fuel oxidizers binders are the major ingredients. In fact, if we even do not need the metallic fuel if we only use the HTPB plus HTPB plus AP it can still work as the propellant.

Because the HTPB will act as fuel as well as binder and this is the oxidizer. So, if you just if you recall we used to draw this picture like if you initially the HTPB is just like a liquid. So, if you add though add the AP crystals and make it a form of let us say this type of a strand or small palette. And if we ignite this if we inhibit the outside surface of the propellant and if we let or allow to burn from this surface only it will definitely going to burn because it is containing the oxidizers it is continuing the fuel. So, here the fuel is the binder itself HTPB will act as fuel and AP will act as oxidizer.

So, the principle ingredient must be like one fuel and oxidizer one fuel and one oxidizers, but the fuel as per the rocket literature the fuel are considered as the metal fuels and we are talking about the binder separately. Because binder is providing the structural group or binding the solid crystals like AP and the metallic fuel. Otherwise if we do not use

aluminum or boron particles or beryllium particles within the propellant grain it is still going to was work because the binder will act as fuel it is hydrocarbon. So, it is going to burn. So, this is the most common ingredients the fuel and the oxidizers.

Now, there are several other ingredients which are also used and I mean according to their use they have this different functionality. For example, like curing agents curing agents role is to cure the uncured propellant means once we have this mixture of the fuel oxidizers and binder we need to form the matrix. So, this pre polymer which is going to be form a cross linking and make sure that it is going to hold the solid crystals within it within the propellant matrix the one kind of agent which is called curing agent which is going to accelerate the curing process or cross linking process. So, the curing agents will act as you know act as a as an agent for accelerating the cross linking and is going to form the you know cross linking of the polymers which is going to hold the solid crystals. So, it has important role although the amount of curing agents may not be very high may be like it may vary from 0.2 to 3 percent, but it has very important role to play in order to you know making the cross linking.

Similarly, like plasticizers are kind of you know low viscous liquid they are going to improve the processing property of the propellant like sometime you know if we put too much of solid oxidizers within the propellant matrix like we add 70 to 80 percent as the solid oxidizers. So, sometime processing is going to be very difficult because we need to mix it thoroughly we need to you know pour it because after mixing our next job is to we need to cast it you know we need to give a proper shape of the grain. If you recall we said that there are various type of you know perforations can be tried which is called grain configurations. Now, it can be cylindrical it can have like a star shape, it can have wagon wheel, it can have multi hole.

So, depending on the requirement of the thrust time profile or pressure time profile this burning surface area initial burning surface area will be designed or will be decided. So, this initial burning surface area is called the grain configuration. So, the next part of the propellant processing after mixing we need to give that shape of the propellant grain or the internal perforation of the propellant grain. So, we have to cast it within the mold and mandrel. So, this is the mandrel and this is the mold.

So, that is giving us the type of you know perforations we are having from the grain I mean sorry within the grain. So, in order to cast this we need to have some certain processing properties that we need to pour it you know we need to pour it within the within the casting system or where with the mold and mandrel is. So, the plasticizer is going to reduce the viscosity in such a way that it will improve the processing properties. Sometime it may actually lead to you know long pot life of the uncured propellant. So, it will remain you know as slurry it will not start you know becoming solidifying it will have some fluidity which will improve the processing property of the propellant.

So, the plasticizer has important role although the very low percentage of you know plasticizers are used for such kind of applications. We can get different examples of plasticizers like di-actyl phthalate DOP, di-actyl adipate as the common oxidizers used for plasticizers sorry common plasticizers used for solid propellant. There are various you know curing agents have been also been tried like IPDI, TDI, toluene di isocyanate then there are IPDI, isophorone di isocyanate. This is like isophorone di isocyanate, this is toluene di isocyanate they are you act as curing agent. They are of course, used in a small quantity just to you know act as cross linkers to you know so that the it will cause the pre polymer to form longer chain of larger molecular mass and is going to interlocks between the chains.

So, the it is going to cure the propellant it will help to cure the propellant. Propellant means it is a mixture of binder, oxidizer and the solid fuels. Now, of course, the minor change in percentage of this type of curing agents may actually change the physical property. So, as I said that it may be used like 0.23 percent, but minor percentage change may actually change the physical properties, it may change the manufacture, manufacture, manufacturability of the propellant or in fact, it may change the ageing characteristics also.

So, depending on the requirement it can be used. So, they are only used to you know only used with composite propellants, because this type of curing agents is going to help to you know make the propellant mixture solidify and become hard. So, it will have common example in common application in composite solid propellant. Now, in case of plasticizer as I said they are low viscosity organic liquid or organic ingredients, which is basically a fuel also they can actually burn, but they are added to improve the you know processing properties. So, that the viscosity sometime it may lower the viscosity, it may actually required for casting you know casting processing during the transfer of the slurry to the you know mold and mandrel system.

So, that it can improve the casting process, it can actually have a longer pot life, it can help to have longer pot life of the mixture of the mixture ingredients, but they are uncured, uncured propellants. Various type of you know plasticizers curing agents have been tried. So, the participants are requested to refer to any kind of you know rocket textbook, it is already listed in the syllabus as well. They can actually get many examples of various curing agents or cross linkers, which can react with polymer and form like long chain. Similarly, they can get example of the plasticizer as well like DOP, DOA.

They there are different you know burn rate modifiers, which have been you know tried for solid propellants. So, they are basically either accelerate or decelerate the burn rate. You know if we have certain ingredients of the you know propellant within the matrix, either they can increase the burn rate or they can decrease the burn rate. So, the role of the burn rate modifiers as the name suggest, it will modify the burn rate of the propellant. You know there are certain you know catalyst, which can actually accelerate the burn rate.

For example, like Fe2O3 ferric oxide catalyst, which can sometime act as the burn rate enhancer. There are certain category of burn rate modifier, which can actually you know decrease the burn rate also. So, we can have like Fe2O3 or ferric oxide, which can actually increase the burn rate. There are some other type of burn rate modifier, which can actually reduce the or inhibit the burn rate. Lithium fluoride for example, so depending on the applications, we can actually either have like accelerating type of burn rate modifier or decelerating type of burn rate modifier, but of course, they are also used in a smaller quantity.

Again as I said like depending on the functionality, they are used or they are not used. But there are number of different ingredients, which have been tried for different solid propellants. And they will definitely you know act as act they will definitely have the different functionality. So, based on the requirement, there may be like 200 plus ingredients, which have been tried in a solid propellants. But the major ingredients as I said the fuel binder and the oxidizers and there are some other ingredients like curing agents, plasticizers, burn rate modifiers etcetera.

And to have other functionalities in the propellant, there may be number of additives, which are used as the ingredients. Now, having you know have some discussion or having discussion on the various type of ingredients, now let us talk about the classification of solid propellants. So, mainly the solid propellants are classified into two, one is called the homogeneous propellants and heterogeneous propellant. This is based on the mixing properties of the propellants. So, homogeneous propellants as the name suggest, if the ingredients are intermittently mixed whereas, in case of heterogeneous propellant, the propellant ingredients are not intermittently mixed, rather they will coexist together and you can individually actually have the you know properties seen individually, they are not intermittently mixed.

For example, like if you have solid crystals mixed in a polymetric binder, you can have like heterogeneous propellant whereas, there are other ingredients, which can actually intermittently mix together and form homogeneous propellant. So, based on this you know homogeneity and heterogeneity of the propellants, they are categorized into various categories. So, we will talk about that and based on the other functionalities, there are different types of propellants. For example, like they may be igniter propellant, there may be gas generator propellant, there may be like reduce smoke propellant. So, we will talk in detail little later. Let us first talk about from this perspective of you know homogeneity of the propellants.

So, they are actually mainly you know homogeneous propellants mainly are termed as the double base propellant. So, the primary ingredients for double base propellant are the nitrocellulose NC and nitroglycerin NG. So, they are mixed together at molecular level to form the homogeneous propellant. Now, the NC or the nitrocellulose, they constitute the

fuel part. You know as I said the major ingredients of fuel and fuel plus oxidizers are formed the propellant.

So, the nitrocellulose form the fuel part whereas, the nitroglycerin they form the oxidizer part. Now, depending on the nitrogen the degree of nitrogen the nitrocellulose part, I mean the molecular structure of the NC may actually change. Because this is basically the cellulose which is which consist of carbon hydrogen nitrogen sorry carbon hydrogen oxygen in the structure, they are substituted with some nitro radical or NO3 radical and that will give the molecular structure of the nitrocellulose. Now, depending on the nitration as I said this structure will depend. Now, similarly the glycerin or the propane trial that is also you know replaced with NO3 radical to form the nitroglycerin.

Now, both the nitrocellulose and nitroglycerin can act as single propellant because they are have the capability of using have the capability to act as both fuel and oxidizers. However, for double base propellant the nitrocellulose part is acting as the fuel whereas, the nitroglycerin part is acting as the oxidizer. Now, once they mix together they are going to form the double base propellant. And, sometime it is known as the homogeneous propellant because they are intermittently homogeneous propellant because they are mixed intermittently. Sometime you know plasticizers are also used in a small quantity in the double base propellant to improve the fluidity of the propellant and the processability of the propellant.

So, it is not that that in case of double base propellant no other ingredients are used rather small amount of you know plasticizers are also used in double base propellant. Of course, still they will not you know affect the homogeneity of the propellant that is why the the double base propellant are also called the homogeneous propellant. Now, coming to the heterogeneous propellant the heterogeneous propellant mainly consist of the solid you know crystalline oxidizer plus the polymeric you know binder. Now, it can have some aluminum particles as fuel as well, but mainly it consist of like the solid crystalline oxidizer and polymeric binder. So, in that sense you know the AP or the ammonium perchlorate is the common solid crystalline oxidizers and the HTPB or hydroxyl terminated poly butadiene is the polymeric binder.

So, they are going to form one of the heterogeneous propellant or they are going to call the composite propellant ok. So, it may have aluminum particles within the propellant matrix. So, they are called composite propellant. Now, typical percentage of you know oxidizer may be like 70 percent oxidizers plus you know 10 to 12 percent of HTPB plus you know around 18 percent of aluminum. So, aluminum particles are fuel 10 to 12 percent HTPB are going to be binder and AP are AP will act as oxidizers.

So, this type of propellant is called composite propellant and it is very much part of the heterogeneous propellant because it is containing the various you know solid crystals and

the solid spherical aluminum particles which is going to create the heterogeneity in the propellant matrix and they are called the heterogeneous propellant. So, this is the most common example of heterogeneous propellant. Now, in order to improve the performance of the double base propellant, sometime additional amount of oxidizers is added in order to improve the performance of the double base propellant. So, if we add AP if we add AP to double base propellant to improve the performance, improved is specific impulse this is called composite modified double base propellant or sometime it termed as CMDB, composite modified double base. So, what additionally we are adding NC plus NG was the main ingredients for double base propellant.

Now, we are adding some amount of ammonium perchlorate to improve its performance and they are going to form. So, since you are adding some solid crystals. So, AP is solid crystals. So, we are actually not maintaining the homogeneity of the double base propellant. So, it is becoming heterogeneous that is why and it is kind of like a composite propellant.

So, it is becoming like composite modified double base propellant. So, this is the basic you know formula sorry basic ingredients for composite. Now, it can have like you know some amount of HMX or RDX also instead of it does not mean that it always have like AP as the additional oxidizer it can have like HMX or even RDX that is also comes under the category of composite modified double base. So, basically we are changing the you know composition of the double base propellant by adding some additional oxidizers. So, these are like some organic oxidizers or some inorganic oxidizers which are added to the double base propellant matrix in order to improve the performance.

So, this is CMDB. The other category of propellant is called nitramine propellants which we have already told our self during the discussion of the oxidizers. So, basically the HTPB plus HMX or RDX. So, some binder and any of the organic oxidizer if they are added together they are going to form the nitramine propellant as we already know the name now by now the her majesty explosive and this is like R and D explosives which we already discussed in the previous class. This is like tetramethylene tetranitramine and this is sorry cyclotetramethenene tetranitramine and this is like R and D explosive which is tricyclotrimethylene trinitramine. Once we add this nitramine type of oxidizers to this binder we are going to form the nitramine propellants.

Now, remember this during the combustion this hydrocarbon gases form from the polymer is going to combine with this fuel rich products of HMX or RDX to form low temperature products. Now, here we need to remember that the it will have like few oxidizing radicals and the binders surrounding nitramine crystals cannot fully oxidized. So, sometime it will so happen that the binder is going to decompose at the combustion temperature and it is going to form the gases rich with hydrogen and carbon monoxide which is going to reduce the molecular weight. So, that will cools the you know combustion chamber temperature, but it is going to have like mostly you know H2 plus CO as the you know gaseous products.

Sometime you know the propellant formulations in addition to like HMX and RDX some small amount of AP is also added to the nitramine propellant just to improve the you know performance of the nitramine propellant.

And this type of propellants will have applications mostly in the strategic side. So, it has applications in the strategic area sometime you know as high as like 85 percent of the oxidizers are added to this type of polymeric binder to form the nitramine propellant. So, it is actually highly you know solid loaded propellant sometime AP is added to improve the performance ok. So, these are the major you know classification of the solid propellant. Now, we can talk about the another other type of we can talk about some othertype of propellant.

For example, like gas generator propellant. Ok what are the other type of other propellant categories? So, major categories we have said like homogeneous propellant, hydrogenous propellant based on the you know mixture of the fuel and oxidizers, but based on the applications there are other propellant categories for example, like we can have gas generator propellant. So, the main motive of gas generator propellant is to produce hot gas, but not thrust. So, these type of propellant are not not thrust. So, they are going to produce hot gas not for producing that they usually have you know low combustion chamber temperature, low T C of the order of like you know 800 to 1600 Kelvin. So, their purpose is to you know different applications not like for you know launching theany kind of satellite launch vehicle not like that.

So, they are having different type of applications. The typical ingredients for this type of you know propellants are like this it can have like ammonium nitrate. Let us say it can have like 78 percent of ammonium nitrate, it can have like some polymeric binder let us say H T B B or any kind of polymeric binder which will takes about you know 17 percent. It can have some additives like processing aids for example, like plasticizers you know some processing aids stabilizer that may contain like 5 percent of that. Oxidizers typical size may be like 150 to 200 micron. Now, if you look at the combustion side the combustion products is going to form you know typically like carbon monoxide, it can have carbon dioxide, it can have nitrogen, it can have hydrogen, it can produce some amount of methane etcetera.

So, these are the typical you know combustion gases and the temperature you know flame temperature will be in the range of like 1400 Kelvin. So, they are in they are not intended for you know applications where thrust is the prime objective rather it is going to produce hot gas by burning the different propellant ingredients ok. So, this is like another category is called gas generator propellant. Other category of propellant is called smokeless or reduced smoke propellant.

Smokeless or reduced smoke propellant. So, generally you know this if we have aluminum particles in the ingredients they will form like Al2O3 aluminum oxide and they are very

smoky. If we add aluminum particles into the fuel into the propellant matrix they are kind of very smoky in nature like the exhaust products are very smoky. In fact, if you use some kind of you know burn rate modifier like aluminum, zirconium or iron oxides or any kind of metallic species generally they form like visible you know cloud trails or small solid metal or metal oxide particles in the exhaust. So, they are going to you know going to form some they are going to form some you know smoky exhaust. So, if you have metallic species in the ingredients they will give the you know smoky exhaust.

So, there are certain military applications where we need to have smokeless or even reduced smoke propellant. So, that type of category is called low smoke or you know minimum smoke propellant. So, it will almost have like a faint you know faintly visible flame. So, this is you know fine applications in mainly like military applications where you know smokeless exhaust will help in you know dodge the enemies radar or it will not be easily detected by the enemies radar. So, there are different kinds of you know oxidizers have been tried or even you know has have been researched on just by looking at how to minimize the exhaust smoke.

For example, like if we do not use any kind of solid particles within the you know double base propellant matrix and modify with some HMX or even RDX this may actually give very few or even no solid particles in the exhaust. So, like we can have like DB propellant plus modified with HMX this going to give us you know no solid exhaust that may fairly have like a reduce or low smoke propellant because they are they are not containing any kind of aluminum particles there. If we use some AN composite propellant ammonium nitrate composite propellants they are also going to give like you know low smoke propellant. So, this is you know category of propellant based on the applications. The other type of propellants we can also need to know is the igniter propellant.

We will remember that see the propellant once it is there we must need to ignite it using some igniter. So, we have the igniter here. So, igniter plumes will be created. So, there are certain category of propellants where the choice of propellant is depend on the applicability. For example, like the for the igniter we need to have like very fast you know high heat release or high gas evolutions.

So, that it can actually give the plume hot plume to the propellant surface and it is going to ignite it. Of course, it need to have like a stable operation or stable initiation of the ignition. It can operate over the required ambient temperature range. Of course, you need to have good aging characteristics as it is required for the general propellant characteristics. Low cost ingredients, low you know fabrication cost, the sensitivity of the burn rate to ambient temperature changes should be low.

So, these are the normal thing, but the major thing is that it needs to have like a fast high heat release and high gas evolution per unit igniter propellant mass because that is the main

objective of the igniter propellant. So, this is these are the certain category of propellants where the propellants are used for igniter composition. For example, like some amount of you know boron particles are used as the fuel for igniter propellants. So, one such common example of igniter propellant is like this.

Boron plus ammonium sorry boron plus potassium nitrate. This is the common example of igniter propellant with some binder like boron particles can be like 20 to 30 percent. It will have 20 to 35 percent. It will have like 65 percent of KNO3 and some small amount of binder that is going to form the igniter propellant. There are other ingredients have been tried to form the igniter propellants.

The main objective is to produce the high heat release at a faster rate. Now, the binder typically may include like epoxy resins. It may have like graphite or even vegetable oil or nitrocellulose as the binder, but the common fuel is kind of a boron particles and the oxidizer is potassium nitrate. So, these are the various category of propellants we have talked about like starting with the homogeneous propellants, then heterogeneous propellant, then based on the applications we have smokeless or reduce propellant, reduce smoke propellant. We have the the gas generator propellants. For example, like there are common application of propellants is in the air car bag air bags in the car where the high gas is to be evolved has to be evolved within a very fraction of time or even a fraction of second because when there is a heat on collision like during a high I mean while the car is proceeding or running with a very high speed.

So, there is a very minimum amount of time is required to inflate the the air bag. So, the only option is that some kind of a propellant which can act which can get activated once the collision occurs and it will inflate the balloon which will actually protect the passengers and the drivers from the injury. So, the common application of gas generator propellants is there in the air bag. The military applications the smokeless or reduce smoke propellants are used and then another category we have discussed is the ignitor propellant where the composition is mainly used for the high heat release at a faster rate. So, common ignited propellants we have said like it is a combination of boron and boron as the fuel and potassium nitrate as the oxidizers typical percentage is like 20 to 30 percent of boron and 64 to 65 percent as the potassium nitrate and some amount of binder is of course, of course, used to hold the both the boron particles and ammonium and the potassium nitrate oxidizers ok.

With that I think we closed our discussion on the propellant ingredients. Now, we will try to solve some numerical problems on the mixture ratios the fuel rich side fuel lean side or rather we said like the oxidizer side oxidizer rich fuel rich propellants how to really get into the numbers about different polymeric fuel such as HTPB like the common binder and some ingredients like ammonium perchlorate oxidizers fuel like aluminum particles. So,

we will try to solve some numerical problems on this thing and then you will be pretty much you know ok with the chapter alright. Thank you so much.