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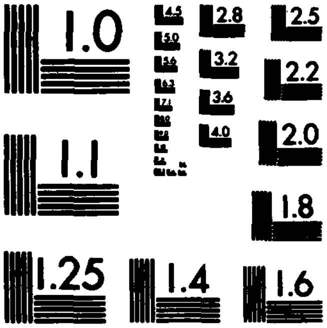

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FOREIGN TECHNOLOGY DIVISION

A COMMENT ON THE PLATEAU COMBUSTION MECHANISM OF THE DOUBLE-BASE PROPELLANTS

by

Ma Xiegi

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A Comment on the Plateau Combustion Mechanism of the Double-Base Propellants*

Ma Xieqi

ABSTRACT

This is a comment on the plateau combustion mechanism of the double base propellants. There are 58 references. In this paper, the experiments, evidence, and viewpoints of each theory were introduced, analyzed, and commented. Furthermore, some viewpoints were presented for future work.

I. FOREWORD

In a certain pressure range, the combustion rate of a double base propellant is almost unrelated to pressure. This is very favorable to the operation of a rocket engine. For this purpose, a large amount of people attempted to understand the plateau combustion mechanism so that plateau propellants can be even better controlled, applied, and developed. This paper gives a brief analysis and comment on the various viewpoints, evidence, and experiments concerning the plateau combustion mechanism of double base propellants.

II. THE SUBSURFACE CONDENSED PHASE THEORY

1. The Photochemical Reaction Mechanism.

Camp, et al(1) (1958) proposed that after the addition of lead compounds into double base propellants, the lead compound can absorb the ultraviolet light emitted from the flame zone and thus become a sensitizer for the dissociation of nitroester. Consequently, the dissociation of nitroester is accelerated. The combustion rate of the propellant is increased and super combustion rate combustion is produced. However, with the rising combustion rate of the propellant, the disapperance rate of the condensed phase becomes faster. The effective photochemical reaction time in the subsurface reaction zone is decreased.

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The extent of super rate combustion is decreased. Thus, plateau combustion is produced. When the pressure increases further, because the condensed aggregates produced by the lead compound block the absorption of ultraviolet light by the subsurface, the combustion rate is decreased and mesa combustion is produced.

Camp(2), et al (1975) used various excitation forms of ultraviolet radiation on catalysts to develop the photochemical reaction theory. Kubota, et al(3) proved experimentally that the increase in combustion rate was related to the amount of external light radiation. However, it is not quantitatively related to the ultraviolet light. But, Camp believed that for some catalysts, which generate high pressure plateaus, the photochemical reaction theory is still effective. At low pressures, the combustion of the propellant does not have a bright flame. However, lead compounds can still increase the propellant combustion rate. Hence, at least under low pressures, super rate combustion is not related to the photochemical theory.

2. The Chemical Stoichiometrical Shift Theory.

Kubota, et al(3,4) (1973) studied the reactions in various zones of the combustion wave by using high speed photography and delicate fine thermocouples. Lead salt leads to the concentration of carbon containing materials on the combustion surface. Correspondingly, the combustion rate increases. However, lead salt does not alter the amount of heat released by the surface. It only causes the heat conduction feedback in the hissing zone to increase by 50-100%. They believed that the appearance of carbon was a result of changes taking place in the decomposition process of nitroester. The amount of aldehyde formed was reduced. Thus the ratio of the aldehyde to NO_2 is even closer to the /49 chemical stoichiometry. However, at the chemical stoichiometry, the reaction between aldehyde and NO_2 is the fastest one. Therefore, the heat of reaction is increased and the combustion rate is raised. As the pressure rises, the effective time for the catalytic effect is shortened, and the amount of aldehyde is increased. The ratio of aldehyde to NO_2 deviates away from chemical stoichiometry. The reaction rate between aldehyde and NO_2 decreases to produce the plateau combustion. Kubota also established a mathematical model. This theory adopted the results of the study on the propagation speed of the combustion flame of formaldehyde and NO_2 by Pollard, et al$^{(5)}$. When the ratio CH_2O/NO_2 is 1/1.4, the combustion rate is the highest. The reaction is as the following:

$$5CH_2O + 7NO_2 \rightarrow 3CO + 2CO_2 + 5H_2O + 7NO$$

This theory did not specifically explain how the lead compound alters the way nitroester decomposes. It was only capable of explaining super rate combustion and plateau combustion. It could not explain mesa combustion. What kind of effect chemical stoichiometric changes have on the combustion process in the actual propellant combustion remains to be proven experimentally. Due to the fact that the reason for super rate combustion and plateau combustion is changes in the nitroester decomposition process, and it occurs in the condensed phase, therefore it is included in the condensed phase theories. However, the effect occurs in the gas phase hissing zone, therefore, it can also be considered as a condensed phase - gas phase theory.

3. The Chelate Compound Theory

Suh and Lenchitz, et al$^{(6)}$ (1974) used explosion heat experiments and a method to simultaneously determine the gas product composition to discover that the NO in the combustion product of a catalyzed propellant was reduced by a half. The total contents of CO_2 and CO remained unchanged. However, the CO_2/CO ratio decreased slightly. Simultaneously, it was also discovered that the explosion heat was raised for the catalyzed propellant at low pressures. The combustion surface temperature also increased. This paper believed that it was caused by the additional NO reduction near the surface. They presented the idea that the lead atoms in the lead salt and the oxygen atoms on the nitroester group formed chelating complexes. The electron on the nitroester is migrating toward the divalent lead, which weakens the $RO-NO_2$ bond. The decomposition of nitroester is accelerated to cause the combustion rate to increase.

As early as 1966, Lenchitz, et al$^{(7,8)}$ had studied the catalytic action mechanism. At that time, the CO_2/CO ratio of the combustion product of a catalyzed propellant was increased according to the measurement. This theory explained that the covalent compound tetrabenzo lead did not have any catalytic action because it could not form chelates. However, it could not explain why tetraethyl lead, lead oxide, and lead powder could make double base propellants produce plateau combustion(9). There is no direct evidence that chelates can accelerate the decomposition of nitroesters. As for the surface temperature rise and the explosion heat increase at low pressure, this could be a result of more NO reduction. Reference (10) believed that the reason for the explosion heat of double base propellants to decrease at low pressure is due to the diffusion of pressurized inert gas. The addition of nickel powder greatly increased the explosion heat at low pressure. Furthermore, it made the bright flame move to the combustion surface. However, nickel powder does not have a plateau effect.

4. The Spectroscopic Method to Study the Catalytic Action Sites and Mechanism.

Dr. Malℓtsev(11) (1973) used infrared emitting spectrum to study the effect and the results showed that there was a strong absorption due to the catalytic combustion product CuH near the combustion surface of a double base propellant with copper salicylate added. The dark zone was relatively narrow. The disappearance of N_2O was unusually fast. The surface temperature rose. Copper compounds make CO and CO_2 appear even earlier. They may even delay the apperance of H_2O. This explains the thermal feedback towards the surface, which accelerates the gas phase reaction. However, with the addition of lead salicylate, the temperature and composition along the flame direction had no apparent change with the exception of the lead spectral line. This explained that lead salicylate greatly accelerated the chemical decomposition and the effect of transformation from solid to gas phase in the condensed phase during the initial stage of combustion. Lead makes H_2O appear even earlier. The carbon containing materials are subsequently burnt.

According to spectroscopic proof obtained by them, lead works in the condensed phase, while copper works in the gas phase. The two work independently at different combustion zones.

However, Androsov , et al, mentioned later, believed that copper had an added effect on lead. It is a non-cumulative effect. Baer, et al(12) in the U.S. also proved that results of Мальцев. Because the experiment was carried out in an actual combustion system, it is more reliable. But the combustion surface was full of holes. It is very difficult to resolve spacings between several to several tens microns. Therefore, the resolution should be improved. A low plateau pressure propellant should be used to further reveal the chemical catalytic nature a step further.

5. Thermal Decomposition - Gas Phase Chromatography Study Results /50

The Androsov study group used thermal decomposition-gas phase chromatography as the basic means to systematically study the mechanism of using lead-copper as the catalysts. On one hand, they studied the characteristics of using a lead-copper composite catalyst, such as the effect of initial temperature and pressure(13), the effect of catalyst composition(14), the effect of lead-copper ratio, etc., in order to obtain some perceptual understanding.(15) On the other hand, thermal decomposition-chromatograph was used to search for chemical evidence(16,17,18) to verify the perceptual understanding obtained. Furthermore, they worked hard to improve the rational understanding. In 1978, a paper entitled, "Mechanism of the Lead-Copper Composite Catalyst on the Combustion of Propellants" was published(19).

Their study showed that CuO does not change the nitroester decomposition rate. However, it decreases the CO content in the combustion product. The CO_2 content increases, which makes CO oxidize into CO_2. In the decomposition of nitrocellulose, it requires the participation of the oxygen in CuO. In the decomposition of nitroglycerin, it requires the participation of the oxygen in NO_2. The effect of lead oxide is to increase the content of CO_2 which has the highest heat in the decomposition products. Furthermore, it increases the content of N_2O which has a higher reactivity than those of NO and NO_2 in combustion. Consequently, super rate combustion occurs. The reinforcement of the lead-copper catalytic effect (exceeding the sum of the two individual effects) is because PbO makes the CO_2 and N_2O in the combustion products increase. The content of CO is decreased. Due to the fact that the reduction of CO is favorable to the catalytic action of CuO, consequently, more CO is converted into CO_2.

Increasing nitroglycerin content in the propellant makes the effect of CuO drop rapidly. When nitroglycerin exceeds 40%, the effect disappears completely. This is because more CO is formed than CO_2 during the decomposition of nitroglycerin, as well as because the CuO surface is poisoned by CO. For a double base propellant containing 52% diethylene/glycol/dinitroester, the effect of CuO is stronger than that of PbO_2 at above 40 atm. If a lead-copper composite catalyst is used, the catalytic effect is greatly improved. However, mesa combustion occurs at 70-100 atm. The decomposiiton of diethylene glycol dinitroester releases large amounts of N_2O. Furthermore, CO is formed. N_2O makes the combustion rate increase, and CO poisons CuO. This indirectly proved the mechanism of the effect of the lead-copper composite catalyst. They used ordinary methods to relatively sufficiently explain the chemical natures which cause super rate, plateau and mesa combustion. Due to the fact that thermal decomposition is related to the combustion process, but there are also differences, it still requires to be verified by other direct experiments.

6. Mass Spectroscopic Study Results

Bauman(20) (1965) and Dauerman(21,22) (1968) first used mass spectroscopy to study the effect of catalysts on the thermal decomposition of double base propellants. Faber(23,24) (1976) used a specially designed quadripole differential pump mass spectrometer to study the products formed in the combustion flame at a constant pressure. Through multiple pressure drops by using nozzles, it is rapidly reduced to 10^{-9}atm. This molecular beam was analyzed by the spectrometer. It was discovered that the oxygen containing acidic salts of lead-copper produced metallic lead and copper upon decomposition. Manganese salts without any catalytic action formed MnO. The covalent bond lead tetrabenzene only vaporized, instead of decomposing. The gaseous lead and copper atoms continued to react with nitroester to form $PbNO_2$ and $CuNO_2$. At the proper temperature, these compounds are stable. The nitrites will react after entering the combustion zone to form metal hydroxides and oxides. This is consistent with the thermodynamic prediction. Therefore, the appearance of $PbNO_2$ and $CuNO_2$ may be a judging standard for plateau combustion.

This study supported the viewpoint that $CO-NO_2$ breaks up into CO and NO_2 during the decomposition of nitroester. It did not confirm the NO_3 discovered by Bauman and Dauerman. It is inconsistent with the oxidation-reduction cycle of Pb-PbO by Prekel. However, it agrees with the assumption of Suh, which is that NO_2 reacts with the lead in the lead salt, but not forming chelates. Instead, $PbNO_2$ is formed. The reaction between gaseous Pb and NO_2 can make nitroester release more NO_2. Consequently, the combustion rate is increased. Mass spectroscopy is a powerful tool to study condensed phase reactions. If the system proposed by White(25) can be used to send the molecular beam instantaneously into the mass spectrometer to carry out the study under high pressure, important contributions toward the plateau catalytic mechanism can be made.

7. Differential Scanning Calorimetric Test Results.

Eisenreich, et al(26,27) (1976) used a differential scanning calorimeter to simultaneously conduct thermal weight loss and thermal analysis experiments. It proved that the first step in the thermal decomposition of double base propellants is the vaporization of nitroglycerin. The second step is the thermal decomposition of nitrocellulose. At low pressures, the heat of reaction with catalysts is higher than that without catalysts. /51
The pattern agrees with that measured with an explosion heat method used by Lenchitz(8,9). The decomposition temperature peak of catalyzed propellants is relatively high. The activation energy is relatively low. Similar work has been done in our country. The pattern obtained was identical.

Eisenreich, et al(28) (1978) continued to study the effect of copper and lead compounds on the decomposition of nitrocellulose.

Beatriz, et al$^{(29)}$ (1978) used a differential scanning calorimeter to discover that the trajectory modifying agents in a double base propellant mainly affect the gas phase or multiple phase reactions in the neighborhood of the combustion surface. The amount of heat measured by the differential scanning calorimeter was not a pure solid phase heat reaction$^{(30,31,32)}$. But, Eisenreich believed that solid phase reactions are primary. The catalyst mainly functions in the solid phase. Differential scanning calorimetry is a modern thermal analysis method. It is more effective in studying the thermal decomposition of propellants. Although its heating speed is far different from that of the actual propellant, yet the results still have a reference value. In recent years a high heating speed (100-20000 deg/sec) thermal analysis has been developed to be used in the study of ignition dynamics of propellants and explosives$^{(33,34,35)}$.

8. Measuring the Eruption Point to Find the Activation Energy.

Bai Mu Lan, et al (1978) used a method to measure the eruption point of an explosive to find the activation energy of the reaction and the factor in front of the exponent. At temperatures between 200-250°C, 0.03 g of propellant specimen was used to measure the explosion delay period at six temperatures. $\ln \tau = \frac{E}{RT} + \ln C$ curves were plotted to obtain E and C as listed in the following table (where: τ - delay period, E - activation energy, R - gas constant, C - factor before the exponent).

4 推进剂 1 计算结果	硝化纤维素 5 (Ⅰ)	6 Ⅰ加 2.6% 苯二甲酸铅	7 Ⅰ加 2.6% 鞣酸铅	某双基推进剂 8 (Ⅱ)	9 Ⅱ加 2.6% 苯二甲酸铅	10 Ⅱ加 2.6% 鞣酸铅
2 活化能E(千卡/克分子)	24.40	23.41	21.40	18.46	16.54	16.02
3 指前因数C(1/秒)	9.4×10^{9}	8.55×10^{9}	3.84×10^{8}	1.37×10^{7}	1.84×10^{6}	6.34×10^{5}

1) Calculated results; 2) Activation energy (kcal/gram molecule); 3) Factor before exponent (1/sec); 4; Propellant; 5) Nitrocellulose (I); 6) I plus 2.6% lead phthalate; 7) I plus 2.6% lead tannate; 8) A double base propellant (II); 9) II plus 2.6% lead phthalate; 10) II plus 2.6% lead tannate.

From the data listed in the table, one can see that catalysts make the activation energies of double base propellants and nitrocellulose decrease. The condensed phase reactions are accelerated. The combustion rate increases.

The activation energy measured using this method apparently is the activation energy in the induction period of explosion. It is not the same as the activation energy concept for explosion reactions or combustion reactions. If the controlling reaction is the same, the activation energy may be consistent. Зенин(36) presented the double base propellant condensed phase reaction layer model. The activation energy of nitroester thermal decomposition was proven to be about 48-50 Kcal/gram·molecule. However, the combustion activation energy was 19 Kcal/gram·molecule. The latter is consistent with the activation energy of 16-20 Kcal/gram·molecule for the oxidation of alkanes by NO_2. Therefore, the controlling reaction in the combustion of double base propellants may be the oxidation reaction involving NO_2. The activation energy measured by the eruption point method is more or less the same as the combustion activation energy. It is highly probable that the controlling reaction is identical, i.e. the oxidation reaction of NO_2. The reaction is not a pure solid phase reaction when the eruption point was measured. It should include the gas phase reactions on the solid phase surface. This can be proven with simple experiments.

9. Another Result of Surface Temperature Measurements. Denisyuk, et al(18) (1971) used thermocouples to measure the temperature distribution curve of catalyzed and uncatalyzed H type powder under 20-90 atm. Furthermore, data such as the surface temperature, thickness of the smoke zone, maximum flame temperature, distance from the surface to the maximum flame temperature, heat released by the condensed phase, heat released by the smoke zone, temperature gradient near the surface, etc. were derived. It was discovered that catalysts did not change the distance between the surface and the maximum flame. They reduced gas phase heat conduction by 4-5%. The heat loss in the smoke zone was also decreased. Therefore, a catalyst must function in the condensed phase to increase the combustion rate. Under high pressure, the solubilities of gaseous products in the condensed phase increase. The catalysts are poisoned. Or, a catalyst becomes a suppressor. Therefore, combustion rate

decreases to cause plateau and mesa combustion.

The authors proved, through temperature measurements by thermocouples, that the catalytic action occurs in the condensed phase. However, the specific physicochemical process was not known. It is difficult to measure surface temperature accurately under high pressure. The fact that catalysts do not alter the distance from the surface to the maximum flame is contrary to the results measured by Kubota in Section 2.

III. GAS PHASE THEORIES /52

1. The Lead-Lead Oxide Cycle Theory

Steiberger(1) (1952) added organic lead salts to propellants after the lead salts had been decomposed in the furnace. It was discovered that the catalytic effect is even better. At 350°C, the thermal decomposition product is lead or lead oxide. They should be the reason for plateau combustion of propellants. The organic portion of the lead salt only has the effect of producing fine metallic lead or lead oxide. Therefore, he presented the gas phase catalysis mechanism:

$$Pb + NO_2(NO) \longrightarrow PbO$$
$$PbO + CO(CH_2O、H_2、C_n) \longrightarrow Pb$$

Prekel(37) (1961) used a sealed erupter to measure the combustion rate. In the plateau pressure range, carbon fragments were observed to drop down. Furthermore, there were melted lead balls. Such phenomenon was not there above the plateau pressure. He believed that the aforementioned reactions occurred in the gas phase zone or the foam zone. Preckel(38) (1965) again explained that inorganic lead compounds and fatty lead compounds could only cause plateau combustion of propellants with low heat values based on the Pb-PbO cycle theory. Aromatic compounds, however, could make plateau combustion occur for propellants with high heat values.

This theory is relatively rough. The lead-lead oxide recycling theory was deduced indirectly. There is no direct evidence. Preckel pointed out the region where the catalyst works.

He also discovered that fragments of carbon are related to plateau combustion. It opened up new avenues for theories of lead and carbon containing matters.

2. The Free Radical Theory.

Sinha, et al(39) (1968) believed that the combustion rate of a double base propellant is determined by the rate of fading of the foaming zone. However, the fading rate is controlled by the heat transfer from the hissing zone to the surface. It is not affected by the flame zone. They adopted the experimental result by Paneth, et al that at 400°C, lead could react with free radicals to form lead alkyls, which could decompose at 600°C into lead and free radicals. In the foaming zone, lead combines with the free radical released by the decomposition of nitroester to form lead alkyl compounds. In the hissing zone, the lead alkyl compounds decompose into free radicals and lead. The free radicals generate a chain reaction to reduce NO and to release large amounts of heat. The heat transfer from the hissing zone toward the foaming zone is accelerated, which increases the combustion rate. It makes super rate combustion occur. However, for a uncatalyzed propellant, NO does not participate in the reaction in the hissing zone. When the pressure rises, the free radical concentration increases in the hissing zone. The terminating collisions between free radicals themselves will increase. The reaction between NO and free radicals is decreased. The heat transfer from the hissing zone toward the foaming zone is decreased. On the other hand, when the pressure rises, the thermal conductivity of the gas increases. The heat transfer from the hissing zone toward the foaming zone increases. In a certain pressure range, the two opposing effects are equal. Then, plateau combustion occurs.

The free radical theory for the decomposition of nitrocellulose has been proposed by Wolfram(40) earlier. Morrow(41) (1976) used a heat platform polarized light microscope to observe the liquified decomposition process taking place with pure nitrocellulose and modified nitrocellulose (by adding free radical suppressor and promoter, combustion rate catalyst, inert additives) when they were heated to 225°C. Experimental results showed that there are important free radical processes taking place. This theory did not actually study the free radical process in real propellants. It could not explain the mesa effect. Furthermore, large amounts of non-lead metals may react with the free radicals to form metallic alkyl radicals without plateau combustion.

3. The Carbon Containing Material-Hot Bright Sphere Theory.

Eisenreich, et al(42) (1978) used microscopic high speed photography and scanning electron microscopy to observe that the color in the solid phase zone 40 microns beneath the extinguished surface varied from transparent to brown or reddish brown. Craters with a maximum diameter of 50 microns were discovered. Carbon was found to cover the entire extinguished surface. The carbon particles have 20-50 micron thick branches and plates with a maximum diameter of 100 microns. The carbon particles are porous. The pore diameter is approximately 5 microns. At above 2 atm the carbon particles begin to emit red light. It seemed to be due to the oxidation of the decomposition product flowing by. In the meantime, the carbon particles became smaller. They flew away from the surface. The quantity was reduced. In the plateau pressure range, the carbon particle diameter is about 20-50 microns, and the density is about 300 particles/cm^2. When the pressure exceeded 5 atm, bright metal spheres began to appear on the carbon particles or the combustion surface. The diameter is approximately 100 microns. The diameter of the bright balls flying away from the surface is about 20-50 microns. The velocity is 15-50 cm/sec. They believed that the trajectory modifier accelerated the decomposition of nitrocellulose under the combustion surface at low pressures. /53 It catalyzed the oxidation of carbon containing materials on the combustion surface. Consequently, more energy was released to produce super rate combustion. Due to the departure of carbon containing and metal containing bright spheres from the combustion surface, the energy transferred to the surface is decreased. This led to the plateau and mesa combustion.

As early as 1956, Brown, et al(1) used microscopic high speed photography to observe the structure of the combustion surface of plateau propellants. They discovered that there were lead spheres 30-60 microns in diameter under plateau pressure. In recent years, many studies in our country have confirmed the carbon containing matter - hot bright sphere theory. Although the chemical nature has not been precisely verified, yet it provided possible clues to the mechanism. The reaction on the carbon particle verified the following carbon-lead catalysis mechanism which leads to the occurrence of super rate combustion.

4. The Lead-Carbon Catalysis Theory.

Hewkin, et al(43) (1971) published the summary of the work of their study group. They used a flame probe to measure the compositions of each combustion zone. Thermocouples and infrared temperature measuring methods were used to determine the temperature at the combustion surface. High speed photography was used to study the structure of the combustion wave. It was discovered that the temperature near the surface increased due to the addition of lead compounds at low pressures. An analysis of the dark zone of the catalyzed propellant indicated that N_2 in the combustion products increased and NO decreased. The exotherm of the NO reduction reaction is very large. The effect of the lead compound produced large amounts of carbon on the combustion surface. There is more carbon during super rate combustion. There is less carbon during mesa combustion. Carbon disappears when the mesa pressure is exceeded. During the combustion of double base propellants without catalysts, there is always carbon formation on the combustion surface in the entire pressure range. However, the carbon content at low pressure is much lower than that of a catalyzed propellant. They beleived that the effect of the lead compound not only increased the formation of carbon, but also activated the carbon. Activated carbon is a solid phase catalyst for the exothermic reduction reaction of NO. Without a catalyst, the rate of the NO reduction reaction in the dark zone is very slow. Therefore, the temperature of the combustion surface increases and the combustion is raised. However, lead also catalyzes the reaction between NO and carbon which makes carbon disappear. When the pressure rises, carbon is removed even more easily. The NO reduction reaction is decreased.

The combustion rate of the propellant is reduced to produce mesa or plateau combustion.

Hewkin, et al (44) (1974) continued to study the correlation between the phenomena on the combustion surface and the catalyst. The aforementioned theory was verified. It was observed that the rate at which carbon is removed by copper compounds is slower than that by lead compounds. Therefore, the catalytic effect can be maintained to high pressures. When both lead and copper are simultaneously used, the removal of carbon is determined by lead. With the addition of oxygen rich materials such as ammonium perchlorate or nitroglycerin, the surface carbon is greatly decreased. The plateau effect is destroyed. The cross-linking of nitrocellulose promotes the formation of carbon. It makes the plateau effect extend to an even higher pressure. RDX does not change the flame structure. There is still a lead and carbon cover. However, the plateau effect is destroyed. This may be due to the poisoning of the catalyst by NO_2 which is the decomposition product of RDX. It indicates that although the formation of carbon is important, yet it is an unique condition for the formation of a plateau. The reaction between NO and CO is very slow at below 1000°C. However, when there is CuO present, the reaction is already very fast at 200°C (45). It is even easier for the reaction to proceed in the simultaneous presence of copper and lead (46). Therefore, the catalytic actions of lead and copper should be considered similar to that of carbon.

This theory can explain many phenomena. But, the lead catalyzed reaction between NO and carbon has a large exotherm, despite the fact carbon is consumed. Therefore, it failed to explain the story. It appeared that the study of Eisenreich can explain plateau combustion, i.e. bright carbon containing and metal containing spheres are leaving the combustion surface so that the energy to be transferred to the surface is reduced to produce plateau combustion.

5. The π Bonding Complex Theory.

Fifer, et al (47) (1975) reported the laser ignition of thin film specimens of nitrocellulose and double base propellants. These specimens were burning at 1, 20 and 40 atm. Infrared spectroscopy was used to measure the final products. In the lead salt catalyzed propellant sample, the CO_2/CO ratio in the combustion product increases under super rate combustion pressures. Consequently, the surface temperature and dark zone temperature increased and the combustion rate increased. The permeation of water and NO_2 into the specimen had no significant effect on the combustion product. However, a small amount of O_2 catalyzed the oxidation of CO into CO_2 and the reduction of NO to N_2. They adopted the π bonding complex theory of Salooja(48,49) (1967), which is that PbO restrains the combustion of alkanes, but forms a π bonding surface complex with oxygen-alkane derivatives to greatly promote the combustion of the oxygen derivatives. The characteristic of a catalyzed reaction is the increase in the amount of CO_2 produced. Sometimes, the amount of H_2 produced also increases. PbO is reduced to Pb and Pb is re-oxidized into PbO. PbO catalyzes the primary and secondary solid phase /54 decomposition reactions in the same manner.

In Fifer's experiment, the amount of carbon found was too little. It was not enough to cause the ratio of NO_2/CH_2O to vary significantly. Therefore, it does not support the chemical stoichiometric shift theory of Kubota. The amount of NO reduced measured by them was extremely little. Therefore, it disagrees with the carbon-lead catalysis theory and the chelate theory, which involve the reduction of NO in large amounts. However, the experimental result was obtained according to the measurement of thin film combustion product ignited by a laser. Its difference with the actual combustion of propellants remains to be studied.

6. Results of Heated Platform Microscopic Studies.

Morrow (1973-1974) used a heated platform microscope to conduct many studies in the areas of heat sensitive macromolecular decomposition, thermal properties of the condensed phase nitrocellulose with different degrees of nitrification, and combustion catalysts(50,51,52). He also specifically studied the effect of catalysts on the combustion of nitrocellulose thin film(53,54). Thin film specimens 180 ±40 microns thick were placed in a melting point apparatus using 1.5 mm outer diameter capillary tubes. They were heated to 250°C and a polarized light microscope was used to observe the phenomena taking place in the heating process. Furthermore, the heating weight loss was measured. In the four sets of experiments at 1 and 34 atm with and without lead salicylate, it was discovered that the emerging temperature, foaming temperature, and foam termination temperature for a rose shaped material were not too different. However, the weight loss was opposite to our prediction. The weight loss with the catalyst was less. He believed that catalysts do not react with the solid phase. They only react in the gas phase over the top of the surface. This is consistent with the viewpoint of Hewkin. It seems that such method is merely an ancillary means and cannot be used to solve the problem completely.

7. Another Piece of Evidence for Gas Phase Theory.

Lenglé et al(55) (1979) used the concept of composite propellant combustion mechanism to study the plateau combustion mechanism of double base propellants. They summarized their own experimental data and previous literature to prove the linear relationship between the surface temperature and the combustion rate. Catalysts do not change this correlation. The condensed phase exotherm, calculated from the surface temperature, increases greatly with increasing combustion rate. But, it is independent of the catalyst. Therefore, the propellant decomposition kinetic is not affected by catalysts. The apparent activation energy for decomposition is about 40 Kcal/gram·molecule. It might be related to the breaking of the $CO-NO_2$ bond. The decomposition of propellants in vacuum was studied using a porous metal plate thermal decomposition apparatus. The gas produced was identified by using a mass spectrometer. It was discovered that catalysts do not affect the gas composition much. Furthermore, from the point of view of decomposition kinetics, lead and copper salts did not begin to react in the condensed phase. From this, one could reach the conclusion that although great amounts of heat are released by the propellant in the condensed phase, yet the catalyst does not react in the condensed phase process. The active products PbO and CuO of the catalysts only react in the initial flame. Therefore, the exact nature and stability of the lead salts are not the major factors. They used the reaction between PbO and formaldehyde in a simulated reactor (duration of stay was about 0.1 sec., temperature 350°C) to prove that this reaction might produce carbon on the surface of the propellant. It was also discovered that the temperature at the tail of the initial flame increased with pressure. When super rate combustion was present, the corresponding temperature at the tail of the initial end was even higher. Therefore, the active position of the active end is located in the gas phase initial flame zone. When there are lead and copper salts, carbon residual is produced by the reaction between PbO and formaldehyde in the initial flame. This makes more NO to participate in the reaction to release more heat to allow super rate combustion to take place.

A porous plate thermal decomposition apparatus was used to study the decomposition product of the vanishing condensed phase when there is no gas phase reaction. Propellants without catalysts had already been studied. Evidence of gas phase catalysis was obtained indirectly. Direct evidence still has to be studied. The methods to study composite propellants are very useful. They can be extended to more areas.

8. The Pressure Independent Reaction in the Hissing Zone Theory.

Kubota(56) (1979) used a special formulation of low plateau pressure, wide range, and low combustion rate, in order to obtain the surface temperature more accurately, as well as to get clearer photographs of each flame zone. This plateau propellant has a very intense super rate combustion characteristic at below 16 atm. At between 16-36 atm, the plateau combustion rate is 0.24 cm/sec. However, the pressure index of the corresponding uncatalyzed propellant is 0.85. It was found by a study that the total reaction order in the dark zone is 2.6. It is not related to the presence of the catalyst. This indicated that the catalyst does not change the dark zone process. In the plateau region, the combustion rate remained unchanged. However, with increasing pressure, the bright flame zone of a catalyzed propellant approached the combustion surface even faster than that of an uncatalyzed propellant. The temperature gradient in the hissing zone of an uncatalyzed propellant rises homogeneously with pressure. However, the temperature gradient of a catalyzed propellant in the hissing zone rises in the super rate combustion section. It remains unchanged in the platform section. The variations of hissing zone temperature with pressure and combustion rate with pressure for the two kinds of propellants are the same. The hissing zone temperature gradient for a catalyzed propellant remains unchanged in the plateau section, i.e. the reaction rate stays the same. Consequently, the heat transfer feedback from the hissing zone toward the combustion surface remains unchanged in the entire plateau section. But, the catalytic activity in the plateau hissing zone varies. Furthermore, it drops rapidly with increasing temperature. This is due to the suppression related to lead in the hissing zone. The total reaction order of a catalyzed propellant in the hissing zone is zero. However, for an uncatalyzed propellant, the total reaction order in the hissing zone is 1.7. In the meantime, it was observed that the surface temperatures and subsurface reaction area exotherms for a catalyzed and an uncatalyzed propellant are identical. Hence, it was believed that reactions, not related to pressure, in the hissing zone caused plateau combustion. /55

Due to the fact that a low pressure, low combustion rate, and wide range plateau propellant was used, the measured surface temperature and the thickness of each zone are more reliable than before. The conclusions derived are more convincing. The result that surface temperature and pressure are not affected by catalysts is different from the earlier result of Kubota(1) and those of Suh(6) and Lengellé(55). However, it agrees with the result of Denisyuk(18). However, based on the observation of Densisyuk, catalysts did not change the distance from the surface to the maximum flame. This is opposite to the observation of Kubota. Because of this, Denisyuk obtained the condensed phase catalysis theory, while Kubota obtained a gas phase hissing zone catalysis theory. Therefore, work must continue to study the mechanism of plateau catalysts by using surface temperature and combustion zone photography. It is hopeful that a commonly recognized theory can be obtained.

IV. VIEWPOINTS REGARDING THE DIRECTION OF FUTURE RESEARCH

1. Objects to Study: The direction should be switched from simulated real combustion systems to real combustion systems. Here, a real combustion system is to burn the actual propellant formulation at high pressure. It does not imply the combustion in a real engine. The studies to date, with the exception of physical studies such as high speed photography, surface temperature measurement, and discontinuity tests as well as flame infrared emission spectroscopy, have great differences with the combustion conditions of real propellants. Thus, only indirect data which is of a reference nature can be obtained. It is not possible to draw positive conclusions. Very frequently, twice the effort only brings about half of the result. The waste is very high. Therefore, from now on we should avoid experiments which deviate from the real combustion conditions to the extent possible. Of course, simulated tests with specific relavance are still necessary complimentary means which we cannot do away with.

2. Experimental Methods: The research work by Eisenreich and Kubota has already reached a relatively high level by using techniques such as high speed microscopic photography, thermocouple temperature measurement, observation of extinguished surface, etc. to obtain a great number of vivid physical phenomena in a plateau effect. Furthermore, physical phenomena were used to predict the chemical nature of the plateau effect. For example, the observation and study of carbon containing matters, lead containing matters, and bright spheres are used to predict the possible chemical reactions. As another example, from the temperature distribution and the thickness measurements of the combustion regions, the pressure index, chemical reaction order, and catalyst activity coefficient in each region can be obtained. This is used as the basis of judgement in the determination of the reaction position of the plateau catalyst and the type of chemical reaction. This type of technique should be further perfected. For example, the accuracy should be raised. The measurement of gas phase temperature distribution of the flame should be developed. Color high speed photography should be used.

The study on extinguished surfaces should also switch from physical effects to chemical compositions, just as some institutions in our country developed electronic probes to study the extinguished surfaces of propellants.

Mass spectroscopy is an important means in the study of condensed phase kinetics. It should be seriously taken into account. Using a molecular beam sampling technique in conjunction with a time lapse mass spectrometer, there is a possibility of studying transient products of the flame under actual combustion conditions. This will be very useful in solving the plateau combustion mechanism. Certainly there are many difficulties yet to be overcome(25).

The laser hologram and laser Raman Spectroscopy are also diagnostic techniques to be developed for combustion(57,58). The advantage is that the actual combustion system is not disturbed in the measurement. The laser hologram can be used to observe the physical structure of the burning surface when flame still exists, as well as the particle size distribution and speed of the catalyst on top of the surface and in the flame. It can also be used to measure the flame temperature distribution. Laser Raman Spectroscopy is capable of measuring the temperature, type of material and concentration at any point in the flame. Apparently, it is an excellent measuring technique for combustion chemical reactions. In which, the correlating anti-Stokes Raman Scattering can be considered to be developed with priority due to high intensity, capability of partial analysis, and absence of fluorescence interference.

3. Scientific Design: When experiments are designed /56 scientifically and delicately, even by using simple experimental methods, it is possible to obtain new and important conclusions. For example, Kubota designed a propellant which underwent plateau combustion at 16-30 atm. This drastically improved the accuracies in photography and temperature measurement. New and reliable conclusions were obtained. As another example, in order to prove the effect of the reaction between CH_2O and NO_2 in propellants, it can be envisioned that such studies can be made through the

delicate design of formulations. There is still much to be done in the experimental design aspect.

4. Investigation on Other Problems Related to Plateau Combustion: For example, the effect of carbon on the combustion of plateau and usual propellants; the mechanism of ultraviolet absorber in raising the plateau combustion rate; the ancillary catalytic action of copper on lead; the effect of inert additives in double base propellants; and non-lead plateau catalysts. These are problems related to the plateau combustion mechanism.

In summary, although the plateau combustion mechanism for double base propellants has been studied for over twenty years by many researchers in the world, and many theories and explanations were given, yet this problem has not been really understood in essence. Much study is still awaiting us to be performed.

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