Platonization in Double-Base Rocket Propellants

Haridwar Singh and K. R. K. Rao
Explosives Research and Development Laboratory, Poona, India

I. Introduction

THE inclusion of small quantities of various lead compounds in the double-base propellant system results in increased burning rate at low pressure, followed by a plateau burning region, where the burning rate remains almost independent of variation in pressure, and the postplateau region, in which the burning rate/pressure relationship is similar to that of an unleaded propellant (Fig. 1). This phenomenon of independence of burning rate to pressure, generally known as "platonization," implies a low value of pressure index n in the plateau region. A low value of n permits the design of lighter rocket motors because of lower safety factors. The magnitude of n is one of the important factors in determining the suitability of a propellant for rocket propulsion applications.

The importance of low-pressure ballistics was realized as early as in 1939 with the widespread use of rockets. Earlier studies centered around low-energy nitrocellulose propellants with a view toward minimizing nozzle erosion, burning rate, and pressure index. However, the real impetus to the platonization of double-base propellants came from the observation that the use of lead stearate as a lubricant in the extrusion of large rocket charges actually had modified their burning characteristics. This paper reviews the literature on platonization of double-base propellant with different inorganic and organic compounds of lead and other metals, and presents various theories to explain the mechanism of the plateau effect.

II. Resumé

Avery and co-workers[1] were the first to observe the unusual behavior of lead compounds on the ballistics of double-base propellants in 1946. Cooley and Bruson[2] patented the use of lead salts of an alkoxy, keto or N-substituted amino acids such as butoxy acetic acid, N-N-bis (2-ethyl hexyl) β-amino propionic acid as burning rate stabilizers. According to them, nitrocellulose propellants, containing lead salts of aliphatic acids, possess burning characteristics substantially unaffected by variations in pressure and ignition temperature during operation. Such propellants are suitable for use in rockets and other guided missiles.

However, Preckel[3] carried out detailed investigations on the effect of oxides of lead, lead stearate, lead-2-ethyl hexoate, etc., on both single- and double-base propellants. He has shown that the lead salts render the burning rate of propellants independent of pressure over a certain pressure range in which pressure index decreases to a value of about 0 to 0.2. Below and throughout this pressure range, the burning rate is increased as compared to the control without lead salt, whereas above the plateau range, the burning rate remains conventional. Furthermore, these salts were effective only with cooler propellants of calorimetric value below about 850 cal/g. Preckel also sought to explain the plateau effect as being due to the catalytic reactions of Pb and PbO. Lead is oxidized by NO or NO_2, and resulting PbO reacts with oxidizable molecules to regenerate lead.

Preckel[4-7] took a number of patents covering the use as ballistic modifiers of various inorganic lead compounds such as PbO, PbO_2, Pb_3O_4, PbS, lead molybdate, lead perchlorate, and lead salts of organic acids such as 2,4-dihydroxy benzoic acid, salicylic acid, acetylsalicylic acid, methoxy propionic acid, ethoxy acetic acid, tribasic maleic acid, or mixtures of lead salicylate or lead acetyl salicylate with lead-2-ethyl hexoate and organo-lead compounds like tetraethyl lead. Lead inorganic compounds and lead salts of aliphatic acids were found to be effective with propellants of calorimetric values less than 900 cal/g, whereas lead aromatic salts were effective at higher calorimetric values. Concentration up to 4% of these additives was effective in producing the desired effects. Furthermore, he reported that addition of carbon black increases the burning rate without

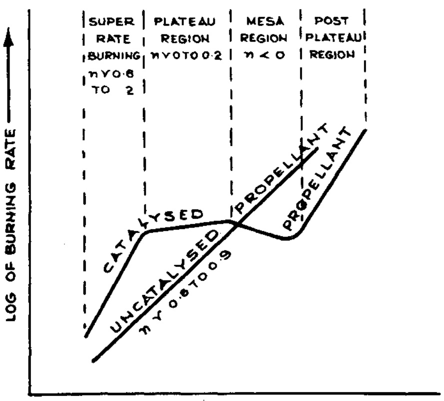

Fig. 1 Graph showing super-rate, plateau, and mesa characteristics.

Haridwar Singh received his M.Sc. (Organic Chemistry) degree from Agra University in 1966. After serving as lecturer in a government postgraduate college from 1966 to 1970, he joined Explosives Research and Development Laboratory in 1971, and since then he has been working in the field of solid rocket propellants. His title is Senior Scientific Officer.

K.R.K. Rao, M. Sc. (Banaras Hindu University), Ph.D. (Poona University), joined Explosives Research and Development Laboratory in 1962, after serving in the Defence Research Laboratory (Materials) and Central Drug Research Institute. At present he is Deputy Director, and his fields of activity are rocket propellants, pyrotechnics, and high explosives.

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affecting the plateau and stressed the importance of the particle size of the carbon black.

Metal-containing additives such as Ag and Ag_2O also were reported by Preckel[8] to minimize the effect of temperature and pressure on the burning rate of double-base solid propellants. Preckel[9] also disclosed that, in addition to lead compounds, the inclusion of a phenolic compound such as 2,4-dihydroxy benzaldehyde, 1- or 2-naphthol, 1,5 naphthalenediol, toluene thiol, Cresol, pyrogallol, phloroglucinol, nitronaphthol, or 2,4-dinitro-resorcinol widened the plateau region.

Camp[10] claimed in a patent that the use of about 2 to 5% of lead salts of aliphatic and aromatic monocarboxylic acids such as lead salicylate, lead stearate, etc., in propellants of calorimetric value less than 1100 cal/g gives mesa characteristics (zero or negative n value, where temperature coefficient is very small). Camp and Crescenzo,[11] in another patent, claimed that by using a combination of lead and copper salts of aliphatic and aromatic carboxylic acids, the mesa region can be extended as compared to lead salts alone, and mesa characteristics were observed with propellants of calorimetric value of 600 to 1250 cal/g. Thus, this invention covered the range for both cooler and hotter propellants. Even inclusion of 10% aluminum did not affect the mesa characteristics. With aluminum, lead and copper salts were supposed to form catalyzing agents for the combustion of aluminum.

Murata and Inagaki's[12] investigations revealed that, by addition of about 4% Pb_3O_4, the n value of double-base propellants is lowered from 0.768 at 20 to 200 atm to 0.474 at 10 to 40 atm and 0.766 at 40 to 100 atm. Ilyana and coworkers[13] claimed uniform and improved combustion of double-base propellants by the incorporation of 2 to 12% of p-phenylene diamine or a mixture of substituted or unsubstituted phenylene diamines, along with lead salicylate, tetraethyl lead, or diethyl diphenyl lead.

Mcewan et al.[14] observed that incorporation of about 2% by weight of short sections of thin wires of metals that are good heat conductors, such as Ta, Pb, Cu, Ag, Al, and Mo, increases the burning rate of double-base propellants containing ballistic modifiers such as lead salts of salicylic and 2-ethyl hexanoic acid, without any adverse effect on the plateau region. The studies of Henry and Mcewan[15] on double-base propellants containing ballistic modifers such as lead salicylate, lead-2-ethyl hexanoate, lead-acetyl salicylate, lead-2, 4-dihydroxy benzoate, and their mixtures have indicated that benzophenone derivatives of the general formula given in Fig. 2, increase the burning rate without affecting plateau and mesa characteristics, stability, and ballistic properties of the propellant.

Preckel[16] published detailed results covering his earlier research. He obtained platonization in propellants of calorimetric values from 850 to 1500 cal/g, by the use of lead salts of aromatic acids such as benzoic, phthalic, tannic, salicylic, thiosalicylic, and anthranilic acids. The addition of carbon black increased the burning rate without adverse effect on the plateau. However, a significant plateau rate increase was observed at low concentration of carbon black (less than 0.5%). Smaller particle size of carbon black resulted in higher burning rates due to surface effects. In this way, by using aromatic lead salts and small particle size of carbon black, he obtained very high-plateau burning rates in high-energy

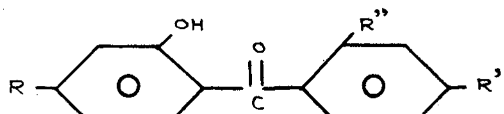

Fig. 2 General formula of benzophenone derivatives (R = OH or lower alkoxy group; R' = H, OH, or lower alkoxy group; R'' = H or OH).

propellants. Svatos and co-workers[17] claimed the superiority of organo-tin compounds such as tetraethyl tin, monoethyl trimethyl tin, tetrabutyl tin, tetraphenyl tin, tin-salicylate, and tin-thio-salicylate over lead compounds as ballistic modifiers, in view of the nontoxicity of their explosion products.

According to Chaill and Walker,[18] potassium or sodium salt of dinitroacetonitrile increases the burning rate of double-base propellants by a factor of 4 or slightly higher, without affecting their thermal stability and calorimetric value. Hewkin and co-workers,[19] in the course of their investigation, studied the effect of a number of metallic oxides. They observed that magnesium oxide and nickel oxide reduced the burning rate, whereas oxides of iron, cobalt, copper, zinc, and tin enhanced the burning rate of double-base propellants over the entire pressure range studied (up to 2000 psi). Litharge was the only oxide that produced a mesa ballistic plot under these experimental conditions. Furthermore, with increasing concentration of PbO, mesa shifted to a lower pressure range, and burning rates increased.

Costa et al.[20] claimed through a patent that good mesa and plateau ballistics are obtained in double-base propellant compositions containing a heterocyclic nitramine explosive such as HMX, RDX, etc., an aryl hydroxide or ester as stabilizer such as resorcinol mono or diacetate, pyrogallol triacetate, p-hydroxy diphenylamine, tetrahydroxy anthracene, etc., and ballistic modifiers such as lead stearate, lead tartarate, and (or) lead cyclopentane carboxylate. Crescenzo et al.[21] patented the use of tin, zinc, lead, manganese, and copper compounds as ballistic modifiers for gas generator compositions and claimed that solid propellant grains containing the compounds of these metals can be formed in a variety of shapes and sizes.

Kubota and co-workers[22] studied the burning rate flexibility of plastisol double-base propellants and observed that burning rates (as high as 400%) and pressure index can be varied by the addition of 2% of lead and copper salts such as salicylates, 2-ethyl-hexanoates, etc. They found that lead and other metallic compounds, metal powders, and carbon powder merely increase the burning rate, whereas only lead salts produce super-rate, plateau, and mesa burning. Inclusion of ammonium perchlorate up to 20% resulted in the increase of burning rate up to 30%. Addition of 0.1% carbon to propellant containing lead salt showed super-rate burning, which decreased on further addition of 0.1% carbon black. However, this is not in agreement with the results of Preckel.[16] According to these authors, PbO, despite its super-rate burning effect, does not produce plateau or mesa burning characteristics, which again is not in agreement with the observations of Preckel[3] and Hewkin et al.[19] Furthermore, they observed that the coupling effect of one lead salt with another lead salt having a different organic moiety, i.e., mixture of lead salts of aliphatic and aromatic acids, is complicated, and a propellant catalyzed with the mixture of lead salicylate and lead 2-ethyl hexoate produced a lower burning rate than that catalyzed with either of two lead salts in the pressure range 8 to 23 atm, with a negative effect on burning rate over 60 atm pressure.

Denisyuk[23] studied the influence of the ratio of PbO to carbon black on the combustion rate of propellants and found that the PbO:carbon black in the ratio of 2-3:1 produced the best effect. In the absence of carbon black, PbO had a weak catalytic effect.

Sumi and Kubota's[24] investigations on composite modified double-base propellants showed that the gradual addition of fine HMX to a platonized double-base matrix resulted in a gradual increase in the pressure index and decrease in the plateau effect and burning rate. Recently, David[25] claimed that inclusion of barium metallo-organic salts such as barium salicylate and barium β-resorcylate or barium oxides produced a plateau in smokeless double-base propellants, with a reduced amount of smoke formation as compared to lead salts.

III. Mechanisms

A number of attempts have been made to explain the mechanism of the action of the lead salts and the phenomenon of platonization. Preckel[3] was the first to suggest the catalytic involvement of lead in the nitrate ester decomposition through the oxidation of lead by oxides of nitrogen to lead oxide, followed by the latter's reaction with the oxidizable molecules regenerating lead in the condensed or gas phase. To account for this, Preckel reported the presence of globules of lead in a window-bomb experiment. According to another theory, lead compound catalysis was supposed to lead to the formation of underoxidized carbon or carbonaceous matter, which liberates much heat in the condensed phase and thereby leads to a higher burning rate in and below the plateau region. The progressive diminution of the carbonaceous surface accounted for the absence of the plateau effect at higher pressures. Preckel concluded that the plateau mechanism occurs in or very near the burning surface, and an easily heat-labile lead compound must be involved. If such a mechanism in which lead merely acts as a carrier of oxygen were operative, one could expect other metal oxides such as Fe_2O_3, MnO_2, Cr_2O_3, etc., to show a similar effect. However, no such effects were observed by Hewkin et al.[19]

On the basis of the mass spectroscopic observation of a number of unstable species and free radicals such as $\dot{N}O_3$, $CH_3CH\dot{O}$, and $CH\dot{O}$, Bauman and Picard[26] concluded that lead salts increase the rate of oxidation-reduction reactions between $\dot{N}O_3$ and $CH_3CH\dot{O}$. They detected these species even prior to the indication of any decomposition of the propellant.

Lenchitz and Picard,[27] through their studies on the thermodynamic properties of a propellant, showed that lead stearate affects the chemistry of the burning process by its influence on the heat of explosion and increase in the intensity of flame radiation. They pointed out that radiation from the flame has no significant effect on the temperature of propellant beneath the burning surface. Lenchitz and Haywood[28] postulated the plateau as the transitional region, in and below which lead stearate increases the heat of explosion, leading to an increase in burning rate, whereas at higher pressures it acts just in the opposite way.

According to Sinha and Patwardhan,[29] lead salts transport short-lived free radicals such as $\dot{C}H_3$ and $\dot{C}_2H_5$, produced by the breaking of $RO\text{-}NO_2$ bonds in nitrate esters, as lead alkyls from the foam to the fizz zone. These lead alkyls decompose into metallic lead and free radicals in the fizz zone, where a chain reaction takes place, and the fizz zone becomes hotter due to reaction between free radicals and NO. The fizz zone transfers heat to the foam zone and thereby increases burning rate. At higher pressures, free radicals are removed due to increased collision, and their reaction with NO becomes less prominent, causing lowering of heat liberation. Thus, the plateau is the result of a balance between the increased heat conduction at the burning surface and the lowering of heat liberation. When the effect of free radicals becomes insignificant at higher pressures, burning rate increases with pressure, thus accounting for the postplateau region. They suggested platonization of hotter propellants by lead aromatic compounds as being due to the heat absorbed for the pyrolysis of lead aromatic compounds in the fizz zone, in addition to the preceding factors. The free radical mechanism also does not explain all of the observed facts, as there are a wide variety of metals other than lead which react with free radicals to form metal alkyls, but no plateau has been reported.

Based on the studies of solid phase reactions of double-base propellants and their thermal decomposition with and without lead salts, Dauerman and Tajima[30] suggested NO_3 rather than NO_2 as the primary oxidation product.[1] Lead stearate was found to be an active catalyst at low pressures. They postulated that lead stearate enhances the oxidation-reduction reaction in the surface reaction zone. Although interesting, it is difficult to explain the formation of NO_3 as the principal product of decomposition of nitric ester $R\text{-}O\text{-}NO_2$, as the energy of the C-O bond will be higher than that of the N-O bond.

Hewkin and co-workers[19] offered an explanation on the basis of the formation of carbon or carbonaceous matter in the condensed phase, projecting into the gas phase. According to them, the basic burning process of double-base propellant involves the formation of a limited amount of carbon in the condensed phase, which catalyzes the exothermic reactions involving the reduction of NO. In the presence of ballistic modifiers, the amount of carbon or carbonaceous material is increased, but in the presence of lead compounds this increase of carbon is confined to a limited pressure range, where the burning rate is higher as compared to that of unleaded propellant composition. In the plateau region, carbon is removed because of oxidation by NO as fast as it is produced. Carbon is not available as a catalyst or catalyst carrier on the surface of a propellant in the postplateau region, and hence the burning rate curve falls. This mechanism of carbon or carbonaceous matter formation explains many of the observed facts, but the greater total heat release in the fizz zone for catalyzed propellants is not in conformity with the findings of Kubota et al.[33] who observed that the final temperature at the end of the fizz zone for catalyzed propellant was the same or less than that for the noncatalyzed one.

From an examination of temperature profiles during burning of ballistite propellant in the presence and absence of a lead-copper catalyst, Denisyuk et al.[31] concluded that the catalyst does not affect the heat evolution in the condensed phase but decreases the flow of heat to the gas phase by 4-5%. The effect of the catalyst on the burning rate was considered to be the result of its influence on the reactions taking place in the condensed phase.

On the basis of the probability of the electronic interaction between lead modifiers and nitrocellulose, Suh et al.[32] proposed that lead forms a chelate-type complex using nitro oxygen of nitrocellulose, and this interaction weakens the $RO\text{-}NO_2$ bond, leading to an increase in the burning rate, by expediting the dissociation of nitrate esters. The weakening of the $RO\text{-}NO_2$ bond, according to these workers, is caused by the shift of π electrons toward the plumbous lead. Based on the preceding hypothesis, they explained that compounds such as tetraphenyl lead, where the lead atom is tetrahedrally hybridized, do not increase the burning rate to the same extent as lead chelate compounds. This mechanism fails to explain how nonchelate lead compounds, such as PbO, can cause a super-rate and plateau effect as observed by Preckel[3] and Hewkin.[19]

To locate the site and mode of action of platonizers in double-base propellants, Kubota and co-workers[33] examined the combustion wave zones (luminous flame, dark, fizz, and surface reaction zones) by means of photography and thermocouples and observed that each zone is altered somewhat in catalyzed propellants by rate-accelerating metal salts. The increase in burning rate is the effect of the enhancement of reactions in the fizz zone. Measurement of the standoff distance of a luminous flame from the propellant surface (dark zone length) indicated extremely small feedback from the luminous flame, and, as against an expected decrease in standoff distance with increase in burning rate, an increase of this distance was observed. The photographs of the flame indicated that, in the presence of a catalyst, a large amount of particulate emission from burning surface is observed, and these particles persist over large distances in the flame. The combination of lead and copper salt yields high emission rates of small particles and higher burning rates. These particles were identified as carbonaceous matter by these workers. The overall results reported by these authors are not fully consistent with the models of Camp or Powling.[19] They further observed that catalyzed propellants exhibit a steeper temperature gradient in the fizz zone, which is because of an increased NO_2/aldehyde ratio, resulting from increased surface carbon formation.

Fifer and Lannon,[34] based on their infrared analysis of combustion products of a propellant, observed that addition of lead salts increases the CO_2/CO ratio and in most cases increases the H_2O/CO ratio also. They explained that the higher CO_2/CO ratio was due to high-energy output for a catalyzed propellant in the superburning region. On the basis of the explanation offered by Salooja[35] for the combustion of hydrocarbons in the presence of PbO, they explained that PbO can interact with nitrate ester molecule to produce a π-bonded surface complex, which may dissociate subsequently, generating lead. Lead can be reoxidized to PbO by oxygen-containing radicals and therefore is available for further reaction.

The mesa and plateau burning characteristics, according to Lee et al.,[36] are due to superimposition of photosensitized decomposition on noncatalyzed thermal degradation of the propellant. Ballistic modifiers have been supposed to undergo thermal and photochemical decomposition at the burning surface, producing legand radicals and metal, which is vaporized and thermally excited. The excited metal undergoes pressure-dependent emission in the flame zone, and the ballistic modifiers, with appropriate absorption characteristics, are photoexcited at the burning surface by uv radiation emitted from excited lead and copper atoms in the flame zone. They further explained the effectiveness of lead salts of aliphatic carboxylic acids at low pressure and that of lead salts of aromatic acids at higher pressure as being due to the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions, at longer wavelength, and higher pressures, because of pressure shifting and broadening effects in the case of lead aromatic salts, where photoexcitation occurs, whereas lead aliphatic salts are capable of being excited only through $n \rightarrow \pi^*$ transition and at low pressures, where short-wavelength uv photon flux is greater before the occurrence of pressure-broadening and shifting emission lines to longer wavelengths.

Thus, all the theories can be grouped broadly under 1) chelate and π-complex theory, 2) free radical theory, 3) carbon or carbonaceous matter formation theory, or 4) photochemical mechanism. Although these theories are interesting and account for some observations, a theory to explain all of the observed facts satisfactorily has yet to be advanced. The primary process in the decomposition of nitric ester is definitely the splitting of the $RO\text{-}NO_2$ bond with an activation energy of about 40 k cal/mole. In a simple way, various reactions taking place in different zones can be represented as shown in Fig. 3. It is also evident from the different studies that ballistic modifiers play their major role in the fizz zone, which is very close to the burning surface.

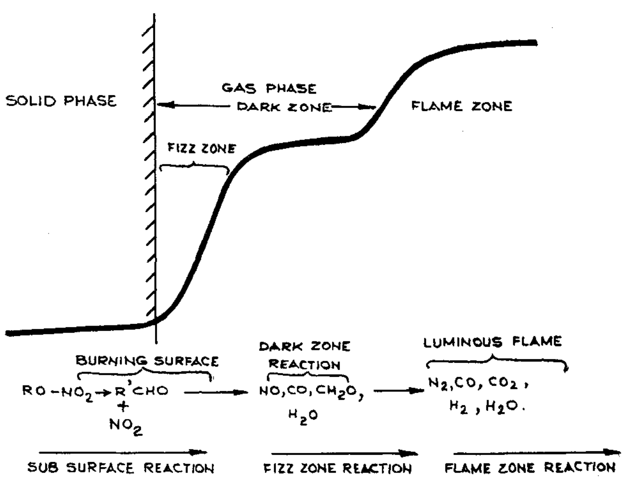

Fig. 3 Representation of various reactions taking place in different zones.

The nature and course of reactions are complex and may not necessarily be the same for super-rate, plateau, or mesa characteristics and even may be different from one catalyst/ballistic modifier to another or even from the low-pressure to the high-pressure region. Even the barrier between the low- and high-pressure regions itself is not a fixed one. A number of factors such as the composition, calorimetric value, concentration, nature and particle size of the catalyst/ballistic modifer, presence or absence and particle size of carbon black, copper salt, etc., affect the burning rate mechanism. Over and above these factors, the effect of lead salts on the plateau of double-base propellants seems to be specific. Hence, the field is still open for further work to offer a really satisfactory and comprehensive theory.

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