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# Studies on Composite Extrudable Propellant with Varied Burning Rate Pressure Index 'n'

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**ABSTRACT**

This paper discusses the development of composite propellant extrusion technique and the study of burning rate pressure indices n with respect to compositional variations. The n is found to vary from 0.35 to plateau and plateau to mesa by suitable compositional modifications. Compositional influence on burning rate with specific reference to plateau and mesaburning additives is described. Details of the process parameters like fluidity of the slurry, extrusion pressure, extrusion rate and die-swell are presented. This propellant is based on ISRO-CTPB binder using ISRO-AP as oxidizer. Ammonium per chlorate (AP) particle size variation and inclusion of additives like PVC, lead stearate, ammonium sulphate, lithium fluoride etc. are found to influence the burning rate pressure index n.

## 1. INTRODUCTION

Processing of double base propellants are generally carried out by solvent extrusion or solventless extrusion technique. The latter is in vogue when the charge diameter is high, since the evaporation of process solvents creates porosity, internal cracks as well as dimensional variation as the grain web thickness is increased. On the other hand composite propellants are processed by casting technique. When smaller size grains are required in large numbers, the choice is in favour of extrusion against casting.

PVC-plastisol, DB and CMDB propellants are widely processed by extrusion technique because of their easy workability, thermoplastic nature and physical curing.

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Recent trend is to extend the extrusion technology to cross-linked composite propellants, because of their better physical and mechanical properties, better aging characteristics over a wide temperature range, dimensional stability and better control over ballistics. Considerable work has been reported on CTBN and MTBN based composite propellant extrusion[1].

## 2. FORMULATION

The experiments were carried out using Carboxyl Terminated Poly Butadiene (CTPB) and Ammonium Perchlorate (AP), both manufactured in Vikram Sarabhai Space Centre, Trivandrum. CTPB was selected for the experimentations due to its less susceptibility to moisture and better workability over a wide processing period for extrusion as compared to the urethane class of propellants. Unimodal AP of average particle size 60 and 140 microns and unimodal coolant oxidizer, Ammonium sulphate of average particle size 110 microns were used. Small amounts of ballistic modifiers such as Lithium fluoride, Lead stearate and Poly vinyl chloride were also used in some of the formulations. Diepoxy-triaziridine combination was used as the curing agent. Tri-cresyl phosphate and Dioctyl adipate were incorporated in the propellant formulation as processing aids and carbon black (Phil-black-GRF) 0.5 per cent as a reinforcing filler. Low melting paraffin wax, 0.5 per cent was incorporated as a die lubricant.

## 3. PROCESSING

The process flow chart for extruded CTPB composite propellant is shown in Fig. 1. The process steps except seasoning and extrusion are familier in the field of composite propellant processing and hence are not discussed in detail.

### 3.1 Seasoning

The propellant was mixed in a conventional jacketed sigma mixer with hot water circulation at 55°C and cast through jacketed hopper with hot water circulation at 55°C under vacuum with a residual pressure of 10–15 Torr, in special containers with diameter identical to that of the extrusion basket. The propellant-laden containers were seasoned at 60°C for 6 hrs and then cooled to room temperature (25° to 27°C) for achieving proper consistency for successful extrusion. The propellant slurry seasoning period varied from 5 to 8 hrs at 60°C for different batches of CTPB resin. A consistency diagram (Fig. 2) could be obtained by plotting fluidity (inverse of Brookfield viscosity) versus time.

Figure 2 shows 3 regions, A-B region showing a gradual decrease in fluidity, B-C region, a plateau like fluidity zone and C-D region, a zone of drastic reduction in the fluidity of the slurry. Extrusion of slurry in the A-B region after cooling to room temperature (25°–27°C) caused deformation of the extrudate due to insufficient crosslinking to maintain the dimensions. The slurry in the C-D region after cooling to room temperature had too many crosslinks which caused drastic increase in extrusion pressure and very slow rate of extrusion, leading to surface damages such as blisters,

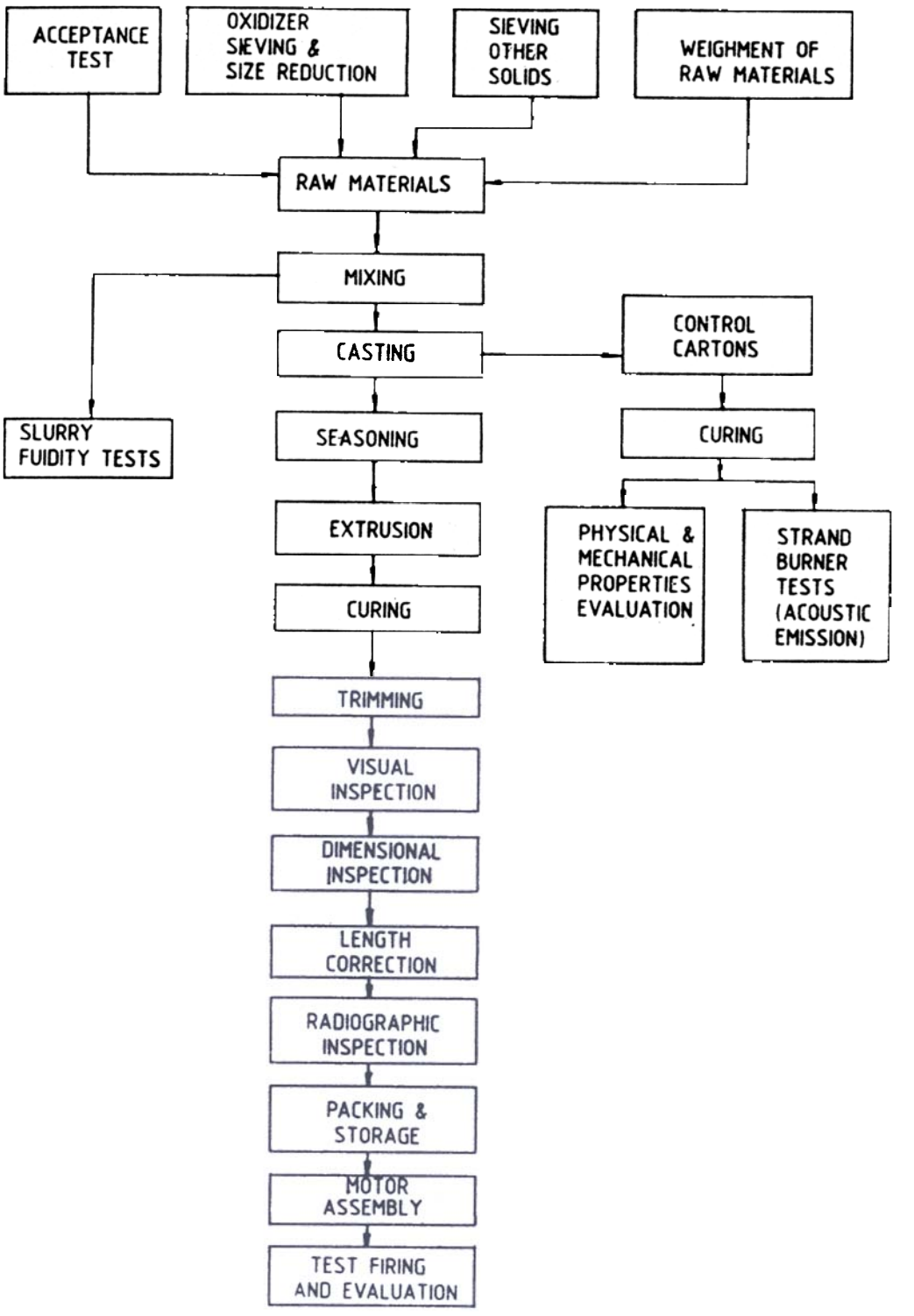


**Figure 1. Composite extruded grain process chart.**

cracks etc. The slurry in the B-C region after cooling to room temperatures was found to be the ideal region for extrusion of small size cartridge grains. The seasoning period in the B-C region for our experimentations was found to be 6 hours and the seasoned slurry after cooling to room temperautre was easily amenable for continuous extrusion for a period of 6 to 10 hrs without much change in the extrusion pressure, extrusion rate and dimensions of the grains as given in Table 1. The seasoning period had to be optimised for a particular lot of CTPB resin before trying for extrusion. The heating

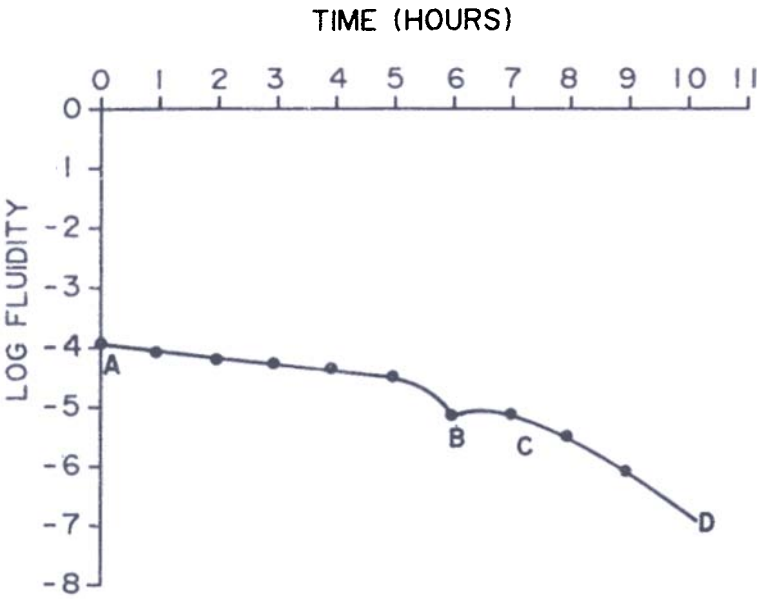


**Figure 2. Fluidity curve.**

**Table 1. A typical extrusion data**

| Extrusion time hours | Extrusion pressure (KSC) | Extrusion rate (mm/s) | Die ID (mm) | Die pin OD (mm) | Cured grains OD (mm) | Cured grains ID (mm) |
|---|---|---|---|---|---|---|
| 0 | 205 | 4.5 | 10.8 | 3.4 | 11.75 | 3.40 |
| | 210 | 4.5 | 10.8 | 3.4 | 11.72 | 3.42 |
| 2 | 210 | 4.3 | 10.8 | 3.4 | 11.75 | 3.42 |
| ٣ | 212 | 4.3 | 10.8 | 3.4 | 11.78 | 3.40 |
| 4 | 212 | 4.3 | 10.8 | 3.4 | 11.77 | 3.41 |
| 5 | 212 | 4.3 | 10.8 | 3.4 | 11.80 | 3.43 |
| 6 | 215 | 4.1 | 10.8 | 3.4 | 11.84 | 3.40 |
| ٧ | 217 | 4.0 | 10.8 | 3.4 | 11.85 | 3.42 |
| 8 | 220 | 4.0 | 10.8 | 3.4 | 11.85 | 3.43 |

up-cooling down method was adopted for our experimentations to minimise the seasoning period and to achieve maximum extrusion time.

### 3.2 Extrusion

The pressure of extrusion depended upon the consistency of the slurry, extrusion rate, die size and die design. Pressures in the order of 200–250 KSC were employed in this work. A typical extrusion data is given in Table 1.

A contoured approach portion for proper consolidation of the propellant, polished die surface, a properly aligned die pin and sufficient land portion which are essential for a good die, were utilised for the extrusion process. A perforated feed portion

before the contoured approach provided for better redispersion of the propellant mix before extrusion, in addition serving as a retainer for agglomerates. A vertical extrusion press (Fig. 3) was used for the extrusion of the propellant grains.

The die used in our extrusion experiments had an ID of 10.8 mm and die pin had an OD of 3.4 mm and is shown in Fig. 4.

To avoid hazards due to friction between the plunger and the press basket, a 5 mm thick paraffin wax buffer disc was provided. The grains were extruded and cut to the required length. The extruded grains underwent dimensional changes after extrusion (die-swell) and during final curing. The die-swell was experimentally found to vary from 7–10 per cent and cure-swell to a marginal value of 1–2 per cent.

### 3.3 Surface Finish

Surface finish of the grain was primarily dependent on the particle size of the oxidizer, nature of the die surface and the extrusion rate. However, better glazing could be obtained by incorporating low melting paraffin wax (m.pt 42–44°C) in the formulation. Paraffin wax, incidentally, acted as lubricant also. Figure 5 shows a set of extruded propellant grains.

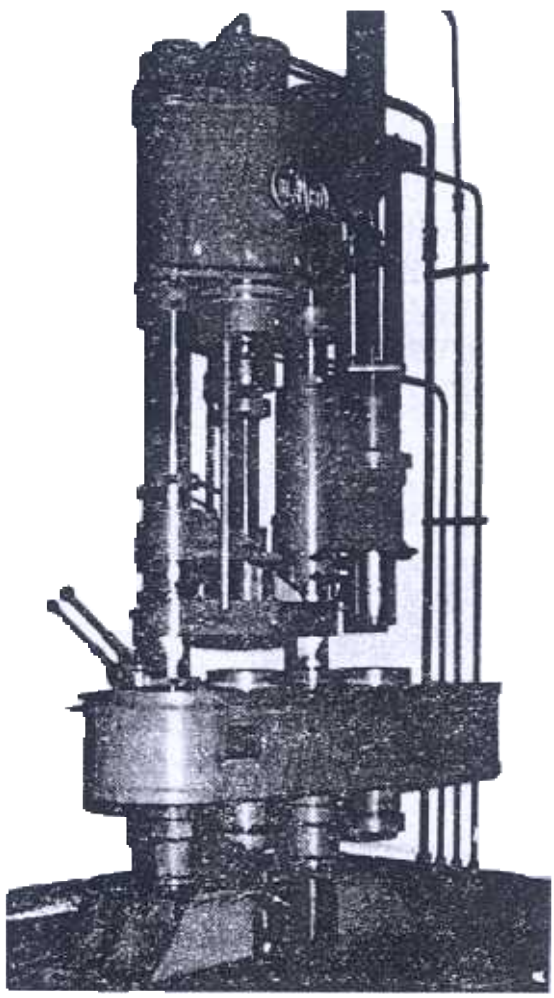

**Figure 3. Vertical extrusion press.**

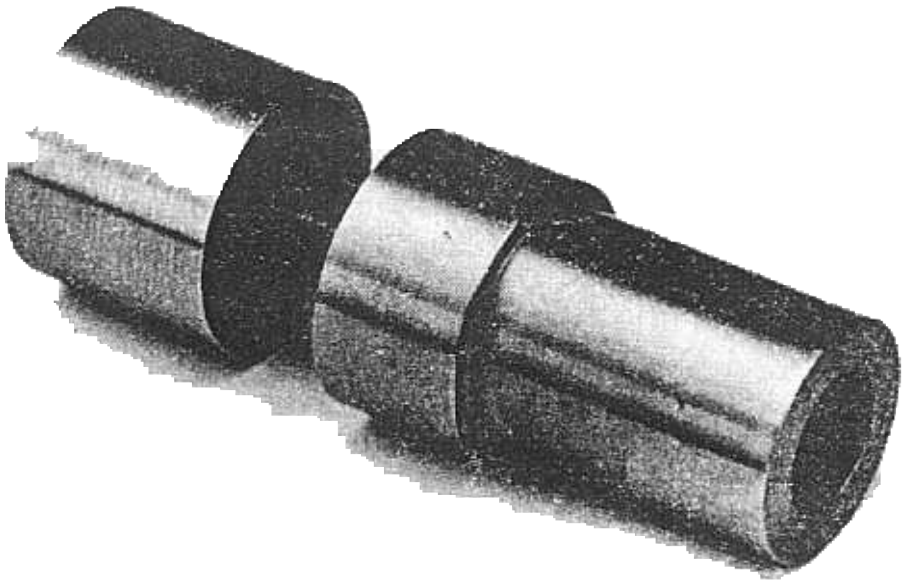

**Figure 4. Die design for extrusion.**

### 3.4 Properties of the Extrudates

Compositional variations and extent of crosslinking was found to influence the propellant properties markedly. Optimum mechanical properties were obtained by curing the propellant at 80°C for 6 days in the case of carton samples and at ambient curing (27°C) for one day which was followed by 80°C for 2 days for the extruded grains. The grains were preserved in stainless steel trays for curing. Table 2 shows the mechanical and ballistic properties of extruded CTPB based composite propellant with some typical formulations.

The extrudate showed slightly lower tensile strength and higher elongation than the carton samples due to the breaking of some of the crosslinks during extrusion, but the variation was of the order of 8–12 per cent. All the mechanical properties were evaluated using INSTRON table model 1121 using die of American Society for testing materials specification D-412-68 'Type C at a cross head speed of 50 mm/minute at 25°C.

## 4. PROPELLANT BURNING RATE AND PRESSURE INDEX 'n'

The propellant burning rate and its pressure dependence were studied using acoustic emission technique[2] and the value of pressure index n was evaluated using Saint Robert's Law, $r = ap^n$ where $r$ is the burning rate in mm/s, $p$ is the combustion pressure in KSC and $a$ is a constant. Five strands at each pressure were used to determine the burning rate in the pressure range 20–68 KSC for all the compositions and the values were plotted in Fig. 6.

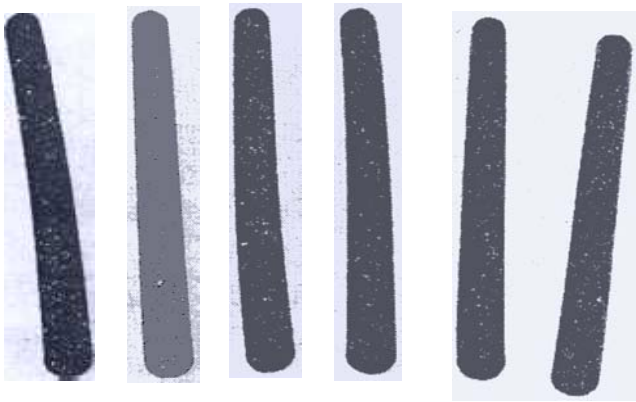

**Figure 5. Extruded grains.**

**Table 2. Mechanical and ballistic properties of some typical extruded compositions**

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| *Mechanical* | | | | | | | | |
| 1. | Code No. | X-101 | X-102 | X-103 | X-104 | X-105 | X-106 | X-107 |
| 2. | Tensile strength (KSC) | 18 | 16 | 16.5 | 16 | 14 | 15.5 | 16 |
| 3. | Elongation % | 16 | 19 | 18 | 19 | 20 | | 19 |
| 4. | Youngs modulus (KSC) | 175 | 160 | 165 | 155 | 150 | 145 | 155 |
| 5. | Hardness (shore-A) | 85 | 85 | 85 | 90 | 80 | 85 | 90 |
| 6. | Density (g/cc) | .63 | 1.61 | .60 | .59 | .61 | 59 | .59 |
| *Ballistics* | | | | | | | | |
| 1. | Code No. | X-103 | X-103 | X-103 | X-103 | X-103 | X-103 | |
| 2. | Motor No. | 1 | 2 | 3 | 4 | 5 | 6 | |
| 3. | Web average pressure (KSC) | 86 | 95 | 118 | 125 | 132 | 198 | |
| 4. | Burning rate (mm/s) | 4.78 | 4.83 | 5.1 | 5.12 | 5.24 | 6.5 | |

The variation in the n values of the various compositions are shown in Table 3

It has been reported that plateau and mesa burning behaviour has been achieved in composite propellants using 12 micron ammonium perchlorate and 525 micron ammonium sulphate[3]. But we have observed that such plateau and mesa burning behaviour could be achieved with varied particle sizes of ammonium perchlorate and ammonium sulphate. The influence of ammonium sulphate on the burning rate pressure index was studied at concentration levels ranging from 0 to 20 per cent, using

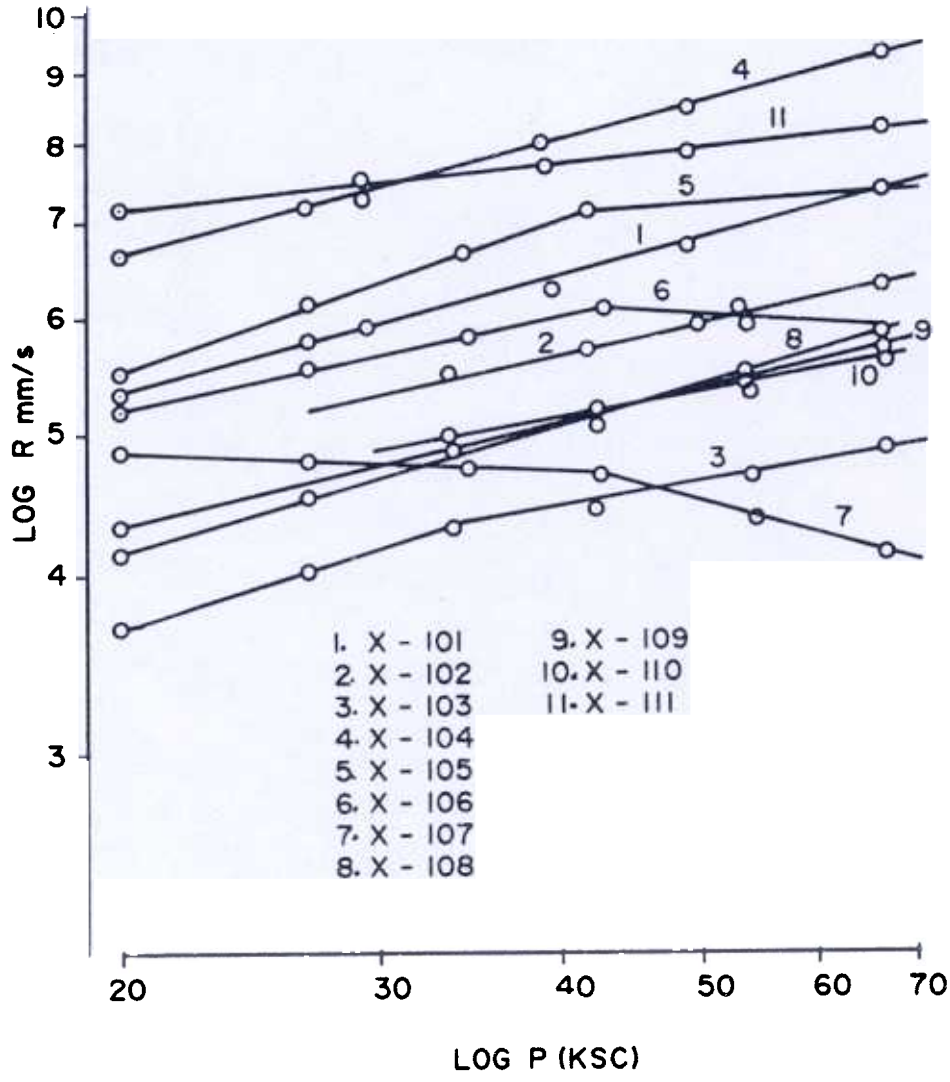


**Figure 6. Burning rate – pressure response.**

two different unimodal ammonium perchlorate of average particle size 60 and 140 microns. The unimodal ammonium sulphate used in the experimentations had an average particle size of 110 microns.

X-102 with 5 per cent ammonium sulphate showed a gradual reduction in the n value from 0.29 to 0.18 in all the pressure ranges studied as compared to X-101 with 0 per cent ammonium sulphate. X-103 with 10 per cent ammonium sulphate gave *n* value of 0.13 in the pressure range of 33–68 KSC. More pronounced near plateau behaviour with n value of 0.09 in the pressure range of 43–68 KSC was noticed in X-105 (with 10 per cent ammonium sulphate) where a smaller particle size of AP (60 microns) was used. X-106 and X-107 with 15 and 20 per cent ammonium sulphate respectively showed mesa burning behaviour. X-106 showed mesa burning behaviour ($n = -0.1$) in the pressure range of 43–68 KSC whereas X-107 showed mesa burning behaviour in all the pressure ranges of 20–68 KSC.

The plateau and mesa burning behaviour with ammonium sulphate at different concentration levels is presumably due to the evaporation of large excess of ammonia gas suppressing the decomposition rate of ammonium perchlorate. It was also noticed

**Table 3. Burning rate and pressure index variation**

| Code No. | Total solids (%) | AP (%) (microns) | Additive (%) | Burning rate at 68 KSC | Pressure Index n | Pressure range (KSC) |
|---|---|---|---|---|---|---|
| X-101 | 80 | 79.5 (140 microns) | | 7.3 | 0.29 | 20–68 |
| X-102 | 80 | 74.5 ( " ) | 5(AS) | 6.25 | 0.18 | 20–68 |
| X-103 | 80 | 69.5 ( " ) | 10(AS) | 4.8 | 0.32<br>0.13 | 20–33<br>33–68 |
| X-104 | 80 | 79.5 ( 60 microns) | | 8.8 | 0.34 | 20–68 |
| X-105 | 80 | 69.5 ( " ) | 10(AS) | 7.2 | 0.20<br>0.09 | 20–43<br>43–68 |
| X-106 | 80 | 64.5 ( ) | 15(AS) | 5.8 | 0.18<br>–0.10 | 20–43<br>43–68 |
| X-107 | 80 | 59.5 ( | 20(AS) | 4.2 | –0.02<br>–0.32 | 20–43<br>43–68 |
| X-108 | 77 | 76.5 ( | | 5.9 | 0.32 | 20–68 |
| X-109 | 77 | 75.5 ( ) | 1(LS) | 5.5 | 0.31 | 20–68 |
| X-110 | 77 | 75.5 ( ) | 1(LiF) | 5.3 | 0.25 | 20–68 |
| X-111 | 77 | 74.5 ( | 2(PVC) | 8.0 | 0.10 | 20–68 |

AS – Ammonium sulphate, LS – Lead stearate
LiF – Lithium flouride, PVC – Polyvinyl chloride

that reduction of n value was more pronounced with coarser AP as seen from Table 3 for X-101 and X-104 where n values are 0.29 and 0.34 respectively whereas in compositions containing ammonium sulphate (X-103 and X-105), the reverse trend was seen at higher pressures.

Incorporation of 1 per cent lead stearate in X-109 reduced the burning rate at 68 KSC by 8 per cent without affecting the burning rate pressure index appreciably. Addition of 1 per cent lithium fluoride in X-110 reduced the burning rate at 68 KSC by 10 per cent at the same time reducing the n value from 0.32 to 0.25. Incorporation of 2 per cent polyvinyl chloride in the dispersed form with plasticizers in presence of 0.1 per cent lead stearate as stabilizer increased the burning rate at 68 KSC by 30 per cent whereas the n value is reduced from 0.32 to 0.1 over a pressure range of 20–68 KSC.

The higher burning rate with polyvinyl chloride additive may be due to the faster pyrolysis of PVC whereas the reduction in n is attributed to the suppression of AP decomposition by HCl gas from the pyrolysis of PVC. The influence of lithium fluoride (reduction in burning rate as well as pressure index) could be due to melt phase decomposition of lithium perchlorate retarding the decomposition of AP.

## 5. BALLISTIC EVALUATION

The ballistic evaluations were carried out using a triple grain clustered motor, made of stainless steel with 200 mm length and 35 mm internal diameter. A perforated grid was provided at the nozzle throat area to screen the combustion gases.

**Table 4. Ballistic Data**

| Sl.No | Web average pressure (KSC) | Burning rate (mm/s) |
|---|---|---|
| | 86 | 4.78 |
| 2 | 95 | 4.83 |
| 3 | 118 | 5.10 |
| 4 | 125 | 5.12 |
| | 132 | 5.24 |
| 6 | 198 | 6.50 |

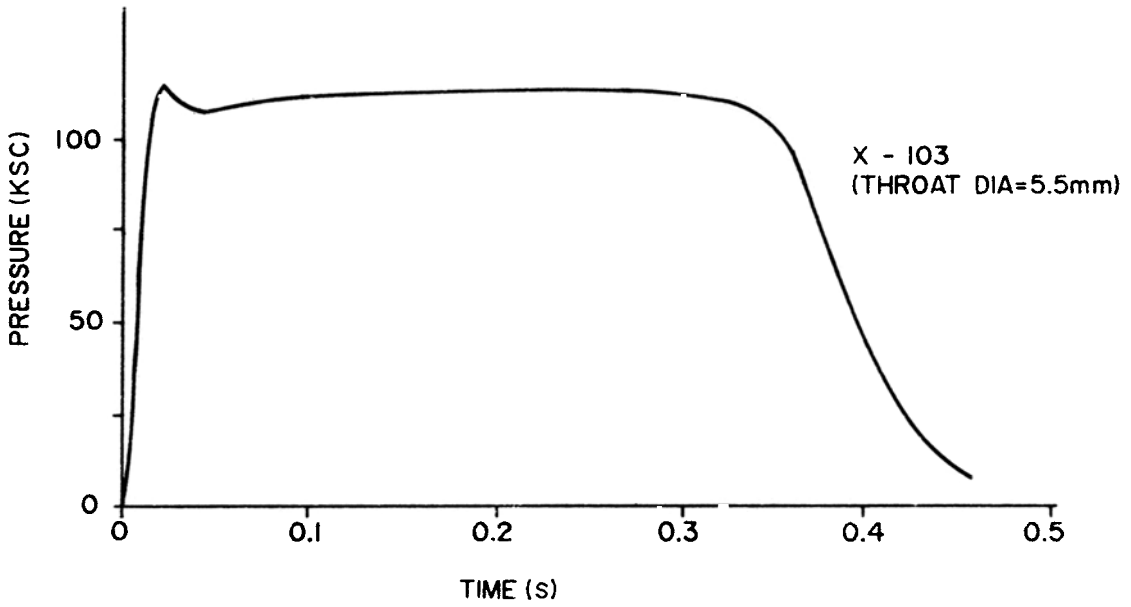


**Figure 7. Pressure time curve of 3 grains clustered**

Typical ballistic evaluation data for a near plateau burning composition (X-103) at different motor operating pressures are given in Table 4 and the thrust-time curve in Fig. 7.

## 6. CONCLUSION

The composite propellant extrusion technology for making large number of grains of smaller diameters was found quite feasible in the case of propellant based on CTPB binder. Suitably controlling the concentration and particle size range of ammonium perchlorate and ammonium sulphate, the burning rate pressure index n of the CTPB propellant could be varied from near plateau to mesa burning for varied end uses.

## ACKNOWLEDGEMENTS

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