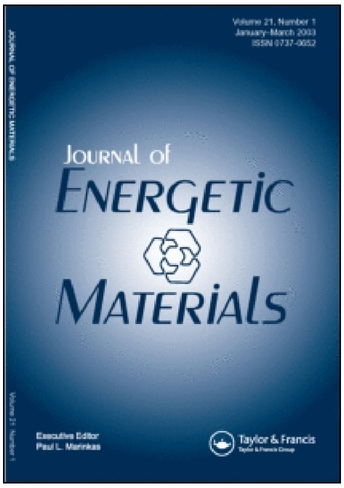

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PRESSURE AND TEMPERATURE EFFECTS ON BURNING RATE OF THE SILICON - RED LEAD SYSTEM

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ABSTRACT

The effects of ambient pressure ranging from 101 up to 3040 kPa and temperature from 233 up to 353 K on burning rate of both high and low fuel content Si-Pb_3O_4 mixtures have been investigated.

Pressure coefficients have not been calculated because of rather irregular shape of pressure - burning rate curves but the dependency is clearly recognizable for both the mixtures although the pressure influence on rate of burning was not very heavy, which is to be expected for this typical delay composition.

Also tests have been made to further reduce pressure effects using additions of metal fluorides. Sodium and calcium fluorides applied diminished the pressure dependency of burning rate for the low fuel content mixture, while for that containing high amount of silicon they left it almost unaffected. This different behavior of the mixtures could be probably attributed to the difference in their combustion mechanism.

Ambient temperature influenced the rate of burning in dependence on fuel content too. Temperature coefficients determined consist well with the assumption on prevailing solid state reaction mechanism of Si-Pb_3O_4 system, which is on the other hand complemented for silicon poor mixes with convective transport of heat.

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INTRODUCTION

Modern pyrotechnic applications demand reliably and precisely burning delay compositions whose rate of combustion is as low as possibly influenced by external conditions - ambient pressure or temperature for example.

To overcome pressure dependency of formerly used gas producing mixtures so called gasless delays have been developed, burning at reproducible rates with the formation of solid and liquid products. In fact most of the gasless compositions are rather low gas systems and they are still pressure dependent although to much less extent.

According to Nakahara[1] the relationship between pressure p and burning rate v can be expressed as follows: $v = a \times p^n$, where **a** is constant and **n** denotes the pressure coefficient. Modern delay systems exhibit values of their pressure coefficients between 0.01 and 0.3 in comparison with the value of about 0.7 for black powder.

Si-Pb_3O_4 mixture represents an example of such a delay widely used in detonators and was chosen to study influence of ambient pressure and also temperature on the burning rate. For the composition it has been shown that the content of silicon is the dominant factor controlling the burning rate[2]. It also governs reaction temperatures, determining in this way amount of gases evolved during combustion[3].

In this study a fuel rich and a fuel lean compositions have been examined to investigate burning behavior of the delay system at different ambient pressures and temperatures. Additives selected from among fluorides that can lower the pressure dependency have bee studied too.

EXPERIMENTAL

Materials, Mixing and Loading Procedures

Three basic binary mixtures were prepared containing 35, 45 and 55 wt% of fuel. Silicon powder was 96% pure with the following particle size distribution: 38 wt% between 10 and 4 μm and 62 wt% less than 4 μm. Red lead was 99% pure (as PbO and PbO_2, with 32.3 wt% as PbO_2) and had the particle size less than 9 μm. Ternary systems were produced by modifying parts of the prepared 35 and 55 wt% silicon mixes with 3 wt% additions of NaF or CaF_2.

The compositions were then mixed by successively eight times repeated hand screening weighed components through a mesh. Delay elements were made by incrementally pressing the mixtures into a metal tube of 3.2 mm ID, 6.3 mm OD and 43 mm length. The loading pressure used to consolidate the compositions was 425 MPa.

Measuring Device

Delay times were measured to calculate burning rates of the mixtures. To learn changes of the burning times under various ambient pressures or temperatures an apparatus shown in Figure 1 was designed. It consists of a delay element holder (2) fastened on a support (1) and used for an accommodation of two delay tubes (3), two fuseheads (5) to ignite the delay mixture in elements and a pair of optical probes (4). Switch (7) closes an initiating circuit (8) of the matches and triggers four channel digital storage LeCroy oscilloscope (6) at the same time. The optical probes are photosensitive transistors which being exposed to the light and heat of combustion front close appropriate electrical circuits, enabling in this way determining the time of burning accomplishment. They are protected from premature exposition caused by light of the fuseheads by means of the sample holder (2). The time span between triggering the oscilloscope and closing the probe circuit represents burning time of the delay element. Reaction time of the fuseheads used was not taken into account because of its shortness and reproducibility.

For measuring pressure dependency of the burning rate the apparatus was inserted into a chamber pressurized with nitrogen from a pressure container. The chamber was equipped with input and output gas valves, a manometer and a sealed connector accommodating lead wires of the initiating circuit and signal wires of the optical sensors.

The influence of ambient temperature on the burning rate was evaluated using SECASI INDUSTRIE temperature chamber in which delay elements were exposed together with the measuring device to a preset temperature for one hour and then tested.

RESULTS AND DISCUSSION

Pressure Dependency

Burning rates of Si-Pb_3O_4 mixtures containing 35 and 55 wt% of silicon at different ambient pressures from 101 up to 3040 kPa are presented in Figure 2 and 3 respectively. For the measurement of burning times six experiments were carried out at each pressure level. It shows that, in the pressure range considered, the burning rate is inclined to increase in accordance with the increase in ambient pressure. The pressure dependency is not explicit and an application of Nakahara's equation[1] would not give reliable results for the pressure coefficients but it is clearly recognizable that the burning rate increase of 35 wt% silicon mixture caused by the ambient pressure applied is about twice higher than that of 55 wt% silicon mix. Even this higher pressure influence is still low however in comparison with gassy delays. The tendency of growing pressure affectability with decreasing fuel content could be explained on the basis of reaction mechanism of the system. According to Al-Kazraji et al.[2] Si-Pb_3O_4 mixtures of low silicon content produce considerable amount of gases, while at those containing large excess of fuel solid-solid reaction mechanism prevails, suppressing gas release. And it is gas that is influenced with the pressure imposed, so higher amount of gas produced means also higher pressure dependency for the low fuel content mix.

Effects of Fluoride Additions

It is known that small additions of some metal fluorides to delay mixtures reduce effects of ambient pressure on the burning behavior[4,5]. Hence NaF and CaF_2 were selected to investigate the performance change resulting from their additions to Si-Pb_3O_4 system.

In Figures 2 and 3 there are besides above discussed mixes shown also results for those which were doped with 3 wt% of one of the mentioned fluorides. At first glance it is evident that, with a small exception at 35 wt% silicon mix, both the fluorides diminish burning rates. This is because of their inert nature, decreasing the amount of heat evolved per gram of mixture. Another notable finding derivable from the figures is that while for the fuel lean mixture presence of the fluorides reduces pressure dependency of its burning rate to a great extent, it is of almost no importance regarding pressure dependency of the fuel rich composition. This behavior can be probably also attributed to the difference in prevailing reaction mechanism. Si-Pb_3O_4 mixtures liberate gases containing oxygen during combustion[6]. The lower content of the fuel is present in the mix the higher the amount of oxygen is evolved and the more important role in transport of heat it plays, making the burning rate more pressure dependent. In Hardt's et al. publication[7] there is mentioned a possibility that an admixture of CaF_2 could inhibit the diffusion of oxygen to unreacted tungsten in W-$BaCrO_4$-$KClO_4$ system. Allowing for similar possibility in case of the composition under consideration we can suppose the fluorides to affect the fuel lean mix by suppressing the oxygen diffusion, thus reducing the relatively high pressure dependency of its burning rate. The mixture containing great amount of silicon is not influenced in this way and its burning rate retains the above mentioned low pressure dependency caused probably by pressure changes of heat transfer coefficients[8].

Temperature Dependency

The effect of ambient temperature ranging from 233 up to 353 K on burning behavior of 35 and 45 wt% silicon mixes is illustrated in Figure 4. The temperature dependencies of the burning rate for both the mixtures follow exponential equations with the best fits having the determination coefficients: $R^2 = 0.955$ and 0.966 respectively. It enabled to make use of the relationship published by Shidlovsky[9] and calculate temperature coefficients **B** defined as follows: $u = e^{BT} + A$, where **u** means burning rate, **T** denotes ambient temperature and A is constant. In this way determined temperature coefficients are of values 1.8×10^{-3} and 2.4×10^{-3} K^{-1} for the fuel lean and fuel rich compositions respectively. The higher temperature influence on performance of the mix containing more silicon is in an agreement with the assumption that higher fuel content supports solid-solid reaction mechanism of this system because the lower amount of gases is involved in a burning process the more temperature dependent it is[10]. According to[10] ordinary temperature coefficients of gasless mixtures lie between 3 and 8×10^{-3} K^{-1} ,while gassy systems exhibit this value less than 1×10^{-3} K^{-1}. Comparison of the above cited values of the temperature coefficients with those obtained in this study shows that the temperature coefficients of Si-Pb_3O_4 mixes fall fairly well in the range which is to be expected for a system reacting mainly in the solid state but burning of which is accompanied at the same time with the convective transport of heat whose importance decreases with fuel content increase.

CONCLUSIONS

Pyrotechnic delay system $Si\text{-}Pb_3O_4$ exhibits a pressure dependency of its burning rate. This influence of ambient pressure on burning performance of the composition is not very strong and it decreases with fuel content increase. On the other hand for fast fuel lean mixtures it can be reduced by introducing small amounts of metal fluorides, NaF or CaF_2 for example, into them.

Also ambient temperature recognizably changes burning behavior of the system. Increasing the temperature causes the mixtures to burn faster. Temperature dependency of the mix containing higher amount of silicon is more significant than of that with small fuel content.

The above mentioned facts support the idea that the silicon-red lead system reacts mainly in the solid state especially if highly abundant amount of silicon, diminishing burning temperatures, is present in the mixture.

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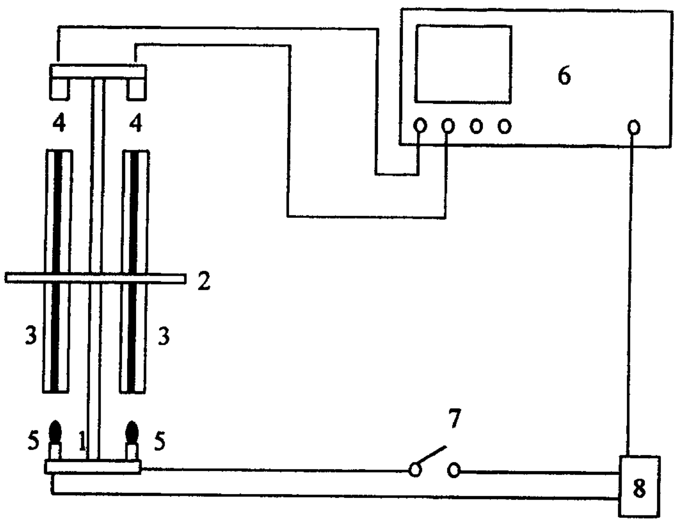

1 - support
2 - holder
3 - delay tube
4 - optical probe
5 - fusehead
6 - oscilloscope
7 - switch
8 - initiating circuit

FIGURE 1
An outline of the device used to measure burning times.

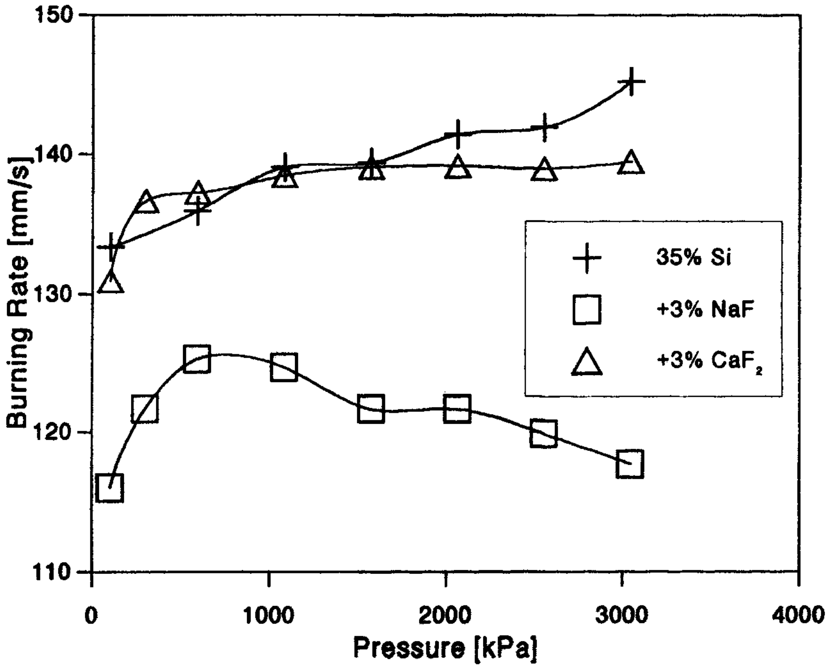

FIGURE 2

Pressure dependency of the burning rate for the mix 35% Si - 65% Pb_3O_4 both alone and doped with 3% of NaF or CaF_2.

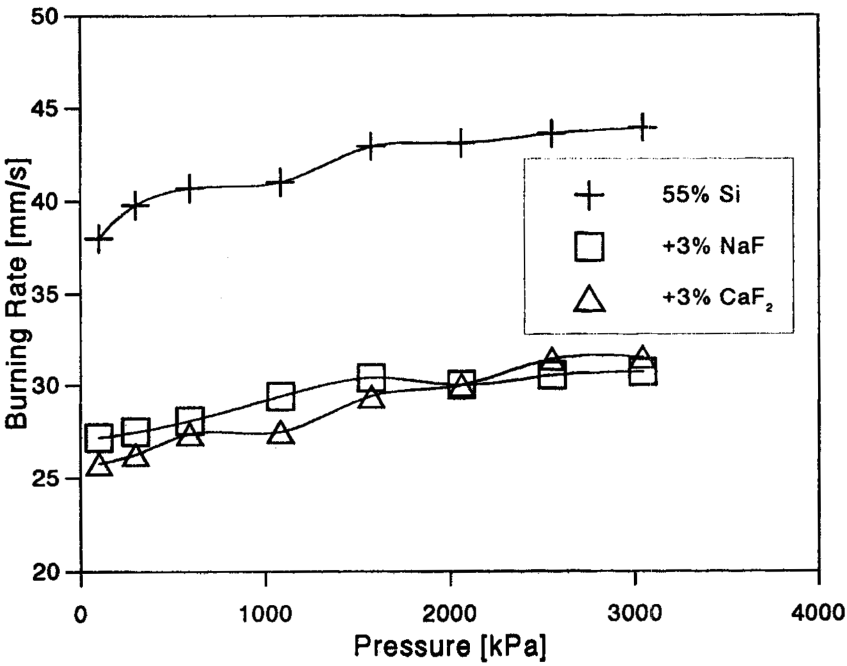

FIGURE 3
Pressure dependency of the burning rate for the mix 55% Si - 45% Pb_3O_4 both alone and doped with 3% of NaF or CaF_2.

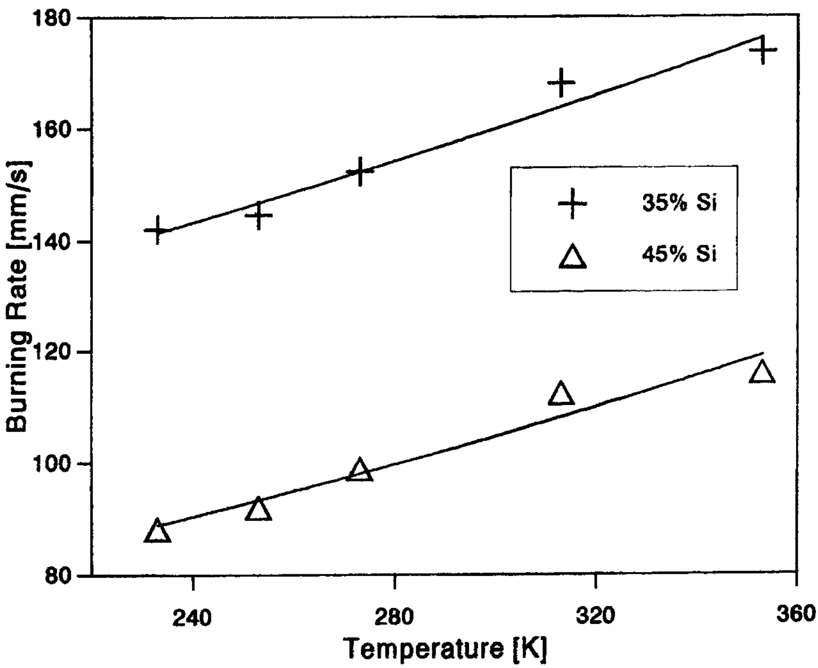

FIGURE 4
Temperature dependency of the burning rate for the mixes 35% Si - 65% Pb_3O_4 and 45% Si - 55% Pb_3O_4.