Fast Burning Rates in Thin Film Propellants

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Burn rates of from 10 in./sec–10,000 in./sec for thin films of some solid composite propellants are reported in this paper. The propellants were composed of McCormick-Selph 510,164 monopropellant, an oxidizer and a polyvinyl chloride binder. The burn rates of the thin films, which were bonded to steel plates on one surface and free on the other, varied with film thickness which ranged from 0.001 in.–0.032 in. There was no significant variation in burn rates between tests made at a vacuum of 5 torr and atmospheric conditions. The substitution of potassium chlorate for potassium nitrate as the oxidizer in the propellant formulation had no apparent effect on burn rates. The increase in the binder (polyvinyl chloride) content from 10%–15% did not decrease the burn rate but may have increased it. Also, the application of a relatively inert, flexible top layer on the propellant film may increase the burn rate of the film slightly. Propellant curing time and propellant mixture age did not affect the burn rates of the thin films.

Introduction

THIS research was initiated during a search for a rapidly burning thin film propellant for a hypervelocity accelerator proposed by Rodenberger.[1] The proposed accelerator concept requires a thin layer of propellant lining a gun barrel as the major energy source for the gas driving the projectile. To obtain projectile velocities of 100,000 fps, it was calculated that the propellant film would require a minimum burning rate of approximately 10,000 in./sec. In searching the literature for a propellant to satisfy this requirement, it was found that Brown[2] had reviewed the literature up to 1967 and did not report any burn rates in the region between 3 in./sec–40,000 in./sec.

No information was found on burn rates of thin layers of propellant restrained on one surface and burned at pressures of one atmosphere and less. Previous burn-rate experiments have reported on propellant samples such as strands, solid cylinders, and some thin films, either completely restrained or unrestrained. Burn rates reported for these experiments are generally below 3 in./sec. or above 40,000 in./sec. Steinz, Stang, and Summerfield's[3] experiments with strands yielded burn rates of less than one in./sec for ammonium perchlorate propellants. Bowden and Yoffe's[4] work with completely restrained sheets of PETN and mercury fulminate yielded detonation rates in excess of 40,000 in./sec.

McCormick-Selph,[5] a Teledyne company, has produced proprietary materials that exhibit burn rates in the region of interest. They have developed some fast-burning composite materials for use in small-column, insulated delays. McCormick-Selph personnel reported that their experimental material (designated 510,164) consistently burns at rates between 7500 and 8500 in./sec in dry powder form.

The Hypervelocity Acceleration Project[1] at Texas A & M Univ. had investigated a large number of propellant films using nitrocellulose as the filmogen. Although propellant admixtures in the nitrocellulose film ranged from lead azide to PETN and black powder, it was observed that the burning rates were constrained to a few inches per second, approximating that of the nitrocellulose. When polyvinylchloride (PVC) was substituted in place of nitrocellulose as a filmogen, high burning-rate properties were observed. The values reported herein resulted from propellants formulated from combinations of McCormick-Selph 510,164 monopropellants, an oxidizer, and the PVC binder. Figure 1 shows that the burning rates reported in this research fall in the intermediate burning region between detonation and deflagration.

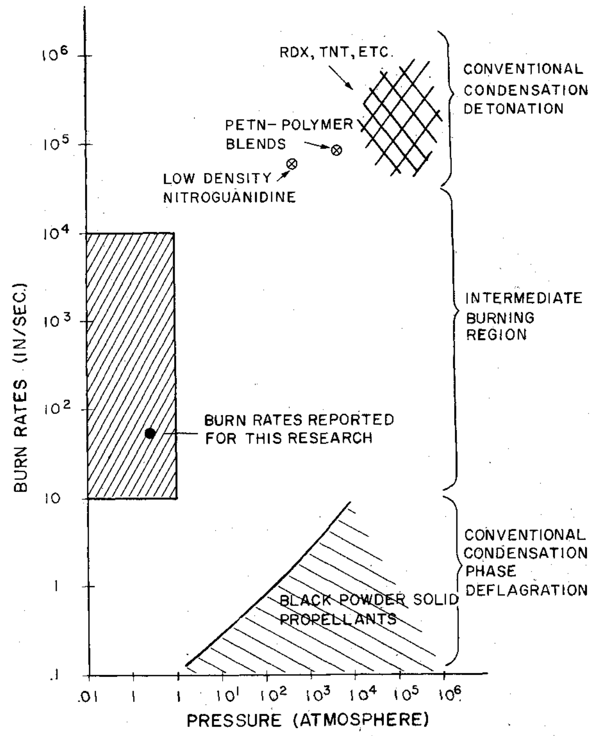

Fig. 1 Reaction rates and pressure of explosives.

Experimental Apparatus and Procedures

The experimental apparatus and tests were designed to obtain information related to the performance of the propellant in the proposed hypervelocity gun. In the gun operation, the inside of a thick walled steel tube is coated with several layers of propellant to build a thickness of 10–15 mils. This surface is then subjected to a vacuum prior to operation of the gun. Although the propellant is not fired until it is subjected to the pressure behind the projectile, there was the possibility that the vacuum would remove the gases from the porous surface and have an effect on the burn-

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ing rate. As a result, tests were performed both at room pressure and at a typical vacuum used in hypervelocity gun procedures to determine if there was an effect on the burn rate. Facilities were not available to test at high pressures.

The propellant specimen to measure the burning rate was prepared in a manner to duplicate the thin propellant coating inside a thick-walled steel tube. The propellant was mixed into a thick paintlike consistency, and was painted in a $\frac{1}{2}$-in.-wide strip 8 in. long in the center of a $\frac{1}{4}$-in.-thick steel plate. The propellant thickness was measured with a micrometer having 0.1-mil gradations. The steel plates had been ground. The thickness was measured at three locations before and after coating. The difference in thickness was the propellant thickness. This configuration provided the massive heat-sink characteristic and thin propellant layer comparable to the gun configuration. No test were made on plates of copper, aluminium or other materials to study the effects of heat loss.

The tests were performed at one of two pressures: either atmospheric or a 5-torr vacuum. A small table-top test chamber was constructed with four opposed ports. Two adjacent ports were covered with plexiglass plates for viewing, with the other two ports utilized for instrumentation.

Several methods of measuring the burn rates were investigated. Consideration was given to using imbedded wires that would burn into two parts, ionization probes that would be located just above the surface, and high-speed movie photography. The imbedded wire was rejected because the thickness of the film is such that the wires could possibly interfere with the burning mechanism, and it is difficult to imbed the wires at a consistent depth within the film. The ionization probe did not prove satisfactory for several reasons. The primary concern was whether the ionization was moving at the flame front. Other difficulties were encountered in positioning the probes consistently. High-speed movies (5000 frames/sec) indicated that the flame front presented a fairly well-defined front as the burning moved along the surface of the specimen. This observation led to the development of a photodiode system to record when the flame front passed a predetermined line. The advantage to the photodiode installation was that readings would be obtained immediately from oscilloscope records. The use of movie films delayed obtaining results because of the required 3 days for processing. The movies did not always give a satisfactory record because the light intensity varied with burn rates. However, two records were used to substantiate the photodiode measurements and establish some degree of confidence in the photodiode approach.

The photodiode sensors assembly used four photodiodes spaced at 1-in. intervals. The first diode triggered an oscilloscope, and the following three each activated a signal-conditioning circuit to display different voltage level for each diode. The displacement setting for the first diode was 1 v, the second 3 v, and the third 5 v, to insure that when two stations were both on simultaneously they would have a reading that would allow identification of the individual station. Consequently, the display indicated when the diode activated and deactivated. However, due to the rapid rise time but relatively slow decay time of the diode, only the activation times were utilized for burning-rate determinations. The use of three diodes gave a check on the consistency of the burning. Measurements were recorded for burning rates between each pair, and the average between the first and last. Any instability or erratic behavior was apparent with the three measurements. The field of view of the photodiodes was collimated using hollow tubes so that the maximum field of vision at the far side of the propellant strip from the photodiode was 0.16 in.

The propellant formulation had been chosen after extensive screening of propellant mixtures containing various additives ranging from primary and secondary explosives to pyrotechnic material. Many of the initial formulations utilized nitrocellulose as the filmogen, with the result that the nitrocellulose apparently inhibited the reaction rate of all the materials. When nitrocellulose was replaced with polyvinylchloride (PVC) as the filmogen and binder, some unusually high burning rates were obtained.

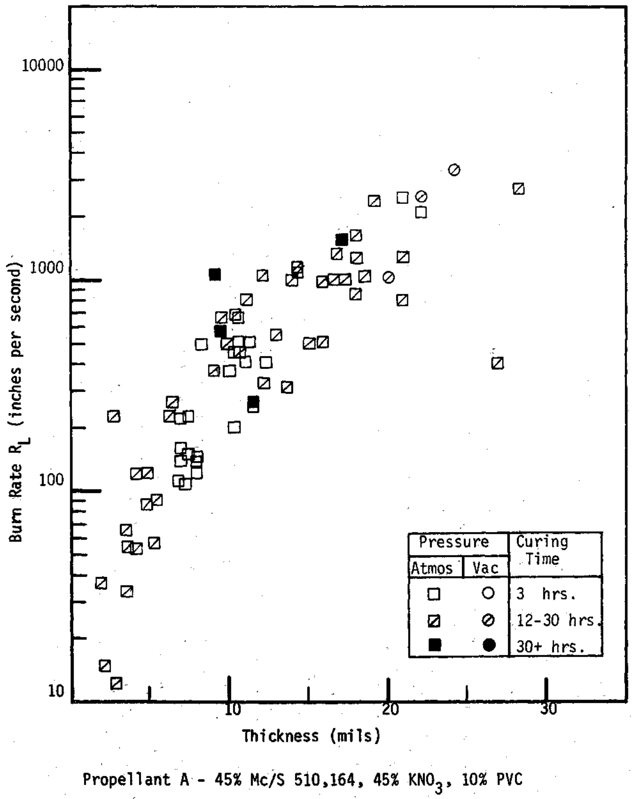

Fig. 2 Burn rate dependence on film thickness—propellant A.

A few of the most promising formulations were selected for use in determining the sensitive parameters. The major ingredient is a proprietary monopropellant produced by McCormick-Selph, designated 510,164. McCormick-Selph personnel stated that the major decomposition products of 510,164 are hydrogen and boron, with minor amounts of nitrogen and oxygen. In order to generate additional gas, an oxidizer is combined in equal weights with the monopropellant. Because conversations with McCormick-Selph personnel had indicated that the burning rate of their propellant was substantially lower under vacuum conditions when potassium chlorate, instead of potassium nitrate, was used as an oxidizer, both potassium chlorate and potassium nitrate were tested under atmospheric and vacuum-test conditions.

The propellant specimen was cast in wet form on the steel plates. The dried strip bonded tightly to the steel surface. The propellant was allowed to cure at room temperature. The propellant was ignited by a hot wire at the end, at least 2 in. from the trigger diode, in order to provide sufficient distance for a well-defined burning front to develop.

Results and Discussion

Tests were run on two formulations designated propellant A and propellant B. Propellant A consisted of 10% polyvinylchloride, 45% McCormick-Selph 510,164, and 45% potassium nitrate. Propellant B consisted of 15% polyvinylchloride and the remainder, equal parts of McCormick-Selph and potassium nitrate. In addition, five tests were made with a formula replacing the potassium nitrate with potassium chlorate. The results of the tests were plotted in Figs. 2 and 3. Figure 2, for propellant A with the 10% PVC, shows a definite trend in the relationship between burn rate and thickness, with higher velocities occuring for the greater thicknesses. There is considerable scatter in the burn rate for any particular thickness. Some of the data had a very close correlation between the three velocity measuring stations (15% of the data varied by less than 10% from the average), and other data points had erratic results between the three measuring stations. There was no apparent correlation of

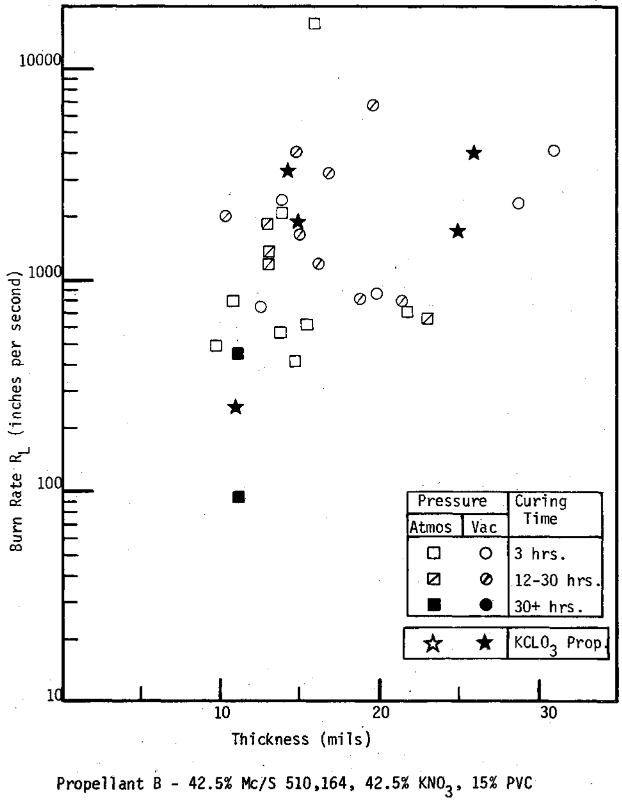

Fig. 3 Burn rate dependence on film thickness—propellant B.

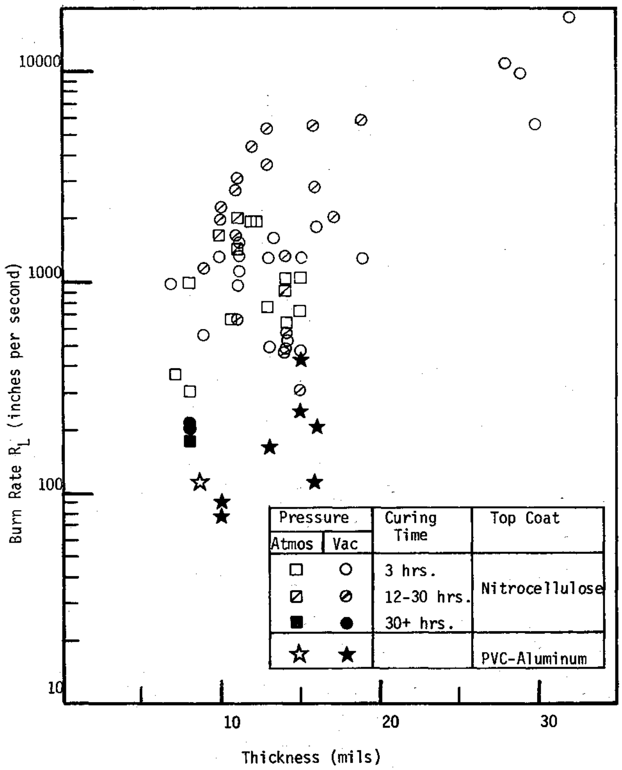

Fig. 4 Effects of top coats on burn rates of propellant B.

the erratic behavior between batches, mixing techniques, curing times, or instrumentation. Figure 3, a plot of the results of propellant B, which has a higher percentage of PVC, indicated considerably more scatter, but also somewhat higher velocities, than the propellant A. This data also includes five specimens in which potassium chlorate was substituted for potassium nitrate as an oxidizer and tested under vacuum conditions. These five points do not indicate that there was any apparent degradation in the burn rate as a result of using potassium chlorate in vacuum conditions. There is also no apparent relationship between curing time and the burn rate for curing times greater than 3 hr.

The change in pressure of the surroundings of the propellant specimens from atmospheric pressure to a vacuum (5 mm of mercury) had no apparent effect on burn rates. This conclusion is supported by information received from McCormick-Selph to the effect that they had observed no adverse effects of vacuums on reactions of their explosive materials using potassium nitrate. Although mixture age and propellant curing age were recorded and graphed as separate parameters, these apparently had little effect on either vacuum or atmospheric burn rates. Thickness measurements were believed to be accurate to within one mil because of the method and consistent values.

An additional series of tests was conducted by applying a top coat of either pure nitrocellulose or a 60–40% mixture of polyvinylchloride with aluminum powder that did not contain other propellant materials. These tests were conducted for two reasons: 1) it had been proposed that various top coats could be used to provide different friction surfaces in the hypervelocity acceleration device and 2) Physics International[6] has proposed using a collapsible inner liner surrounded by a propellant layer inside a rigid tube as a possible method of obtaining hypervelocity accelerations. The burn-rate tests were conducted to determine if such a top coat would have any appreciable effect upon the burn rate characteristic of the propellant.

Some side effects on the coating itself were noted. The nitrocellulose top coat did not increase the total propellant film thickness, but decreased it. No sure explanation for this phenomenon has been provided. The nitrocellulose might possibly have penetrated the PVC propellant layers and, in drying, compressed the layer. In cylindrical tubes, shrinkage of the top coat pulled the previous layers from the tube walls, preventing their use for hypervelocity tests.

The aluminum-PVC top coat was more flexible than the nitrocellulose. Fragments of the unburned top coat were found after several tests using the aluminum-PVC top coat. This top coat also shrinks the total thickness of the film. The thickness of the unburned pieces of top coat were measured to be 1–2 mils thick.

As shown in Fig. 4, the burn rates measured for the propellant strips with top coats were generally higher than for propellant test without the top coat. The burn rates for thicknesses of 10–15 mils were generally in a range from 1000 in./sec for this thickness range. For a 30 mil thickness, burn rates of 10,000 in./sec were observed using the nitrocellulose top coat. The PVC top coat does not burn, and would prevent the flame travel from being a surface phenomena, thereby adding credibility to the accuracy of the burn rates using the photodiode devices.

Conclusions and Recommendations

As a result of research to develop a fast-burning propellant film for the lined hypervelocity accelerator launch tube, some thin film propellant formulations with burn rates in a region not previously reported have been identified. Several important conclusions may be drawn concerning the burning rates of thin films of the propellants tested in this reserach.

1) The longitudinal burn rate is mainly dependent on thickness ranging from several in./sec for film thickness of less than 5 mils, up to the neighborhood of 10,000 in./sec for 30-mil film thickness. 2) There is little or no variation in burn rates between propellants tested at atmospheric pressure and those tested at vacuum pressures. 3) For curing times greater than 3 hr, there is no apparent effect of the length of curing time of the propellant coating or of the age of the propellant mixture on burn rates. 4) A nitrocellulose layer coated over the propellant film will increase its burn rate but will destroy the bond between the propellant film and a steel surface on a curved surface. 5) The McCormick-Selph monopropellant apparently will react equally well under both atmospheric and vacuum pressures in formula-

tions with either potassium chlorate or potassium nitrate as an oxidizer.

No concrete conclusions can be made concerning the effects of the change in percentage of polyvinylchloride on burn rates. The experimental evidence indicates that propellant B (the mixture with 15% PVC by weight) may be capable of producing higher burn rates than the 10% PVC propellant. However, the amount of data taken is not great enough to warrant drawing a sure conclusion.

There are many unexplored areas in the field of burn rates of propellants. The burn rates reported here are in the range between deflagration and detonation. The large variations in burn rates indicate instability in the burning process, and should be subject to further study.

Brown[1] has listed many uses for propellant formulations which would burn in the range intermediate between deflagration and detonation. Among these are explosively-actuated tools, chaff ejectors, gas generators, metal forming and welding, single-grain gun propellants, high-acceleration rockets, and bursters for materials which a detonation would destroy. These are sufficient reasons to institute a more complete search for, and investigation of, propellant formulations in the burn-rate region between deflagration and detonation.

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Comparison of Linear and Riccati Equations Used to Solve Optimal Control Problems

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Optimal control problems can in general be formulated as nonlinear two point boundary value problems. One method of attempting to solve a nonlinear TPBVP is to iteratively solve for the solution of a corresponding linear TPBVP. By successively solving the linear TPBVP, an attempt is made to produce a trajectory which is a solution of the nonlinear problem. Such an approach is referred to as a linear perturbation method. It is reported in the literature that the linear methods suffer from numerical instabilities and that the unstable characteristics can be improved by uncoupling the linear differential equations with a Riccati-type transformation of variables. In this paper, five different methods of solving the linear TPBVP are discussed. Two of these methods involve integrating a coupled set of linear differential equations. The other three require the integration of a Riccati equation and associated linear equations and quadratures. These systems are used to calculate optimal solutions for the Brachistochrone problem and for a three dimensional Apollo-type re-entry problem. The results show that, for the examples considered, the linear system of equations is more effective in obtaining the solutions to nonlinear two point boundary value problems than algorithms based on the Riccati transformation.

Introduction

NECESSARY conditions for unconstrained optimal trajectories can in general be reduced to a nonlinear two point boundary value problem (TPBVP). Attempts to solve the nonlinear TPBVP usually involve successively solving a linear TPBVP. The linear TPBVP may be solved either by superimposing solutions of a system of linear differential equations or by the integration of a Riccati matrix and associated linear differential equations and quadratures. Much of the recent literature has favored the integration of Riccati equations instead of linear equations because of the improved stability properties.[1,2] For many optimization problems, the linear equations have eigenvalues which vary considerably in magnitude and are often positive. If the equations are integrated over a sufficiently long time interval, instability is a definite problem. For linear problems, however, the Riccati equation can be shown to be asymptotically stable in some regions where the linear equations are unstable.[2] Hence, it is reported that it is easier to integrate the system of Riccati equations than linear equations for many problems.

The purpose of this paper is to present a comparison between two linear systems of differential equations and three Riccati systems of equations which may be used to solve linear TPBVP. The standard perturbation method[3,4] and the adjoint method,[5] which integrate linear equations, are considered. Then two Riccati methods are derived, which in some cases are equivalent to the perturbation and adjoint methods, respectively. The standard Riccati method[2,6] is considered also. Finally, all of the methods are compared numerically for two example problems. A simple example, the Brachistochrone problem, is considered

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