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THE UNIVERSITY OF ARIZONA PROGRAM IN SOLID PROPELLANTS

p30

Introduction - Kumar Ramohalli

The University of Arizona program is aimed at introducing scientific rigor to the predictability and quality assurance of composite solid propellants. As already noted, the main program in this area is conducted for NASA Marshall Space Flight Center. The statement of work is available in ref. 14. Two separate approaches are followed concurrently. One is attempting to use many of the modern analytical techniques to experimentally study carefully controlled propellant batches to discern trends in mixing, casting, and cure. The other is examining a vast bank of data, mostly obtained at JPL as part of a NASA MSFC study, that has fairly detailed information on the ingredients, processing, and rocket firing results, including mechanical property values of JANNAF standard dumb-bells (dog-bones). The experimental and analytical work is described briefly by Daniel Perez in this report. The principal findings have been that pre- (dry) blending of the coarse and fine AP can significantly improve the uniformity of mixing, the Fourier transformed infrared spectra of the uncured and cured polymer have valuable data on the state of the fuel, there are considerable non-uniformities in the propellant slurry composition near the solid surfaces (blades, wall) compared to the bulk slurry, and in situ measurement of slurry viscosity continuously during mixing can give a good indication of the state of the slurry.

In the related study of the voluminous data bank, several observations are important. First, this is perhaps the single most carefully controlled set of solid composite propellant data. Close scrutiny revealed that many of the "identical" batches had variations in the iron oxide particle size, concentration, source, batch size, motor size, etc. Thus, we found only a small fraction of the initial data bank to have been really "identical" within the available information records; there could be variations that were not noted. Even in this small fraction (approximately 31 data points), variations are apparent. The fundamental advance made at the University of Arizona has been the careful logging of all available data with a color-coded entry into a popular spread-sheet program for easy manipulations and the generation of graphs to show trends more readily. This work is currently continuing.

Arthur Mazer, a student in the Department of Applied Mathematics, has approached the problem of mixing in a mathamatical way. His work is described later in this chapter in a highly abridged manner. The question of mixing of various ingredients has to be properly understood. In some mathematical formulations and approach, the mixture becomes homogeneous in the limit of infinite time of mixing. This is simply not the case in composite propellants. Even in the limit of infinite time, the propellant continues to be heterogeneous but more uniform than at the start. Thus, the concept of the smallest scale for uniformity has to be established. Is this the size of the coarse particles? Is this several multiples of the coarse particle diameter? Is there a fundamental spatial scale that is truly representative of the homogeneity of the end product? Art Mazer and Professor Vincent will answer these questions. For now, it is most interesting that we may have to evolve the concept of **heterogeneous homogeneity** in order to mathematically characterize the mixing in composite propellants.

The importance of quantitatively accurate color displays cannot be overemphasized. Here, Mike Hicks (with Professor Nikravesh) is programming the governing equations on the computer specifically to identify **dead zones** that could lead to improper mixing. His work is also briefly described here.

As part of the studies being conducted at the University of Arizona's NASA Center, extraterrestial propellant production is examined by Paul Schallhorn. Although this is not part of the MSFC program, it is felt worthwhile to include his work here to indicate the important steps being taken to automate composite propellant processing and to minimize questionable human judgmental factors.

Some of these studies are less than six months old, but already indicate the promise of a better understanding of composite propellants.

An Interim Progress Report on Mixing - Dan Perez

Introduction

No research is readily available on high solid concentration mixing. Yet problems evident in the processing of such materials are well known. Data on the variations in mechanical properties and burn-rate performance have been given in the literature.[9,11] Under "identical" procedures and with material from the same lots, propellants have been manufactured with distinct and discernible differences in performance.

A recent review of the process has opened the door to speculation on the culprits in the problem. Many causes of the variations have been listed, covering the areas of mixing, casting, and curing. Even the accepted testing techniques of the finished product (i.e., strand burn rate and uniaxial tensile tests) have been criticized. Any and/or all of these variables could be the culprit(s); the volume can be, and is, overwhelming.

Furthermore, the percentage of solid particles within composite solid propellants is extraordinarily high. With the addition of metals, concentrations within 80 to 88 percent by weight of solid material have been manufactured. The understanding of such material processing has an added complication due to the use of multidispersed particle-size systems.

It is quite evident that an endeavor to analyze the entire process at this time would be fruitless. Therefore, work will be pursued on one stage of the process in order to assist in the establishment of the proper route for research in the others.

Work within this research has been, and will continue to be, on the first stage of the process mixing. Since this first step defines the state of the propellant, it must be well understood. Any imperfections which arise within this stage will have to be dealt with in the following stages. In addition, the complexity of the mixing stage, as compared to casting or curing, allows future work to be minimized. Findings in the mixing stage may have the potential of being applicable to the less chaotic behavior of the other stages.

In the following sections, three areas will be briefly stated. These cover those areas of the investigation which are most crucial in the efforts to resolve this problem. The first will describe the JPL data base established to guide and substantiate any findings. The second will state the rheological understanding of the material presently available. Last is the series of testing techniques developed to define the state of the mixture.

Data Base

The data under review were acquired by JPL and consist of a series of 60 batch runs of ammonium perchlorate/PBAN propellant. Each batch constitutes 150 gallons of material. The mixing was done with a Baker Perkins Model 16-PVM vertical planetary mixer with a thermal jacket surrounding the mixing bowl. This is a two-blade dual planetary mixer.

The batch runs were vacuum cast into 48-inch-diameter cartridge molds. Small samples were taken from these molds for analysis. Samples for tensile, density, and burn rate tests were allowed to cure in separate molds. The detailed data sheets on which this information was supplied are included in Appendix F.

The ingredients were received from two sources, and the lots were examined for adherence to specifications. The ingredients and their respective weight percentage within the propellant are given in Table 2.

Table 2. Listing of propellant ingredients.

Ingredients	Wt. %
Ammonium perchlorate (200 microns)	48.99
Ammonium perchlorate (10 microns)	21
Aluminum (granular)	16
Ferric oxide[a]	0.01
PBAN	11.49
DOA	0.7
ECA	1.81

[a]First 36 runs: 0.01; next 18: 0.04; next 6: 0.27 (AP coarse subsidized for %Wt. balance).

The standard operating procedure is shown in Fig. 7. Actual run schedules were recorded. Automated monitor readings were also noted and hand measurements for propellant temperature and viscosity taken.

An additional 11 runs on identical ingredient lots were completed for 1-gallon batches. These were used as a comparison for the end-product properties of the large batches.

Figures 23 through 26 show samples of several findings which have proven important. Each indicates strong correlations with respect to certain parameters.

Rheology

Unlike mixing, work on high solid concentration rheology is available. From these works, two regions are quite apparent in the rheology. The first lies in the shear rates below 1.0 sec-1, where the material is extremely well behaved in the sense of flow mechanics, and is pseudoplastic in nature. The second is not so hospitable, with sudden viscosity jumps and shear thinning and thickening behavior. The maximum shear rate behavior recorded was as high as 1000 sec-1, so the entire spectrum of shear rates experienced in the mixer was certain to be covered.

A list of the most dominate parameters is mentioned below with respect to each particular region. Note that these are the predominant factors which govern the flow mechanics and, that for high shear rates, two more parameters must be considered in addition to those for low shear rates. In decreasing order of importance, the parameters are:

<u>Low Shear Rates</u>

1. Volumetric solid concentration
2. Particle size distribution
3. Particle shape

<u>High Shear Rates</u>

4. Shear thinning
5. Wall effects

The most interesting and important work is on the rheology of bi-dispersed particle size distributions identical to those within solid composite propellants. Figures 27 and 28 show the behavior of this material based on the theoretical model of synthetic flow.[22] This model has proven successful in mapping the viscosity characteristics of the material and plays a large role in future work.

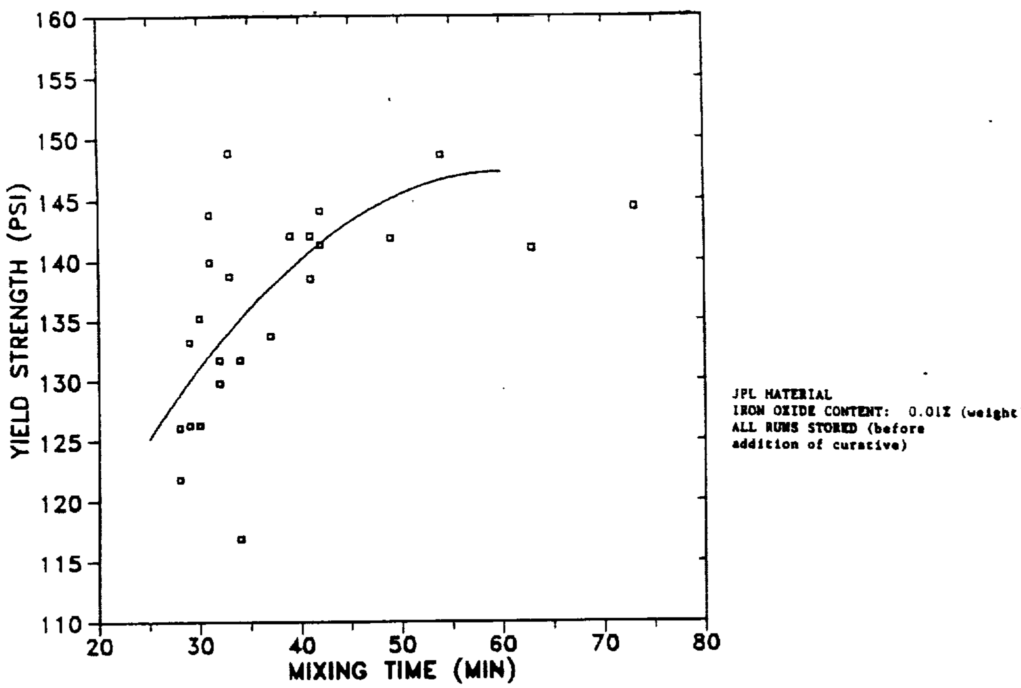

Fig. 23. Yield strength dependence on mixing time.

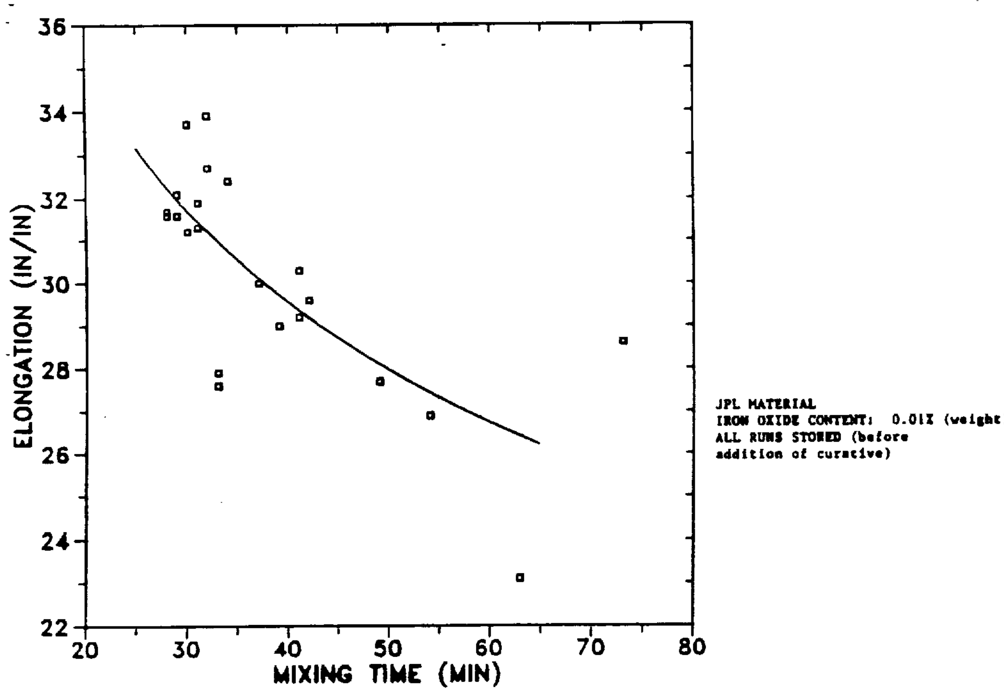

Fig. 24. Elongation dependence on mixing time.

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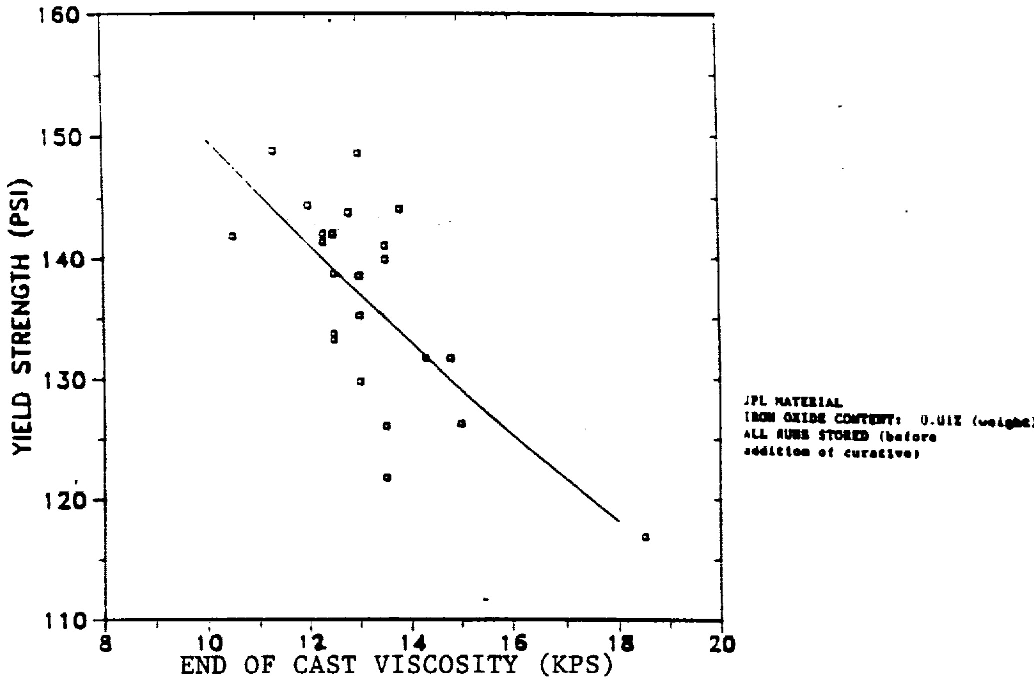

Fig. 25. Yield strength correlation with cast propellant viscosity.

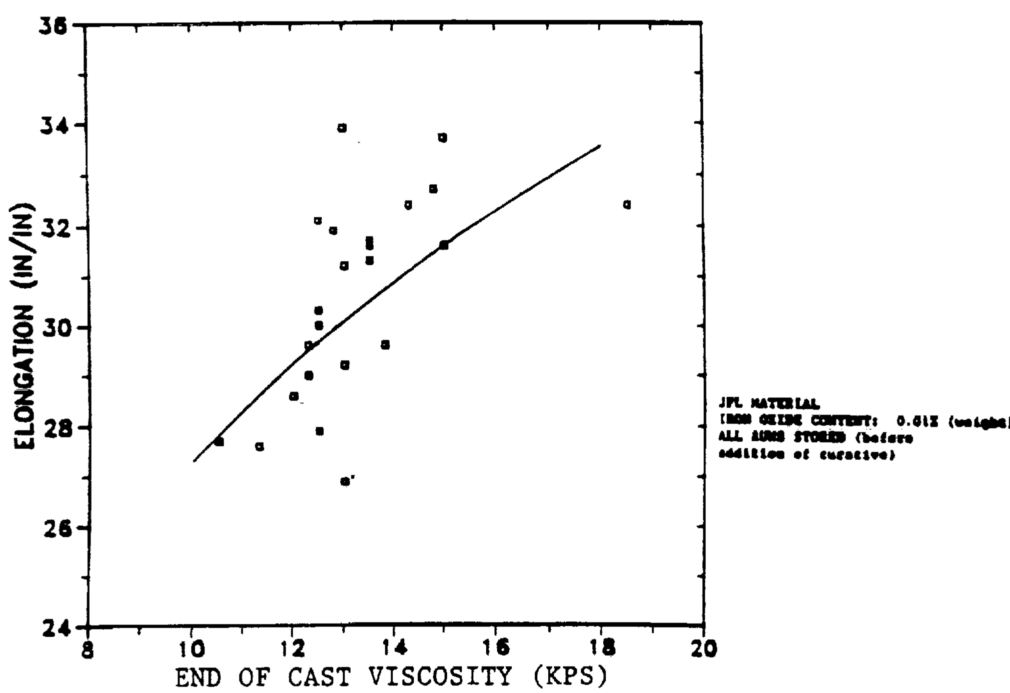

Fig. 26. Elongation correlation with cast propellant viscosity.

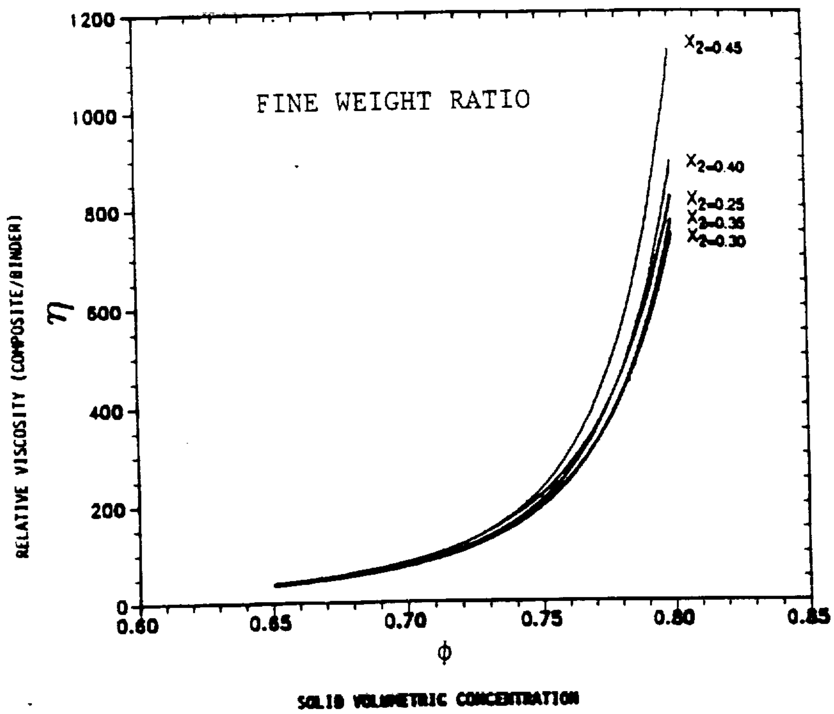

Fig. 27. Relative viscosity with solid volumetric concentration.

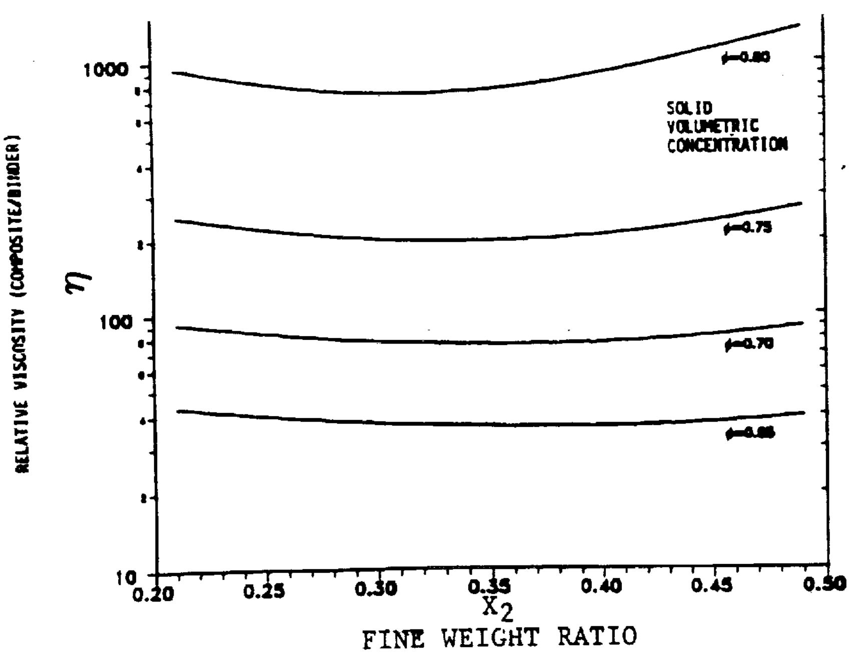

Fig. 28. Relative viscosity with fine weight ratio.

Testing Techniques

Let it be assumed that, in the manufacture of a solid composite propellant, all the starting materials are properly inspected and conform to the specifications. Furthermore, curing is to be done as per the specifications without any variations. Under these conditions, it is therefore evident that to ensure reliable performance of a propellant from batch to batch, the final mix before curing needs to be well defined. In other words, the final mix has to be properly and fully characterized with reference to

a. critical solid ingredients by way of particle size, particle size distribution, concentration, etc., and
b. the binder matrix in terms of its cure stage (molecular weight buildup and cross-linking) in addition to the concentration of various ingredients.

If every propellant mix batch, whether small or large, is brought to conform to this definition before curing, batch-to-batch variation and scale-up problems can be further understood. To achieve this end, very fast and quick techniques have to be established for evaluation of the propellant. These tests have been developed. The analysis includes drawing samples of the mix and extracting, with a suitable solvent, the solid particles from the binder. With this complete, the constitutents of the mixture can be inspected as follows:

a. Insoluble portion--consisting of solid inorganic ingredients such as AP or AL--can be analyzed for particle size and distribution (i.e., with microtrac, microscope, and coulter counter).
b. Soluble portion--consisting of primarily the binder--can be analyzed for ingredient concentration and polymer growth (i.e., with FTIR spectroscopy and GPC analyzer).

Figures 29 and 30 show the inferred spectrum of the soluble portion of the propellant. Figure 9 has been processed through the extraction technique and therefore in a solution of solvent.

<u>A Mathematical Formulation of Mixing</u> - A. Mazer and T. Vincent

In this section, we present a brief introduction to the design and analysis of a bladeless mixer. The motivation for designing a bladeless mixer is to overcome the shortcomings associated with the blades used in the mixing of solid fuel propellants.

The dynamics of mixing systems has interested mathematicians since Poincaré introduced a geometric viewpoint to the study of differential equations. More recently, the search for chaos has spawned many examples of mixing dynamics. The common feature in all mixing systems is the presence of a positive Lyapunov exponent which indicates that the dynamics stretches trajectories as they pass through certain regions of the domain.

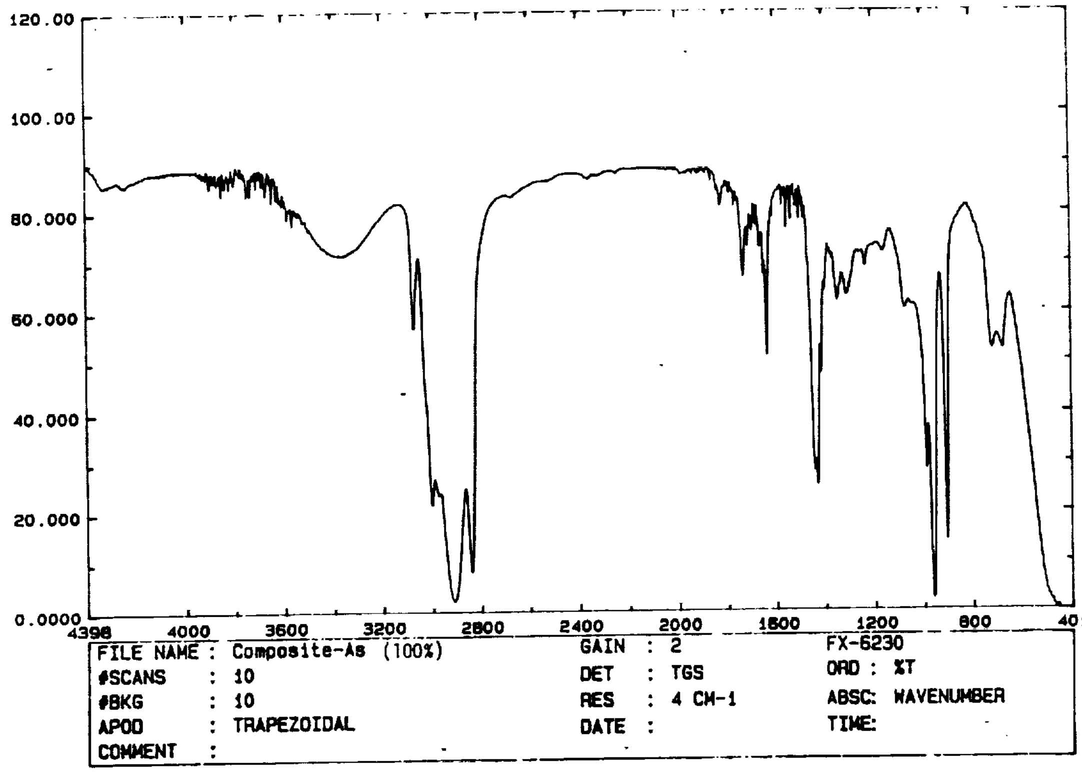

Fig. 29. FTIR spectrum for composite binder.

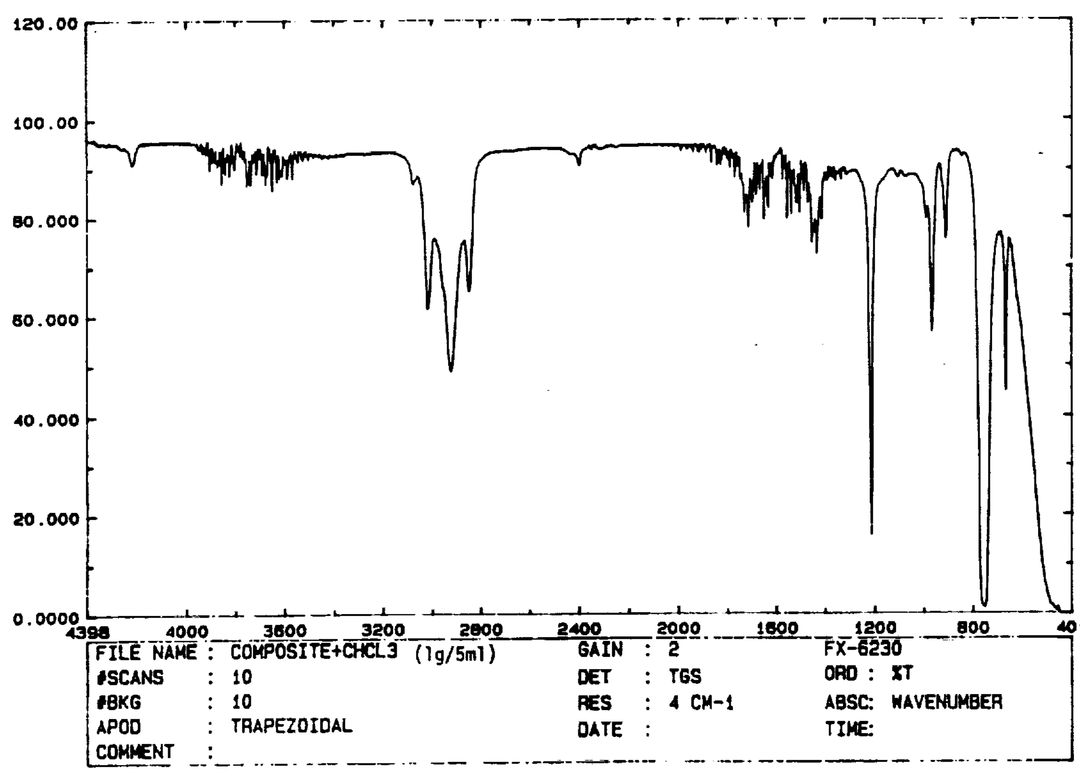

Fig. 30. FTIR spectrum for extracted composite binder.

As an example of a mixing system, consider the "Baker's Transformation." The Baker's transformation is a mapping of the unit square back to the unit square which is performed in two steps (Fig. 31) In step one, the domain is stretched by a factor of two. In step two, regions 2 and 4 are stacked on top of regions 1 and 3.

Figure 32 illustrates that the Baker's transformation creates a mixing system. The unit square is partitioned into 16 cells and the orbit of the shaded region is tracked through four iterations of the transformation. After only four iterations, the shaded region, which was initially contained within one cell, is distributed uniformly in all 16 cells.

Figure 33 is a photograph of a bladeless mixer inspired by the Baker's transformation. The mixing medium is corn syrup, which is circulated in a clockwise direction. The narrowing of the tank, along with viscous effects and the manner of reinserting the fluid into the tank, induce the necessary stretching to create a positive Lyapunov exponent.

After running several experiments using different designs, we found that the most critical design criteria is the avoidance of stagnant regions where the fluid does not circulate through the pump. Such regions are known as invariant subsets. Figure 33 represents a design which produces no invariant subsets.

A portion of the corn syrup has been stained and visually monitored. (Our mixer is made of Plexiglas.) Stretching is observed and it is apparent that the stained region becomes mixed throughout the tank.

The analysis of the mixing process is an application of the branch of mathematics known as ergodic theory and can be carried out on other mixing systems.

We have two mathematical models of the mixer, a discretized and a continuous model. The first step in realizing the discretized model is to partition the domain of the mixer into n cells of equal size and label each cell uniquely with an integer between one and n. Define the number m_{ij} as the proportion of the mixing medium that is transported from cell i to cell j after mixing for a standard unit of time denoted by τ. (We take τ to be the average time it takes a fluid element to circulate clockwise through the mixer.)

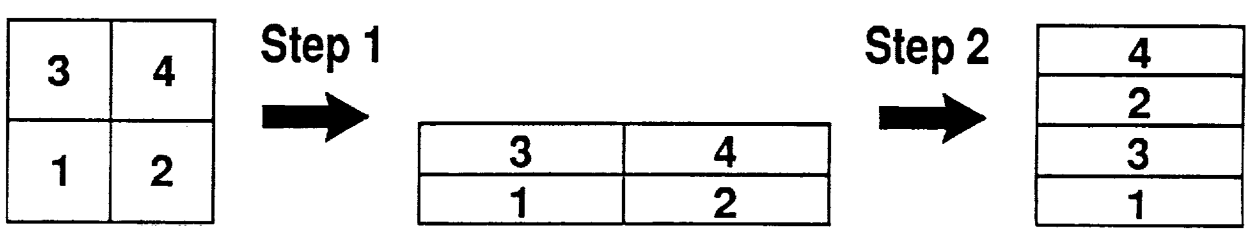

Fig. 31. The Baker's transformation.

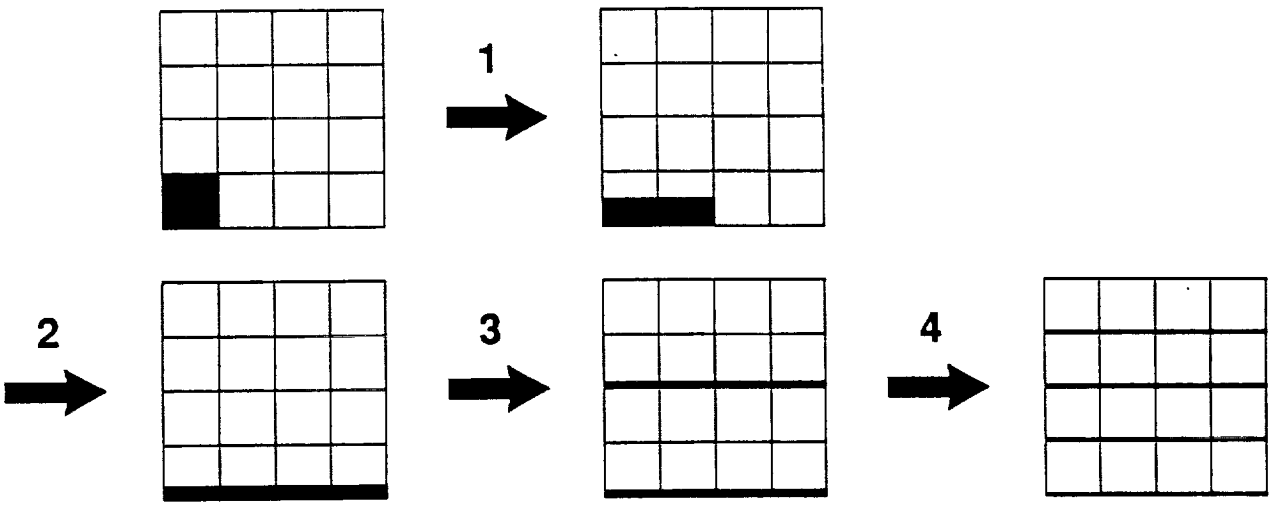

Fig. 32. Mixing system created by the Baker's transformation.

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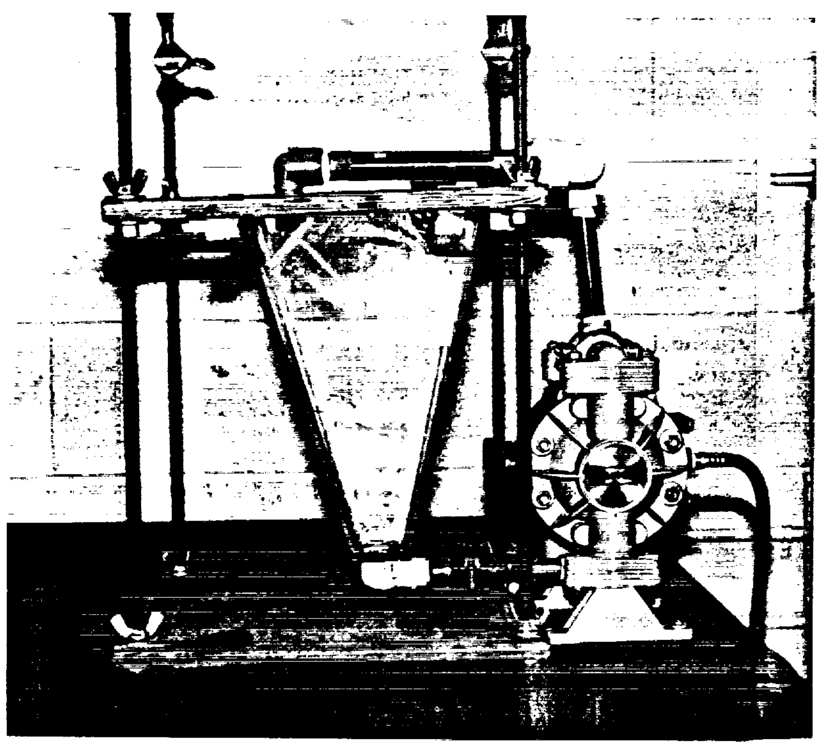


Fig. 33. The mixer.

The set of numbers, m_{ij}, forms a matrix called the transition matrix and is denoted by M. We say that the medium is being mixed if

$$\lim_{k \to \infty} M^k = [1/n] \,,$$

where [1/n] represents the n × n matrix in which every entry of the matrix is 1/n. Physically, this condition states that the limiting proportion of mixing medium transferred from cell i to cell j is 1/n for any two cells.

A necessary and sufficient condition for mixing is that the magnitudes of all the eigenvalues for the matrix, $P = M - [1/n]$, are less than one. From the transition matrix, one can also address the following questions about the mixing properties of our system:

i. What is the rate of mixing?

ii. If we assign an initial density to the medium, what will the density distribution be at different times?

The continuous model is obtained by letting the cell size of the partition approach zero. Then, the transition matrix becomes a linear operator on the square integrable functions over the domain. We call this operator the transition operator. It provides more detailed information about the mixing process than the transition matrix does. To describe the features of this model would require a lot of background that cannot be provided here. Henceforth, we will only consider the discrete model.

We can determine the transition matrix for our mixer experimentally using the concept of ergodicity. If f is any function over the domain of the mixer such that $\int_\Omega |f(x)|\, d^3x < \infty$, then the mixer produces an ergodic system provided that

$$\lim_{k \to \infty} (1/k) \sum_{j=0}^{k-1} f[\phi_j(z)] = \int_\Omega f(x) d^3x \,,$$

where Ω is the domain of the mixer. Also, z is considered to be any element of the domain and $\phi^j(z)$ is the position of this element after τ_j units of time. Physically, the system is ergodic provided that the time average coincides with the space average. We have determined that the mixer induces an ergodic system.

The experiment to determine the transition matrix is performed as follows: Place a particle in the mixer and take a measurement of its position at every τ^{th} time interval for many iterations. Let the number λ_i be the total number of times that the particle is located in cell i. Also, let the number γ_{ij} be the total number of times that the particle is transferred from cell i to cell j in succeeding measurements. Using the definition for the value m_{ij} and the definition of ergodicity, one can show that

$$m_{ij} \cong \gamma_{ij}/\lambda_i \ .$$

Dr. Summerfield, Dr. Hermance, and Dr. Dowler were concerned that the above model treats the medium within the mixer as if it were a fluid and that it does not account for distributions of solid particles such as one finds in fuel propellants. However, the ratio of particle size to domain size is so small that the mixing properties of the actual propellant should be similar to those of a fluid and so the model should remain reasonable. This conjecture could be verified by experimental observation.

Quantitative Computer Representation of the Governing Equations - Mike Hicks

It is possible to consider the mixing process in an abstract sense as the operation of a function, F, which maps a domain back upon itself. Computational fluid dynamics are notoriously complex and time consuming, and this approach allows us to simplify the problem to a great degree and yet still be able to investigate certain fundamental and important aspects of mixing on the whole.

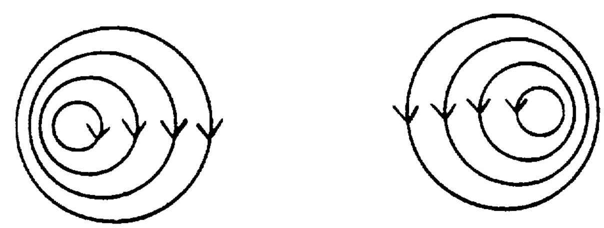
A two-dimensional mixing model has been developed using this approach. The equations were designed by Arthur Mazer (see his section of this report) to satisfy continuity and incompressibility conditions of two-dimensional flow in a unit circle. The differential equations of motion were solved numerically using the Rung-Kutta algorithm to obtain the mapping function. The results of this mapping were then displayed graphically on an IRIS workstation. The computational work was performed by this author.

The equations which were to be integrated are as follows:

$$\dot{X} = [1 + \sin(t)]\left\{\frac{2Y[4X - 2 + [(2 - X)^2 - 3(1 - x^2 - Y^2)]^{1/2}]}{3[(2 - X)^2 - 3(1 - X^2 - Y^2)]^{1/2}} + 2Y\right\}$$
$$+ [1 - \sin(t)]\left\{\frac{2Y[4X + 2 - [(2 + X)^2 - 3(1 - X^2 - Y^2)]^{1/2}]}{3[(2 + X)^2 - 3(1 - X^2 - Y^2)]^{1/2}} + 2Y\right\}$$

$$\dot{Y} = [1 + \sin(t)]\left\{\frac{2}{9}\,[2X - 2 - [(2 - X)^2 - 3(1 - X^2 - Y^2)]^{1/2}] \times \left[2 + \frac{4X - 2}{[(2 - X)^2 - 3(1 - X^2 - Y^2)]^{1/2}}\right]\right\}$$
$$+ [1 - \sin(t)]\left\{\frac{2}{9}\,[2X - 2 + [(2 + X)^2 - 3(1 - X^2 - Y^2)]^{1/2}] \times \left[4 - \frac{4X - 2}{[(2 + X)^2 - 3(1 - X^2 - Y^2)]^{1/2}}\right]\right\}$$

When we consider the streamlines generated by this velocity function, we see that the flow consists of two superimposed vortices rotating in opposite directions:



The two components of the flow are modulated by sinusoidal forcing functions which are 180 degrees out of phase. It is the periodic forcing functions that give rise to the chaotic behavior of the flow. By examining the graphical output generated (Fig. 34), we see that our model demonstrates mixing behavior very well. The photograph shows the results of 30 successive applications of the mapping function upon 4 sets of points initially very tightly spaced. Each mapping is overlaid in this output to demonstrate the mixing. There is one dead zone located in the lower right corner of the domain. This agrees with set theory, which states that there must be at least one invariant set, or in terms of mixing processes at least one dead zone, in any two-dimensional mapping of a domain upon itself.

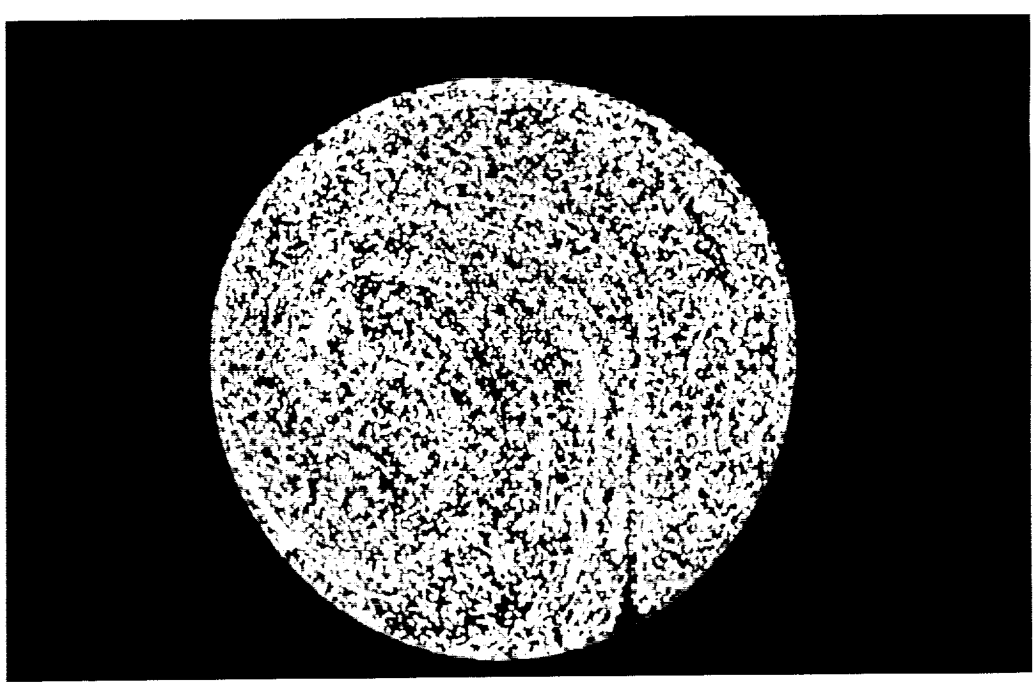


Fig. 34. Two-dimensional model after 30 mixing cycles.

Preliminary Work on Automation of Batch Processing - Paul Schallhorn

Abstract

For space-based propellant production, automation of the process is needed. Currently, all phases of terrestrial production have some form of human interaction. A mixer has been acquired to help perform the tasks of automation. We have designed, built, and installed a heating system to be used with the mixer. Tests performed on the heating system verify design criteria. An IBM PS/2 personal computer has been acquired for future automation work. It is hoped that by the end of the next academic year, the mixing process itself will be automated. This is a concept demonstration task--proving that propellant production CAN be automated reliably.

Introduction

The research work deals with the autonomous production of propellants. Because 80% to 90% of a spacecraft's weight is propellant, it is advantageous to produce propellants in strategic locations en route to, and at, the desired mission destination. This will then reduce the weight of the spacecraft and the cost of each mission. Since one of the primary goals of the space program is safety, a totally automated propellant production system is desirable. This system would thereby remove the constant human intervention currently required in production of many propellants from hostile, high-risk extraterrestrial environments. This enables the exploration of space to be more than the search for, and production of, propellants. As a proof-of-concept demonstration, one specific case was chosen for this study--composite propellant production; the principle is more important than the application.

Background

Currently, composite solid propellant production is done with constant human intervention. Using a control room, man has total control over all aspects of the propellant production. This is fine on Earth, but it is too costly in space. Thus, the need for automated composite propellant production exists.

Approach

We are currently completing testing of a heating system, which was designed by the student (Paul Schallhorn), for the one-pint mixer that is to be used for this project. Because composite propellant production requires mixing the ingredients at two constant temperatures (160 and 140°F), a self-contained water-heating system is required for space-based operation. Such a system is shown in Fig. 35. This system provides the required temperatures and only needs an electric power source to drive the pump motor and heat the water heaters. This is not unrealistic considering that electricity is also required for the mixer and controlling computer.

One approach, therefore, is to use a personal computer to control the introduction and mixing of the composite propellant ingredients to the mixer (making sure that temperature is constant on the walls of the bowl, detecting local "hot spots" within the mixture, and taking in-situ measurements of the viscosity of the mixture to check if it is within an acceptable range). Then, pump the mixture, via computer programs, into a cast which will be placed in an oven for curing and then stored for future use.

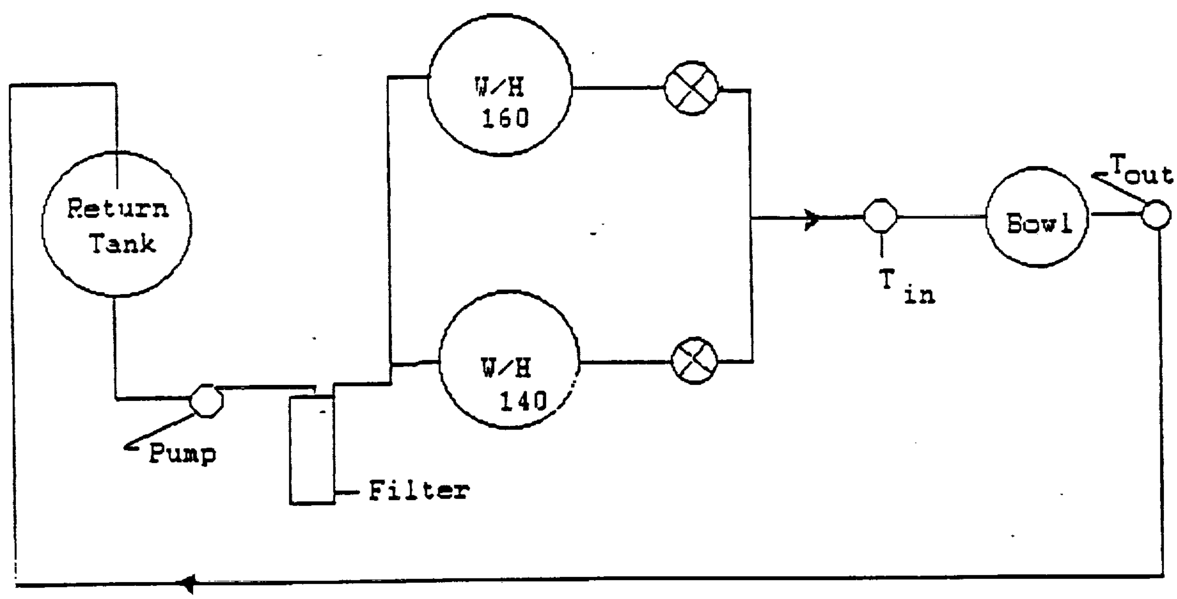


Fig. 35. The heating system.

Results to Date

The major results to date are as follows:

1. A used Baker-Perkins PX-2 mixer was acquired; this introduces a factor of 6 cost reduction (see Fig. 36 for the complete mixer setup). A heating system was required for its operation.
2. In September 1988, Schallhorn designed the heating system to be used for the mixer (see Fig. 35). It was determined that the minimum volumetric flow rate for the heating system for a 1-degree temperature drop across the mixer operating at steady state was 2.5 gallons per minute. Therefore, we selected a pump with a volumetric flow rate of 4.4 gallons per minute to ensure a negligible temperature drop across the mixer bowl. Since only two temperatures are needed, it was logical to have two separate reservoirs, each at

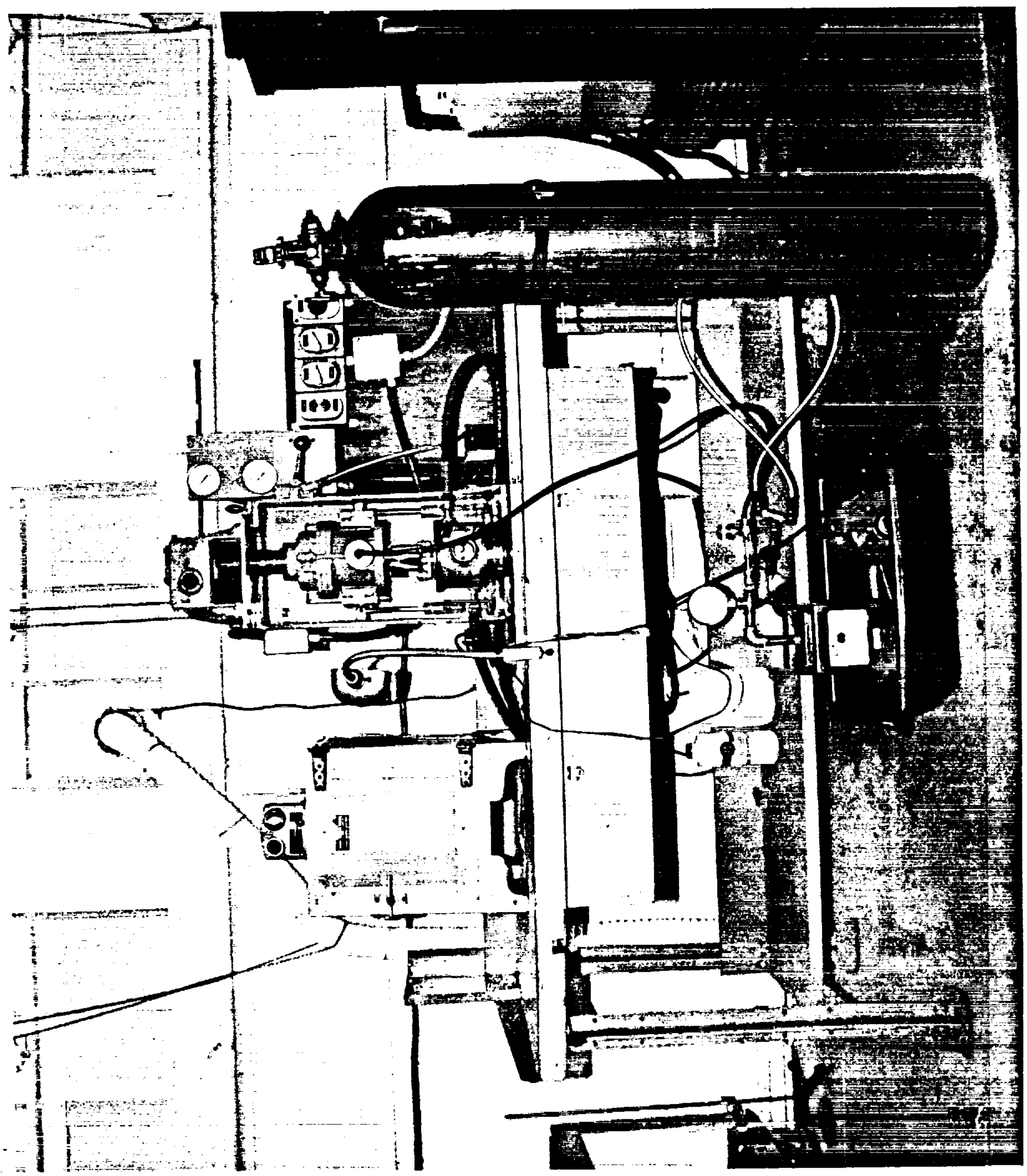


Fig. 36. University of Arizona's solid composite propellant production facility (including mixer, oven, vacuum pump, and heating system).

one of the required temperatures. We chose to have both reservoirs be hot water heaters. Because we only had 120-volt a/c power available, we had to choose the most efficient heater size on the market. As we began to search for heaters for the project, it was discovered that the same heating element was commonly used in different-sized 120-volt water heaters. This made it clear that for maximum water heating, the smaller the water the heater, the more advantageous. That was the basis for the selection of two 10-gallon water heaters (see Fig. 37). The system uses distilled water to eliminate the possibility of scale buildup in the system. To further ensure the cleanliness of the water in the system, a filter is placed in the system immediately following the pump (see Fig. 38).

3. Acquisition of the components of the heating system was begun in October 1988. By the middle of November, all of the components were in and the heating system was assembled.
4. Initial verification of the temperature profile of the heating system was begun in December 1988. Verification of the heating system continued through March 1989, including verification of flow rate and the time required to heat the system from a cold start.
5. In August 1988, research was begun to determine which personal computer to purchase for this project. By the end of September, an IBM PS/2, Model 80 was selected, with an Intel 80386 microprocessor operating at 20 MHz, a 115-megabyte hard disk drive, and 2 megabytes of RAM. The computer was ordered at the end of September, along with the following peripherals: a 14-inch monitor, a 80387 math coprocessor, a modem, a 5.25-inch external diskette drive, additional memory, a mouse, and a Hewlett Packard Laserjet II printer. Due to shipping problems from IBM, the computer did not arrive until late in January, and the peripherals did not arrive until early February. By the middle of February, the computer system was operational. This computer system will be used on various other NASA Center projects, also.

Summary and Future Work

In summary, this task has shown that there is a need for automated production of propellants for space-based propellant production. We have also seen that there is no current system to produce composite propellants without human intervention. A mixer has been acquired to help perform this task. We have designed and built a heating system to be used in conjunction with the mixer to maintain constant mixing temperature. The heating

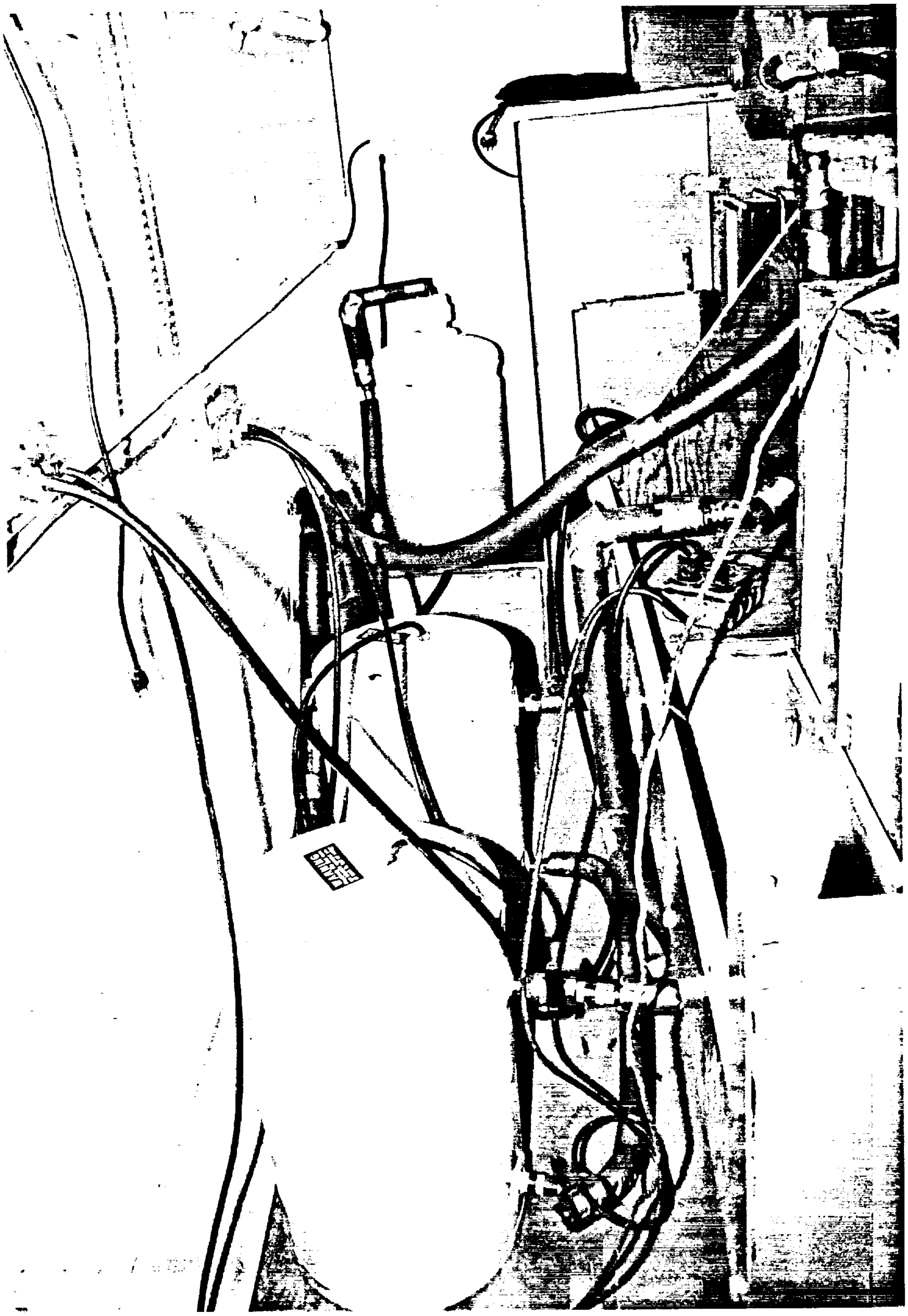


Fig. 37. Side view of the heating system.

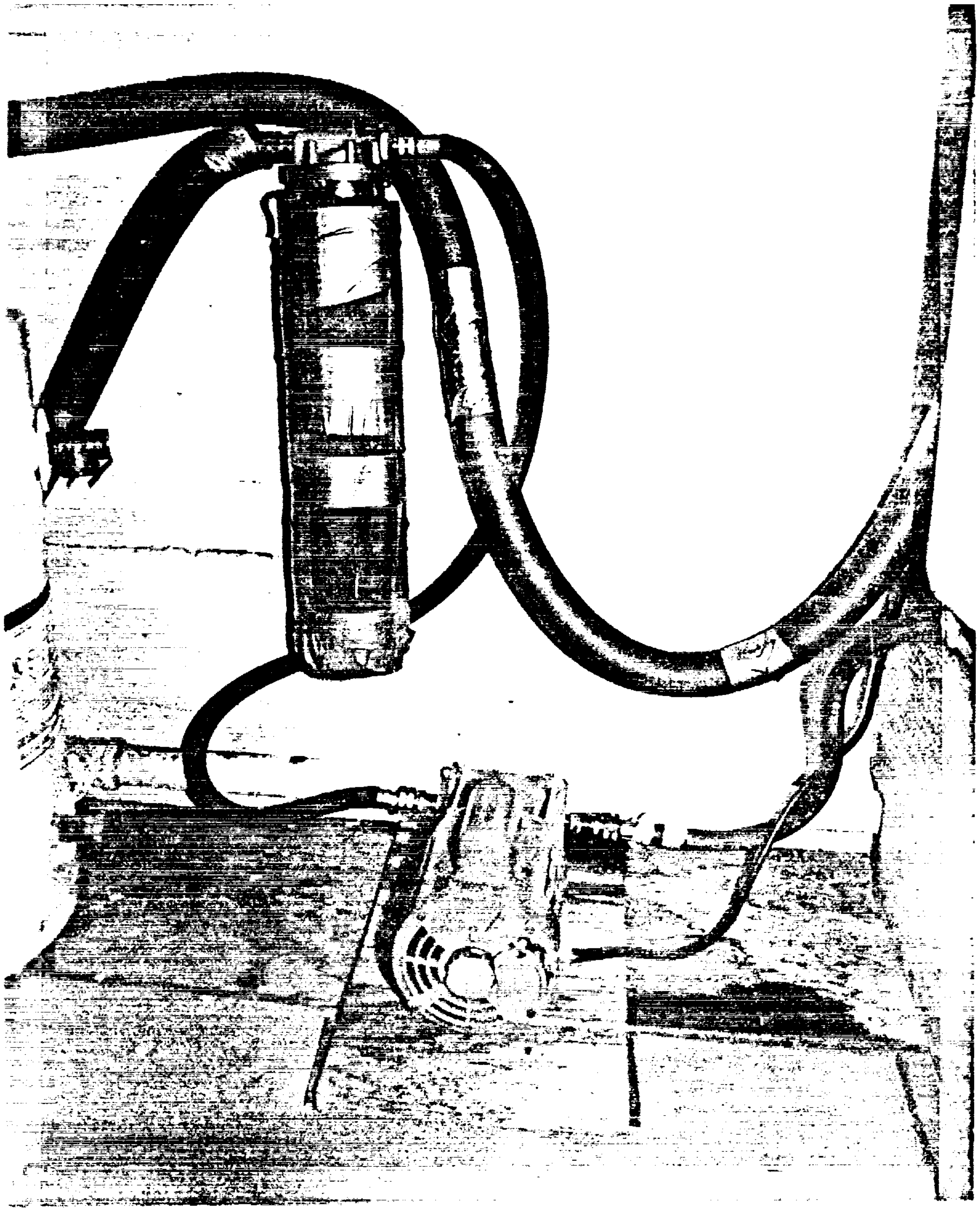


Fig. 38. Heating system pump and filter.

system has been, and is continuing to be, tested under operational conditions for design verification. We have acquired an IBM PS/2 personal computer for the computer portion of the automation.

For the 1989-90 academic year, the student plans to begin his Ph.D. research, which will consist of the actual automated propellant production. During the year, we will begin to automate the mixing process itself. It is hoped to have the computer control the addition of each ingredient from a "hopper" (yet to be built) to the mixer at required times and have the computer control the mixing of the ingredients for the required amount of time. We also plan on building and installing the in-situ viscosity measuring device for future integration into the automation system.

DISCUSSION AND COMBUSTION

Discussion

When discussing malfunctions, or less-than-desired performance, we would like to learn the way these are approached in similar programs. Fortunately, Code Q established a program to specifically explore failures, and to recommend improvements, in the closely related field of **pyrotechnics**. Larry Bement[23] has conducted a detailed study, for Norm Schulze, surveying the recent failures and substandard performance in NASA, DoD, and the Space Division. It is instructive to recall here the classification used to characterize the failures and anomalies. This is shown in Table 3. Extensive data accumulation is also systematically tabulated and catalogued. A typical example is shown in Table 4. Similar surveys of composite solid propellant rockets will be most valuable.

The rest of the discussion is best stated concisely in the form of the principal findings and recommendations, with one exception. It was felt by all that the end use, combustion, is poorly understood and that this must be rectified. Thus, the next section discusses combustion.

Combustion

An inescapable feature of solid propellants is that their end use will be through combustion. Thus, all of our efforts at understanding the ingredients, specifications, mixing schedules, processing, casting, and cure will be of little help in accurate predictions of performance unless the final combustion can be predicted accurately, too. Here again, many models are available and some have indeed proved useful in formulating good propellants with desired characteristics. Nevertheless, these combustion models are approximate at best, and none can claim to predict as simple a parameter as the time-independent burn rate purely from a specification of the ingredients. Some of these deficiencies, which may be adequately concealed in time-independent burning, are revealed when the propellant combustion becomes time-dependent, or unstable. For an adequate understanding of the solid propellant predictability and quality assurance, we must develop a better understanding of combustion.

Combustion of a composite propellant is inherently a heterogeneous, time-dependent process that involves key interactions among the condensed and vapor phases and physical and chemical processes, all within a time scale of milliseconds and within a spatial region of a few hundred microns. The conversion of the "room temperature" solid into vapors and gases that frequently exceed 5,000°F in temperature must be understood, at least to the extent of predicting the overall rates from the fundamental constituent rates. Hopefully, some of the constituent rates, such as the depolymerization rate of the binder, the

Table 3. Definitions for survey on pyrotechnic problems and failures.[23]

1. Manufacturer's Poor Quality Control--All quality controls in place, but not followed.
2. Manufacturer's Bad Procedures--The quality control procedures or manufacturing methods are inadequate and in need of improvement.
3. Manufacturer's Decision--Unilateral decision by manufacturer affecting customer.
4. Bad Design--Technology exists, but not followed.
5. Lack of Understanding--Technology did not exist at the time of problem.

Table 4. Typical example of data collected--firing circuits.[23]

Date	Project	Problem	Impact	Source of Problem	Resolution
1983	Aircraft Crash Test	Aircraft crash test program discovered stray voltage in facility firing circuits in flight checkout (poor grounding and corrosion of cables/connectors	Delay of experiment and potential loss of life and loss of experiment	Bad test procedures	Rebuilt checkout/firing cables and consoles
1982	Shuttle	SRB decelerator parachute released prematurely in flight at frustrum separation (pyrotechnic shock activation of water impact sensor)	Loss of spent SRBs	Lack of understanding	Redesigned, requalified
1972	Centaur	Shroud separation joint fired primary and secondary charges simultaneously in qualification and ruptured containment (connectors on firing circuits swapped)	Delay of system qualification, damaged test hardware, potential damage to spacecraft and flight vehicle	Bad design	Redesigned, different connectors

decomposition rate of the oxidizer; and the melting rate of the metal, can be accurately determined through combinations of modern experiments and data analyses. The popular Arrhenius kinetics may be adequate to describe these, but the variations of the activation energy and pre-exponential factor as influenced by temperature, species, and pressure in the presence of intense radiation may need further study. The physical constants, such as the thermal conductivity coefficient, specific heat, and absorptivity, are usually averaged over all of the ingredients, and this procedure must also be examined. Many of the details of composite propellant combustion were reviewed and the more important theories presented in ref. 24, which describes time-independent (steady-state) burning. The time-dependent combustion aspects form the subject of a book (in press) in which the suppression techniques are scientifically described.[25] These books cover only those aspects of combustion that are known; more work is needed on the unknowns.

While the natural heterogeneity of composite propellants was adequately described, most combustion models used a "suitably averaged" homogeneous material when it came down to actual mathematical analyses. Clarke Hermance was the first to introduce heterogeneity explicitly in the analysis. The success of his model started a series of variations by other researchers. We now need another such step forward to improve the accuracy of our understanding and predictions. Many modern sensors, diagnostic tools, and microprocessors should all be constructively used in conjunction with powerful computational capabilities to evolve better combustion models. Such models should specifically address the importance of the following:

1. Condensed phase reactions, including those of the ingredients, between ingredients, and among the products of initial reactions (here, reactions include depolymerizations also).
2. Surface reactions, including the very definition of the "surface" itself.
3. Near-surface vapor phase reactions, including those within one fine (particle) diameter distance from the surface. What is the influence on heat transfer to the condensed phase from such close zones?
4. Main-flame reactions, including the proper definition of the flame, or the vigorous combustion zone.
5. Post-flame reactions, relaxation reactions, condensation reactions, and their importance to the overall burn rate.
6. Possible control of some of the "nature-prescribed" reactions through the powerful influence of free radicals and free radical donors.
7. Unambiguous verifications, independent checks, and repeatable tests; ability to predict small variations as influenced by ingredient or processing variations.

8. Realistic combustion experiments that reproduce the essence of solid composite propellant combustion without actually using solid propellants (the perforated porous plate burner provides one example).

PRINCIPAL FINDINGS

1. Unplanned variations in solid propellants have been quite prevalent.
2. With so many ingredients, each characterized by so many physical and chemical properties, quality control of the end product is subject to several uncertainties at the present time.
3. Parameters during processing (for example, the temperatures and mixing times) have varied around the desired values by magnitudes whose significance is not yet fully understood.
4. There does not appear to be a single case of a propellant that was scientifically studied, formulated, processed in various scales of mixers, cured, and tested in various sizes of rocket motors--all under conditions where nothing was changed in the formulation. We cannot fault the production specialists, because changes in the formulation of scaled-up batches are made on the basis of documented experience common to the industry.
5. The enormous "data base" in solid propellants is really unusable for a scientific study.
6. Most solid propellant rocket motors have been evolved based on empirical corrective procedures during development.
7. Bonded interfaces can be trouble spots.
8. The important **end use** invariably involves combustion; the current combustion models are too naive.
9. Even in academia, traditionally recognized for fundamental research away from the pressures of developmental programs, there are practically no universities in the nation capable of experimental pursuit of propellant formulation and rocket motor tests, even on small scales.
10. Extremely useful and revealing data may have been, and are continuing to be, lost when "unsatisfactory" propellant batches are simply discarded.
11. Unfortunately, many of the procedures followed in solid propellant formulation, processing, and production suffer from the legacy of black art; even the mixers we use are really borrowed from the bakers.
12. Eliminating solid propellant rockets in favor of liquid propellant rockets is hardly the solution, since there are even more serious problems with liquid rockets.

PRINCIPAL RECOMMENDATIONS

All of the deliberations and the consensus of the authorities (on solid propellants) present at this meeting are available in the transcript (Appendix A) and the body of this report. Here, the main recommendations are listed in the interest of concisely stating what is needed for increasing the quality and reliability of solid rocket motors. It is understood that long-term quality and reliability can only be ensured through better predictability which, in turn, can only be the result of a thorough understanding of the key parameters; it is important to note that thoroughly understanding the key parameters is distinctly different from an attempt to thoroughly understand all of the fundamental physical and chemical processes relevant to solid propellants.

Such an ambitious goal--to understand all of the fundamentals--would probably be instructive but would be prohibitively costly, besides detracting from intelligent and economical approaches that can identify and clarify the key parameters that directly affect the end-use performance. The recommendations of this working group are:

1. Establish at least one end-to-end facility where propellants can be formulated, processed, cast, cured, and tested in different size motors--all under strict control. [KR notes here that the only such facility in the U.S. still with an independent university is JPL; however, all of the experimental propellant processing capability has been moved from Pasadena to Edwards. In any case, support of this facility has been very meager in the last 15 years.]
2. Seek and establish a data bank from industry; this should include not only the mainstream successful programs, but also all of the seemingly secondary details that include failures, too.
3. Scrutinize the data bank for meaningful trends.
4. Since the end use will always involve vigorous combustion, establish a good combustion program in composite solid propellants. [KR notes that the establishment of a small number of highly focused, competitive, and selective grants in combustion will be much more productive than the establishment of a large program.]
5. Carefully study bonded interfaces. [KR notes that MSFC has recently started (with SAIC as the prime contractor) the SPIP Bondline program. More is needed to specifically study the propellant composition.]
6. Evolve the fundamental mathematical models for mixing and flow of heterogeneous mixtures, including chemical (curing) reactions.
7. Establish the bounds of physical and chemical variations of interest in practical composite propellants and exceed these bounds in the laboratory. These out-of-

bounds behaviors can be of immense value in understanding some of the unplanned variability in practice.

8. Utilize all of the latest high-technology developments in micro devices (sensors, processors, and chemical activators) to scientifically gather more information on composite propellants to help modeling.
9. Formulate one simple, model composite propellant and thoroughly study it at various independent facilities, including industry, universities, NASA, DoD, and other government laboratories. The results of such a study can be very valuable in understanding the bases of some of the baffling variations.
10. The last recommendation is very profound. All of the participants noted a general decline in the number of students and faculty actively working in solid propellants. To obtain and maintain a reasonable working knowledge of composites, it takes competence in several disciplines, dedication, and careful attention to details--all spread over at least twenty propellant families; and a careful, first-hand study is needed over the entire propellant program life, from uncured strand burn rates to full-scale motor firings. Cursory supervision in a bystander role will simply not suffice; neither will any amount of theoretical work on model (ideal) systems. We must have more involvement by competent researchers, who should spend time actually working with the processing and end use (combustion).

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