Table 5 Change in properties after 24 hr exposure to various gaseous environments

Material	Volume resistivity, Ω, cm			Weight change, %			Volume change, %			
	Control	Air	N_2	"Venus"	Air	N_2	"Venus"	Air	N_2	"Venus"
Kapton 100 (polyimide film)	1.24×10^{17}	5.6×10^{16}	8×10^{16}	1.20×10^{17}	−0.1428	−1.373	+1.950	−0.98	−1.36	...
Fiberglas 91LD (glass filled phenolic)	1.44×10^{14}	1.0×10^{14}	9×10^{14}	1.03×10^{14}	−1.859	−2.389	−0.1488	+1.49	−0.28	0.00
Exp 820 (glass fiber reinforced benzimidazole)	...	...	...	...	−1.671	−1.541	−1.202	0.00	−1.64	−2.52

<1. The steadily rising gas pressure, resulting from heating of the environmental chamber, was adjusted to its desired value (18.5 ± 1 atm) after the test temperature of 550 ± 10°F was reached. A cam-type timer was set to turn off the heat automatically after the required exposure period of 6, 24, or 72 hr. Gas flow through the simulator was carried on during the entire course of an exposure, at the rate of 10 ml/min. Sampling for mass spectrographic analysis was made after externally reducing the pressure in the simulator. The foregoing gas mixture and conditions, first thought to exist on the equatorial surface of Venus, most probably describe the conditions at some distance from the surface. Arguments seem to support the hypothesis that Venera 4 had not reached the planet's surface when it stopped sending information.[4–6]

The materials tested were the commercial products listed in Table 1, and test specimens were prepared in accordance with the sizes and shapes specified in the standard test methods used. Some of the products, for example, the encapsulants and adhesives, required such preliminary handling as mixing and degassing before castings or testing specimens could be prepared. Weight losses were measured to an accuracy of ±0.1 mg and dimensional change measurements were accurate to ±0.1 mil.

Results and Discussion

Only six products (4–6, 10, 12, and 13 in Table 1) met the compatibility criteria set for the screening program. Two materials, Teflon FEP and Exp 820, had melted at the exposure temperature, and therefore, the test specimens were deformed. However, the mechanical properties seemed intact, after the specimens were brought to room conditions, and the small weight loss indicated that chemical degradation was practically absent. If these two plastics were reinforced by fibrous materials, they probably would have been dimensionally stable. Later on, a glass-cloth-reinforced polybenzimidazole showed adequate resistance to the test conditions and was rated compatible with the environment.

The six products were then exposed for 24 hr to the "Venusian" atmosphere. Three of these, Viton 77-545, GP-77, and Pyre-ML-RK 692, failed to meet the compatibility criteria, which consisted essentially of retaining at least 70% of the original mechanical, physical, and electrical properties, and losing less than 2% weight (see Tables 2 and 3). The three remaining materials, Teflon TFE, Fiberglas 91 LD, and Kapton 100 were exposed 72 hr to the simulated conditions. Kapton 100 retained 40% of its original elongation and 63% of its original tear strength after this treatment. Its tensile strength was well retained. The other two compounds were affected very little by the 72-hr exposure.

Kapton 100, Fiberglas 91LD, and Exp 820 also were exposed to N_2 and air, as well as again to the "Venus" atmosphere, at 550° ± 10°F and 18.5 ± 1 atm for 24 hr. Some of the values obtained (averages of at least three tests) are given in Tables 4 and 5. Table 4 indicates that the "Venus" atmosphere reduced the mechanical properties of the materials more than did air or N_2; however, with the exception of percent elongation, the mechanical properties were not reduced more than 10%. The improvement in the tensile strength of Kapton and Fiberglas 91LD in nitrogen is worthy of notice, as is the tensile property of Exp 820 after exposure to air.

No dramatic changes in the volume resistivity of Kapton and Fiberglas 91LD were encountered after any of the exposures. There was not sufficient amount of Exp 820 to perform the volume resistivity measurement. The weight of Kapton increased after the "Venus" exposure. Also the weight loss of the other two materials was less after exposure to this atmosphere. Absorption or an actual chemical combination between the imide nitrogen of the Kapton and the acidic CO_2 is a possibility. Although the "Venus" atmosphere affected the properties of the tested materials more than nitrogen or air did, its affect was not severe enough to rate these materials to be incompatible with this atmosphere for the duration of the test.

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Assessment of the Explosive Hazards of Large Solid Rocket Motors

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THE conventional sensitivity tests for the hazard classification of propellants and explosives are generally arbitrary in nature and based on previous experience. With 260-in.-diam motors containing over 4 million pounds of propel-

Received November 11, 1969; revision received January 16, 1970. This study was conducted under NASA MIPR-W-11, 870; and the technical direction of W. Cohen and R. Wasel. Reviews and suggestions made to the paper by L. A. Dickinson and A. T. Camp are gratefully acknowledged.

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lant proposed for space missions, an accurate evaluation of the hazards involved in large motor systems is in order. On the one hand, the composite solid propellants being considered for use, when handled with normal precautions, can be looked upon as being safe. On the other hand, even materials such as coal, flour, sugar dust, and even solid sugar[1] can be made to detonate, and explosions of commonly used fertilizer (ammonium nitrate) have been reported.[2] This Note discusses the need for, and an nonconventional approach to, an analysis of the potential hazards of large solid motors.

Although tests have been developed and/or adopted by the Interstate Commerce Commission[3] and the Armed Services Explosives Safety Board[4] to determine the sensitivity limits of propellant for various stimuli and the predictable damage if fire, explosion, or detonation occurs, these hazard classification tests and procedures may not be appropriate for very large and costly motors. The military classification tests were in fact, intended to determine shipping and storage hazards only; launch hazards were specifically excluded. The tests were designed for laboratory characterization of the material, and scaleup from small to large tests is not always permissible. For instance, the traditional Naval Ordnance Laboratory (NOL) Card Gap Test for determining sensitivity to explosive initiation was not designed for application to large composite motors,[5,6] and results have little significance. Results from negative small-scale detonability and impact-sensitivity tests cannot be extrapolated to motors of 156 or 260 in. in diameter, and so far, no reliable means is available to predict critical diameters from subscale testing.[7]

Problems Areas in Assessing the Hazards

Explosive reactions

Most of the work in this area concerns critical diameters of propellant systems.[8,9] The Air Force in its Solid Propellant Hazard Program (Project Sophy) developed a scaling model for critical diameter using an RDX-adulterated composite propellant, but the model has not been tested on any different propellant system. The detonation (low velocity) of unadulterated composite propellant was demonstrated at a diameter of 72 in. by applying an initiating detonation of 9 tons of TNT.[10] However, such a large stimulus would constitute nearly as great a hazard as that of the propellant detonation itself.

The threshold initiation pressure for a composite propellant of ideal diameter (larger than critical)§ has been extrapolated from detonation initiation pressures for propellants adulterated with RDX to be approximately 10 kbars. In an accident involving large masses of composite propellant, the matching conditions between donor and acceptor will certainly not be optimized as in the case of the experiments, and a much higher stimulus will be required for a detonation to take place. The more probable hazard arises from explosions. In malfunctions of Polaris and Minuteman missiles, as well as in composite propellant testing, violent explosions but not detonations were observed.[11]

It is clear that factors other than critical diameter and detonability must be considered. When a rocket motor strikes the Earth at velocities in the range of 100 to 1000 fps, for example, the resulting pressure will be below 15 kbar, which is probably too low to initiate detonation but high enough to cause violent explosions after break-up and/or partial confinement of the propellant. Propellant break-up could lead to thermal explosion by creating a very large burning surface. Without a significant burning surface increase, extreme confinement is necessary to obtain transition from burning to explosion or detonation. It has not yet been determined whether propellant burning after motor impact on ground can be confined to such an extent that detonation could occur. A sled test of a 120-in.-diam motor produced a low explosive yield[12] but did not allow burial and confinement of the motor, since it was impacted into a re-enforced concrete wall, backed up by a mount of earth. In tests at the Naval Ordnance Station (NAVORDSTA), Indian Head, ground confinement of Sidewinder motors being struck by flying plates at varying velocities did not affect the explosive yield. Nevertheless, it must be assumed that confinement after an aborted motor has penetrated into the Earth will affect the explosive yield.

The influence of porosity on the detonability of propellants is well known.[13,14] Changes in volume and thus in porosity upon elongation of the propellant have been reported.[15,16] However, it has not been established yet that such elongations can be obtained with large masses of propellant, e.g., upon impact during a fall back.

Small scale tests in which PBAN propellant samples were shock-loaded up to 15 kbar showed a surface increase up to only approximately 100% under the given test conditions.[17] Permanent dewetting or separation of the binder from the oxidizer was not observed. Much more testing is needed to obtain more insight into the mechanical behavior of composite propellants under shock loading, since a combination of effects such as shock loading with ensuing surface increase (break-up of propellant, increase in porosity) and confinement (partial or complete burial in ground) may lead to uncontrollable, violent consumptions of the propellant grain but not necessarily to a true detonation.

Temperature effects

The explosive hazards classification tests so far have been specified at ambient temperature only. However, propellants are more apt to react violently at elevated temperatures, and the critical diameter decreases with increasing temperature. Malfunction or premature ignition of an upper liquid stage could expose the solid motor to extremely high temperatures and thereby increase greatly the sensitivity of the solid propellant to pressure stimuli.

Blast effects

Because of their longer reaction times, explosions can produce air blast effects which cause as much or more damage than that caused by a detonation. For a self-sustained, steady-state detonation, the relationship between over-pressure and distance is known. For lack of better methods, it has been common practice to express damage hazards of propellant in terms of TNT equivalence; i.e., it is assumed that the blast potential of a given quantity of propellant is equivalent to that amount of TNT having the same total energy of explosion. This concept is weak in that it does not consider the rate of energy release and assumes that the energy that contributes to the air blast is as great as the thermochemical heat of explosion, which may not be the case. The type of reaction (combustion, deflagation, and/or detonation) and the energy release as a function of time depend not only on the magnitude of the stimulus but also its geometry and location with respect to the motor and the geometry of the motor. For example, propellant explosions tests carried out at the Naval Weapons Center in 1964–1965 (Ref. 18) resulted in TNT equivalence at locations more than 150 ft from the motor that were 20% greater than those obtained much nearer the motor.

Systems Approach to Hazards Analysis

Since a reliable measure of the safety of large solid motors cannot await the lengthy accumulation of operational experience, we have applied a logical approach[19] for determining potential hazards and describing the expected consequences. As shown in Fig. 1 the systems approach called a hazard tree begins with a definition of the system; in this case, the large solid motor and its surroundings. The motor's life is segmented into the operational modes as the initial basis for analyzing hazards. The potential accidents considered

§ At critical diameter this pressure will be much higher.

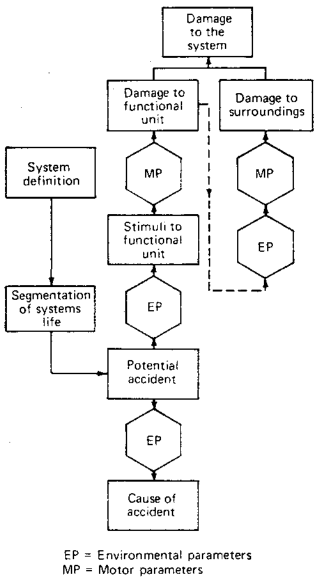

Fig. 1 Sequence of analysis for hazards evaluation.

reasonably probable for an operational mode are identified and a hazard tree is constructed for each, making use of standard logic gates and descriptive symbols. Special notation permits restrictions to be designated for both "in-put" and "output."

If a missile is dropped in transit, ignites prematurely, or malfunctions during launch, structural damage, propellant fracturing, burning, explosion, or detonation may result. These possibilities are assessed on the basis of theoretical aspects of initiation, deflagration, explosion, and detonation that are believed to be applicable to the large solid motor situation. Finally, the hazard tree shows the degree of damage to the motor and to the surroundings. The effect on the surroundings would be determined by the energy-release rate, blast effects, and fragmentation including burning pieces of propellant. A gross hazard analysis of the operational modes of the large solid motor has indicated that launch oper ations present a high-risk area. Results also show that propellant fracturing and associated phenomena are as yet inadequately defined for very large systems.

Concluding Remarks

The Joint Services Hazard Classification Procedure is not sufficient to completely assess the hazards of very large motors. For economical reasons full-scale tests are not recommended, and there are presently no correlations for extrapolating the results from small-scale tests to varying sizes, configurations, and propellant formulations used in large solid motors.

Too much emphasis has been put on the ability of a propellant to detonate, while hazards caused by nondetonative reactions have been neglected. Hazards of composite polybutadiene acrylonitrile propellants are most likely to result from uncontrollable burning and explosions rather than detonation. There is a need for investigating the mechanical behavior of composite propellant under shock loading. At NAVORDSTA, small propellant samples are being shock-loaded up to 15 kb and recovered to determine the increase in surface area as a function of shock pressure and combustion transients as a function of surface increase. A theoretical program has been initiated to develop a two-dimensional numerical analysis procedure for the stress wave propagation from end impact of cylinders using linear viscoelastic properties of composite propellants.

The TNT equivalence should be replaced by a more meaningful prediction method for blast damage. The approximate shock wave theory can be applied if magnitudes of the explosion process such as initial shock wave pressure and energy release as a function of time are available. Such a model would provide information on the influence of propellant defects on burning rates and transient phenomena besides the boundary information needed for blast wave evaluation.

A systems approach called the hazard tree can be used to describe the "prior-to-the-fact" safety for the life cycle of the motor. Efforts to apply it for large motors have revealed vital areas where information is lacking, but qualitative results have been obtained.

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