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Effect of Cyclic Loading on Solid Propellant Grain Structures

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Dynamic Failure Criteria

DESIGN of a solid rocket propulsion system inevitably involves the solution of many structural problems, which are related intimately to the ultimate performance of the system. The solid rocket is perhaps unique in that the source of propulsive energy is an integral part of the total structure. Accordingly, reliability of the system will depend on how well one can predict the integrity of the propellant grain structure under various environmental conditions. This consideration implies also that adequate methods of failure analysis must be available. Such analysis requires 1) rigorous, yet practicable methods of grain stress analysis, 2) definitive and accurate description of propellant mechanical behavior, and 3) formulation of definitive propellant failure criteria. In the past several years, considerable progress has been made toward achieving adequate failure analysis of solid propellant grains subjected to strains resulting from 1) high-rate pressurization, 2) application of gravitational forces, and 3) thermal cycling. Evidence of this progress can be found in the work of Williams and his co-workers,[1] in a recent review of evaluation of solid propellant mechanical properties by Wiegand,[2] and in papers presented at meetings of the Joint Army-Navy-Air Force Panel on Physical Properties of Solid Propellants.

However, even with such progress, much remains to be done, as pointed out by Hart in a recent state of the art review.[3] The development of failure criteria is mentioned as a critical need. A number of approaches to establishing such criteria have been proposed,[4–9] and it has been suggested[1, 10] that the effects of variable strain rates or past strain history could be treated by a concept of cumulative damage much like the one that has been developed for

During more than 16 years in the chemistry of solid and liquid rocket propulsion, John F. Tormey has played a significant part in the early research and development of chemical rocket motors. Now Chief Engineer for Rocketdyne's Solid Rocket Division, Mr. Tormey received his B.S. degree in Chemical Engineering at the University of Notre Dame in 1941 and his M.S. degree from the Massachusetts Institute of Technology. With the Navy in World War II, 1942–1946, Mr. Tormey was attached to the Bureau of Ordnance, where he was assigned to underwater ordnance research, development, and test at torpedo stations in the United States and at the Bureau, participating in aircraft torpedo development and the application of hydrogen peroxide to torpedo powerplants. He was Chief of Research for Rocketdyne in Canoga Park, Calif., from 1955 until 1958, when he transferred to McGregor as Chief Engineer of Astrodyne. He assumed his present position in October 1959, when Rocketdyne formed its Solid Rocket Division. Mr. Tormey is a Regional Director of AIAA and was named an ARS Fellow in December 1957. He also is a member of the American Chemical Society, American Institute of Chemical Engineers, and American Association for the Advancement of Science.

S. C. Britton's association with research on aerospace engine fuels began over 30 years ago when he was a laboratory assistant in the Materials Laboratory at Wright Field while a cooperative student at the University of Cincinnati. He received his professional degree in Chemical Engineering at that university in 1936. Mr. Britton is now Propulsion Research Specialist reporting to the Chief Engineer of Rocketdyne's Solid Rocket Division, following three years as Supervisor of Propellant Chemistry. Previously, with Phillips Petroleum Company's Research and Development Department, he was responsible for combustion research on aircraft gas turbine, ramjet, and reciprocating engine fuels and for industrial and automotive lubricant product development. He was transferred to the McGregor Plant in 1956 and placed in charge of the Solid Propellant Laboratory. From 1940 to 1945 in World War II, Mr. Britton first was assigned to high explosive plant technical administration by the U. S. Army Ordnance Department. He later was transferred to the Army Air Force and assigned to Wright Field, where he was active in research and engineering projects on the application of fuels, lubricants, and hydraulic fluids to aircraft and aircraft powerplants. Mr. Britton is a member of AIAA, the Society of Automotive Engineers, the Combustion Institute, and the Society of Rheology. He has been active on several Joint Army-Navy-Air Force Solid Propellant Panels since 1956.

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Table 1 Estimates of service cyclic loading of solid propellants

Service condition	Strain reversal frequency	Possible total strain reversals before firing
Vibration in flight	100 to 500 cps	5×10^7
Vibration during ground transport	10 to 500 cps	5×10^8
Temperature cycling	1 per day	2×10^3
Rotation in storage	1 per month	5×10

metals.[11–13] Application of this concept requires data on the effects of time-dependent loading, for example, fatigue test data on solid propellants. Generally, such data have not been available.

Failure criteria for extended application of dynamic loads therefore have more than academic interest. Propellant grains are subjected to cyclic strains during the handling, shipment, and storage of rocket motors which ultimately might produce enough structural damage to result in mission failure. Repeated strain reversals are encountered when a motor is transported on the ground and in the air, during temperature cycling, and when a motor is rotated in storage to counteract the effect of slump. Typical conditions for such environment are summarized in Table 1.

What is the response of the propellant when cyclic loads such as those indicated are imposed? What happens to propellant properties? Do these change enough to affect structural integrity of the grain significantly? The following illustrations and data give some indication of the answers to these questions. Figures 1 and 2 depict what can happen to a solid propellant grain after extended moderate frequency vibration. This particular grain was vibrated for about 6×10^6 cycles at 5 g input and resonant frequency. A typical plot of amplification ratio (grain accelerometer reading divided by input accelerometer reading) against frequency at 5 g input for this motor is shown in Fig. 3.

At 1 g input, the amplification ratio and frequency at the peak are slightly higher. In most instances the bending natural frequency for a grain with a case or support made of steel or plastic is changed less than 5% if the contribution of the propellant modulus is neglected. Thus a change in propellant properties during vibration will have less effect on resonant frequency than changes in other structural components.

Another example of a failure after extended cyclic loading, with a different propellant and a different grain configuration, is shown in Fig. 4. The fracture appearing at the base of the points occurred after longitudinal vibration for about 11×10^6 cycles at 200 cps.

Propellant failure after extended slow mechanical cycling is more difficult to demonstrate. However, in exploratory studies, internal damage has been detected, leading to ultimate failure after repeated strain reversals at 1 cycle/day. In these studies, cyclic application of maximum uniaxial strains up to about 75% of the strain at maximum stress (e_m) resulted in a steady reduction in area under the stress-strain curve, indicating an energy change resulting from cumulative damage to the internal structure of the propellant. When the maximum applied strain was increased, failure was found to occur in 3 to 10 cycles. Drastic changes in propellant properties on extended vibration, ultimately culminating in structural failure, also have been demonstrated in the laboratory. In recent experiments, a $1 \times 1 \times 2$ in. block of propellant was vibrated at 5 g acceleration and resonant frequency with the apparatus shown in Fig. 5 mounted on a Ling shaker. As cycling proceeds, the specimens gradually soften as shown by the change in complex modulus indicated by frequency scans such as those in Fig. 6. Ultimately, the propellant properties will change to the point that the sample slumps or cracks as shown in Fig. 7. These results are typical of composite solid propellants.

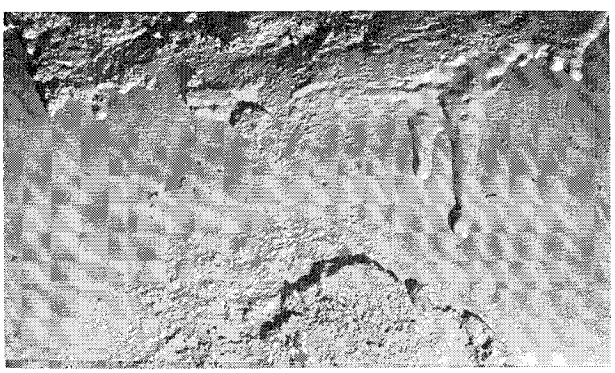

Fig. 1 View of solid propellant grain surface after extended vibration.

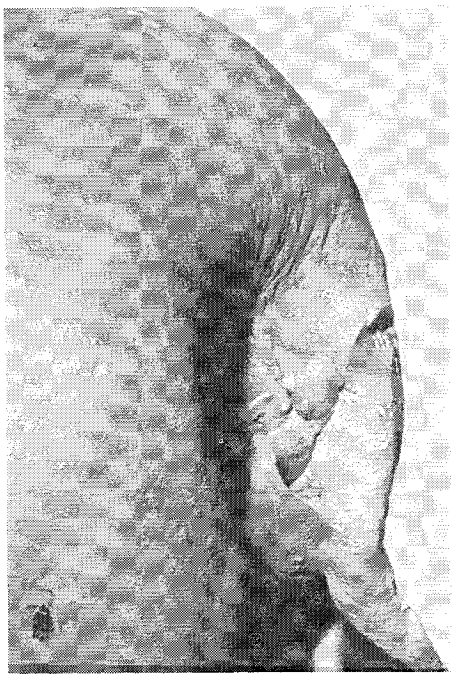

Fig. 2 View of grain end after extended vibration.

Some Basic Considerations

From the evidence presented in the foregoing discussion, it is evident that any failure criteria for solid propellant grains must take into account the effect of previous stress-strain history on the propellant properties. Some exploratory research on the effects of extended dynamic loading on solid propellants has been carried out, such as the experiments briefly described in the foregoing discussion and that reported by Lindsey,[34] who showed the feasibility of using a rotating beam test to obtain S-N fatigue curves for filled elastomers. However, very few definitive data are available. On the other hand, the fatigue of metals is understood reasonably well, and endurance and heat buildup tests have been run on rubber vulcanizates and other high polymers for some time. Additionally, the relation of high polymer structure to mechanical behavior has been described in some detail.[14–17] From such background, one can devise a logical approach to the elucidation of the mechanism of failure of solid propellants when subjected to mechanical cycling. In this discussion, the problems of fatigue or endurance of solid propellants will be discussed from the viewpoint of both internal (molecular) structure and engineering mechanics.

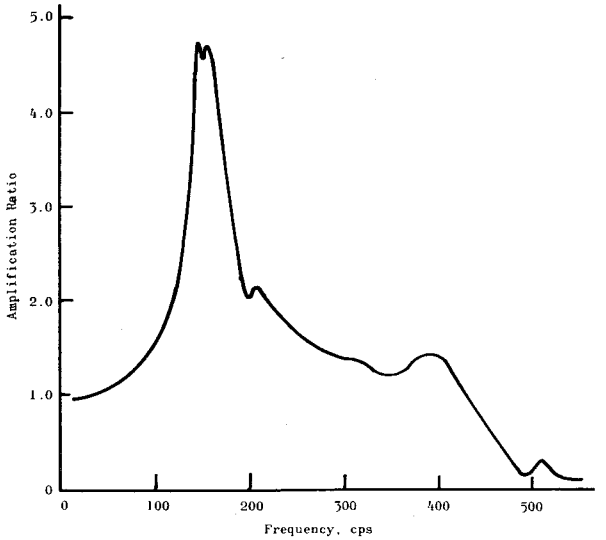

Fig. 3 Typical resonance response curve of a solid propellant grain.

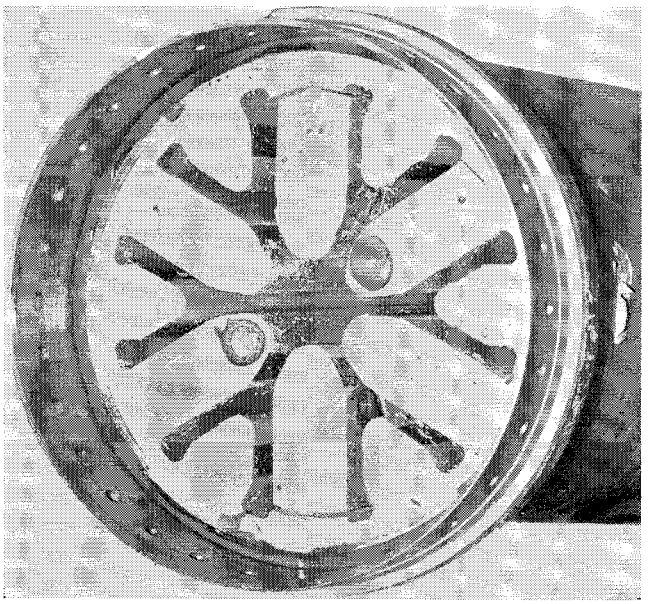

Fig. 4 View of solid propellant grain after extended vibration.

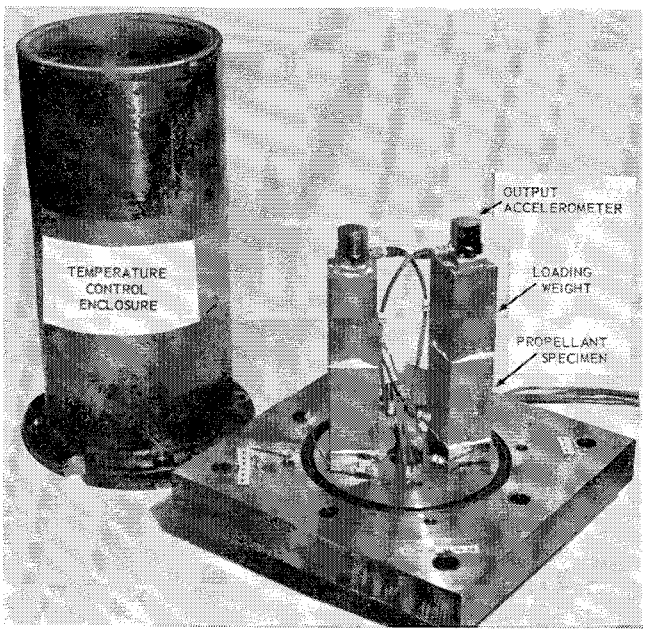

Fig. 5 Apparatus for vibrating solid propellant specimens.

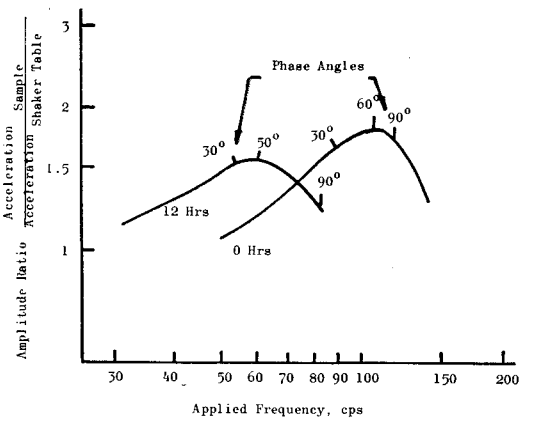

Fig. 6 Effect of vibration on amplitude ratio.

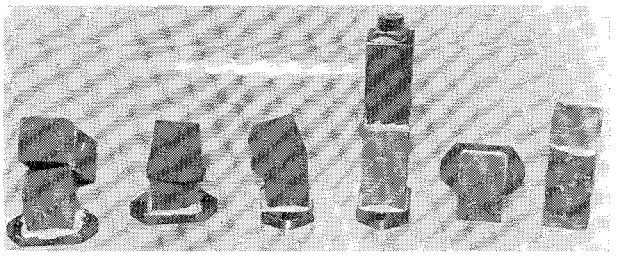

Fig. 7 Representative failures obtained on propellant vibration test.

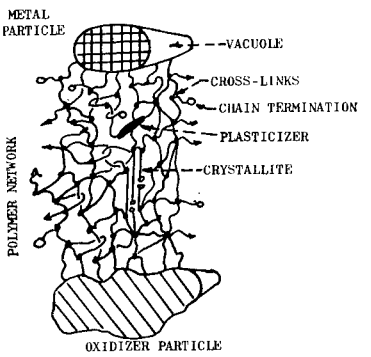

Fig. 8 Schematic representation of a composite propellant internal structure.

Internal Structural Analysis

Study of failure from the viewpoint of internal structure of a solid propellant immediately poses basic questions as to what holds the structure together and as to how this structure may be changed by application of external forces so that observable changes and ultimate deterioration result. Since failure or fracture implies moving a force through a finite distance, energy (bond energies, surface energy, etc.) should be considered rather than either force (stress) or displacement (strain) alone. Most current solid propellants are not homogenous and thus have a fairly complex internal structure, and so it will be convenient to refer to a very much simplified picture, such as shown in Fig. 8, in this discussion.

Referring to this diagram, let us examine the processes that will result in an energy interchange when a piece of solid propellant is extended. These processes include those which occur 1) within the binder polymer, 2) within the crystalline solid components, and 3) at interfaces. When a force is applied which causes a displacement, some of the mechanical energy added to the system will appear as heat (temperature rise), some will result in a change in molecular structure, and some will alter the surface energy at the various interfaces. In this part of the discussion, the latter two processes will be examined.

In the binder polymer, the following processes can become energy sources or sinks: 1) bond interchange, 2) bond scission: crosslink cleavage or chain cleavage, 3) viscous flow or diffusion, 4) formation of crystallites, 5) orientation

of crystallites, and 6) release of distortion of molecules and crystallites.

All of these changes are subject to the laws governing rate processes, and, if the network system could be described with sufficient precision and the various activation energies stated, one would be able to estimate what happens to the internal structure when stress is applied. Unfortunately, this approach is rarely possible. However, the magnitude of the activation energy is indicated (from relaxation data on polysulfide rubbers) by Tobolsky[17] to be about 24 kcal/mol. It is interesting to note that Dillon[18] indicates that a fatigue life-temperature law in the form of $L = c \exp(E/RT)$ is the only one possible for general application to rubber and fibers. The importance of the bond scission mechanism also is indicated by evidence of reaction with chemical agents external to the polymer network in fatigue tests: Gehman[19] showed that the antioxidants and antiozonants frequently improve the fatigue life of rubber vulcanizates before appreciable aging has occurred.

Where the specific mechanism responsible for polymer network behavior under stress cannot be deduced, a thermodynamic phenomenological approach has been found to be useful. A number of investigators have shown that stress-strain phenomena of elastomers may be related to a single function expressing the elastically stored energy per unit volume in terms of the strain variables. Mooney[21] developed an empirical equation in which the stored energy W is written as

$$W = C_1(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) + C_2[(1/\lambda_1^2) + (1/\lambda_2^2) + (1/\lambda_3^2) - 3]$$

where C_1, C_2 are material constants, and λ_i is the extension ratio $(1 + e_i)$ along a principal axis in the i direction.

This relation subsequently has been generalized by Rivlin,[20] who has shown that

$$W = W(I_1, I_2, I_3)$$

where the I's are called strain invariants, defined by

$$I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2$$
$$I_2 = \lambda_1^2 \lambda_2^2 + \lambda_2^2 \lambda_3^2 + \lambda_3^2 \lambda_1^2$$
$$I_3 = \lambda_1^2 \lambda_2^2 \lambda_3^2 = (V/V_0)$$

where V is system volume, and V_0 is unstrained volume.

Treloar[16] discusses a statistical approach that results in expressing the total entropy of deformation for an incompressible system as

$$S = -(NK/2)(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3)$$

where N is the number of chains per unit volume and K is Boltzman's constant, and from which the free energy or work of deformation (assuming no change in internal energy of the system) becomes

$$W = (NKT/2)(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) = (NKT/2)(I_1 - 3)$$

For an incompressible system, the constant C_1 in the Mooney equation corresponds to $\frac{1}{2}NKT$; thus this constant is related to crosslink density.

Work by Bills reported by Wiegand[22] indicates that the following relation is valid for filled polymers, such as solid propellants:

$$I_1 - 3 = M(I_2 - 3)$$

where M is a constant characteristic of the material. Assuming isotropic lateral deformation for uniaxial tensile extension (making $\lambda_3 = \lambda_2$), a simple relation between λ_1 and Poisson's ratio could be predicted from M. Thus it appears that, when changes in a plot of $(I_1 - 3)$ against $(I_2 - 3)$ are observed, one would expect to find irreversible alterations in the internal structure of a propellant, and thus such a plot might be useful in assessing the result of continued cyclic strain application.

It is well known empirically that, where plasticizers are used, they are associated intimately with the binder portion of a propellant and thus will influence the mechanical behavior. The manner in which this influence is exerted is complex and thus difficult to predict exactly, but the ways in which plasticizers will respond when external mechanical energy is added to the system can be considered qualitatively. Many plasticizers are known to be bound tightly as a sol fraction of the polymer network. Accordingly, the crosslink density will be altered, and thus the mechanical properties will be influenced. A plasticizer also can exist as a separate discreet phase. When this occurs, the controlling factors will be the number and size of these liquid particles and their viscosity and interfacial tension or surface energy. When a propellant is subjected to repeated strains, the plasticizer will tend to migrate from the polymer network into a discreet phase and ultimately will work its way to internal and external propellant surfaces. If the plasticizer has a positive partial molal volume of solution, its chemical potential will be decreased in regions of mechanical stress. The resultant potential difference is responsible for the flow of plasticizer, and repeated stress reversals will tend to have a pumping action. Appearance of plasticizer at solid-polymer interfaces will tend to weaken the bonding and thus soften the propellant.

The strength and modulus of crystalline solids in a propellant, such as oxidizer and metal particles, are much greater than the corresponding properties of the polymer network. Thus, such solid fillers usually are considered as unyielding components that influence the mechanical properties of a propellant by their surface interaction with the binder. This probably is not strictly true in the case of ammonium nitrate oxidizer, where the well-known phase changes will tend to affect the morphology of this solid phase when a grain is temperature cycled.

Considering, therefore, the very high loading of crystalline solids, one would expect that the binder-solids interaction will exert a controlling influence on solid propellant mechanical behavior. This interaction should be a particularly important factor in the response of a propellant to cyclic loading. Bills, Sweeny, and Salcedo[23] propose a failure mechanism based on formation of vacuoles around the solid particles when a propellant is extended, resulting from failure of the binder-solid bond or from particle dewetting. Landel[24] points out that the maximum in the stress-strain curve and the upswing observed in creep compliance curves are due largely to this dewetting process. He also indicates that the point at which vacuole formation occurs can be detected, through dilatometric measurements, by determining where Poisson's ratio (defined by logarithmic strains) departs from 0.5. Particle dewetting and formation of vacuoles is indicated similarly by dilatometric data reported by Smith.[25] Additionally, it has been shown that additives that affect the bond can have a significant effect on propellant mechanical properties.

Thus it is evident that, as dynamic loading is sustained, one can expect a continuing change in propellant mechanical properties (a softening) as solid particle dewetting proceeds. It is interesting to speculate at this point whether or not the

Table 2 Reversion of vibration-induced propellant softening

Time after end of vibration, hr	Propellant hardness around periphery of failure spot Shore A at 77°F
24	55 to 60
96	60 to 70
120	60 to 80
430	65 to 80
Original propellant	80

dewetting process might be reversible and thus be one of several processes that will introduce the variable of recovery time in fatigue experiments. It is clear that such reversibility will complicate application of a concept of cumulative damage. Preliminary indications of such reversibility already have been indicated in our work. These have been confirmed by measuring the hardness of the propellant around a vibration-softened spot on the grain shown in Fig. 1. The data in Table 2 were obtained in the laboratory.

A similar indication has been obtained in the laboratory vibration tests of 1 × 1 × 2 in. blocks of propellant previously described. Both continuous and intermittent vibration with recovery periods were applied in this series of experiments. The general trend of the results is shown in Fig. 9. The tendency of the propellant to regain its structure during recovery periods is indicated by the course of the amplitude ratio and resonant frequency curves.

Formation of vacuoles by dewetting of propellant solids will be important also because such defects are sites for the initiation of crack propagation. This consideration suggests a comparison that might be made of the fatigue failure processes of metals, unfilled plastics or rubber, and composite solid propellants. Continued application of stress-strain reversals ultimately results in formation of internal defects and then in crack growth and fracture. Let us consider only that part of the process which results in crack initiation, as shown in Table 3. From such a comparison, the special role played by the dewetting process in composite solid propellants is evident. and, additionally, it will be clear

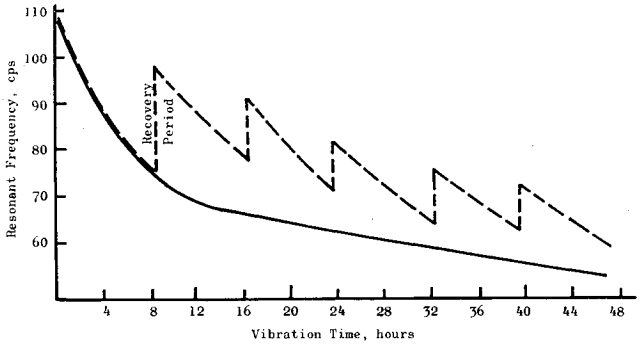

Fig. 9 Generalized results of laboratory vibration tests.

that fatigue failure data and theories applied to metals, plastics, and rubber will be applicable only in part to solid propellants. However, once dewetting has occurred and the number, size, and shape of the defects thus formed are determined, crack propagation will be controlled by the binder matrix. Tear criteria for the matrix such as the stored energy theory proposed by Rivlin and Thomas[26] probably will be useful. This concept is extended further by Williams,[27] with particular attention being given to the effects of strain rate, temperature, and curvature of crack tip on crack acceleration and stable crack propagation. Furthermore, the work of Knauss[28] leads one to hope that a prediction of crack initiation characteristics is imminent. It is worth noting that his initial results permit one to predict fracture in principle for an arbitrary loading or cumulative history, although at the present time the computations are somewhat formidable.

In summary, propellant fatigue, from the viewpoint of internal structure, will be governed by a number of energy-absorbing processes including 1) binder polymer network degradation, 2) plasticizer migration, 3) binder-solids dewetting, and 4) crack propagation in the binder. Presently available knowledge is adequate to do little more than describe these processes qualitatively, and when they occur in combination it is not possible to make even an ad hoc prediction of the response of a solid propellant to sustained dynamic loading from compositional data alone. However, many of the insights from consideration of internal structure, as have just been discussed, will be quite useful in guiding acquisition and interpretation of experimental data. For example, the indicated role of the binder-solid dewetting process suggests that changes in the Poisson's ratio-extension curve and deviations from properties predicted by the Guth-Gold equation (and others) will be useful in determining the mechanism of propellant fatigue failure. Similarly, solvent swell and gel fraction measurements will be useful in determining how much of the change in propellant mechanical properties is the result of changes in polymer network structure.

Table 3 Crock initiating processes

Material	Structural change resulting in defect formation
Metals	Crystal sliding
Plastics, rubber	Polymer degradation, chain scission, etc.
Composite solid propellants	Polymer degradation, polymer-solids dewetting

Engineering Mechanical Analysis

Some of the viscoelastic parameters required for engineering mechanical analysis of solid propellant grain structures can be obtained conveniently by measuring the complex moduli or compliances by dynamic test procedures such as those described by Fitzgerald,[29] Baltrukonis,[30] and Nicholson.[31] As useful as these procedures are, they do not establish failure criteria, nor are the test and methods of data analysis concerned with the behavior of the propellant on sustained dynamic loading.

On the other hand, considerable attention has been given to empirical dynamic fatigue tests for rubber and other high polymers. For example, a test developed by Gehman[19, 32] subjects a specimen of tire rubber to an alternating biaxial strain, and the number of cycles to failure at a fixed applied strain (either 60 or 80%) is determined, but *S-N* fatigue curves are not developed. However, he notes the apparent anomaly that, although the fatigue life of a rubber vulcanizate generally is independent of frequency (as in metals), the characteristic relaxation time at zero strain has a significant effect on results. He also notes that raising the ambient temperature has a much less than proportional effect on the temperature of the test piece because the decrease in hysteresis with increase in ambient temperature tends to offset the direct effect of the change in temperature. Characteristic *S-N* curves are obtained by Roelig[33] from cylindrical rubber test pieces under a constant flexing load. Data are correlated on the basis of an L/D form factor and the total energy input per unit volume of sample according to the relation

$$I/V = \sigma_f^2/2\,E_{\text{eff}}$$

where the energy input I is proportional to the area under the load-deflection curve for the test piece, σ_f is the fatigue strength, and $E_{\text{eff}} = CL/A$ is the effective elastic modulus of the material obtained from the slope of the load-deflection curve C, the length L, and cross section A of the test piece. In a simple elastic situation, this energy correlation relates the applied work to the total strain energy stored in the specimen volume.

Many other fatigue tests have been devised for rubber, fibers, and plastics. However, in a very complete review of such tests and the resultant data, Dillon[18] notes that experimental conditions seldom are chosen which will yield data necessary for a clear understanding of fatigue phenomena. He indicates particularly the need for study of the effects of wide variations in frequency and temperature in elucidating the important fatigue-strain relationship. Additionally, it appears that even the data that are available on high poly-

mers will have limited application in the study of solid propellant fatigue because of the following:

1) Compared with solid propellants, none of the other commercial high polymer systems studied are highly solids loaded. As already indicated, binder-solid interactions are expected to play an important role in the response of solid propellants to sustained cyclic loading.

2) Few data appear to be available on which failure criteria could be based; the complicating factor of recovery time has not been investigated adequately.

3) The cycling frequency spectrum has not been explored fully, particularly at the low end, nor has the validity of time-temperature superposition been explored in fatigue tests.

A beginning has been made as illustrated by the work discussed here and in a report by Lindsey.[34] However, the need for additional study in this area is evident. The nature of and approach required for such research is indicated by the following simplified analysis.

The first premise is that fatigue failure takes place as a result of the degradation of material properties which is accelerated by the tendency for the internal temperature to rise. Consider, therefore, that mechanical cycling of a viscoelastic propellant leads to the input of energy into irreversible microstructural changes, flaw formation, or viscous dissipation. Evidence of such hysteresis loss is the temperature rise observed on cycling resulting from the lag of strain

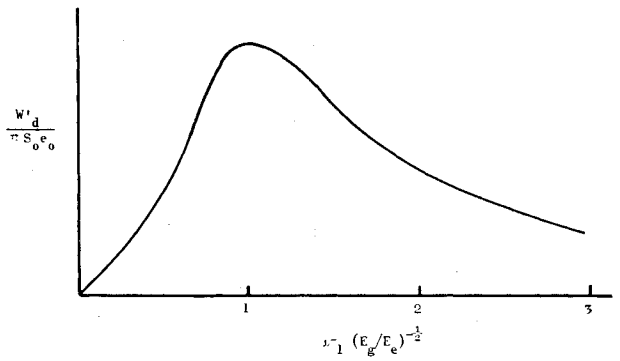

Fig. 10 Work input as a function of frequency.

behind stress. The energy input W_d per unit volume and each cycle can be expressed as follows:

$$W_d = \int S\, de = \int_0^{2\pi} S \frac{de}{d\,(t\omega)}\, d\,(\omega t) \qquad (1)^*$$

$$W_d = \pi S_0\, e_0 \sin\delta \qquad (2)$$

where S_0 is stress amplitude, e_0 strain amplitude, and δ lag angle.

If the viscoelastic compliance K^* is specified through the complex form

$$e = K^* S \qquad (3)$$

where

$$K^* \equiv k' - ik'' \equiv |k^*|\, \exp^{-i\delta} \qquad (4)$$

the sine of the lag angle in Eq. (2) may be expressed such that, alternatively,

$$W_d = \pi S_0\, e_0 \frac{k''}{|K^*|} = \pi S_0\, e_0 \frac{k''}{[(k')^2 + (k'')^2]^{1/2}} \qquad (5)$$

As a particular example, consider a simple three-element model consisting of a spring in series with a Voigt element to represent propellant viscoelastic behavior. With such representation, Eq. (5) becomes

$$\frac{W_d}{\pi S_0\, e_0} = \left[1 + \left(\frac{k_g}{k_1}\right)^2 \left(\omega\tau_1 + \frac{1 + (k_1/k_g)}{\omega\tau_1}\right)^2\right]^{-1/2} \qquad (6)$$

Where k_g ($\equiv 1/E_g$) and k_1 ($\equiv 1/E_1$) are the spring compliances of the model and τ_1 the relaxation time of the viscous element. Noting that the long term rubbery compliance is $k_e = k_1 - k_g$,

$$\frac{W_d}{\pi S_0\, e_0} = \left[1 + \left(\frac{E_e}{E_g - E_e}\right)^2 \left(\omega\tau_1 + \frac{E_g/E_e}{\omega\tau_1}\right)^2\right]^{-1/2} \qquad (7)$$

This equation can be plotted to give a curve with the characteristic shape shown in Fig. 10. The significant thing to note is the maximum energy input at $\omega\tau_1 = (E_g/E_e)^{1/2}$, which one can find by differentiating Eq. (7), at which point

$$W_d \max = \frac{\pi S_0\, e_0}{\{1 + [4(E_g/E_e)/(E_g/E_e - 1)^2]\}^{1/2}} \qquad (8)$$

$$W_d \max \approx \pi S_0\, e_0 \text{ for most rubbery materials}$$

Accordingly, within the quantitative restrictions imposed by a simple three-element model of viscoelastic behavior, one would anticipate the most rapid deterioration in the vicinity of the maximum shown in Fig. 10 if, as indicated by Roelig,[33] the fatigue strength is proportional to the square root of the energy density per cycle. For many rubber binder solid propellants, $\tau_1 \approx 10^{-2}$ sec, and the frequency for maximum energy input will be about 100 cps. It is interesting to note that the propellant deterioration indicated in Figs. 1 and 2 occurred after vibrating the grain at a resonant frequency of about 150 cps.

The effect of temperature clearly is a very important consideration. First, the critical frequency will depend on a shift factor as may be indicated by a plot of $k''T_s/T$ vs ωa_T. One thing that should be established by experiment is whether or not the so-called universal shift factor defined by the *WLF* equation[1, 24] is valid in this case. Second, temperature will influence the various processes leading to degradation of mechanical properties, including the effect of temperature on binder-solid surface energy and on chemical mechanisms such as bond scission. Third, the temperature rise resulting from the heat produced can be sufficient to affect directly mechanical properties to the point where the applied stress will be high enough to cause distortion or flow and ultimate failure. The magnitude of the temperature rise per cycle $\Delta T'$ can be estimated from the following:

$$\Delta T' = W_d/C_p \qquad (8a)$$

In usual engineering units (that is, where W_d is in inch-pounds per cubic inch and temperature in degrees Fahrenheit), one obtains the following for a typical propellant:

$$\Delta T' = 7 \times 10^{-3}\, W_d \qquad (8b)$$

With a loss modulus (E'') of 1500 psi and e_0 of 10%, a temperature rise of about 0.03°F/cycle is indicated. Under adiabatic conditions, it is evident that a propellant quickly would reach a temperature where failure would result. In the usual case, heat flow from the propellant will result in a much lower equilibrium temperature. For example, in the apparatus shown in Fig. 5, a sample surface equilibrium temperature of 260°F has been measured when the ambient temperature was 200°F, frequency was 115 cps, and e_0 was 1%. The combined effects of temperature thus appear to be quite complex; it would be fortuitous if the fatigue life-temperature relation for solid propellants would be as simple as the Arrhenius law proposed by Dillon[18] for high polymers.

In this discussion, it already has been pointed out that, for solid propellants, the influence of recovery time must be taken into account and the effect of partial reversibility of structural degradation would influence the ways which a ni con-

* See the Appendix for a discussion of the simplifying assumptions made.

cept of cumulative damage might be applied. Although this effect eventually might be treated by extending the cumulative damage concept for viscoelastic materials suggested by Williams[1] in conjunction with its more usual, Miner[11] form as applied to the fatigue of metals, the development of such a theory only can be suggested in this discussion.

Assuming no recovery, Eq. (2) can be written for N cycles:

$$W_N = N\pi S_0 e_0 \sin\delta(\omega) \tag{9}$$

or, since $e_0 = S_0/E_{\text{eff}}$ and $N_f = \omega t_f/2\pi$,

$$W_f = \omega t_f(S_0^2/2E_{\text{eff}}) \sin\delta(\omega) \tag{10}$$

where the f subscript denotes quantities at the point of fatigue failure (t_f is time to failure at a given value of S_0). One can assume that a first-order rate process controls recovery of internal damage so that

$$x = 1 - \exp(-t_R/\tau_R) \tag{11}$$

Where x represents the fraction of damage recovered, t_R is recovery time, and τ_R is a characteristic time of the recovery reaction; t_R should be understood as comprising both the part of t_f during which recovery takes place and a rest time t_r, which is determined upon how often and how long the cyclic process is interrupted; thus

$$t_R = f(t_f) + t_r \tag{12}$$

Correcting W_f for the energy involved in the recovery of internal damage, one obtains

$$W_f^* = W_f - W_R \tag{13}$$

but, from Eq. (11),

$$W_R = \gamma W_f x = \gamma W_f[1 - \exp(-t_R/\tau_R)] \tag{14}$$

where γ is the proportion of damage recoverable

$$W_f^* = \omega t_f(S_0^2/2E_{\text{eff}}) \sin\delta(\omega)\{1 - \gamma[1 - \exp(-t_R/\tau_R)]\} \tag{15}$$

or

$$S_0 = \left\{\frac{2E_{\text{eff}} W_f^*}{\omega t_f \sin\delta(\omega)\{1 - \gamma[1 - \exp(-t_R/\tau_R)]\}}\right\}^{1/2} \tag{16}$$

and

$$t_f = \frac{2E_{\text{eff}} W_f^*}{S_0^2\omega \sin\delta(\omega)\{1 - \gamma[1 - \exp(-t_R/\tau_R)]\}} \tag{17}$$

Equation (17) illustrates the increased time to failure t_f at a constant stress amplitude as the recovery time increases. Note also that, if t_R is zero, S_0 is proportional to $t_f^{-1/2}$ and thus to $N^{-1/2}$, which is qualitatively the shape of the usual S-N metal fatigue curve.

The foregoing brief consideration of the response of solid propellants to extended cyclic loading, from the viewpoint of engineering mechanics, has indicated in a general way 1) how deterioration of mechanical properties will be strongly dependent upon the energy input per cycle, which in turn depends upon the frequency, the viscoelastic parameters, the stress amplitude, and the strain amplitude, 2) the manner in which temperature will influence the process, and 3) how the effect of the recovery time variable may be handled. The results of preliminary experiments have indicated that most of the basic premises are correct, but it is evident that considerably more research will be needed before a failure analysis of a solid propellant grain in a cyclic stress environment can be made.

Conclusion

Although fatigue failure of solid propellant grains is not a common occurrence, the importance of developing failure criteria and methods of analysis for such structures under extended dynamic loading has been indicated. Additionally, it is evident that an endurance limit, analogous to fatigue strength of metals and other materials, is a significant mechanical property of solid propellants. However, the knowledge of cyclic mechanical effects in solid propellant grain structures is rather primitive at the present time. Nevertheless, the path that pertinent research should take can be indicated clearly at this point. In conclusion, therefore, the following areas appear to be of primary importance:

1) Identify the mechanisms or internal processes that cause solid propellant mechanical properties to change and cause ultimate failure in extended cyclic loading.

2) Identify the important variables involved in the foregoing processes, and determine their relative importance and interrelationships.

3) Measure the critical propellant (material) properties that best reflect the fatigue characteristics.

4) Establish realistic design criteria and specifications leading to a rational failure analysis scheme for solid propellant grains subjected to sustained dynamic loads.

In pursuing these objectives, extended dynamic loading tests should be conducted on representative propellants, unfilled polymers, and polymers filled with "idealized" solids such as glass beads. The stress field imposed is an important consideration. In actual practice, it often is multiaxial and quite complex. However, at this time much can be learned from experiments carried out under simple uniaxial stress. Such testing must be planned so that the independent effects of the principal variables can be determined, particularly the following: 1) cyclic frequency, both fixed and programmed, 2) temperature of both the specimen and environment, 3) stress and strain amplitude, 4) recovery time, and 5) environment: principally chemical composition of gas around sample and humidity.

Curves indicating the change in properties with the number of cycles are essential; an endurance endpoint can be defined as either ultimate failure, a given amount of "permanent" distortion of the sample dimensions, or a specified amount of change in a property or combination of properties. The properties to be measured should be selected to identify the type and measure the extent of internal structural damage as well as to measure change in the mechanical capability of the propellant. The following measurements, not all of which are peculiar to dynamic analysis, are expected to be definitive for this purpose: 1) complex dynamic modulus, 2) creep modulus, 3) relaxation modulus and equilibrium stress, 4) shape and endpoints of the stress-strain curve, at various temperatures and rates of strain, 5) hardness, 6) specific volume change vs extension ratio, 7) energy for tear propagation, 8) solvent swell, and 9) gel fraction.

It is evident that some ingenuity and effort will be required to make the indicated measurements. For example, both destructive and nondestructive determinations are indicated; these must be combined judiciously in any test plan. It also is clear that a critical evaluation of failure criteria will require endurance tests with programmed combined frequencies and stress (or strain) amplitudes. Some of the specific objectives and methods of analyzing such data have been indicated in the foregoing discussion; others should evolve as research in this area proceeds.

Appendix

Equations (1–17) represent a simplified analysis that assumes that neither S_0 nor e_0 is a function of ωt. It applies qualitatively to the specimens shown in Fig. 7 but neglects acceleration and body force terms in the equations of axial equilibrium such that the internal strain is identical with the applied strain. For some purposes, it will be desirable to consider the effects of acceleration, in which case an analysis developed by Williams[35] can be applied.

In this analysis, the governing equation is

$$\partial^2 u/\partial x^2 = [1/(E/\rho)](\partial^2 u/\partial t^2) \quad \text{(A1)}$$

which is recognized as the equation for the propagation of a wave through an elastic material; E/ρ is the square of the one-dimensional speed of sound in the material: $C_0^2 = E/\rho$.

This equation is Laplace transformed for zero initial conditions to give

$$\partial^2 \bar{u}/\partial x^2 = \{1/[E(p)/\rho]\} p^2 \bar{u} \quad \text{(A2)}$$

where

$$\gamma = \frac{\rho' l'}{\rho l} = \frac{\text{weight of end mass}}{\text{weight of viscoelastic bar}}$$

and condition at forced end is

$$\bar{u}(o, p) = u_0 \left[\frac{\omega^2}{p(p^2 + \omega^2)} \right]$$

and $K^2(p) = p^2/[E(p)/\rho]$. The transformed solution of Eq. (A2) can be shown to be

$$\bar{u}(x, p) = \frac{u_0 \omega^2}{p(p^2 + \omega^2)} \left\{ \cosh[K(p)x] - \frac{\sinh Kl + Kl \cosh Kl}{\cosh Kl + Kl \sinh Kl} \sinh[K(p)x] \right\} \quad \text{(A3)}$$

The inverse transform will give the physical displacement

$$u = u(x, t; u_0, \omega) \quad \text{(A4)}$$

Similarly, the transformed strain can be shown to be

$$\bar{\epsilon}_x(x, p) = \frac{\partial \bar{u}(x,p)}{\partial x} = \frac{u_0 \omega^2}{p(p^2 + \omega^2)} \left\{ K(p) \left[\sinh Kx - \frac{\sinh Kl + Kl \cosh Kl}{\cosh Kl + Kl \sinh Kl} \cosh Kx \right] \right\} \quad \text{(A5)}$$

The method for inversion of these transforms is indicated in Ref. 35 for both the elastic situation where E = const and for the viscoelastic case where $E = E(p)$. The solution will vary, depending on the value of γ, which in the limit is zero for no added end mass and infinity for a rigid end support when the end of the bar is clamped. The stress may be found in various ways, depending upon the kind of material property data available.

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