NOTES

Mechanism of the Oxidative Degradation of Binder During the Aging of Composite Solid Propellant

Composite solid propellant contains a polymeric binder and an inorganic oxidant. It has been established that the propellant undergoes aging during storage. Normally, propellant is stored in air, which results in oxidative degradation of the binder. The oxidative attack on the binder is due to (1) the interaction between the binder and the oxidizing species generated from oxidizer decomposition or (2) air oxidation of the binder. The present note is aimed to clarify the above problem.

The inhibitor- (hydroquinone) free styrene monomer was fractionally distilled by using a long fractionating column at reduced pressure (~10 mm) to get pure styrene. A given amount of pure styrene with 1% (by weight) of benzoyl peroxide was placed in a flask fitted with a condenser and placed in a thermostat maintained at 50°C. After 12 hr, the condenser was removed, and a mechanical stirrer was used to obtain a homogeneous viscous prepolymer of the desired viscosity for propellant processing. The prepolymer was mixed at low speed with freshly sieved oxidizer in a stainless-steel beaker. The dough was then poured into soft-glass test-tubes. These test-tubes were kept at room temperature for 24 hr, and cured in an incubator maintained at 50°C for 15 days. After 1 week, the bottom portion of the test-tubes was broken, and the test-tubes were then cracked at several points to allow homogeneous curing of the strands. Finally, after 15 days the test tubes

TABLE I
Comparison of Percent Change in Weight-Loss and Burning Rate for PS/AP (75%) Propellant During Aging[a]

Storage temperature, °C	Storage time, hr	Weight-loss, %	Change in $\dot{r}$, %
150	24	0.420	7.50
	48	0.500	17.50
	72	0.640	27.50
	96	0.740	41.00
	120	0.750	48.00
120	48	0.320	6.00
	96	0.350	12.60
	144	0.370	18.50
	192	0.390	25.00
	240	0.420	31.50
100	48	0.260	2.00
	96	0.270	3.50
	144	0.280	5.00
	192	0.285	6.50
	240	0.350	8.00
63	360	0.44	5.50
	480	0.50	7.00
	600	0.54	9.25
	960	0.58	14.85

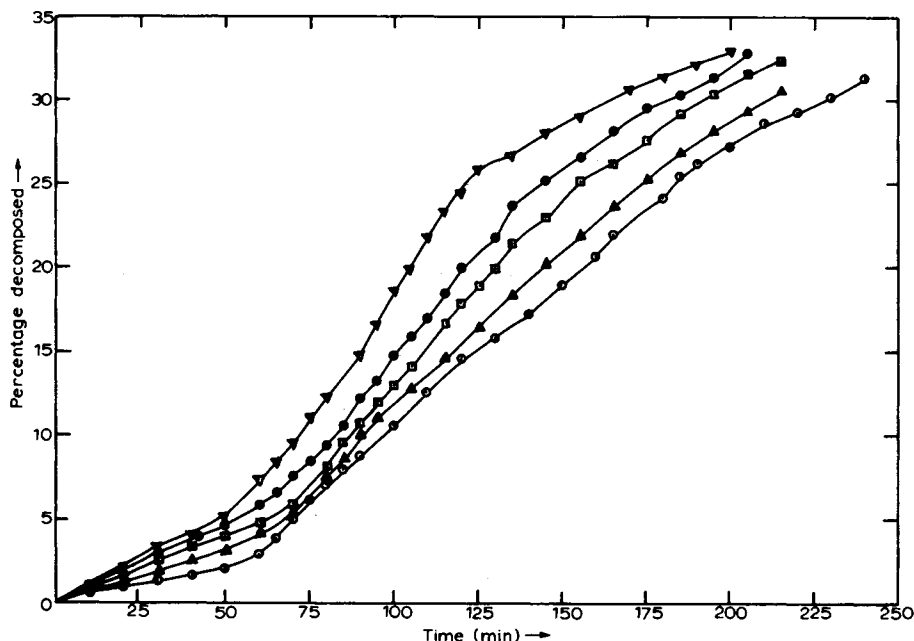[a] AP particle size, 172–204 μm.

Fig. 1. Percent decomposition vs time plot at 230°C for PS/AP (75%) propellant aged in air at 100°C for different storage times: unaged propellant (⊙), 5 days (▲), 10 days (□), 15 days (●), and 20 days (▽).

were completely broken to get cured propellant strands. The method of aging, determination of propellant burning rate ($\dot{r}$), and thermal decomposition (TD) studies have been described in our recent papers.[1,2]

Two sets of experiments were carried out. In the first set, polystyrene (PS) ammonium perchlorate (AP) propellants were aged at 100°C in vacuum, air, and nitrogen atmospheres. The aged propellants were removed, cooled in desiccator, and then $\dot{r}$ and TD were determined. We have recently established[2,3] from detailed aging studies in the storage temperature range of 63–150°C that slow decomposition of the propellant was responsible for increased in $\dot{r}$ during the course of aging. To investigate the role of the porosity of the propellant in increasing the $\dot{r}$ during aging, measurements

TABLE II
TD Data for the PS/AP (75%) Propellants Aged at 100°C in Air, Vacuum, and Nitrogen[a]

Atmosphere	Storage time, days	TD rate, min^{-1} × 10^{-3} (25% decomposition)	ΔTD rate, × 10^{-3}	Change in TD rate, %
Air	Unaged	5.43	0.00	0.00
	5	5.75	0.32(+)	5.89
	10	6.49	1.06(+)	19.52
	15	6.94	1.51(+)	27.81
	20	8.13	2.70(+)	49.72
Vacuum	5	5.68	0.25(+)	4.60
(20 mm)	10	6.33	0.90(+)	16.57
	15	6.80	1.37(+)	25.23
	20	8.00	2.57(+)	47.33
Nitrogen	5	5.71	0.27(+)	4.96
(1 l/min)	10	6.37	0.93(+)	17.09
	15	6.90	1.46(+)	26.84
	20	8.00	2.56(+)	47.06

[a] TD temperature, 230°C; AP particle size, 53–105 μm.

TABLE III
Burning Rate Data for the PS/AP (75%) Propellants Aged at 100°C in Air, Vacuum, and Nitrogen[a]

Atmosphere	Storage time, days	$\dot{r}$ (cm/sec)	Change in $\dot{r}$	Change in $\dot{r}$, %
Air	Unaged	0.088	0.000	0.00
	5	0.095	0.007(+)	7.96
	10	0.100	0.012(+)	13.64
	15	0.105	0.017(+)	19.32
	20	0.109	0.021(+)	23.86
Vacuum	5	0.094	0.006(+)	6.82
(20 mm)	10	0.099	0.011(+)	12.50
	15	0.103	0.015(+)	17.05
	20	0.106	0.018(+)	20.46
Nitrogen	5	0.094	0.006(+)	6.82
(1 l/min)	10	0.099	0.011(+)	12.50
	15	0.104	0.016(+)	18.20
	20	0.107	0.019(+)	21.60

[a] Error in $\dot{r}$ = 2–4%; AP particle size, 53–105 μm; room temperature, 26 ± 1°C.

on weight-loss and density changes were carried out as a function of storage time and temperature (Table I). Table I shows a comparison of the percent change of weight-loss (which in fact is proportional to the change in porosity) and the percent change in $\dot{r}$. It may be seen that the percent change in weight-loss, and hence in porosity, is almost negligible when compared to the extent of change in $\dot{r}$; hence porosity has very little effect on the change in $\dot{r}$ during the course of aging.

TD studies of the aged and unaged propellants were carried out at 230°C (Fig. 1). At this stage, it is relevant to define two types of TD behavior encountered in the present note. First there is TD
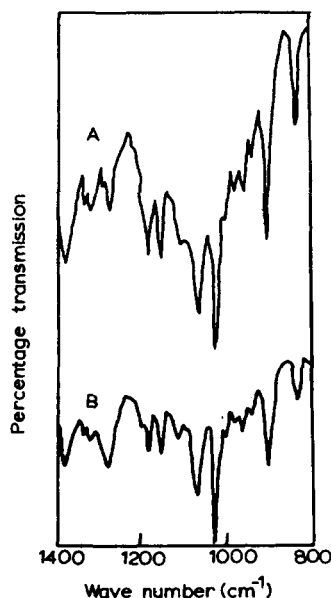

Fig. 2. The ir spectra of the binder films of the PS/AP and PS/NaCl (control) propellants aged in air at 100°C: A, separated binder from aged PS/AP; B, separated binder from aged PS/NaCL.
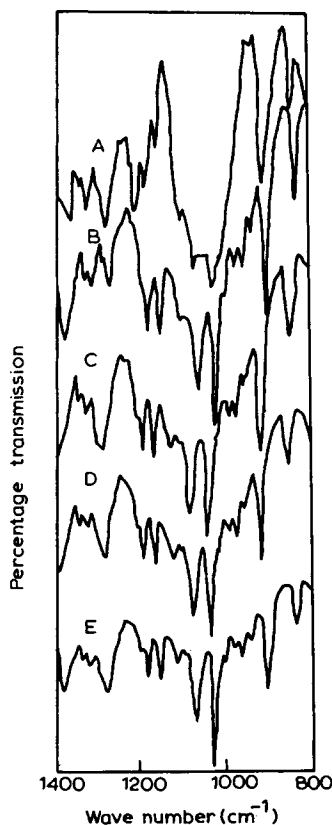
Fig. 3. The ir spectra of the binder films of the PS/AP (70%) propellant aged in air at 100°C in the range 800–1400 cm^{-1}: A, poly(styrene peroxide); B, separated binder from propellant aged 20 days; C, binder from propellant aged 15 days; D, binder from propellant aged 10 days; and E, binder from propellant aged 5 days.

caused by the aging process (Table I). The second type of TD is the technique (TG studies) employed to study the decomposition behavior of the aged and unaged propellants at 230°C. Average TD rates were calculated for 25% decomposition from plots of percent decomposition versus time. There is very little difference in the aging characteristics in vacuum, air, and nitrogen atmospheres (Table II). The contribution of air oxidation is almost negligible, and the cause of aging is the decomposition of AP, which subsequently attacks the binder. The same trend is also observed for changes in burning rate (Table III).

Two types of propellants were aged under similar conditions. The propellants were PS/AP and PS/NaCl (control). After storing at 100°C for about 25 days, it was observed that the sample containing AP turned yellow homogeneously throughout the bulk of the material, while the sample containing NaCl resembled that of the unaged propellant. The NaCl sample developed a slight yellow coloration only on a very thin outer layer exposed to air, while the color of the bulk remained unchanged. The slight yellow color on the surface may have been due to air oxidation.

The bulk portions from the aged PS/AP and PS/NaCl (control) propellants were removed and subjected to chemical analysis in the following manner. Benzene was used to extract the binder portion from the propellant, which was subsequently evaporated to yield the binder. A thin film of the binder of known weight and size was made by drying the benzene solution over mercury contained in a stainless-steel vessel. Infrared spectra of binder film were taken on a Carl-Zeiss UR-10 spectrometer (Fig. 2). The presence of a broad, intense peroxy band[4,5] in the binder of the aged PS/AP propellant could be seen in the range of 1000–1200 cm^{-1}. This is absent in the corresponding PS/NaCl (control) propellant. Figure 3 shows the ir spectra of the binder portion of propellants aged for different storage times. The intensity of the peroxide band increases with the storage time.

These two experiments clearly indicate that air oxidation is not related to the aging of the propellant. Therefore, the storage of the propellant in vacuum, air, and nitrogen atmospheres have similar effects on the aging characteristics of the propellant.

It is now established that the oxygen for the oxidative attack on the binder comes from AP decomposition. One may argue that the AP does not decompose significantly at temperatures below 200°C. The following facts support that AP decomposition does occur at low temperatures: (1) Mass spectrometric studies by Hackmann et al.[6] have shown that AP decomposes at temperatures as low as 80°C. Similarly, Heath and Majer[7] reported the formation of oxygen as a product during the decomposition of AP at 110°C. (2) Oxidizers such as AP and $KClO_4$, decompose below the normal range of decomposition temperature in the presence of various carbonaceous fuels.[8]

References

1. G. Prasad, K. Kishore, and V. R. Pai Verneker, *Proceedings of Fourth National Conference on I.C. Engines and Combustion, Faculty of Mechanical Engineering, College of Engineering, Guindy, Madras, India, Dec. 9–11*, Vol. 2, (1977), C4-7 to 14.

2. K. Kishore, V. R. Pai Verneker, and G. Prasad, *Fuel,* **56,** 292 (1977).

3. V. R. Pai Verneker, K. Kishore, and G. Prasad, *AIAA J.,* **14,** 1330 (1976).

4. A. A. Miller and F. R. Mayo, *J. Am. Chem. Soc.,* **78,** 1017 (1956).

5. K. Kishore, V. R. Pai Verneker, B. K. Chaturvedi, and V. Gayathri, *AIAA J.,* **15,** 114–115 (1977).

6. E. Ellsworth Hackmann, III, Henery H. Hessor, and Harold C. Beachell, *J. Phys. Chem.* **76,** 3545 (1972).

7. G. A. Heath and R. J. Mejer, *Trans. Faraday Soc.,* **60,** 1783 (1964).

8. M. M. Markowitz and D. A. Boryta, *J. Phys. Chem.,* **69,** 1122 (1965).

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