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Storage of Solid Propellants in a Dry Environment

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ABSTRACT

Storage of solid propellants in either a dry or a vacuum environment causes a significantly greater increase in the propellants' modulus and maximum tensile strength than does ambient storage. It is postulated that these physical property changes can be attributed to the effect trace amounts of moisture has on the bond between the propellants' binder and oxidizer.

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I. INTRODUCTION

Future long duration space missions will use high performance solid propellant rocket motors. On these missions, the solid propellant on board may be exposed to space vacuum for long periods, up to two or three years. To date, solid propellant motors have not been used in this application.

Based on data obtained in vacuum and in dry storage test programs, it is anticipated that solid propellants exposed to space for long periods of time will undergo significantly greater physical property changes than they would during a comparable ambient Earth storage period. Short term, 32 day, vacuum storage tests caused a propellant's modulus to increase significantly, whereas that of parallel samples stored under ambient conditions changed negligibly (Reference 1). Additional tests under dry storage, <100 ppm water, indicate similar results. In either case, vacuum or dry, returning the samples to the ambient environment caused the physical property changes, which had occurred during the vacuum or dry storage, to decrease.

The test program described herein has an ultimate goal of determining the extent of physical property changes which will result from extended (two years or more) space exposure, with a primary emphasis on determining the effects of space vacuum. The data indicate that the loss of trace amounts of residual moisture from cured propellant is the apparent cause of the observed propellant property changes. Therefore, initial screening tests were carried out under dry storage conditions. Upon completion of the dry storage tests, it is planned to propose an experiment to expose appropriate propellant samples to an actual space environment using the Long Duration Exposure Facility (LDEF) (Reference 2), which will be launched by the Shuttle. In this experiment, propellant samples will be exposed to space, then returned to Earth in a sealed canister for physical property testing without exposure to the ambient environment.

II. EXPERIMENTAL APPROACH

Four propellants were prepared and subsequently tested under both dry and ambient storage conditions. The propellant formulations are given in Table I. Propellant #1 is the same as that used in Reference 1, and was included to provide a comparison. Propellant #2 is similar to that which will be used in the Shuttle solid propellant booster motors. Propellant #3 is a candidate heat sterilizable propellant, the type which will be required on missions within our solar system when the spacecraft will contact another planet. To simulate the expected propellant treatment for missions requiring sterilization, all samples of this propellant were put through the current Viking sterilization requirement, which is one 40 and two 25 hour exposures at 113°C. Propellant #4 is typical of the type which may be used on deep space missions which will not require sterilization.

All testing was done on standard JANNAF tensile bars which were machined to size prior to exposure to their test environment. All propellant testing was carried out within its storage environment. This in situ testing is necessary to prevent reduction of any changes, which occurred during storage, by re-exposure to the ambient environment. To accomplish this, the dry storage tests were carried out in a 3 x 3 x 3m dry room. Within the dry room a remote controlled table model Instron was mounted above a carousel which could be rotated. The carousel held 42 JANNAF bars plus calibrating weights. From outside the dry room the carousel was rotated to the proper position for testing the desired sample or for calibrating the Instron. Periodically, once every four to six months, a technician would have to enter the dry room to remove broken samples from the carousel and replace them with samples being stored on a table within the room. This operation took 50 to 60 minutes, during which time the moisture content of the air in the room would rise to 1000 to 1500 ppm. Recovery time was fast; within an hour the room moisture content would be back to its normal operating level, between 50 and 100 ppm of water. Throughout the test program the dry room temperature was maintained between 22 and 24°C. The ambient storage samples were stored in a temperature controlled oven at 22 to 24°C, the relative humidity was maintained between 20 and 40 percent. All samples were tested at a strain rate of 5.08 centimeters/minute (two inches/minute).

III. RESULTS AND DISCUSSION

Previous work indicated that the modulus of a PBAA-MAPO propellant increased significantly while stored under vacuum, and to a lesser degree while stored under dry nitrogen; while parallel tests indicated no change occurred in samples stored at ambient (Reference 1). After 32 days storage, the modulus changes were as follows: vacuum storage, 1240 N/cm^2 to 2070 N/cm^2 (1800 to 3000 psi); dry nitrogen storage (∿2000 ppm water), 1240 N/cm^2 to 1380 N/cm^2 (1800 to 2000 psi). Furthermore, when the vacuum or dry storage samples were returned to ambient, much of the modulus increase was eliminated after only 24 hours. It is readily apparent that the only component which could likely cause this phenomenon is water. Minute traces of moisture within the propellant would be caused to outgas by either a vacuum or a dry storage environment. Greenwood (Reference 1) and Evans (Reference 3) also reached this conclusion. They state "Since water was the major outgassed product, the observed increase in maximum tensile strength with vacuum time was attributed to the evaporation of water from the propellant sample. The proposed reason for the increase in tensile strength with vacuum time was an increase in binder-oxidizer (filler) bond strength due to this evaporation of water." This was additionally supported by the fact that the crosslink density was found to be essentially constant throughout the vacuum exposure.

Based on these findings, a storage test of longer duration (two years) in a dry environment (100 ppm water), as a screening test for propellants which would later be tested in an actual space environment, was initiated. Physical property data obtained during the 140 week storage period of that test are given in Figures 1 to 12 (modulus, Figures 1 to 4; maximum tensile strength, Figures 5 to 8; and, strain at maximum stress, Figures 9 to 12). Several observations can be made from the data. First, the modulus of the samples stored in the dry environment always increased significantly. However in only two of the cases is there a significant difference between the dry and ambient storage samples. Propellant #1, PBAA-MAPO binder, the dry storage modulus increased by 80 percent, the ambient by 35 percent. Propellant #3, saturated HTPB binder, the dry storage modulus increased by 100 percent, the ambient by 25 percent. Propellant #2, PBAN binder, and #4, HTPB binder each showed similar modulus increases, about 50 percent, but there were no discernable differences between the modulus increase in the dry or ambient storage conditions.

The maximum stress data present a slightly different result. Again, in all four propellants the maximum stress increases as a result of dry storage. However, in each case the increase is significantly, or at least measurably greater after dry storage than it was after ambient storage. As with the modulus changes, propellant #1, PBAA-MAPO binder, showed the greatest increase, 80 percent, while the ambient samples did not change at all. Propellant #3, saturated HTPB binder, the maximum stress increased by 40 percent after dry storage, a 5 percent increase occurred during ambient storage. Propellants #2, PBAN binder, and #4, HTPB binder, which showed no discernable difference in modulus value as a function of storage type, each have a distinctly greater increase in maximum tensile strength as a result of dry storage than as a result of ambient storage. In propellant #2, the tensile strength increased by 40 percent during dry storage, by 20 percent during ambient storage. In propellant #4, the tensile strength increased by 25 percent during dry storage, no increase (actually a slight decrease) during ambient storage.

When the storage time reached 83 to 86 weeks (∿1-1/2 years) the maximum tensile strength and the strain at maximum stress, of the ambient storage samples, began to drop in three of the four propellants. Only the propellant with the saturated HTPB binder did not. None of the samples stored in the dry environment show this trend. The only significant difference in the storage conditions of the two sets of propellants is the moisture content of the air. In each case the air around the samples was continually being changed, and the storage temperatures were nearly the same. These data suggest that moisture plays a significant role in the aging process of solid propellants, even when it is controlled between 20 and 40 percent relative humidity. In addition, the absence of physical property change in the propellant with the saturated HTPB binder suggests that the property changes caused by longer term ambient aging are not associated with the binder-oxidizer bond, as it is believed that the initial changes associated with dry or vacuum storage are, but instead with chemical changes to the binder, possibly at the unsaturation points. Unfortunately, no chemical tests, such as measuring the crosslink density, were made on either the dry or the ambient storage samples.

In addition to the measured physical property changes, it was observed that significant color changes took place in the ambient storage samples, except propellant #3, saturated HTPB binder. The dry storage samples did not undergo any noticeable color changes. The greatest color change was with propellant #1, PBAA-MAPO binder; a lesser change occurred in propellant #2, PBAN binder; and only a slight change was noticed on propellant #4, HTPB binder.

Weight loss measurements were obtained on propellant #3, saturated HTPB binder, in the dry room. A machined JANNAF bar was placed on an automatic recording analytical balance and the weight followed for 100 hours. The total weight loss was 0.003 percent. Greenwood (Reference 1) measured the weight loss on a PBAA-MAPO propellant tensile bar and found that it lost 0.14 percent after 400 hours at 10^{-7} torr. These data indicate that the magnitude of moisture lost during storage in a dry or vacuum environment is quite small, in fact, almost insignificant.

After completion of the dry storage period, several samples of each propellant type were removed from the dry storage, re-exposed to ambient, and the properties periodically measured out to 144 hours. The maximum tensile strength data from these tests are plotted in Figures 13 to 16. In each case the tensile strength dropped from its final dry storage value to a value near its original as-cast value.

In Table II the values of modulus, maximum tensile strength and strain at maximum stress are tabulated for each of the four propellants for three time points, initial (after cure), at the end of dry storage (140 or 143 weeks), and after re-exposure to ambient for 144 hours. As previously shown in Figures 13 to 16 the greatest changes occur in the maximum tensile strength. Re-exposure to ambient shows a slight trend to reduce the modulus in all four propellants, but the decreases are not considered significant (almost within the scatter of the data), except for propellant #3, where the decrease is 22 percent. The strain at maximum stress changes very little during dry storage on propellants 1 and 2, however, re-exposure to ambient causes the strain value to decrease by 32 and 24 percent, respectively. Propellants #3 and #4 show essentially no change in strain value as a result of re-exposure to ambient after dry storage.

IV. PLANNED FUTURE WORK

It is planned to expand this testing with an emphasis on understanding which binder parameters significantly affect the magnitude of the observed physical property changes. This may lead to propellants in which propellants' physical property changes that result from dry storage or vacuum exposure can be minimized. This will then be followed by exposure of the most likely candidate propellants, for use in lengthy space missions, to space conditions. It is planned to use the Long Duration Exposure Facility (LDEF) which will be launched by the Shuttle for this purpose. In this experiment selected propellants will be placed in a near Earth orbit for several months. At the completion of space exposure the samples will be sealed in a canister (while still in space) and returned to Earth where they will be tested without re-exposure to the ambient environment.

V. CONCLUSIONS

The variation in the results obtained with the different propellants is probably a function of the effect trace amounts of moisture has on the role the different binders play in the bond mechanism of the binder to the oxidizer. The following specific conclusions can be drawn from this work.

A. Exposure of solid propellants to vacuum or very dry (<100 ppm water) environments for extended periods can significantly affect their physical properties.

B. The loss of trace amounts of moisture from propellants containing PBAA-MAPO or a saturated HTPB binder will significantly increase both the propellant's modulus and its maximum tensile strength.

C. Dry storage had no discernable effect on the modulus of propellants containing PBAN or HTPB binders, yet it measurably increased the maximum tensile strength of each above that of ambient stored samples.

D. Dry storage eliminates the tensile strength losses observed during ambient storage of PBAA-MAPO, PBAN, and HTPB binder propellants for significantly longer storage periods (>143 weeks, the duration of the test).

REFERENCES

1. Greenwood, L. R., "The Effect of Vacuum on the Mechanical Properties of a Solid Rocket Propellant During Space Storage," Virginia Polytechnic Institute, Ph.D. Thesis, May, 1967.

2. "Long Duration Exposure Facility (LDEF) - Guide for Experiment Accomodations," LDEF-101, NASA, December 1975.

3. Evans, M. L., "Investigation of Vacuum Effects on the Mechanical Properties of Composite Materials," Virginia Polytechnic Institute, Ph.D. Thesis, July 1972.

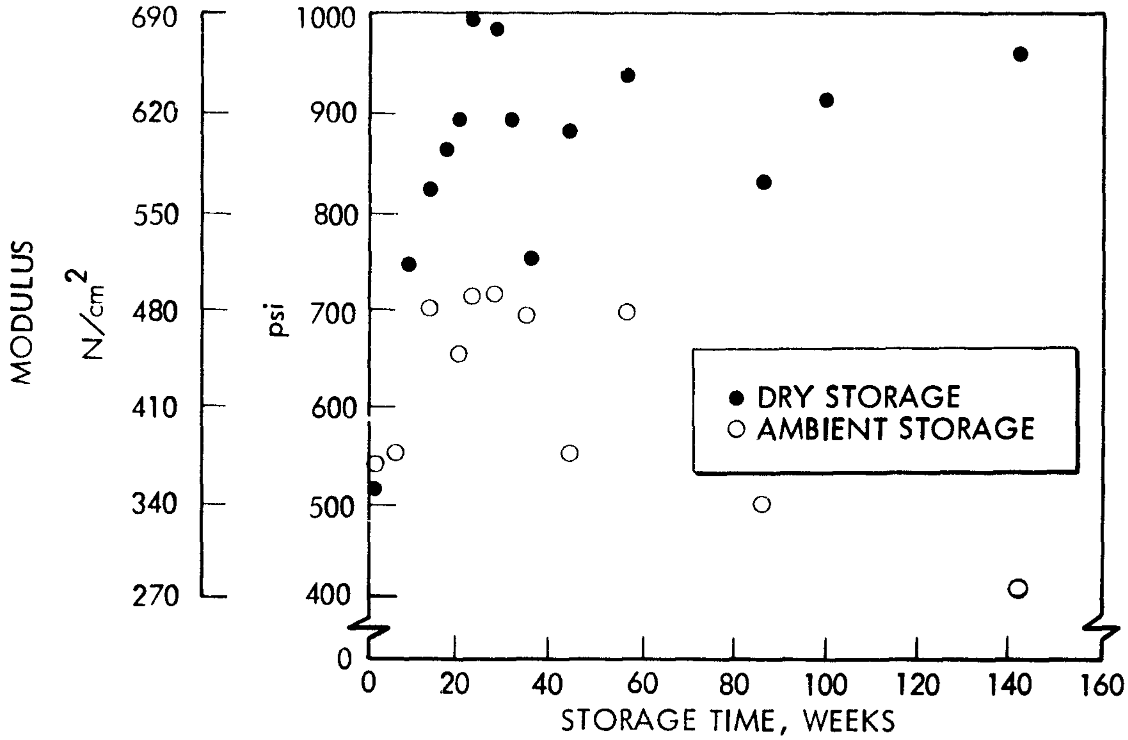

Figure 1. Modulus vs Storage, Propellant #1, PBAA-MAPO Binder

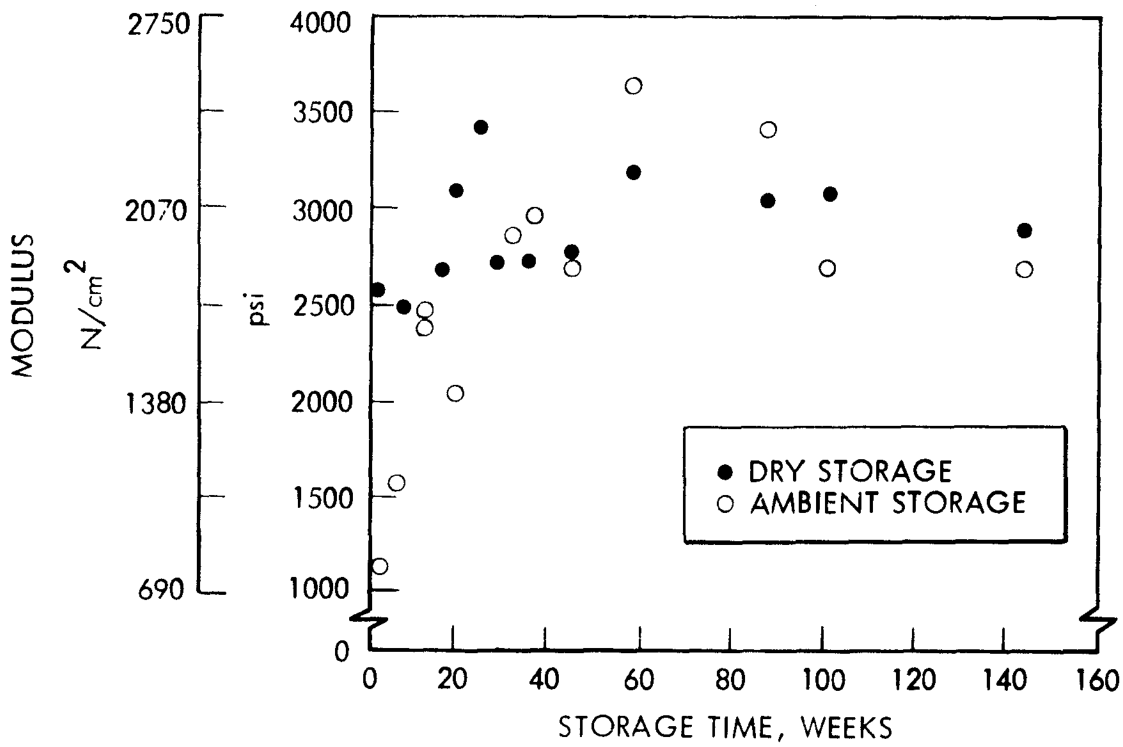

Figure 2. Modulus vs Storage, Propellant #2, PBAN Binder

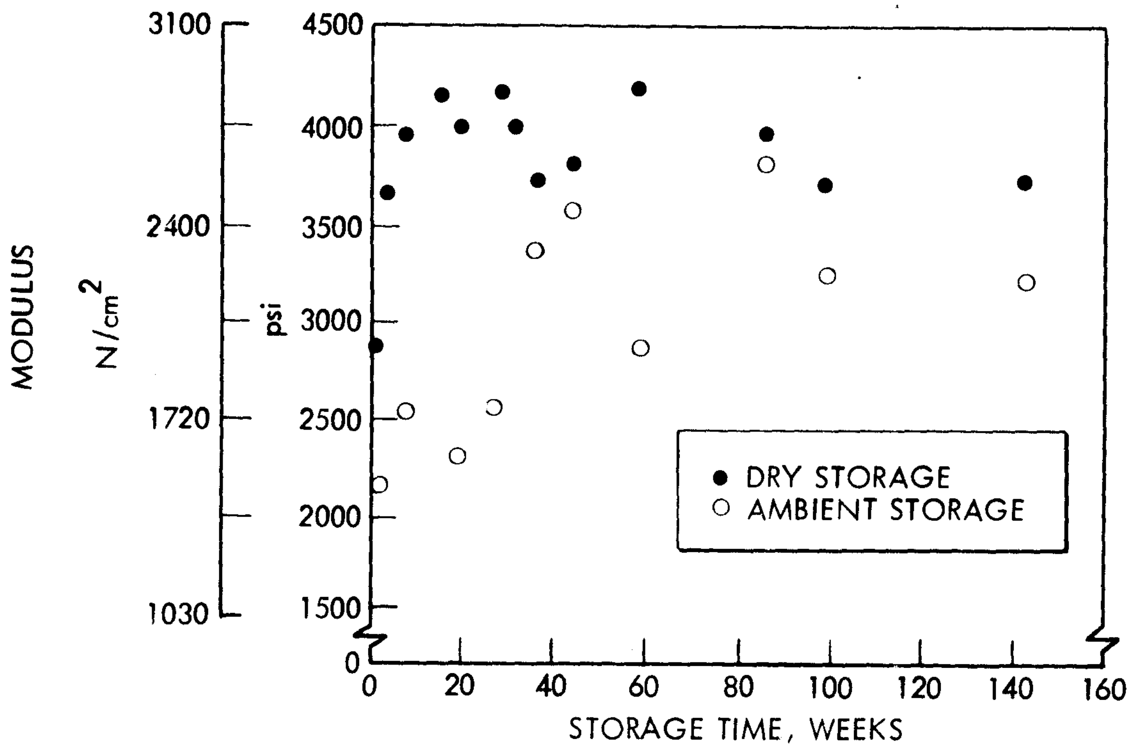

Figure 3. Modulus vs Storage, Propellant #3, Saturated HTPB Binder

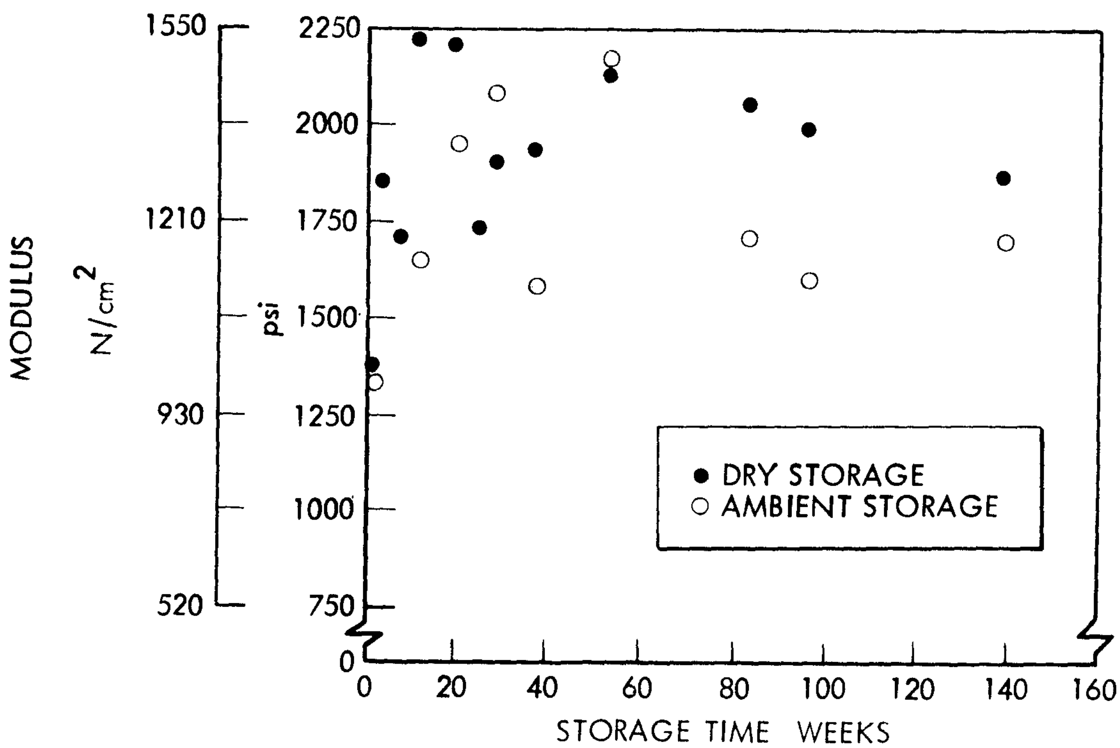

Figure 4. Modulus vs Storage, Propellant #4, HTPB Binder

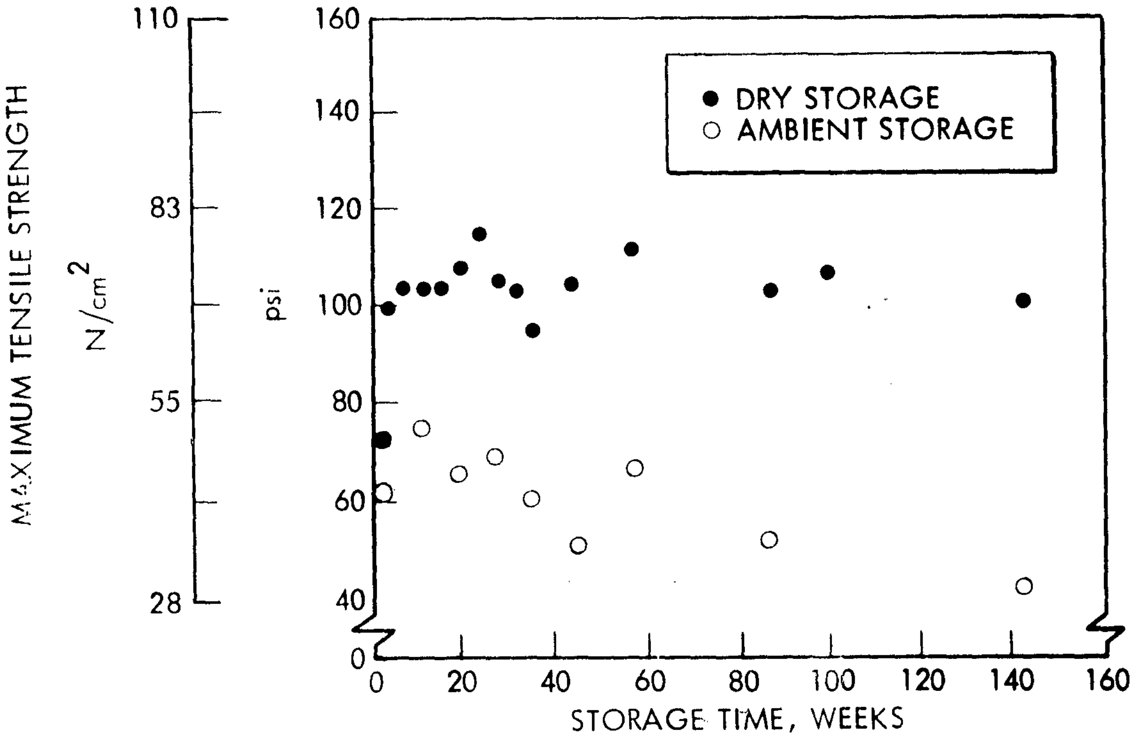

Figure 5. Maximum Tensile Strength vs Storage, Propellant #1, PBAA-MAPO Binder

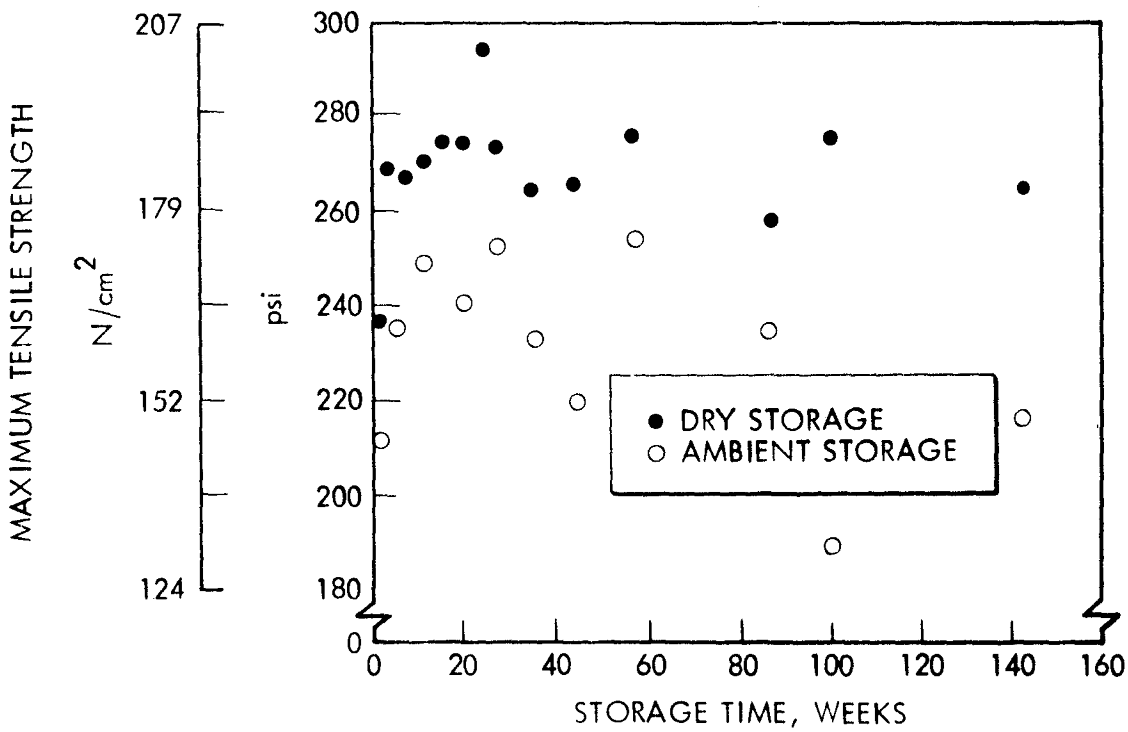

Figure 6. Maximum Tensile Strength vs Storage, Propellant #2, PBAN Binder

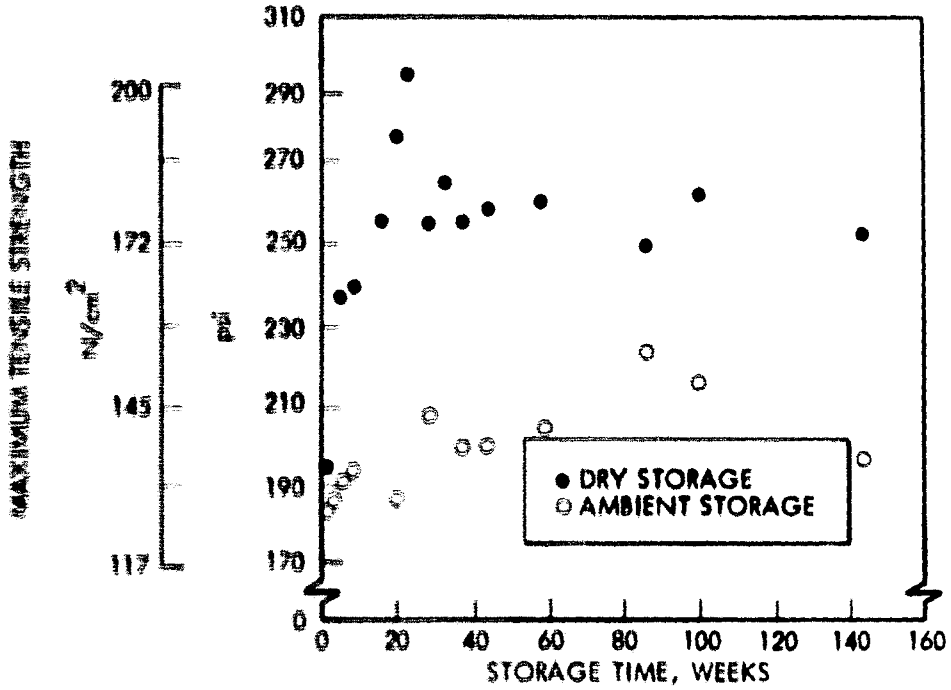

Figure 7. Maximum Tensile Strength vs Storage, Propellant #3, Saturated HTPB Binder

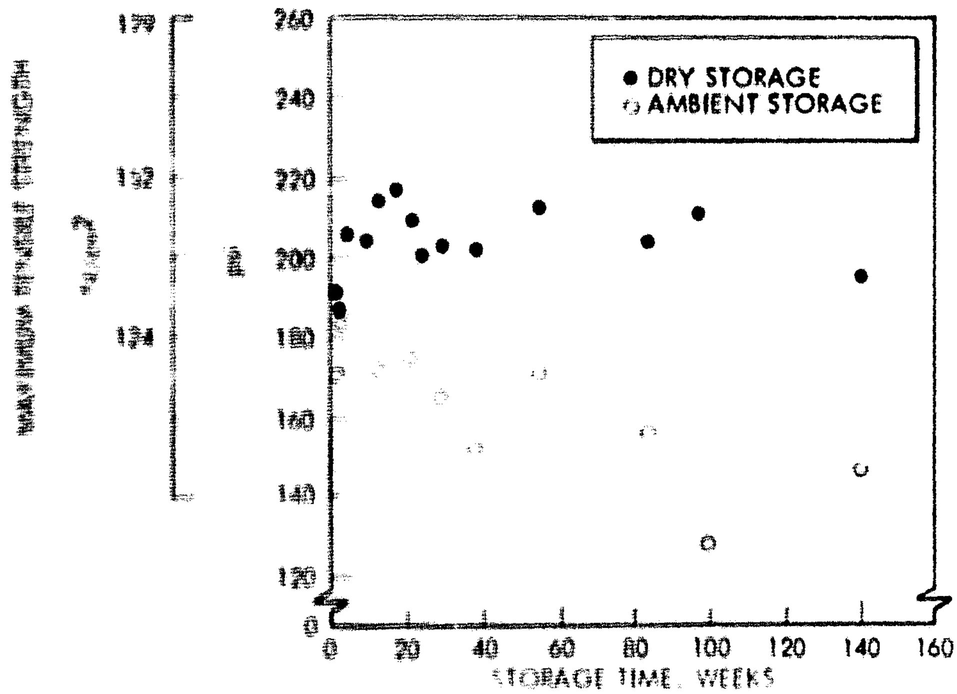

Figure 8. Maximum Tensile Strength vs Storage, Propellant #4, HTPB Binder

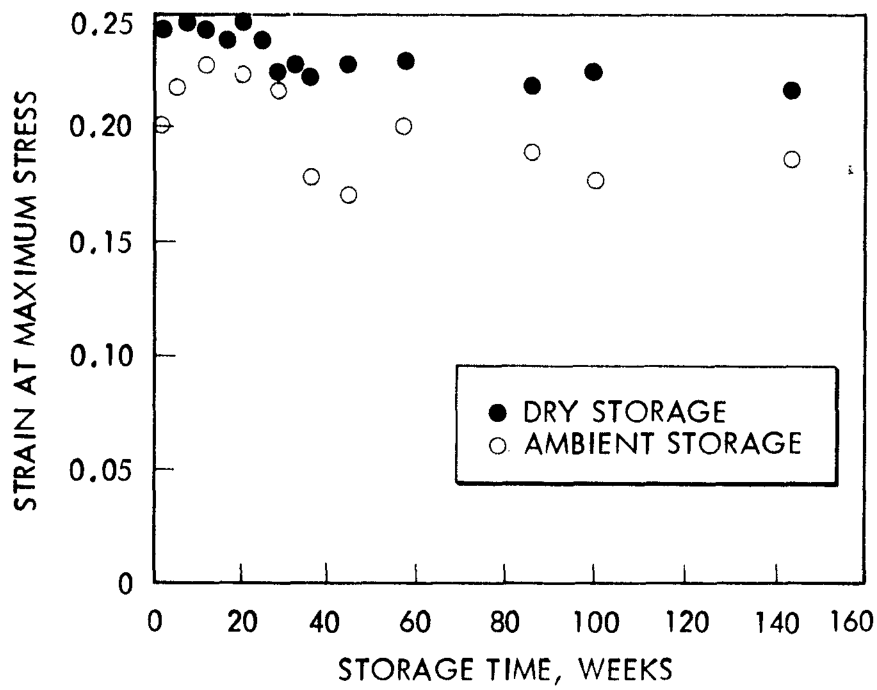

Figure 9. Strain at Maximum Stress vs Storage, Propellant #1, PBAA-MAPO Binder

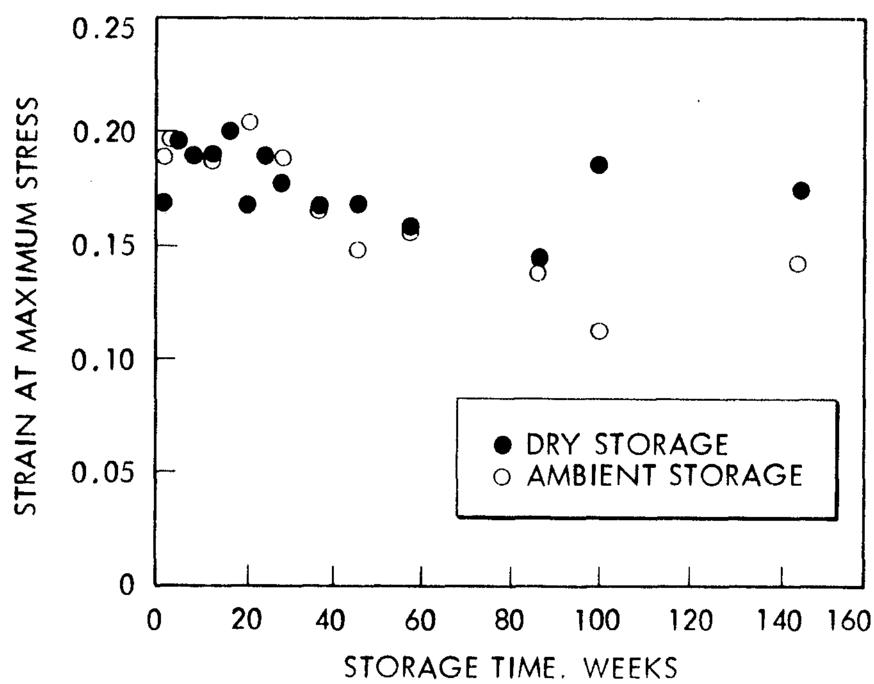

Figure 10. Strain at Maximum Stress vs Storage, Propellant #2, PBAN Binder

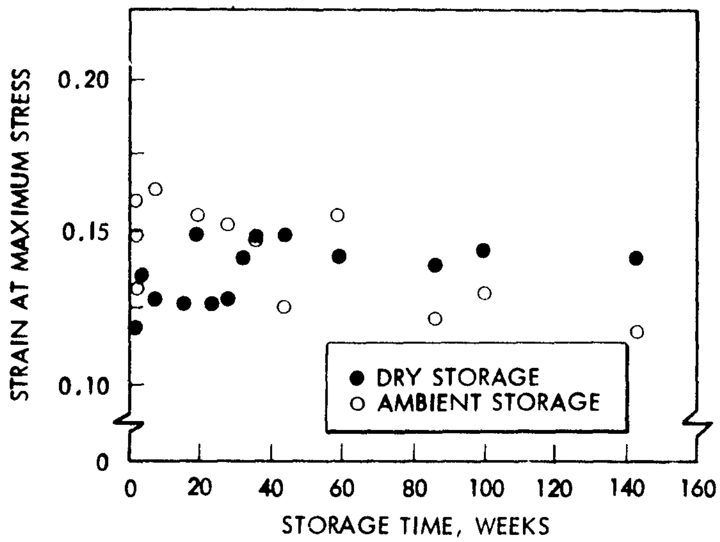

Figure 11. Strain at Maximum Stress vs Storage, Propellant #3, Saturated HTPB Binder

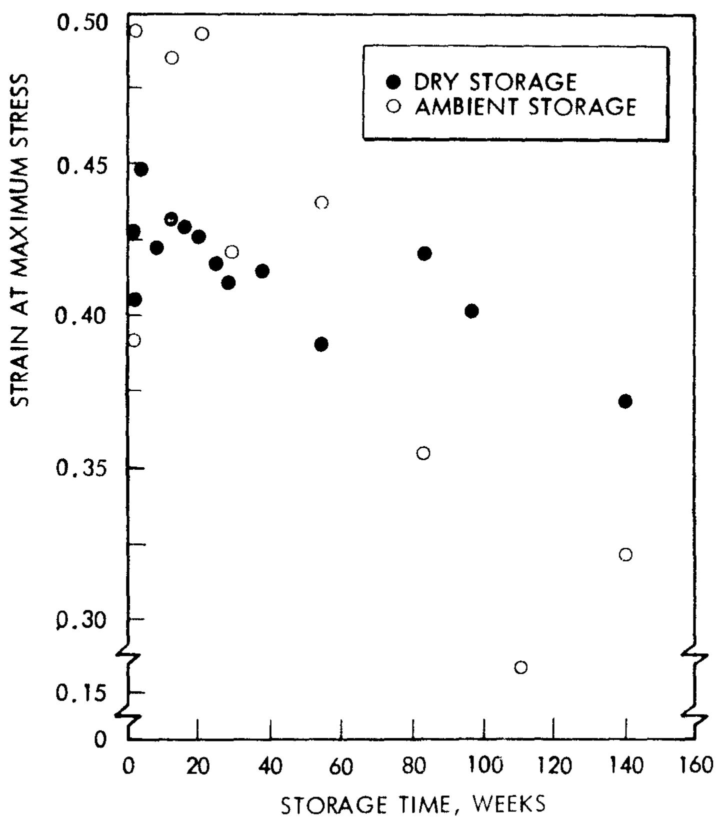

Figure 12. Strain at Maximum Stress vs Storage, Propellant #4, HTPB Binder

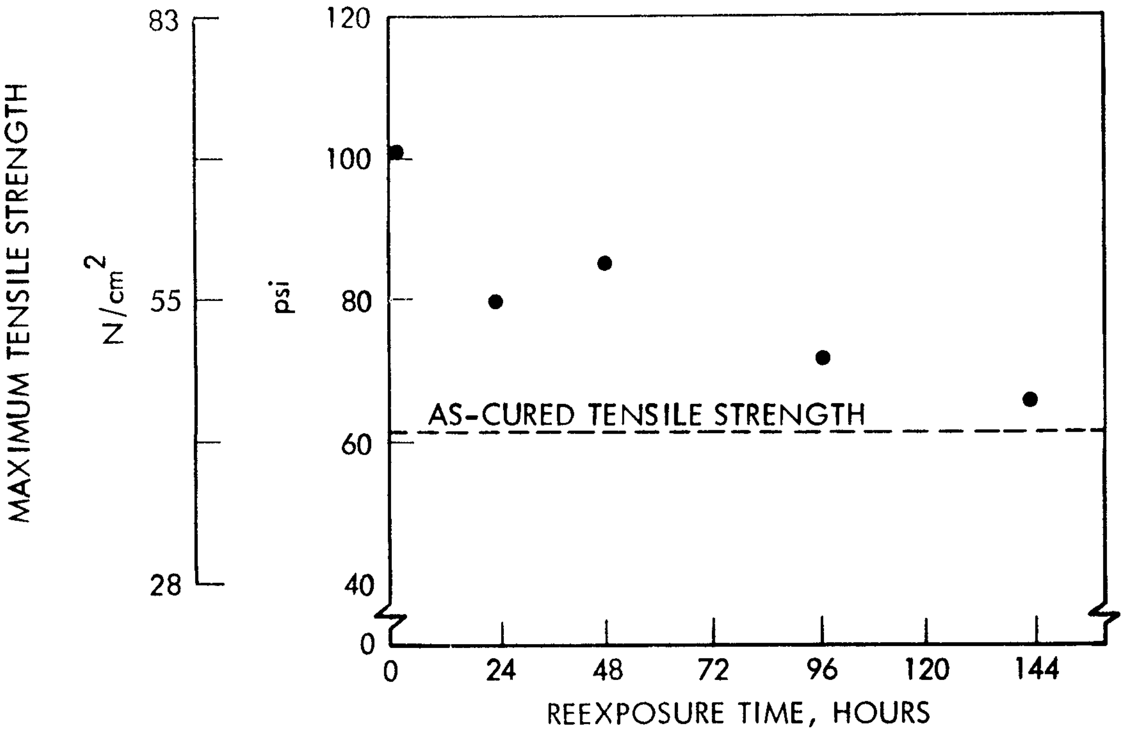

Figure 13. Maximum Tensile Strength vs Reexposure Time to Ambient After Dry Storage, Propellant #1, PBAA-MAPO Binder

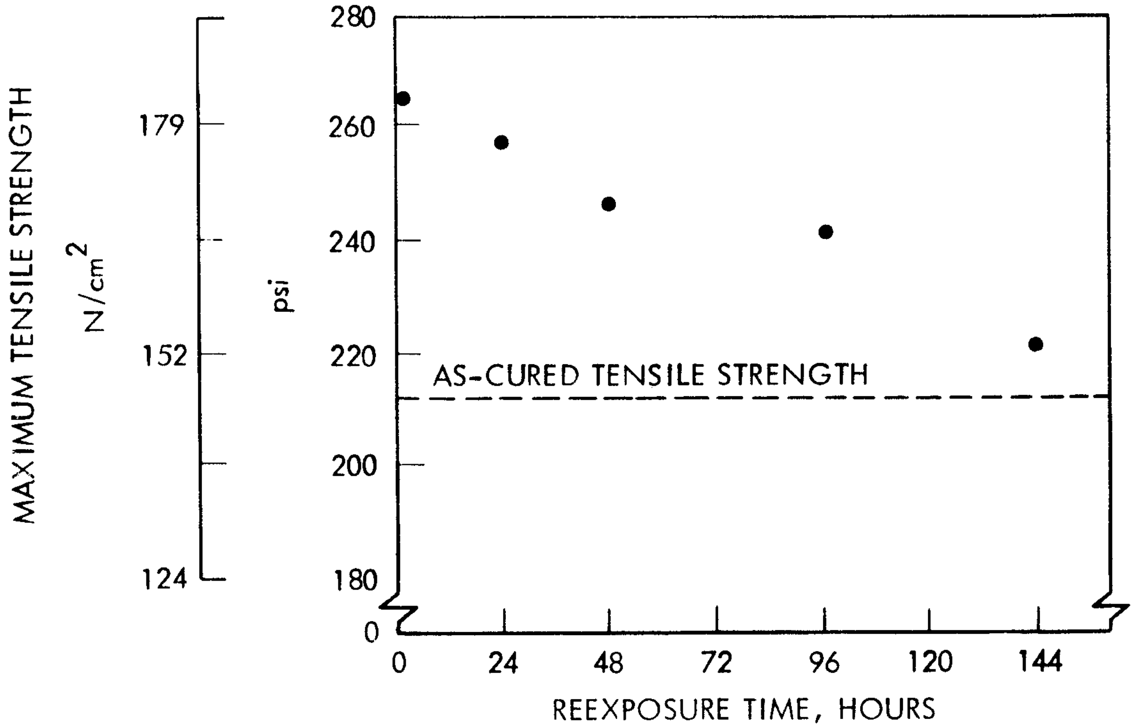

Figure 14. Maximum Tensile Strength vs Reexposure Time to Ambient After Dry Storage, Propellant #2, PBAN Binder

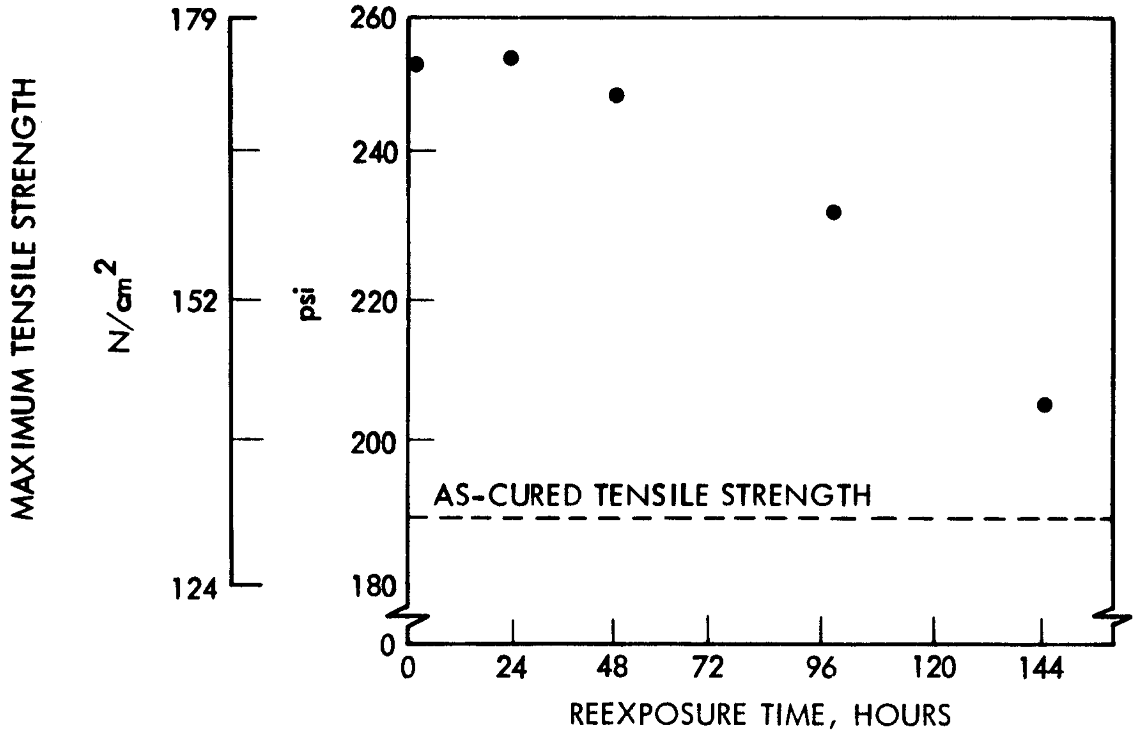

Figure 15. Maximum Tensile Strength vs Reexposure Time to Ambient After Dry Storage, Propellant #3, Saturated HTPB Binder

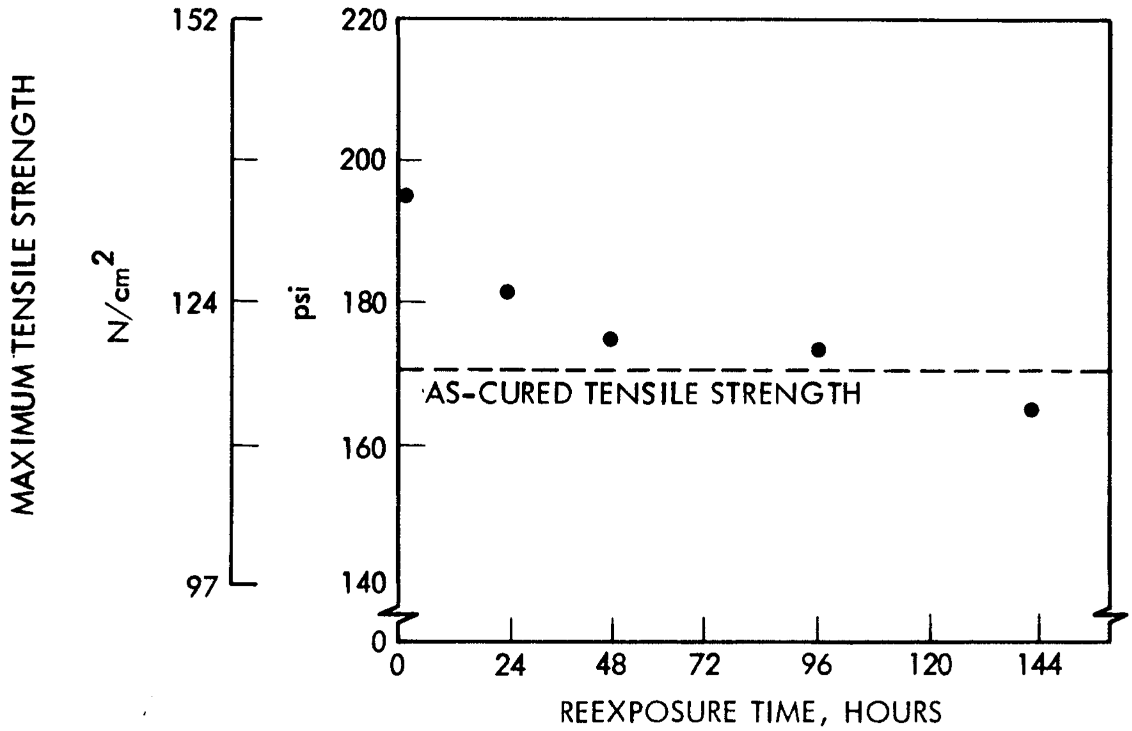

Figure 16. Maximum Tensile Strength vs Reexposure Time to Ambient After Dry Storage, Propellant #4, HTPB Binder

	Ingredient	Wt.%		Ingredient	Wt.%
Propellant #1			Propellant #3		
	PBAA	20.16		Telagen	13.84
	MAPO	0.84		Trimethylol Propane	0.13
	A.P., 200μ	54.40		DDI	5.03
	A.P., 13μ	24.60		AI	16.00
				A.P., 13μ	65.00
Propellant #2			Propellant #4		
	PBAN	12.04		Butarez HT	4.145
	DER 331	1.96		R-45M	7.640
	Fe_2O_3	0.40		Alrosperse 11P	0.218
	Al	16.00		Isostearyl Alcohol	0.547
	A.P., 400μ	8.40		AO-2246	0.140
	A.P., 200μ	31.30		MT-4	0.200
	A.P., 13μ	29.90		IPDI	1.310
				Al	18.0
				A.P., 200μ	47.60
				A.P., 13μ	20.40

Alrosperse 11P, Giegy Chemical Company
Aluminum, Alcoa 1230, Aluminum Company of America
A.O. 2246, Anti-oxidant, American Cyanimid Company
A.P., Ammonium Perchlorate, Kerr McGee Chemical Company
Butarez HT, Hydroxyl terminated polybutadiene, Phillips Petroleum Company
DDI, Diisocyanate, General Mills Chemical Company
DER 331, Liquid Epoxy resin, Dow Chemical Company
IPDI, Isophorone Diisocyanate, Thorson Chemical Corporation
MAPO, Interchemical Corporation
MT-4, Reaction product of MAPO, Tartaric Acid, Adipic Acid, Mfg. at JPL
PBAA, Polybutadiene Acrylic Acid, American Synthetic Rubber Company
PBAN, Polybutadiene Acrylonitrile, American Synthetic Rubber Company
R-45M, Hydroxyl terminated polybutadiene, Arco Chemical Company
Telagen, Saturated hydroxyl terminated polybutadiene, General Tire and Rubber Company

TABLE I. PROPELLANT FORMULATIONS

PROPELLANT NO.	INITIAL			AT END OF DRY STORAGE			AFTER 144 HOURS RE-EXPOSURE TO AMBIENT		
	E(1)	Sm(2)	εm(3)	E	Sm	εm	E	Sm	εm
	psi/N/cm^2	psi/N/cm^2	%	psi/N/cm^2	psi/N/cm^2	%	psi/N/cm^2	psi/N/cm^2	%
1	540/370	61/42	20.3	860/590	101/70	21.8	750/520	66/45	14.8
2	1310/900	212/146	18.9	2900/2000	265/183	17.4	2810/1940	222/153	13.3
3	2070/1430	185/127	17.1	3740/2580	253/174	14.3	2920/2010	206/142	13.7
4	1340/920	170/117	39.1	1860/1280	195/135	37.2	1780/1230	165/114	41.4

E = Initial Modulus

Sm = Maximum Tensile Strength

εm = Strain at Maximum Strength

TABLE II. PROPELLANT PROPERTIES,

INITIAL, AT THE END OF DRY STORAGE AND AFTER REEXPOSURE TO AMBIENT