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USE OF WEIBULL DISTRIBUTION STATISTICS IN ASSESSING LONG TERM COMPATIBILITY OF PROPELLANTS WITH POLYMERIC MATERIALS

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ABSTRACT

The long term compatibility of propellants with polymers may be evaluated by statistical means. The Weibull distribution function was used in an effort to provid a more accurate means of estimating the effect of aging of the inert material in contact with the propellant.

This method was applied to several systems exhibiting different degrees of compatibility. Exposure at 140°F of the RTV 680 rubber with M30 propellant in the XM735 projectile displayed no apparent adverse effects. Distribution analysis supported the conclusion that the RTV 680/M30 system is compatible at ambient temperatures. Another silicone displayed an initial decline in mechanical properties followed by a period of stability when stored with M30 at elevated temperatures over a period of 12 months.

A fair amount of incompatibility was displayed by 30% glass filled nylon which had been exposed to a double base propellant WC870 for an extended time. The Weibull distribution plots indicate that the propellant exerts a damaging effect on both Nylon 12 materials, particularly at elevated temperatures.

Thermal aging may contribute to the ultimate failure of a polymer, as well as direct contact with an energetic. This is illustrated in the case of the M205 non-metallic cartridge case used in the projectile of a 152mm round, with M26E1 propellant. Although it is difficult to separate the effect of these variables upon the lifetime of the system, Weibull statistics provide some measure of prediction.

INTRODUCTION

In an earlier report (1) it was shown that a Weibull distribution function was useful in evaluating compatibility data for a polypropylene in contact with M9 and M2 propellants. Although usually there was some difficulty in evaluating the data due to a pronounced scatter, it was shown statistically that there was essentially no difference* between control and with-propellant data.

In the present work we extend this type of treatment to several polymer-propellant systems showing varying degrees of compatibility (or incompatibility).

RESULTS AND DISCUSSION

The Weibull distribution is a statistical distribution that has been shown to have wide applicability, especially in treating mechanical property results (2,3). The cumulative distribution function may be written (2,3)

$$\log \log \left[\frac{1}{1-F(X)}\right] = \log \alpha + \beta \log (X-\gamma) \qquad (1)$$

where F(X) is the distribution function, i.e., the fraction of samples showing a mechanical property value of X or below. α is the scale parameter (y-intercept), β is the slope and γ a location or threshold parameter. A plot of the left hand side of Equation (1) vs. log $(X-\gamma)$ should give a straight line of slope β and intercept α, γ may be selected on an iterative basis by making trial plots. In the present work satisfactory results were obtained by taking $\gamma=0$ and thus using a two parameter distribution.

Weibull differential distribution curves may be calculated by using the equation

$$f(X)=\frac{b}{a}\left(\frac{X}{a}\right)^{b-1} \exp \left[-\left(\frac{X}{a}\right)^{b}\right] \qquad (2)$$

where the parameters a and b are related to those in Equation (1) by $\beta=b$ and $\alpha=-b \log a -0.36$. Constant a and b in Equation (2) are calculated in each case from the least squares values of α and β in Equation (1).

Case I

Generally the most desirable case is one of complete compatibility. This would correspond to the situation where the mechanical property for the controls and for the polymer after storage with propellant are statistically the same. Exposure of the silicone RTV-680 with M30 propellant appears to fit this case. The silicone was stored in the propellant at 150°F for 18 months and silicone samples were tested (tensile strength and elongation) at 3,6,9,12 and 18 months. Controls were treated in exactly the same way except that they were not in contact with propellant. Figures 1 and 2 show the linear plots according to Equation (1). The correlation coefficients are shown in Table 1. One very wild point in the control tensile strength was not

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*For tensile and elongation properties.

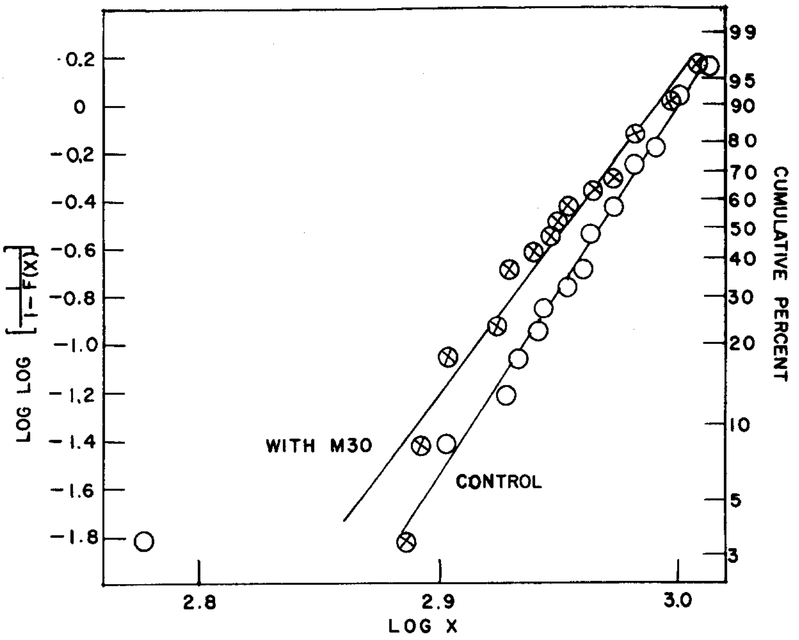

FIG. 1 LINEAR WEIBULL DISTRIBUTION PLOTS FOR CONTROL AND FOR M30-TREATED RTV-680 DATA. X = TENSILE STRENGTH.

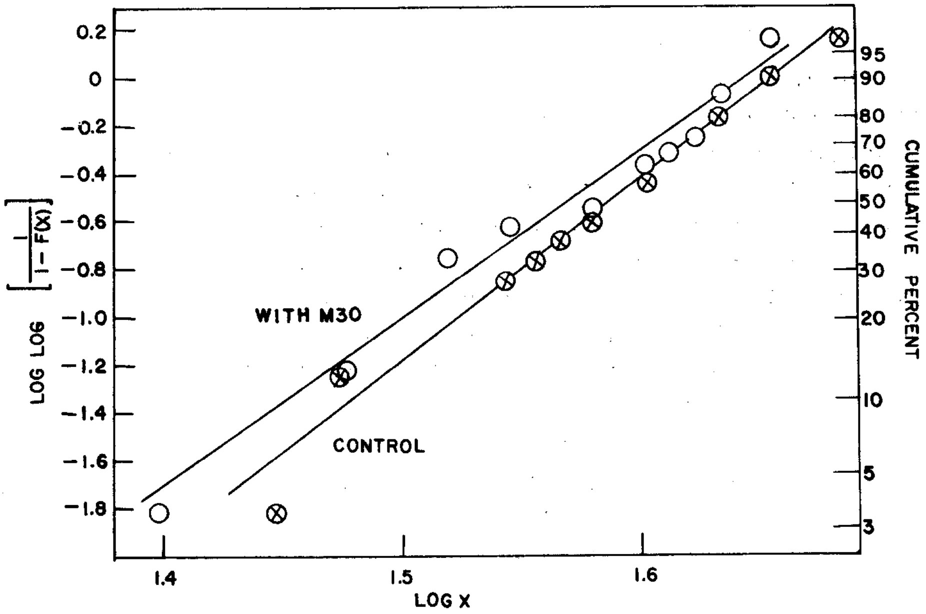

FIG.2 LINEAR WEIBULL DISTRIBUTION PLOTS FOR CONTROL AND FOR M30-TREATED RTV-680 DATA. X= ELONGATION.

TABLE 1

Correlation Coefficients for the Linear Weibull Distribution Plots

System	Correlation Coefficient
RTV-680 Controls Tensile	0.995
RTV-680-M30 Tensile	0.968
RTV-680 Controls Elongation	0.984
RTV-680-M30 Elongation	0.989
Nylon 12 (Huls) Controls	0.949
Nylon 12 (Huls)-WC870 6 Mo.	0.963
Nylon 12 (Huls)-WC870 12 Mo.	0.946
Nylon 12 (Huls)-WC870 18 Mo.	0.888
Nylon 12 (Huls)-WC870 24 Mo.	0.986
Nylon 12 (Nylatron) Controls	0.975
Nylon 12 (Nylatron)-WC870 6 Mo.	0.982
Nylon 12 (Nylatron)-WC870 12 Mo.	0.990
Nylon 12 (Nylatron)-WC870 18 Mo.	0.938
Nylon 12 (Nylatron)-WC870 24 Mo.	0.951
Silgan Controls	0.970
Silgan-M30	0.960
M205 Case Controls 1-25 Mo.	0.974
M205 Case-M26E1 1-25 Mo.	0.943
M205 Case Control 30 Mo.	0.944
M205 Case-M26E1 30 Mo.	0.964

used in the correlation (see Figure 1). An illustrative differential distribution plot according to Equation 2 is shown in Figure 3. Figures 1 through 3 show that difference between controls and exposed samples are very small.

An independent test for any significant differences between the populations was also performed. The Wilcoxon Sum of Ranks (4) is simple and convenient for this purpose. This test involves ranking the data in order of increasing values and numbering accordingly. The smallest sum of ranks is compared with appropriate tables and the probability (P) of getting the two sets of data in the actual order is determined. Usually anything greater than one chance in 20 (i.e., P=5%) is taken to mean that there is no difference. For the system under consideration it turns out that $P > 10\%$. It seems reasonable to conclude that there are no statistical differences between the populations.

Since after 18 months at 150°F the RTV 680 - M30 system showed no statistically adverse effects, one could reasonably conclude that this system is compatible and could be expected to have a long lifetime under ambient conditions.

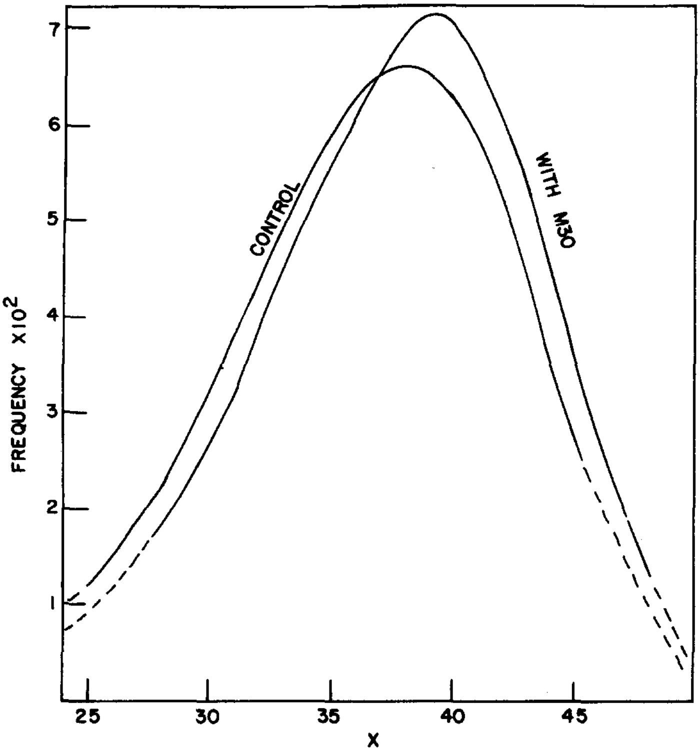

FIG. 3 DIFFERENTIAL WEIBULL DISTRIBUTION CURVES FOR CONTROL AND M30 TREATED RTV-680.

Case II

A second case involves fundamental incompatibility with a progressive decrease in mechanical properties with time. Some studies of two commercial Nylon 12-30% glass-filled specimens with WC870 propellant for the 30mm Plastic Cartridge Case program fall in this category. The studies were accomplished at 140°F and tests were made after contact times of 6, 12, 18 and 24 months. The tensile strength versus time curves are shown in Figures 4 and 5 and the linear Weibull plots are given in Figures 6 and 7. Correlation coefficients for the Weibull lines in Table 1 indicate that this treatment is adequate. It is noteworthy that the mechanical properties fall off slowly at first with propellant exposure time and then the drop appears to accelerate, with some levelling off at the longer exposure times. The decrease in Weibull slope with exposure time is indicative of a greater data scatter as the propellant interacts with the Nylon 12.

The foregoing would indicate that Nylon 12 should not be used with this type of propellant. Indeed, any nylon should be tested thoroughly before use with WC870 or related propellants.

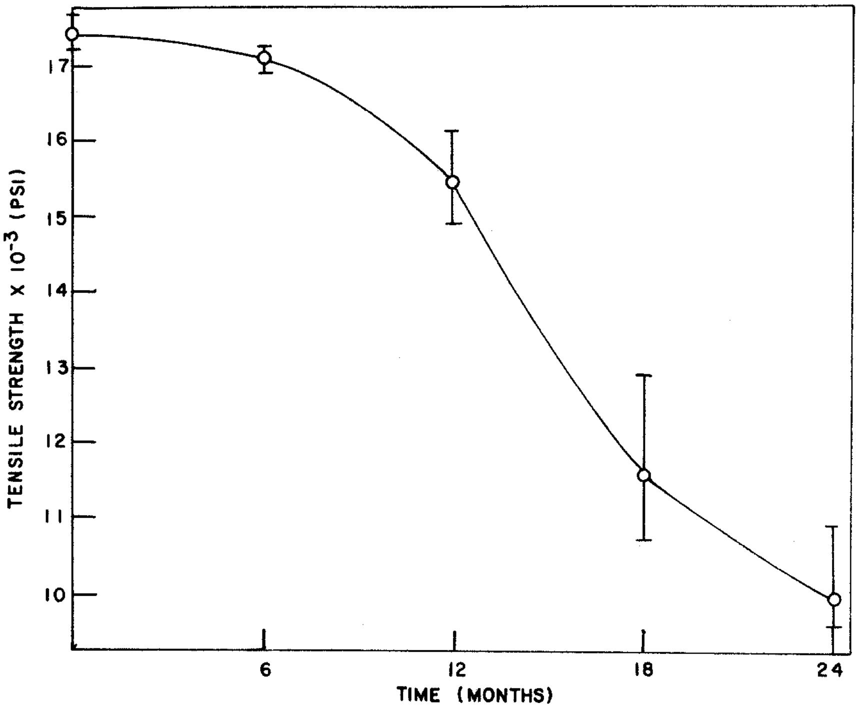

FIG.4 STRENGTH VS. STORAGE TIME AT 140°F WITH WC870 FOR NYLON 12 (HULS)-30% GLASS.

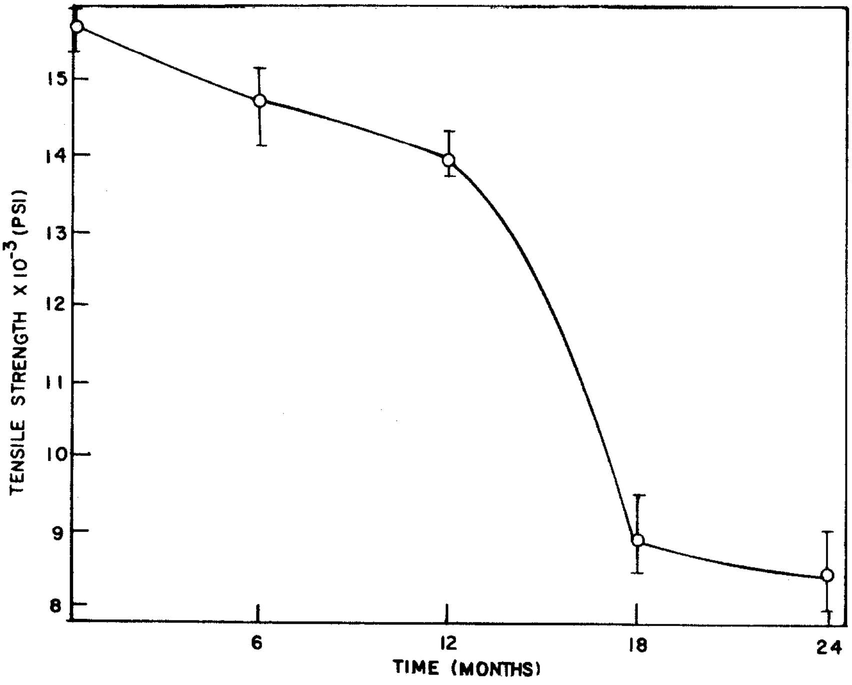

FIG.5 STRENGTH VS. STORAGE TIME AT 140°F WITH WC870 FOR NYLON 12 (NYLATRON)-30% GLASS.

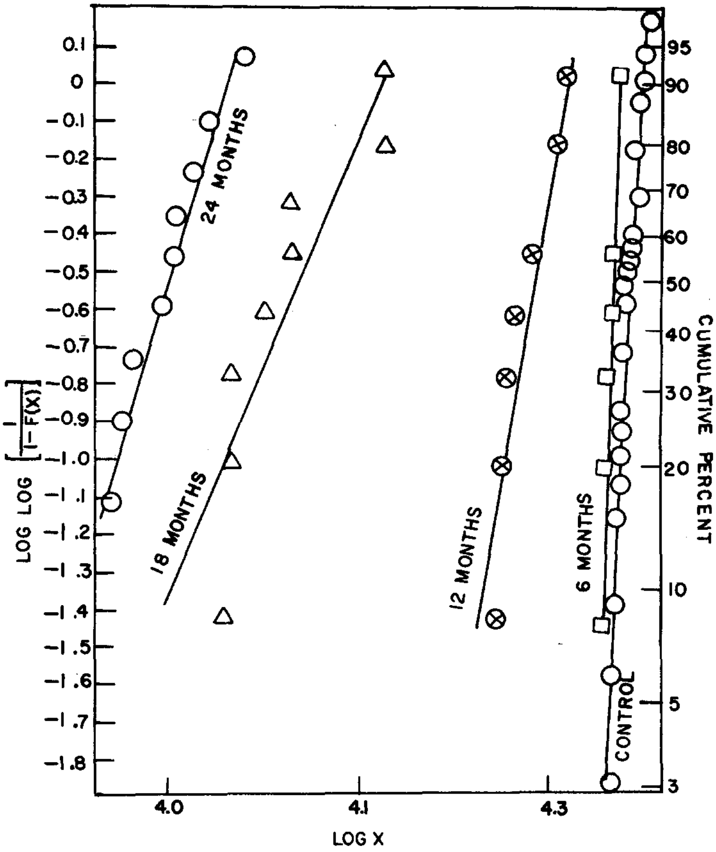

FIG.6 LINEAR WEIBULL DISTRIBUTION PLOTS FOR CONTROL AND WC870-TREATED NYLON 12 (HULS)- 30% GLASS. X= TENSILE STRENGTH.

Case III

A third case involves some degree of incompatibility as evidenced by an initial sharp decline in mechanical properties upon exposure to propellant. However, this reduction is followed by a period of stability in which the properties remain essentially constant. A good example of this situation involves the system Silgan silicone potting compound with M30 propellant. Figure 8 shows the comparison of the controls with polymer exposed to M30 for 3 months at 140°F and for 12 months at 150°F Data for the two storage periods are indistinguishable. However, the exposed population has much lower strength values than the controls. Such a system could be cautiously used if the reduction in properties is tolerable under use conditions. Under ambient applications the life would be much larger than under the accelerated testing conditions.

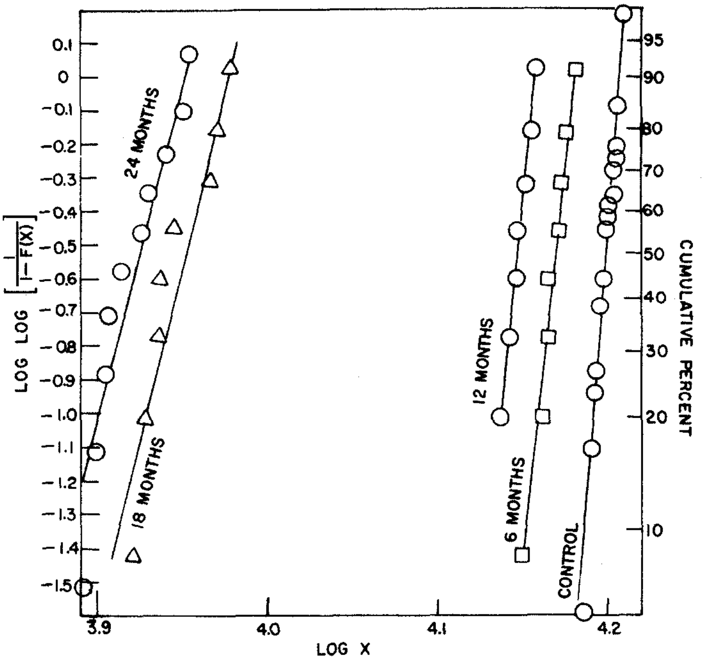

FIG. 7 LINEAR WEIBULL DISTRIBUTION PLOTS FOR CONTROL AND WC870-TREATED NYLON 12 (NYLATRON)-30% GLASS. X = TENSILE STRENGTH.

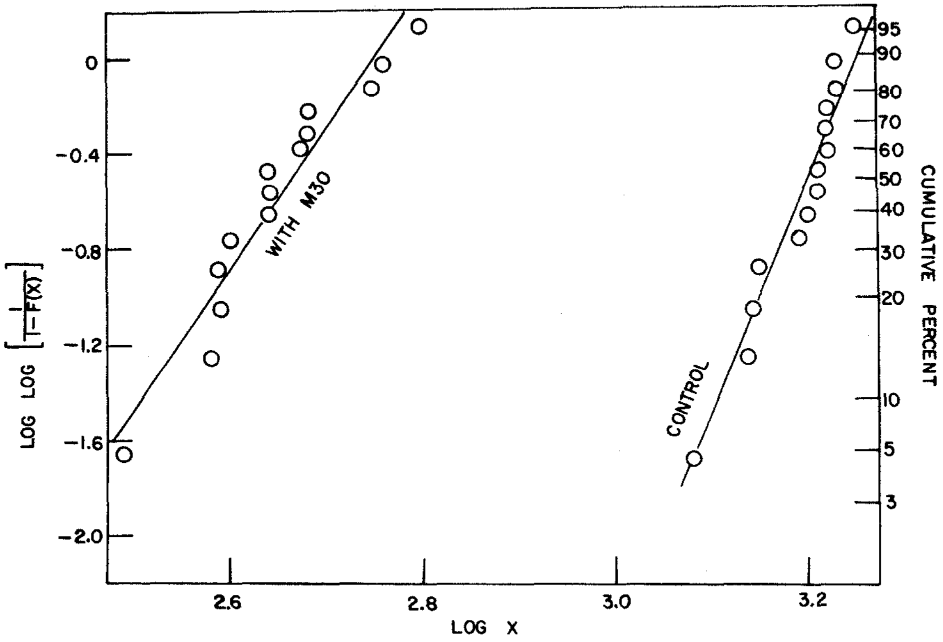

FIG. 8 LINEAR WEIBULL DISTRIBUTION PLOTS FOR CONTROL AND FOR M30-TREATED SILGAN SILICONE. X= TENSILE STRENGTH.

Case IV

In this case there is a decrease in mechanical properties, followed by a levelling off as in Case III. At longer temperature accelerated times there is a further decrease in properties. This may be due to further polymer-propellant interaction, to thermal aging of the polymer, or to both. Where there are multiple effects the situation may be quite complex. Such a case is illustrated by the M205 nonmetallic cartridge case in contact with M26E1 propellant (5). The averages and data value ranges are shown in Figure 9. Although there might be a slight downturn at the highest storage value for the ambient controls, the data overlap indicates that probably there is no change.

In the case of the accelerated tests, the downturn (Figure 9) both for the controls and for the propellant treated would seem to indicate that changes are occurring between 25 and 30 months. Figure 10 perhaps gives a better indication of the magnitude of these changes. In this Figure the experimental points are omitted in order to reduce the clutter. An idea of the goodness of fit in each case can be obtained from the correlation coefficients in Table 1.

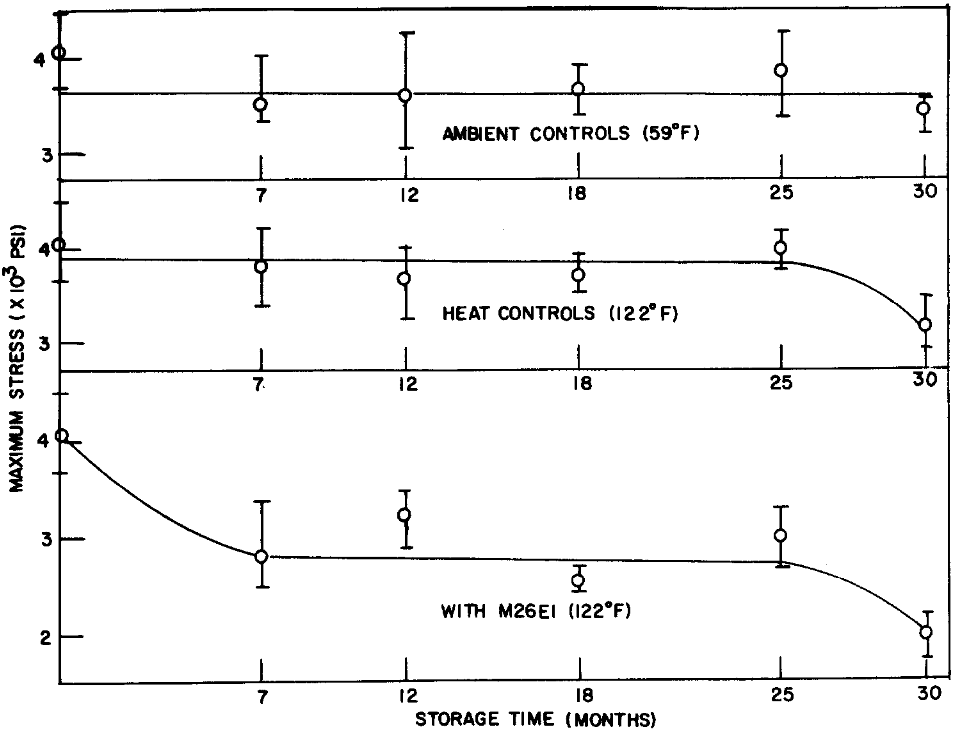

FIG. 9 EFFECT OF STORAGE OF M205 CARTRIDGE CASE WITH M26E1 PROPELLANT

From Figure 10 it is hard to draw definitive conclusions. It does appear that both thermal and compatibility effects contribute to the strength reduction at the longest exposure times. However, from the data in hand it does not seem possible to quantitatively separate these effects. It is interesting to note that the reduced strengths after storage are higher than those required by the item in field use. Thus this combination could well be acceptable for use in a temperate zone. Indeed, this item has been in the field for several years and has been reported to be mechanically satisfactory (5).

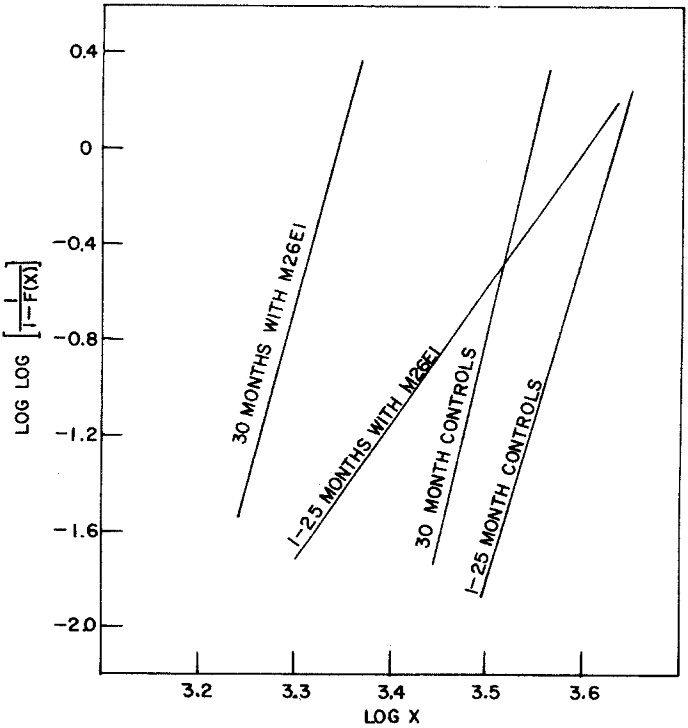

FIG. 10. EFFECT OF STORAGE TIME AT 122°F ON TENSILE STRENGTH OF THE M205 CASE.

MATERIALS AND METHODS

RTV 680 is a two component silicone rubber (available from General Electric), which was studied as a potential replacement for the polyurethane seal in the 105mm XM735 projectile. The M30 propellant used in this system has the following formulation (in percent):

Nitro cellulose (12.6% N)	28.0
Nitroglycerin	22.5
Nitroguanidine	47.7
Ethyl Centralite	1.5
Graphite	0.1

Tensile bars made from the RTV 680 elastomer were stored at 66°C (150°F) in direct contact with the M30 propellant in a closed glass container. The samples were periodically removed at intervals of 3, 6, 9, 12 and 18 months and mechanically tested. Tensile strength was determined according to ASTM-D412 "Tension Testing of Vulcanized Rubber" using an Instron Universal testing machine at a rate of 5 inches/minute.

Silgan silicone was also evaluated as a candidate for the aft seal in the XM735 projectile. Silgan (SWS Silicones Corp) long-term compatibility with M30 propellant was evaluated using the same procedures as described above for the RTV 680 silicone.

Commercial Nylon 12 containing 30% glass filler (Hüls and Polymer Research) was evaluated for long-term stability with WC870 double base propellant at intervals of 6, 12, 18 and 24 months. This system was considered for the 30mm plastic cartridge case. The WC870 propellant composition (in percent) is:

Nitrocellulose (13.15%N)	79.0
Nitroglycerine	10.0
Dinitrotoluene	0.5
Diphenylamine	1.0
Dibutyl Phthalate	7.0
Calcium Carbonate	0.6
KNO_3	0.7
$Sn\ O_2$	1.0
$Na_2\ SO_4$	0.1
Volatiles and Moisture	1.0

The tensile strength of the nylon samples was measured on the Instron machine at room temperature with a crosshead speed of 0.2 inch/minute.

The M205 non-metallic cartridge case is used in conventional 152mm ammunition. The propellant charge for such ammunition is a double base M26E1 propellant whose formulation is (in percent):

Nitrocellulose (13.15% N)	68.7
Nitroglycerine	25.0
Ethyl Centralite	6.0
Graphite	0.3

The cartridge case has the following nominal composition (in percent):

Nitrocellulose (12.6% N)	55.0
Kraft Fiber (cellulose)	9.0
Acrylic Fiber (fibrillated)	25.0
Polyvinyl Acetate Resin	10.0
Diphenylamine	1.0

The cartridge case was stored(5) in the form of tensile specimens at 122°F in contact with the M26E1 propellant. After storage for various time intervals the specimens were subjected to tensile stress at a crosshead speed of one inch/minute until failure

All the control samples (those not exposed to propellant) were treated in the same manner as the test specimens.

ACKNOWLEDGEMENTS

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