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M549A1 PROJECTILE DELAY ASSEMBLY PREDICTIVE ENGINEERING ANALYSIS IN SUPPORT OF THE AMMUNITION STOCKPILE RELIABILITY PROGRAM

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14. ABSTRACT

Experiments were conducted on M549A1 High Explosive Rocket Assisted projectiles to evaluate the effects of thermal degradation and moisture on the delay assembly, and on the potential for premature rocket ignitions. Accelerated aging experiments for up to 25 days at 75°F did not induce premature rocket motor ignitions. Higher temperatures and conditioning times were recommended in order to cause this type of failure mechanism to become active. Delay assemblies required very high temperatures (375°F and 475°F) to cause failure due to temperature alone. When humidity was introduced into the test matrix, the delays failed at much lower temperatures (155°F to 230°F). Because of the high susceptibility to failure of the delay assembly due to humidity exposure, the recommendation was made not to fire any M549A1 projectiles which do not have the Rocket Off Cap present on the projectile.

15. SUBJECT TERMS

ASRP, Predictive engineering, M549A1, Artillery ammunition, 155-mm projectile, Rocket motor, Delay assembly, Accelerated aging, Firing test, Predictive analysis, Reliability

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SUMMARY

The original project objective was to predict the life of the M549A1 155-mm High-explosive Rocket Assisted (HERA) projectile stockpile as a function of two potential failure mechanisms:

- Rocket motor (RM) delay assembly snuff out resulting in non-ignition of the rocket motor

- Migration of nitroglycerine (NG) from the rocket motor propellant grain resulting in premature ignition of the rocket motor

Conditioned (high temperature or high temperature with high humidity) projectiles for both failure mechanism experiments were fired at Yuma Proving Ground (YPG) to detect induced failures.

Accelerated aging tests were executed on rocket motor delay assemblies for the M549A1 projectiles. Failures were induced by subjecting the delays to elevated temperatures alone and a combination of elevated temperatures and humidity levels.

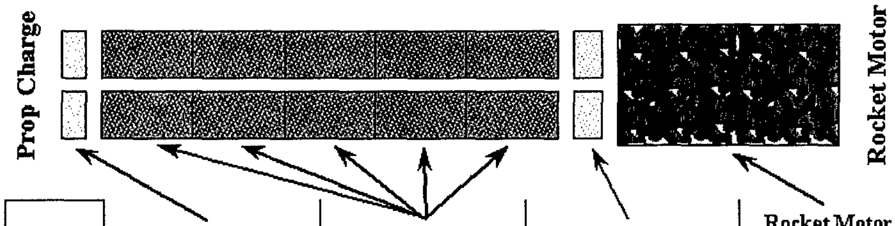
The results indicate that the delay assembly is very susceptible to failure due to elevated humidity exposure. Failure was not a function of the type of delay assembly design. The original design delay assembly and the alternate design delay assembly are not significantly different in their resistance to moisture or thermal stress. Therefore, there is no reason to separate or remove rounds from the stockpile based on their delay type.

Accelerated aging tests were executed on rocket motors. Premature RM ignitions could not be induced by subjecting the RMs to an elevated temperature (75°C) for up to 25 days.

Higher temperature and/or longer conditioning times would be required to reproduce the failure mechanism. Without failures, a predictive analysis can not be accomplished. Since additional funding was not provided to pursue a life prediction based on premature RM ignition caused by the NG migration failure mechanism, there are no conclusions or recommendations with respect to the stockpile.

BACKGROUND

Two types of delay assemblies were investigated in this study. One is designated the original design and the second is designated the alternate design. The basic composition is shown in figure 1.



Delay Design	Increment 7 Igniter Composition	Increments 2-6 Delay Composition	Increment 1 Flash Composition	Rocket Motor Igniter (Pellets)
Original	Zirconium (65.0±1.0%) Iron Oxide (25.0±1.0%) Diatomaceous Earth (10.0±1.0%) VAAR (1.0±0.1%)	Tungsten (45.0±5.0%) Barium Chromate (40.5±5.0%) Potassium Perchlorate (14.50±0.25%) VAAR (1.0±0.1%)	Zirconium (58.0±1.0%) Chromium Oxide (16.0±1.0%) Molybdenum Trioxide (25.0±1.0%) VAAR (1.0±0.1%)	Boron (23.7±2.0%) Potassium Nitrate (70.7±2.0%) Resin (5.6±0.5%)
Alternate	Boron (10.0±0.5%) Barium Chromate (90.0±0.5%) VAAR (1.5±0.1%)		Boron (10.0±0.5%) Barium Chromate (90.0±0.5%) VAAR (1.5±0.1%)	
	250±15mg	950±10mg each	300±15mg	5.75±0.75g

Figure 1
Alternate and original delay assembly compositions for the M549A1

Note that the igniter and flash compositions are different for the two designs. The basic difference is the substitution of boron in the alternate formulation for zirconium, which is used in the original formulation.

The initial experimental design consisted of delay assemblies from four projectile lots (table 1), which were conditioned at elevated temperatures (375° to 475°F) for different time durations, and then fired to determine the dud rate.

The second experimental design consisted of delay assemblies from two projectile lots (IOP84C032-001A and IOP82H031-074A), which were conditioned at elevated temperatures (165° to 230°F) and various humidity levels for different time durations. The rounds were then fired to determine the dud rate.

The NG migration experiment conditioned five samples from one M549A1 lot (IOP81E030-118) at 75°F (a sixth control sample was not conditioned) for 5 to 25 days. The projectile warheads consisted of an inert fill during the conditioning process.

Two research papers, which were written based on these experiments, are provided in appendices A and B.

EXPERIMENTAL DATA

Delay Assembly Experiment

The delay assemblies used in these experiments were obtained from the projectile lots identified in table 1. For the thermal stress experiment all four lots were used. For the thermal and humidity stress experiment only the lots not exposed to Operation Desert Storm (ODS) deployment were used.

Table 1
Lots used in the delay experiments

Lot history	Projectile lot number	
	Original design	Alternate design
Exposed to ODS	IOP81B030Y109	IOP84F032Y005C
Not exposed to ODS	IOP84C032-001A	IOP82H031-074A

Part I: Temperature Conditioning Test

The results of the thermal stress experiment for the delay assembly samples from each of the four lots of M549A1 projectiles are shown in table 2. The failures are designated by no rocket motor (No RM) which indicated that the delay did not function.

Table 2
Thermal stress delay experiment results

Lot number	Serial number	Conditioning		Results
		Temperature (°F)	Duration (days)	
IOP84C032-001A	51	No conditioning/delay not removed		OK
	1	375	5	OK
	2	375	10	OK
	3	375	15	OK
	4	375	20	OK
	5	375	25	OK
	6	475	5	No RM
	7	475	10	No RM
	8	475	15	No RM
	9	475	20	No RM
	10	475	25	No RM
IOP81B030Y109	49	No conditioning/delay out-in		OK
	1	375	5	OK
	2	375	10	OK
	3	375	15	OK
	4	375	20	No RM
	5	375	25	OK
	6	475	5	No RM
	7	475	10	No RM
	8	475	15	No RM
	9	475	20	No RM
	10	475	25	No RM
IOP82H031-074A	51	No conditioning/delay not removed		OK
	1	375	5	OK
	2	375	10	OK
	3	375	15	OK
	4	375	20	OK

Table 2
(continued)

Lot number	Serial number	Conditioning Temperature (°F)	Duration (days)	Results
IOP82H031-074A (continued)	5	375	25	OK
	6	475	5	OK
	7	475	10	OK
	8	475	15	OK
	9	475	20	OK
	10	475	25	No RM
	49	No conditioning/delay out-in		OK
IOP84F032Y005C	1	375	5	OK
	2	375	10	OK
	3	375	15	OK
	4	375	20	OK
	5	375	25	OK
	6	475	5	OK
	7	475	10	OK
	8	475	15	OK
	9	475	20	OK
	10	475	25	OK

The data in table 2 shows multiple delay assembly failures for lots IOP84C032-001A and IOP81B030Y109 with a single failure for lot IOP82H031-074A. The failures were primarily observed in the original design delay compositions. This was unexpected, since all previous delay assembly failures during the stockpile and ODS testing were of alternate delay composition. In order to get some feel for the degradation rate (or service life) at ambient storage conditions, the data were modeled using a lognormal failure distribution.

Since only lot IOP81B030Y109 had failures at both of the conditioning temperatures, those data were used to supply an estimate of the degradation rate. The results indicate that thermal degradation alone occurs at a very slow rate. The lognormal failure distribution and the Arrhenius plots indicated a lifetime of about 11,000 years at ambient. This means that thermal degradation alone could not have caused the delay failures that were observed in previous testing (app A). Therefore, the effect of moisture was investigated in the second experiment.

Note: Appendix B contains the paper that addresses the stabilizer degradation behavior of Aryl Hydrocarbon Hydroxylase (AHH) propellant, which is cast into the rocket motor of the M549A1.

Part II: Temperature and Humidity Conditioning Test

Firing resulted in four observed delay failure modes. The most common failure mode, as observed in the temperature only conditioned test, is No RM. The three other delay failure modes were early ignition (Early Ign), ignition in the tube or projectile break up. It is assumed that the early ignition occurred due to a degradation of the delay element. This led to a shorter delay column, and consequently, an early ignition. When the delay element was severely degraded due to moisture exposure, it formed a loose column of oxidized delay components. This resulted in a whitish substance that became loosely packed inside the delay column. An ignition in the tube or projectile break up was assumed to be a phenomenon caused by the propellant gases/flame burning through the column much more quickly than normal and igniting the rocket motor. In some cases, the in-bore rocket motor ignition resulted in a separation of the rocket motor body from the projectile main body, which was designated projectile broke-up.

The results of the humidity experiments are summarized in tables 3 through 7. After each data set, a comment is included as to what happened in the experiment and a contrast between the original and alternate delay formulation is made.

Table 3
Humidity test results at 230°F and 100% RH

Days of conditioning	Projectile lot	
	IOP84C032-001A	IOP82H031-074A
5	No RM	No RM
8	No RM	No RM
12	No data	Early Ign
14	Early Ign	No RM
19	No RM	Ignition in tube

Observation: No difference between alternate and original delay designs in this test.

Table 4
Humidity test results at 205°F and 100% RH

Days of conditioning	Projectile lot	
	IOP84C032-001A	IOP82H031-074A
4	OK	No RM
4	OK	No RM
8	No RM	No RM
10	No RM	No RM
17	No RM	No RM
25	No RM	No RM
32	Early Ign	No RM
58	Projectile broke-up	No RM
71	No RM	No RM
81	Projectile broke-up	Projectile broke-up

Observation: On day 4, the original delay designs still functioned, whereas, the alternate design failed. Otherwise both lots were approximately the same.

Table 5
Humidity test results at 155°F and 100% RH

Days of conditioning	Projectile lot	
	IOP84C032-001A	IOP82H031-074A
27	OK	OK
49	OK	OK
68	No RM	OK
68	No RM	OK

Observation: On day 68, the original delay designs failed whereas the alternate designs functioned.

Table 6
Humidity test results at 185°F and 85% RH

Days of conditioning	Projectile lot	
	IOP84C032-001A	IOP82H031-074A
9	No data	OK
30	OK	OK
65	OK	OK

Observation: No failures of either delay type during this test sequence.

Table 7
Humidity test results at 70°F and 100% RH

Days of conditioning	Projectile lot	
	IOP84C032-001A	IOP82H031-074A
27	No data	No data
39	No data	OK
49	OK	No data
68	OK	OK

Observation: No failures of either delay type during this test sequence.

Nitroglycerine Migration Experiment

The NG migration experiment employed six inert warhead M549A1 projectiles. Five projectiles (one control projectile was not conditioned) were conditioned at 75°C with a conditioning duration per projectile of 5, 10, 15, 20, or 25 days. The projectiles were fired at YPG with no observed premature RM ignitions. Table 8 contains the summary of results.

Table 8
NG migration test results

Round	Conditioning environment	Conditioning duration (days)	RM ignition
Control	None	0	Normal
1	75°C	5	Normal
2	75°C	10	Normal
3	75°C	15	Normal
4	75°C	20	Normal
5	75°C	25	Normal

No premature RM ignitions indicate a higher temperature and/or longer conditioning duration are required to induce premature ignition (failure).

CONCLUSIONS/RECOMMENDATIONS

Both types of delay assemblies are susceptible to failure when exposed to high levels of moisture at elevated temperatures. The original and alternate designs do not seem to exhibit any differences in their susceptibility to failure from either the thermal experiments or the thermal and humidity experiments.

M549A1 projectiles with both types of delay assemblies (original and alternate designs) should remain in the stockpile. If it is known that the Rocket Off Cap has been removed from the base of the projectile (allowing the delay assembly to be exposed to moisture intrusion), that projectile has an increased risk of rocket motor (RM) failure (short round) and should be put into condition code H (unserviceable - condemned).

Since RM conditioning at 75°C for up to 25 days did not induce a premature RM ignition, a higher temperature and/or longer duration experiment(s) is required to conduct a predictive analysis. A new experiment can be safely conducted at 85°C for up to 50 days, which could precipitate failures (premature ignition) that would provide sufficient data to predict life as a function of premature RM ignition.

APPENDIX A

EVALUATION OF AGE RELATED DEGRADATION FOR M549A1 ROCKET MOTORS

Evaluation of Age Related Degradation for M549A1 Rocket Motors

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ABSTRACT

This paper addresses two potential failure mechanisms for the M549A1 Rocket Motor. The first failure mechanism involves migration of NG (Nitroglycerine) from the rocket grain onto the surface. Then upon launch, the grain spins and auto-ignites producing an auto-ignition of the rocket motor and a resulting short round. The second failure mechanism being investigated is failure of the delay assembly. The effect of temperature on the degradation of the delay assembly has been characterized in this paper.

A series of experiments have been initiated which study the two failure mechanisms. The experiments involve accelerated aging of the rocket motor, and the subsequent firing of the M549A1 projectiles at Yuma Proving Ground (YPG). Similarly, accelerated aging has also been conducted on the delay assemblies in order to induce failure of the delay. This would cause a non-ignition of the rocket motor and produce a short round.

The results indicate that higher stress levels are required to induce the NG migration failure mechanism in order to produce early ignition of the rocket motor. For the delay failure mechanism extremely long lifetimes resulted when using only temperature as the accelerant. Additional experiments that subject the delay to high humidity are required to fully characterize the delay failure mode.

INTRODUCTION

Upon return from Operation Desert Storm, the test firing of M549A1 projectiles resulted in rocket motors that did not function. Using radar it is possible to detect whether or not the delay functioned. It if functions correctly, it ejects out the back of the round. For the rocket motors that did not function, it was observed that the delay did not eject out the back of the round and was the cause of the failure. The result of a delay failure is a non-ignition of the rocket motor and, consequently, a short round. The rocket motor non-ignitions were all attributed to delay failure. Those test firing results with the delay failures are shown in Table A-I.

Short rounds are a safety hazard during tactical maneuvers in a wartime situation. The M549A1 is fired over the heads of our troops. The high explosive warhead on the M549A1 is aimed at stopping the advancing opposing troops. Thus, a short round could fall on our troops and cause "friendly fire" casualties. This study was initiated to study the failure mechanisms and modes of the M549A1 rocket assisted projectile.

In addition to the delay assembly failure mode, another failure mode involving premature rocket ignition was also investigated. Premature rocket ignition can also result in a short round since the rocket motor ignites too early. The trajectory of the projectile at the early stages of firing has a large component in the upward direction. Ideally, the rocket motor goes off when the projectile is flying horizontally. If it goes off early, the projectile goes up higher but does not get the required extended range. This also results in a short round. This was reported in a number of test firings of the M549A1 but the data were not available at the time of the writing of this paper.

Table A-I. M549A1 Rocket Motor Non-ignition Observed During Test Firings

	Selected from Depot/Not ODS (fail)	Selected from PREPO/Not ODS (fail)	ODS Deployed (fail)	Total (fail)
Original Delay Design	830 (0)	104 (0)	48 (0)	982 (0)
Alternate Delay Design	235 (0)	40 (1)	105 (4)	380 (5)

EXPERIMENTAL

Experimental Designs

Three different experimental designs were used in this study. The first was a propellant stabilizer depletion study. The experimental design involved the two factors temperature and humidity with each of the factors present at two levels. The factor levels and experimental designs are shown in Table A-II below.

Table A-II. Experimental Design for the Propellant Stabilizer Depletion Study

Temperature Levels	70°C	85°C
Humidity Levels	0% Relative Humidity	100% Relative Humidity
	0% Relative Humidity	100% Relative Humidity

Then a nitroglycerine migration study was done. In this experiment a single level of temperature was used. Samples from an M549 Projectile lot (IOP81E030-118) were conditioned at 75°C. The humidity was low. Only ambient air entered the chamber and it was heated to 75°C. The warhead of each of the projectiles was filled with an inert fill during the conditioning process. The only factor which was varied in that experiment was the conditioning time. Samples were withdrawn at the start of the experiment and at 5 day intervals. The warhead of each of the projectiles was filled with an inert fill during the conditioning process. The experimental design for the rocket motor experiment is shown in Table A-III.

Table A-III. Rocket Motor Experiment at 75°C and Ambient Humidity

Conditioning Times in Days	0
	5
	10
	15
	20
	25

A delay experiment was also conducted. That experiment was done at two levels of temperature. Two delay configurations were used. The delay configurations were designated as alternate design and original design and had chemically different makeup. Samples were obtained from four different lots of M549A1 projectiles. Two were designated as Y lots. The Y lots were produced with an alternate and an original design configuration. The lots are designated as Y lots because they are lots of material that were in Operation Desert Storm (ODS) and then shipped back to the continental United States. The lots without the Y designation had never seen the ODS environment. The lots used in that experiment are shown in Table A-IV. The experimental design for that experiment is shown in Table A-V.

Table A-IV. Lots Used in the Delay Experiment

Lot History	Original Design	Alternate Design
Exposed to ODS	IOP81B030Y109	IOP84F032Y005C
Not Exposed to ODS	IOP84C032-001A	IOP82H031-074A

Table A-V. Sampling Times and Temperatures for Delay Experiment for Each Lot

Temperature Levels	375°F					475°F				
Sampling Times in Days	5	10	15	20	25	5	10	15	20	25

RESULTS

Predicted and Observed Stabilizer and NG Concentrations

The earlier study on the propellant degradation kinetics (Bixon, 2001) resulted in reaction kinetic (Fogler, 2000, Levenspiel, 1972) models. The models were formulated to describe the reaction of 2NDPA and the formation of some of its derivatives. The data obtained from those experiments were correlated and the results were used to set the accelerated aging conditions (temperature and duration or exposure) for use in the nitroglycerine migration study. Some of the data generated during the propellant stabilizer depletion study are shown in Figures A-1 and A-2. Data for the derivatives and daughter products were also correlated during that study.

Based on earlier models and the experimental data generated in the propellant stabilizer depletion study, stabilizer profiles and NG concentrations were estimated at 70 and 85°C at times of 10 and 25 days based on the data. It was estimated from the data that at 75°C, a 25 day experiment would be safe enough to run without blowing up the rocket motors in the chamber. Samples were taken at 10 and 25 days from the 75°C experiment at YPG and sent back to ARDEC for analysis using HPLC. The predicted and observed stabilizer concentration results are shown in Table A-VI. The observed results at 75 °C were based on samples cut from the rocket motors during the NG migration experiments conducted at YPG. The observed results indicate a large amount of 2NDPA present. This indicates the experiment could be carried out at higher stress levels with no danger. The predicted and observed NG concentrations are shown in Table A-VII. For that situation, the observed NG concentrations were lower than the predicted NG concentrations.

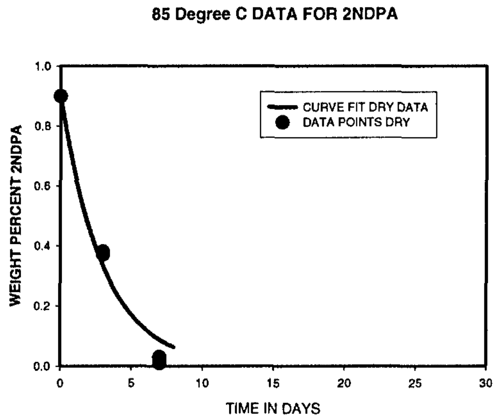

Figure A-1. Weight percent 2NDPA vs. time

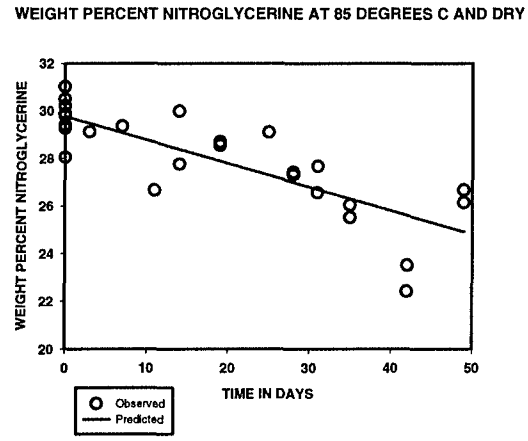

Figure A-2. Weight percent NG vs. time

One factor that could result in the difference between predicted and observed results is the sample size. The original study was done using small disks of propellant cut from the rocket grain using a hole saw and sliced into thin segments. In the current study, the complete rocket motor assembly was aged. The ratio of surface area to mass for the two experiments is very different. The diffusion rates of NG and the kinetics of the propellant degradation products depend on the sample size to some degree.

Table A-VI. Predicted Stabilizer Concentrations

	2NDPA		NNO -2NDPA		2-2' DNDPA		2-4' DNDPA	
Temperature	10 day	25 day	10 day	25 day	10 day	25 day	10 day	25 day
70°C (predicted)	0.6	0.32	0.14	0.08	0.06	0.15	0.1	0.23
85°C (predicted)	0.0	0.0	0.07	0.06	0.24	0.06	0.35	0.05
75°C (observed)	0.395	0.455	0.22	0.49	0.085	0.035	0.11	0.05

Table A-VII. Predicted and Observed NG Concentrations

	NG Concentrations		
Temperature	0 day	10 day	25 day
70°C (predicted)	29.8	29.5	28.2
85°C (predicted)	29.8	29.0	27.2
75°C (observed)	–	25.6	25.5

Nitroglycerine Migration Test

As indicated, the nitroglycerine migration test involved exposing complete M549 rounds in the test chamber and conditioning them for a period of [up to] 25 days at 75°C. Samples were obtained every 5 days. The rounds were then fired in a test sequence at Yuma Proving Ground (YPG) and the firing data was examined for any evidence of an early ignition. The test results are shown in Table A-VIII. No failures were observed. That indicates higher temperatures and/or longer conditioning times are required to reproduce the failure mode of early rocket motor ignition.

Table A-VIII: Nitroglycerine Migration Test Results

ROUND NUMBER	TEMP (°C)	DURATION (DAYS)	RESULTS
Control	No Conditioning	None	OK
1	75	5	OK
2	75	10	OK
3	75	15	OK
4	75	20	OK
5	75	25	OK

Delay Test

The delay assemblies were removed from the rounds and were conditioned at very high temperature with no humidity. Samples were withdrawn periodically every five days. Then the delays were put back into the corresponding M549A1 rounds and fired at Yuma Proving Ground. A number of controls were also used to make sure that the delay removal process did not affect the results.

The complete test results are shown in Table A-IX. Note that in Table A-IX additional results on unconditioned delays are also shown. Those samples were done in order to verify that the delay removal procedure did not affect the reliability of the delay elements. The out-in designation indicates delays were taken out and then put back into rounds that were tested.

The untouched delays were not removed from the rocket motor. The rounds using the untouched delays were not "tampered" with in any way. The results indicate that the procedure of delay removal and then reinsertion did not affect the reliability. Those results are based on very small sample sizes, however, there is no reason to suspect that the delay removal and reinsertion process would cause a reliability problem with the delays.

Table A-IX. Delay Experiment Results

LOT NUMBER	SERIAL NUMBER	CONDITIONING TEMPERATURE (°F)	CONDITIONING DURATION (DAYS)	RESULTS
001A	51	No Conditioning Delays Untouched		OK
001A	1	375	5	OK
001A	2	375	10	OK
001A	3	375	15	OK
001A	4	375	20	OK
001A	5	375	25	OK
001A	6	475	5	NO RM
001A	7	475	10	NO RM
001A	8	475	15	NO RM
001A	9	475	20	NO RM
001A	10	475	25	NO RM
001A	49	No Conditioning Delays Out-In		OK
Y109	1	375	5	OK
Y109	2	375	10	OK
Y109	3	375	15	OK
Y109	4	375	20	No RM
Y109	5	375	25	OK
Y109	6	475	5	No RM
Y109	7	475	10	No RM
Y109	8	475	15	No RM
Y109	9	475	20	No RM

Table A-IX. Delay Experiment Results (continued)

LOT NUMBER	SERIAL NUMBER	CONDITIONING TEMPERATURE (°F)	CONDITIONING DURATION (DAYS)	RESULTS
Y109	10	475	25	No RM
074A	51	No Conditioning Delay Untouched		OK
074A	1	375	5	OK
074A	2	375	10	OK
074A	3	375	15	OK
074A	4	375	20	OK
074A	5	375	25	OK
074A	6	475	5	OK
074A	7	475	10	OK
074A	8	475	15	OK
074A	9	475	20	OK
074A	10	475	25	No RM
074A	49	No Conditioning, delays out-in		OK
Y005C	1	375	5	OK
Y005C	2	375	10	OK
Y005C	3	375	15	OK
Y005C	4	375	20	OK
Y005C	5	375	25	OK
Y005C	6	475	5	OK
Y005C	7	475	10	OK
Y005C	8	475	15	OK
Y005C	9	475	20	OK
Y005C	10	475	25	OK

The data in Table A-IX show delay failures for lots 001A and Y109. There was also a single failure for lot 074A. The failures were primarily observed in the original design delay compositions. This was not expected since most of the failures during the stockpile test occurred with the alternate delay composition. In order to get some feel for the degradation rate (or service life) at ambient storage conditions, the data were modeled using a lognormal failure distribution. Only lot Y109 had failures at both of the conditioning temperatures. Those data were used to supply an estimate of the degradation rate.

Modeling of the Failure Data for the Delay Test

For the experimental cells in which failures were observed, the censored data were modeled using a lognormal distribution. The lognormal cumulative distribution function for the population fraction failing by age y is

$$F(y,T)=\Phi\{[\log(y)-\mu(T)]/\sigma\},\ y>0 \qquad (1)$$

Here $\Phi(\ )$ is the standard normal cumulative distribution function. The parameter $\mu(T, \%RH)$ is the mean of the log of life and is called the log mean. It is a function of the accelerated aging conditions to which the item is exposed. For this system it is a function of temperature. The data for lot Y109 at 375°F is a censored data set. Maximum likelihood methods (Nelson, 1982, 1990) were used to compute the log mean and the log standard deviation for the censored data sets in which failures were observed. The means, standard deviations and median times to failure for the lognormal distribution can be determined from the log mean and the log standard deviation. The median time to failure is related to the logmean and is given by the following expression.

$$\tau.50 = \exp\left[\mu(T, \%RH)\right] \tag{2}$$

At 475°F failures were encountered at each of the 5 sampling periods. From these type of data, it can be assumed that all of the items were failed by day 5. The samples were pulled at later times, but they all could have failed by day 5. Using the "interval" method (Nelson, 1982) of estimating the failure time, the time to failure can be estimated as halfway between the interval. This corresponds to a failure time of 2.5 days at 475°F. The data at 375°F can be analyzed using the referenced Maximum Likelihood techniques. This results in a lognormal mean of about 25 days at 375°F. The predicted failure distribution for that data set is shown in Figure A-3.

The two lognormal means obtained from the data generated for lot Y109 can be correlated using the Arrhenius equation shown as Equation (3). In Equation (3), $\mu(T)$ is the log mean at temperature, T, and T is the absolute temperature. A rough estimate of the lifetime can be

$$\mu(T) = A + B/T \tag{3}$$

supplied using the two lognormal means. Application of Equation (3) to the two data points generated for lot Y109 predicts a lifetime at ambient of greater than 11,000 years. This implies that temperature alone did not cause the delay failures observed during the test firings shown in Table A-.

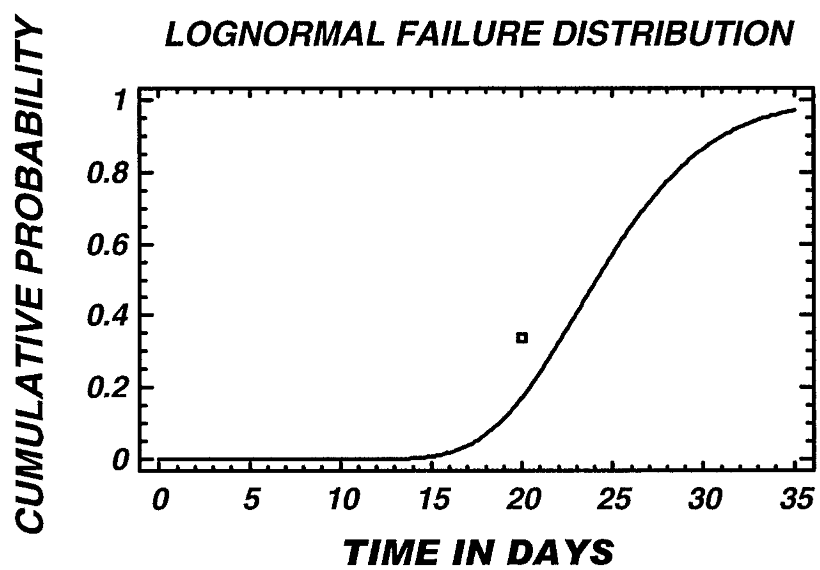

Figure A-3. Lognormal Failure Distribution for the Y109 Lot at 375°F

CONCLUSIONS

Reaction kinetic models were used to correlate accelerated aging data for M549A1 rocket motor samples. The models were used to predict safe aging conditions for the experimental determination of NG migration as a potential cause of premature rocket motor ignition. One set of experiments was conducted at a temperature of 75 °C that did not cause the premature ignition to take place. Higher temperature experiments need to be conducted in order to reproduce this failure mode based on the NG migration mechanism. Those experiments can be conducted very safely since the observed stabilizer depletion rates for the 75°C experiment indicated plenty of stabilizer left. The next experiments should be conducted at 85°C for up to about 50 days. There is some risk of low stabilizer at that condition. If that experiment is conducted successfully, samples should be taken in the middle and the end of the experiment to determine the actual stabilizer levels, and to see if the experiment can be run at an even higher stress condition.

For the delay experiments an Arrhenius correlation of the median times to failure based on the lognormal distribution indicated an extremely long lifetime (11,000+ years). This implies that the thermal degradation of the delay element proceeds at an extremely slow rate at 21.1°C. Therefore, the failures that were observed in the returned ODS M549A1 assets were probably due to humidity or moisture environmental stresses. High humidity exposure experiments are currently being conducted to reproduce the delay failure mode at much lower temperatures than those used in this study[1].

REFERENCES

1. Eric R. Bixon, "Accelerated Testing of M549A1 Rocket Motors", Proceedings of the 50th JANNAF Propulsion Meeting, Salt Lake City, Utah, 11-13 July 2001.
2. H. Scott Fogler, May 2000, "Elements of Chemical Reaction Engineering", New Jersey, Prentice Hall.
3. Octave Levenspiel, 1972, "Chemical Reaction Engineering", New York, John Wiley & Sons.
4. Nelson, Wayne, (1982), Applied Life Data Analysis, John Wiley & Sons, New York.
5. Nelson, Wayne, (1990), Accelerated Testing, John Wiley & Sons, New York.

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[1]Note: The "high humidity exposure experiments" results are presented under "Part II: Temperature and Humidity Conditioned Test" pages 4 through 8 of this report.

APPENDIX B
ACCELERATED TESTING OF M549A1 ROCKET MOTORS

Accelerated Testing of M549A1 Rocket Motors

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ABSTRACT

This paper addresses the degradation behavior of AHH propellant, which is cast into rocket motors for use in the M549A1 Rocket Assisted Projectile. A study on the stabilizer depletion rates that occur in small samples taken from an M549 rocket grain has been conducted. Reaction kinetic models have been formulated to describe the reaction of 2NDPA and the formation of some of its derivatives. Data obtained from the experiment have been correlated. The models have been developed as part of a larger effort to characterize the degradation behavior of the propellant and to provide stability data at elevated temperatures.

BACKGROUND

The M549A1 rocket grain is a double base propellant. The grains are formulated from AHH propellant made in accordance with MIL-P-60432 and casting solvent (MIL-C-13609B). The compositions of the AHH grains and the composition of the casting solvent are given in Table B-I. The rocket motors have a composition that results from a mixture of the two compositions.

Table B-I: Composition of AHH grains and casting solvent in weight percent

MATERIAL	SPECIFICATION (AHH)	SPECIFICATION (Casting Solvent, TYPE III)
Nitrocellulose	83.0 ± 1.3	
Nitroglycerine	11.4	75.0 ± 1.0
Lead Salicylate	2.3	
Lead 2-Ethylhexoate	2.3	
2-Nitrodiphenylamine	1.0 ± .15	1.0 ± 0.10
Graphite (glaze)	0.03 to 0.06	
Triacetin		24 ± 1.0

EXPERIMENTAL

Procedure

Small samples were taken from each of the three sections of rocket grain, which make up the M549A1 Rocket Motor. Cores about 30 mm in diameter were drilled out with a hole drill bit. Slices between two and three millimeters in thickness were then sliced off of the core. The samples were not exactly symmetrical. The diameters were very consistent but the heights (when they were sliced off the core) varied from one side of the sample to the other. Typical dimensions and weights of several of the samples are shown in Table B-II.

Table B-II. Dimensions of the samples cut from the M549A1 rocket grain

CONDITION	Diameter (mm)	H1 (height on small side)	H2 (height on large side)	Mass in grams
Not conditioned	30	3	3	4.0301
Not conditioned	30	2.5	3.5	3.9957
70 C, 8 weeks, dry	30	3.0	3.5	3.8472
70 C, 8 weeks, dry	30	2.4	3.5	3.6695
70 C, 8 weeks, wet	30	2.4	3.0	3.3338
70 C, 8 weeks, wet	30	2.0	3.0	3.4577

TABLE B-III - Composition of samples aged at 85°C and 100% relative humidity

TIME IN DAYS	2NDPA	2-4'	2-2'	N-NO-2NDPA
0	0.9	0	0	0.14
3	0.52	0.2	0.1	0.06
3	0.57	0.2	0.11	0.06
7	0.4	0.26	0.15	no data
7	0.43	0.27	0.16	0.02
11	0.28	0.29	0.16	no data
11	0.31	0.29	0.18	0.02
14	0.21	0.31	0.19	0.08
14	0.2	0.38	0.23	0.09
19	0.11	0.38	0.23	0.12
19	0.09	0.43	0.26	0.12
25	0.07	0.45	0.29	0.05
25	0.04	0.4	0.25	0.08
28		0.4	0.26	0.09
28		0.41	0.26	0.1
31		0.39	0.26	0.12
31		0.39	0.26	0.11
35		0.37	0.25	0.13
35		0.36	0.24	0.1
42		0.31	0.24	0.11
42		0.31	0.24	0.02
49		0.08	0.11	0.03
49		0.04	0.1	no data

Results

In order to provide a good baseline five samples were analyzed for weight percent 2NDPA (2-nitrodiphenylamine) and the daughter products on 2 separate occasions. The results indicated 2NDPA and some N-Nitroso-2NDPA were present. The averages of those ten analyses are shown in Table III at time equal to zero days. Additional samples were conditioned at 85°C and 70°C at 0 and 100% relative humidity. The samples were placed in weighing dishes on desiccator plates inside desiccators that were then placed in the chambers. The 100 % relative humidity condition was maintained with a reservoir of distilled water in the base of the desiccator. The 0% relative humidity was maintained in another desiccator filled with drierite in the bottom.

Samples were periodically withdrawn and analyzed using HPLC. The results of those analyses for the experiments conducted at 85°C and 100% relative humidity are shown in Table III. The data in Table III are the weight percent of 2NDPA, 2-4' DNDPA, 2-2' DNDPA and N-Nitroso 2NDPA expressed as the equivalent weight percent of 2NDPA. The actual weight percents of the compounds in Table B-III were multiplied by the molecular weight of the 2NDPA divided by the molecular weight of the compound.

Correlation of Experimental Data

Reaction kinetic[1,2] models have been used to correlate the data shown in Table B-III for the 2NDPA and each of the daughter products. Reaction kinetics is based on the development of rate expressions. The rate expressions are used to model the progress of the reaction as the concentration changes with time. A generalized reaction scheme for the degradation of 2NDPA in the presence of excess NOx is shown in Equation (1) where A represents the 2NDPA and R represents a product that results from the reaction of 2NDPA and the NOx species generated by the decomposing nitrocellulose molecules. The rate expression for the first order irreversible decomposition of reactant A is shown in equation (2). The symbol C_A is used to represent the concentration of A in weight percent.

$$A \xrightarrow{k1} R \tag{1}$$

$$dC_A / dt = -k1 * C_A \tag{2}$$

Another reaction scheme used to correlate the data generated in this study is based on irreversible reactions in series. That reaction scheme is given in Equation (3).

$$A \xrightarrow{k1} R \xrightarrow{k2} S \tag{3}$$

The reaction scheme in Equation 2 shows the reactant, A, being converted to an intermediate product, R, which in turn gets converted to a subsequent product, S. The rate expression for the component R based on first order kinetics used to represent that reaction scheme is given in Equation (4). Note that C_R in Equation (4) is expressed as the equivalent weight percent of 2NDPA.

$$dC_R / dt = k1 * C_A - k2 * C_R \tag{4}$$

The solutions to equations (2) and (4) are given below in Equations (5) and (6) respectively.

$$C_A = C_{A_0} * \exp(-k1 * C_R) \tag{5}$$

$$C_R = \{k1 * C_{A_0} / (k2 - k1)\} * \{\exp(-k1 * t) - \exp(-k2 * t)\} + C_{R_0} * \exp(-k2 * t) \tag{6}$$

Equations (5) and (6) were used to correlate the experimental data. Equation (5) was used to correlate the data for 2NDPA and Equation (6) was used to correlate the data for the N-Nitroso-2NDPA, the 2-2'-dinitroDPA and the 2-4' dinitroDPA. The rate constants for each of the components are given in Table B-IV.

Table B-IV: Rate Constants for the 2NDPA and the daughter products at 85°C

Component	Desiccator Condition	Rate Constant, k1 in day^{-1}	Rate Constant, k2 in day^{-1}
2NDPA	Distilled Water	0.1137	–
2-4' DINITRODPA	Distilled Water	0.0636	0.0424
2-2' DINITRODPA	Distilled Water	0.0336	0.0550
N-NITROSO-2NDPA	Distilled Water	0.0104	0.1052
2NDPA	Drierite	0.3317	–
2-4' DINITRODPA	Drierite	0.2165	0.1376
2-2' DINITRODPA	Drierite	0.1170	0.1789
N-NITROSO-2NDPA	Drierite	0.0133	0.1845

Discussion of Results

The rate constants in Table IV have been determined by regressing the data onto the models given by Equations (5) and (6). Equation (5) was used to correlate the data for 2NDPA and Equation (6) was used to correlate the concentration-time data for each of the products formed by the reaction of the 2NDPA with the NOx given off by the decomposing nitrocellulose. Note that in Equation (6) the rate constants k1 and k2 have been allowed to vary, and have not been constrained by the value of k1 found from Equation (5). This allowed for a better fit for the kinetic data. The results are shown in Figures B-1 through B-4.

In these experiments it is desirable to run the experiment long enough so that the products (like 2-2' DNDPA and 2-4' DNDPA) have a chance to be completely formed and completely reacted. If the full concentration vs. time curve is available, the model fitting procedure is more accurate. From the plots it looks like more time is needed to completely exhaust the dinitro derivatives as well as the n-Nitroso-2NDPA. The time can be calculated from the models.

The models appear to fit the data well with the exception of the N-nitroso 2NDPA model. That model does not fit the initial decrease in the concentration of the N-nitroso 2NDPA when the experiment first starts. Both the wet and the dry data sets have this feature.

The fact that the reaction rates are much slower in the desiccator with the distilled water in the base is obvious from the concentration vs. time plots for all the components. One explanation for the fact that the reaction rates (2NDPA degradation) are so much slower in the wet desiccator than the dry desiccator is that the presence of the water in the base of the desiccator acts as an absorbent for the NOx. This would tend to decrease the concentration of the NOx gases in the vapor phase inside the desiccator. That would decrease the partial pressure, and lower the driving force for the trapped NOx gases to equilibrate with the propellant sample and react with the stabilizer (and its daughter products).

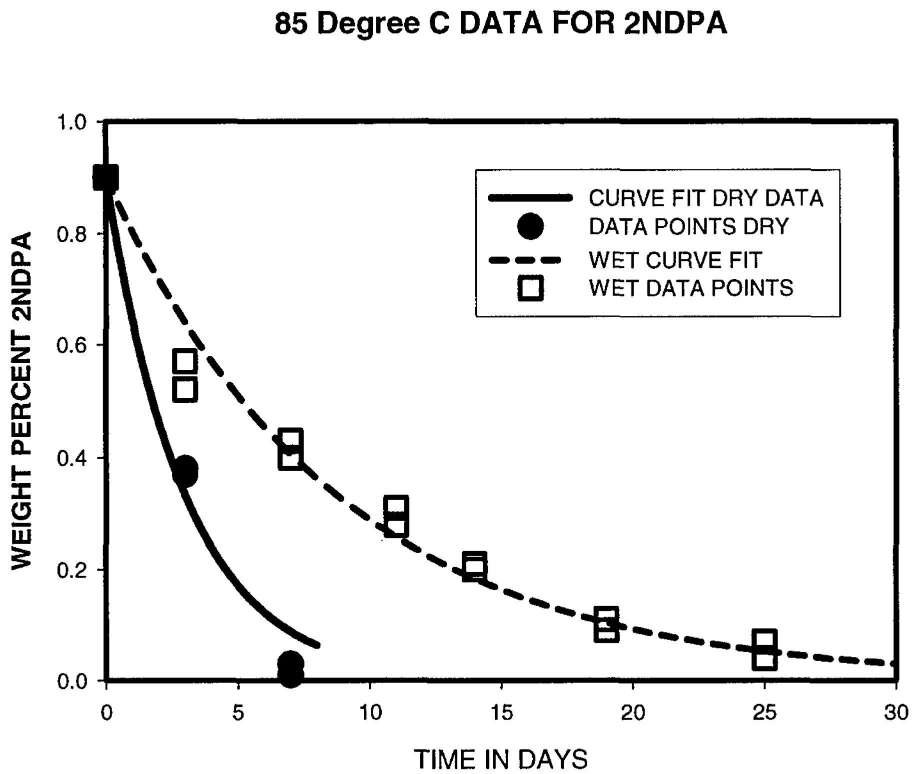

Figure B-1. Weight percent 2NDPA vs. Time

CONCLUSIONS

Reaction kinetic models have been used to correlate accelerated aging data for M549A1 rocket motor samples. The data was obtained using HPLC analysis for 2NDPA and its daughter products. The correlations were based on irreversible first order reaction kinetics for the correlation of the 2NDPA degradation data. For the daughter products, which are formed and then react to produce further nitration products, a reaction kinetic model based on irreversible reactions in series was used to correlate the data. The presence of moisture in the desiccator lowered the reaction rates for the 2NDPA and all its daughter products when compared with the desiccator filled with drierite.

FUTURE WORK

Future work in this area includes extending the models to the data at 70°C (at 0 and 100% relative humidity). In any future experiments using desiccators filled with distilled water, the pH and the acidity (by titration with a base) of the distilled water should be evaluated before, during and at the conclusion of the experiment. This would also be a useful test method for determining the amount of NOx gases that escape from the propellant grain and are not picked up by the stabilizer.

Experimental methods other than using desiccators filled with distilled water may be more useful for evaluation of the effect of moisture on the stabilizer reaction rates. Environmental chambers might be more useful in subjecting the system to moisture. In an environmental chamber there would not be a reservoir of water in the bottom to act as an absorbent. Also the effect of turnover time and air velocity in the chamber is probably important when considering the gas phase concentration of NOx species.

It is useful to develop a predictive model to estimate the degradation rate of the stabilizers as a function of storage conditions. To be more generalized such a model might include temperature, pressure, relative humidity and air flow rate. It should also include the stabilizing effect of all the daughter products.

Models of this type can be correlated with the experimental variables using forms of the Eyring equation. These models can be used to help evaluate the remaining life of the propellant based on various storage scenarios.

NOMENCLATURE

A	Symbol for reactant used in reaction kinetic models (2NDPA)
DNDPA	Dinitrodiphenylamine
R	Symbol for intermediates formed by the reaction of 2NDPA and NOx which include the N-Nitroso 2NDPA, 2-2' DNDPA or 2-4' DNDPA
S	Symbol for products that form after the 2NDPA and the dinitro derivatives have reacted.
CA0	Initial value or concentration of reactant A in weight percent
CR0	Initial value or concentration of reactant R in weight percent of 2NDPA equivalents
CA	Concentration of reactant A in weight percent
CR	Concentration of intermediate R in weight percent of 2NDPA equivalents
k1	First order rate constant in weight percent per day
k2	First order rate constant in weight percent per day
NNO-2NDPA	N-Nitroso 2NDPA
NOx	Decomposition products due to degradation of the nitrocellulose in the propellant
t	Time in days
2NDPA	2-nitrodiphenylamine
2-2' DNDPA	2-2' dinitrodiphenylamine
2-4' DNDPA	2-4' dinitrodiphenylamine

REFERENCES

1. Octave Levenspiel, 1972, "Chemical Reaction Engineering", New York, John Wiley & Sons.
2. H. Scott Fogler, May 2000, "Elements of Chemical Reaction Engineering", New Jersey, Prentice Hall.

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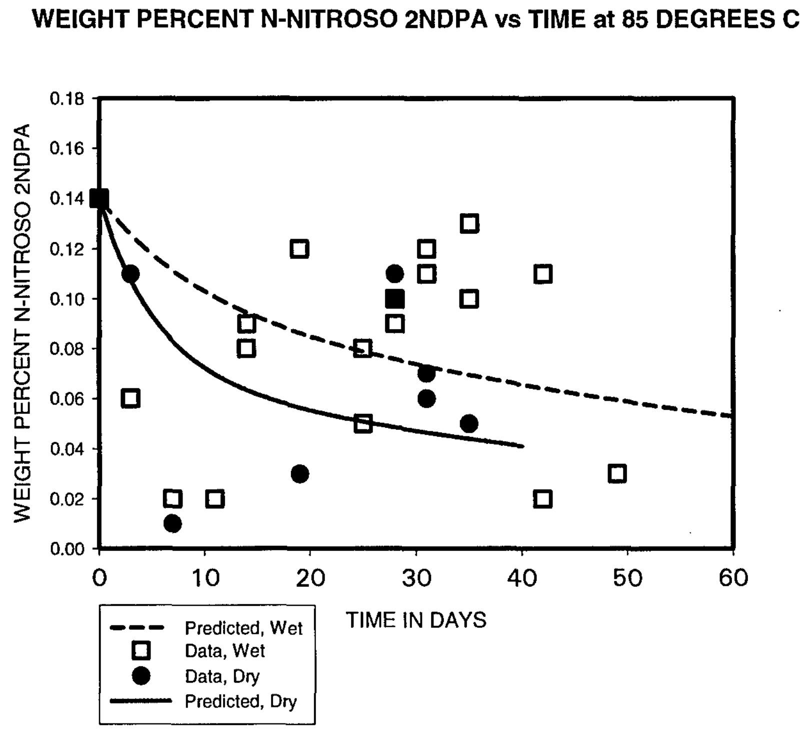

Figure B-2. Weight percent n-nitroso-2NDPA vs. time

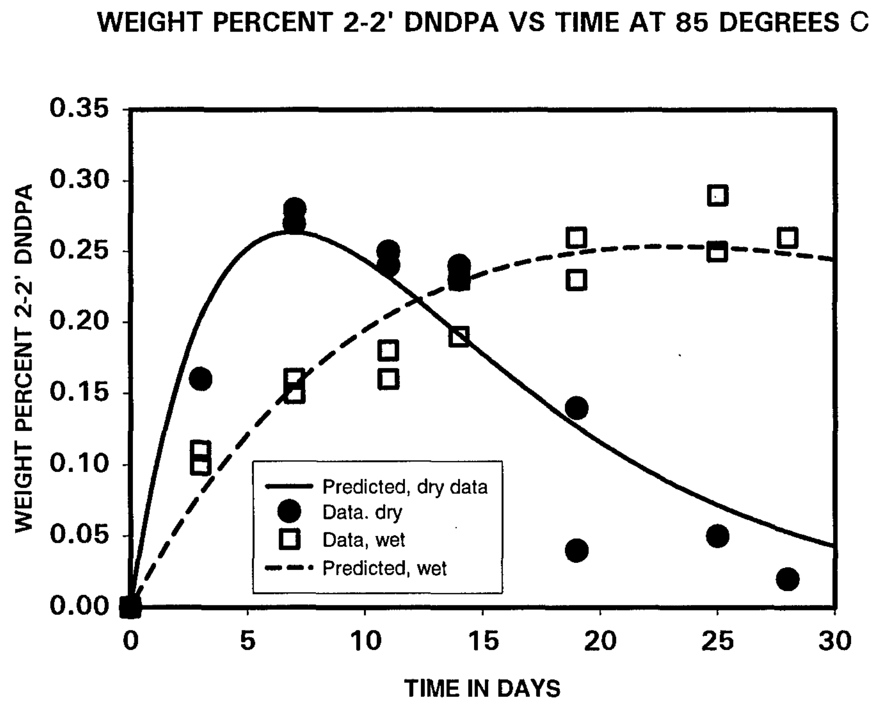

Figure B-3. Weight Percent 2-2' DinitroDPA vs. time

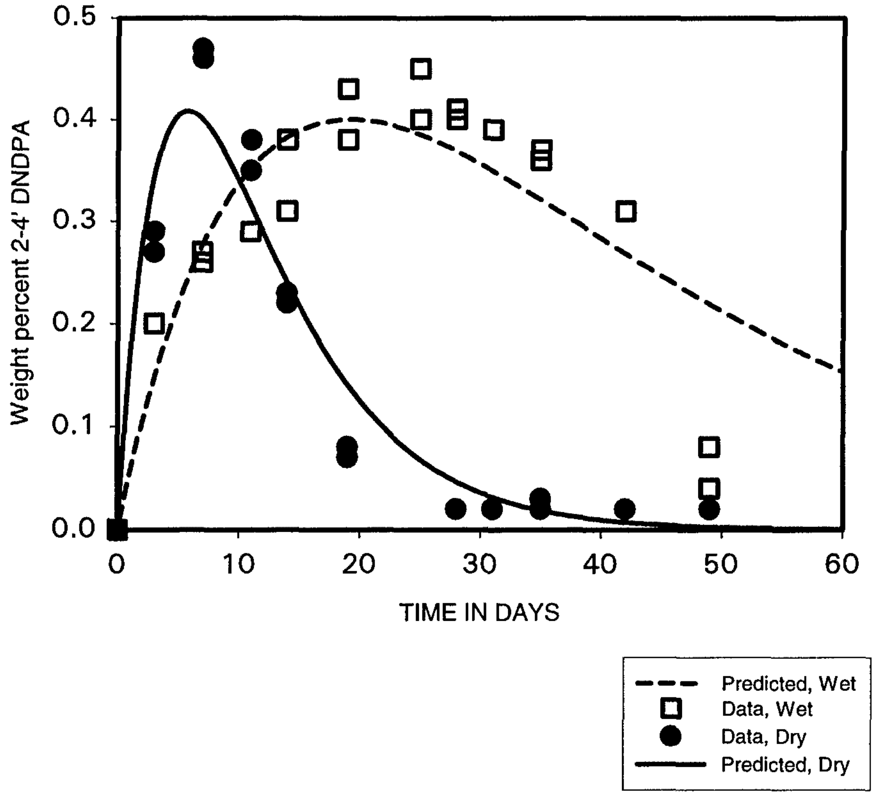

Figure B-4. Weight Percent 2-4' Dinitro DPA vs. time

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