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AN INFORMAL REPORT

The Effects of Long-Term Storage at 60°C on Small Cylinders of PBX 9404

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The Effects of Long-Term Storage at 60°C on Small Cylinders of PBX 9404

by

William H. Rogers*
Louis C. Smith

*Deceased.

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ABSTRACT

Small cylinders of 9404 were stored at 60°C in sealed ampoules partially filled with air or argon. At various times some of the ampoules were removed from storage and opened; the volume and composition of the evolved gases were determined, and various tests were run on the explosive cylinders. Our principal findings were as follows: a) The density and compressive strength decreased abruptly during the first 70 days, and continuously, but slowly, thereafter; b) the impact sensitivity and vacuum thermal stability remained unchanged; c) at the end of the test (331 days) the samples had evolved approximately 1 ml of gas/g of 9404, of which some 30% was oxides of nitrogen (primarily N_2O); d) the oxygen in the air samples was consumed at the rate of about 6×10^{-4} ml/g of 9404/day, and we estimate that the diphenylamine stabilizer was exhausted in about 300 days.

AUTHOR'S NOTE (LCS)

The work described here was carried out in the late 1950's by William H. Rogers, with the assistance of various other LASL personnel. A draft of this report was written by Mr. Rogers shortly before his final illness and untimely death in February 1960. Continuing requests for the experimental results, and a recent decision to repeat the experiment, in slightly modified form, on a new composition, have prompted me to complete the report and issue it at this late date.

I. INTRODUCTION

The thermal stability of PBX 9404 molding powder has been investigated extensively at 100 and 120°C. A long-term exposure of pressed 9404 at 60°C was undertaken so as to collect data more directly related to its behavior under various conditions of storage and use.

II. EXPERIMENTAL

A. Material

Molding powder from a current lot of PBX 9404 was pressed to high density in the form of large cylinders by customary production procedures. These cylinders were machined to provide the test cylinders. A complete description of the material used and a summary of the inspection data follow.

1. Molding Powder
    a. Identification

    PBX 9404, Lot 75

    b. Analytical Data (w/o)

Cellulose nitrate	3.05
tris(β-Chloroethyl)phosphate	3.09
HMX	93.73
Diphenylamine	0.09
Moisture	0.04

2. HMX
    a. Identification

    Lot 41-57, Blend "O"

    b. Analysis

    93.5% HMX, 6.5% RDX

    c. Particle Size Distribution

Screen Size	Percent Passed
45	98.7
60	80.5
80	55.0
120	25.0
170	14.7
230	9.6
325	5.5

3. Pressed Stock

GMX-2 Mold Type 113, vacuum-pressed 4/14/58

Charge Number	Immersion Density (g/cm^3, 26°C)
1154-1	1.826
1154-2	1.826
1154-3	1.826
1154-4	1.825
1154-5	1.827

4. Machining

Forty-five 1-in.-dia x 3-in.-long test cylinders were machined from the stock charges according to the following scheme:

Stock Charge Number	Test Piece Numbers
1154-1	1154-1 to 15
1154-2	1154-16 to 30
1154-3	1154-31 to 45

5. Dimensional Inspection

The height of each piece was measured on the axis and at two or three equally spaced points near the edge, and the diameter of each piece was measured at several points around the cylinder at each end and at the middle. The results of these measurements are reported in Table I.

6. Immersion Density and Dry Weight

The dry weight of each piece was determined to 0.1 mg, and the immersion density (water) to 0.001 g/cm^3. These data are reported in Table II.

7. Radiographic Inspection

All the pieces were radiographed. Pieces showing high-density inclusions greater than 0.015 in. in maximum dimension were put aside to be used as controls. Of the remaining pieces, 24 were selected for testing. The rest were stored with the rejects from radiographic inspection. All stored pieces were kept in individual glass bottles in a magazine. The temperature in the magazine ranged from 53°F in the winter to 72°F in the summer.

B. Sample Preparation

Each piece to be tested was placed in a separate, sealed container in an atmosphere of either argon or dry, CO_2-free air. The gas pressure in the containers was adjusted to approximately 200 mm Hg at room temperature. The containers were entirely of glass so as to avoid the presence of materials that might contribute to the products of decomposition or react with them. The all-glass ampoule used in these tests is shown in Fig 1. The piece was placed in the body of the ampoule, and

---

TABLE I

DIMENSIONAL INSPECTION

9404 - Charges 1154-1,2,3 - 16 April 1958

Piece No.	Diameter (in.) Top	Middle	Bottom	Height (in.)
1	1.0000	1.0002	1.0003	3.0012
2	1.0003	1.0002	1.0003	3.0018
3	1.0002	1.0001	1.0002	3.0008
4	1.0002	1.0002	1.0002	3.0010
5	1.0002	1.0002	1.0004	3.0011
6	1.0002	1.0003	1.0005	3.0008
7	1.0003	1.0002	1.0004	3.0010
8	1.0001	1.0002	1.0003	3.0001
9	1.0002	1.0002	1.0004	3.0009
10	1.0005	1.0004	1.0006	3.0010
11	1.0005	1.0003	1.0004	3.0012
12	1.0004	1.0005	1.0006	3.0010
13	1.0004	1.0003	1.0005	3.0010
14	1.0002	1.0002	1.0003	3.0010
15	1.0002	1.0004	1.0005	3.0012
16	1.0002	1.0002	1.0003	3.0005
17	1.0003	1.0002	1.0005	3.0010
18	1.0005	1.0003	1.0006	3.0010
19	1.0004	1.0003	1.0006	3.0000
20	1.0004	1.0004	1.0007	3.0001
21	1.0006	1.0005	1.0006	3.0008
22	1.0006	1.0005	1.0005	3.0005
23	1.0005	1.0005	1.0006	3.0014
24	1.0000	1.0000	1.0001	3.0012
25	1.0000	1.0000	1.0001	3.0015
26	1.0001	1.0001	1.0001	3.0012
27	1.0002	1.0001	1.0002	3.0010
28	1.0000	1.0000	1.0001	3.0013
29	.9998	.9999	1.0000	3.0012
30	1.0000	1.0000	1.0001	3.0012
31	1.0001	1.0000	1.0001	3.0010
32	1.0000	1.0000	1.0001	3.0015
33	1.0000	1.0000	1.0000	3.0015
34	1.0000	1.0000	1.0001	3.0012
35	1.0001	1.0000	1.0001	3.0015
36	1.0001	1.0000	1.0000	3.0015
37	1.0000	1.0000	1.0000	3.0012
38	1.0002	1.0002	1.0003	3.0015
39	1.0002	1.0001	1.0002	3.0015
40	1.0003	1.0002	1.0002	3.0010
41	1.0000	1.0001	1.0002	3.0002
42	1.0003	1.0003	1.0004	3.0005
43	1.0002	1.0002	1.0003	3.0009
44	1.0001	1.0002	1.0003	3.0012
45	1.0001	1.0001	1.0002	3.0010

TABLE II

CHARGE WEIGHTS AND DENSITIES

Piece No.	Weight in Air (g)	Volume (cm^3)	Density (g/cm^3)
1	70.4140	38.5384	1.827
2	70.4508	38.5542	1.827
3	70.4362	38.5512	1.827
4	70.4532	38.5516	1.828
5	70.4760	38.5568	1.828
6	70.4876	38.555	1.828
7	70.4720	38.5491	1.828
8	70.4679	38.5548	1.828
9	70.4531	38.5585	1.827
10	70.5053	38.5571	1.829
11	70.4980	38.5582	1.828
12	70.4910	38.5589	1.828
13	70.4870	38.5552	1.828
14	70.4466	38.5505	1.827
15	70.4740	38.5595	1.828
16	70.4530	38.5549	1.827
17	70.4660	38.5569	1.828
18	70.4608	38.5567	1.827
19	70.4492	38.5490	1.828
20	70.4614	38.5518	1.828
21	70.4724	38.5605	1.828
22	70.4837	38.5558	1.828
23	70.4934	38.5658	1.828
24	70.4304	38.5288	1.828
25	70.4343	38.5362	1.828
26	70.4413	38.5300	1.828
27	70.4375	38.5284	1.828
28	70.4285	38.5103	1.829
29	70.4408	38.5206	1.829
30	70.4520	38.5238	1.829
31	70.4254	38.5188	1.828
32	70.4204	38.5261	1.828
33	70.4210	38.5289	1.828
34	70.4340	38.5304	1.828
35	70.4300	38.5336	1.828
36	70.4617	38.5205	1.829
37	70.4581	38.5236	1.829
38	70.4520	38.5509	1.828
39	70.4773	38.5512	1.828
40	70.4890	38.5489	1.829
41	70.4705	38.5318	1.829
42	70.4948	38.5467	1.829
43	70.4790	38.5439	1.829
44	70.4921	38.5420	1.829
45	70.4801	38.5390	1.829

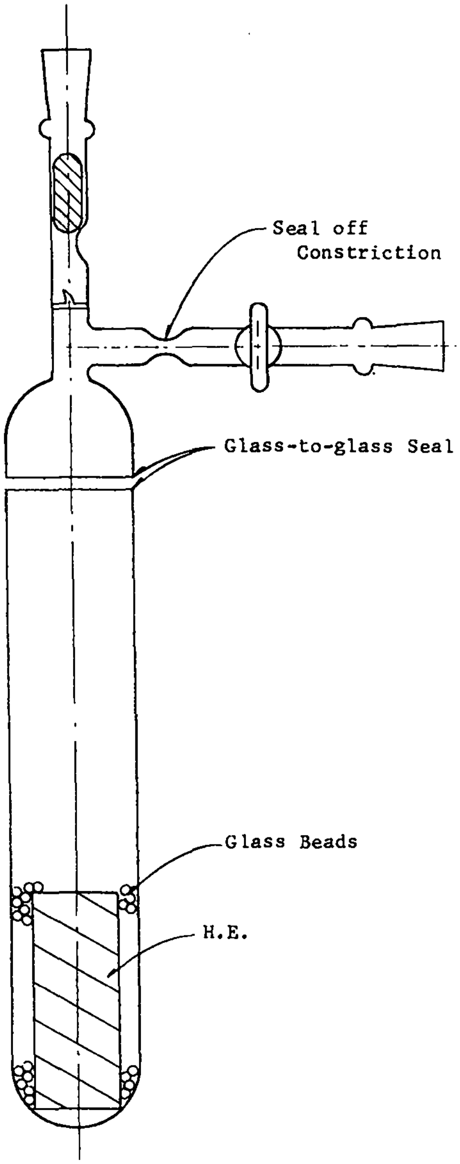


Fig 1

glass beads were added to cover the piece to a depth of several inches. The top was then sealed to the body with a hand torch. The body was kept cool during this operation by immersing it in ice water. The beads served as a barrier against an accidental incursion of flame from the torch. The seal was carefully annealed with the hand torch and subsequently tested for leaks under vacuum with a helium leak detector.

Before filling the ampoules with gas it was necessary to determine the free volume of each ampoule in order to measure the pressure and volume of the gases in the ampoule at the end of the surveillance period. The volume up to the stopcock was determined by PVT measurements with the aid of a calibrated 1-liter volume and a mercury manometer. The ampoule was then filled with the appropriate gas and the pressure was measured with a mercury manometer. The stopcock was closed and sealed off at the constriction shown in Fig 1. The small volume removed with the stopcock was determined by filling the volume with mercury and weighing the mercury. This volume was subtracted from the calculated volume of the ampoule. Table III contains all the data relative to the filling of the ampoules.

C. Surveillance Conditions

All 24 samples were placed in a 60°C oven on 26 May 1958. The oven was an electrically heated, forced-draft oven manufactured by Precision Scientific Company, cat. no. S-2018-B-HAZ, with both control and safety thermostats. The safety thermostat was ascertained to be operative at the start and was set for 70°C. The knobs were removed from both control shafts to prevent an accidental change in setting. The temperature was monitored by a liquid-filled recording thermometer located in another room to minimize personnel exposure. The thermometer was checked, in place, against a carefully prepared thermocouple and a mercury-in-glass thermometer. The liquid-filled thermometer was found to be accurate, and the oven was observed to cycle between 60.8 and 61.2°C with a period of 3 min. A long-period fluctuation was observed during the 11-month surveillance period. The limits were observed to be 59 and 61°C, and the period was quite variable -- often as long as 12 h. The recorder chart was changed daily except on weekends. The temperature dropped significantly each time the oven door was opened to remove samples. The maximum drop was about 10°C, and control was resumed after about 20 min.

TABLE III

FILLING DATA

Flask No.	Piece No.	Gas	Flask Vol at Seal-off (ml)	Gas Pressure at Seal-off (mm Hg)	Temp (°C)	Gas Vol (ml STP)
1	1	Argon	159	202	26.5	38.5
2	2	Air	144	203	26.6	35.0
3	5	Argon	146	201	27.0	35.1
4	6	Air	153	205	27.0	37.5
5	7	Argon	163	203	25.6	39.9
6	8	Air	145	200	26.0	34.8
7	9	Argon	158	204	26.2	38.8
8	11	Air	153	206	27.0	37.7
9	12	Argon	150	206	27.6	36.9
10	14	Air	145	204	27.2	35.4
11	15	Argon	156	200	26.8	37.3
12	16	Air	143	200	26.8	34.2
13	17	Argon	152	196	26.8	35.7
14	18	Air	182	209	26.4	45.6
15	19	Argon	176	196	27.2	41.2
16	20	Air	173	205	27.6	42.3
17	21	Argon	184	204	29.0	44.6
18	33	Air	181	205	28.9	44.1
19	23	Air	166	205	28.4	40.5
20	24	Argon	173	204	27.0	42.2
21	27	Air	172	202	28.8	41.3
22	28	Argon	162	192	27.2	37.2
23	29	Air	182	195	26.8	42.5
24	30	Argon	164	205	26.2	40.3

The test was originally scheduled for 24 months, but pressure buildup in the ampoules was more rapid than had been expected, and the test was terminated after 331 days. At that time the pressure in the ampoules was about 600 mm Hg.

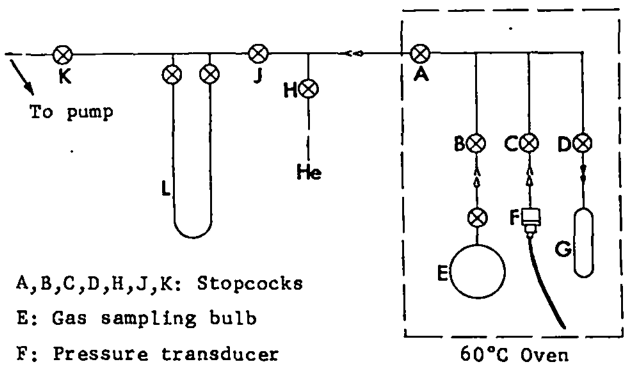
D. Postsurveillance Examination

At appropriate intervals ampoules were removed from the oven to the laboratory where they were opened at the break-seal in order to measure the volume and composition of the gases produced. A gas sample was taken for mass-spectrometric analysis at that time.

The ampoule was placed in a Dewar flask filled with hot water during the transfer from the surveillance oven to a similar oven also at 60°C in the laboratory. The laboratory oven was equipped with a small, calibrated gas-transfer line, which was part of a larger vacuum system. The complete system is shown in Fig 2. The procedure for measuring the gas pressure in the ampoule was as follows:

a) Calibrate the pressure transducer F against the mercury manometer L at several pressures in the range of pressures to be measured (helium was used for all calibration and PVT measurements).

b) Determine the volume between stopcock D and the break-seal in G as follows: Evacuate the entire system with all stopcocks open except H. Close stopcocks B, D, and K. Admit helium through H to provide about 100 mm Hg pressure as measured by the transducer F. Close A and H. Open stopcock D and redetermine the pressure with transducer F. Calculate V_2, the unknown volume, from $P_1V_1 = P_2(V_1 + V_2)$ (V_1 was determined previously by filling the system with mercury and weighing the mercury). P_1 is the pressure before opening D, and P_2 is the pressure after opening D.



A,B,C,D,H,J,K: Stopcocks
E: Gas sampling bulb
F: Pressure transducer
G: Ampoule
L: Mercury manometer

c) Determine the volume between stopcock B and the sample-bulb stopcock in the same manner (the volume of the sample bulb was determined previously by filling it with water and weighing the water).

d) Open A, B, and C and evacuate the system again, including the gas sample bulb. Close A and break the break-seal in G. Measure the pressure with transducer F. Calculate the pressure in the ampoule from $P_1 = (P_2/V_1)(V_1+V_2)$, where V_1 is the volume of the ampoule determined at the start of the experiment and V_2 is the combined volume of the sample bulb and the calibrated system in the oven with A closed. P_2 is the pressure measured in this system when the break-seal is broken. Using P_1, V_1, and the temperature of the oven, calculate the STP volume of gas in G.

The ampoule was removed from the oven, cooled, and opened. The test cylinder was placed in a screw-cap bottle and sent for radiographic inspection. After inspection the piece was weighed and an immersion density was determined. A dimensional inspection was made according to the scheme for presurveillance inspection previously outlined, and finally the end surfaces were machined flat and perpendicular to the axis of the cylinder. Strain gages were attached to the cylinder, and the ultimate compressive strength was determined on a Baldwin testing machine. The cylinders were then machined to provide a powder to be used for drop-weight impact sensitivity and vacuum thermal stability. At the end of the surveillance period the residue was extracted with trichloroethylene, and the extract was examined for stabilizer by a chromatographic technique.

The gas samples for mass-spectrometric analysis were collected in a 1-liter bulb equipped with a hollow-plug, slant-bore precision stopcock and a side arm fitted with a break-seal so that the stopcock could be sealed off if it became necessary to store the samples for an appreciable period. This was never necessary. The analyses were performed by E. D. Loughran. His description of the procedure used is as follows:

> It was anticipated that the samples could contain significant amounts of H_2, N_2, O_2, Ar, CO, CO_2, NO, N_2O, H_2O, H_2CO, $(CH_3)_2CO$, and NO_2. Consequently, calibration runs were made on pure samples of each of these gases, except NO_2, at various times during the course of the experiment. N_2, O_2, and Ar, in particular, were run in conjunction with each set of samples.
>
> In general, sample pressures were such that fractionation effects during introduction into the mass spectrometer inlet system could be minimized. The samples were submitted in 1-liter flasks having a stopcock and a 12/30 $ male joint as described above. Since the samples contained approximately 200 mm Hg of Ar or air originally, there was no problem in obtaining sufficient material for any number of runs.
>
> The spectra were resolved by the so-called "artichoke" technique. Starting with a peak that was unique - ie, characteristic of only one species - constituents were successively eliminated or "peeled" from the spectrum by utilizing the fragmentation patterns obtained in the calibration runs. In all samples CO_2 was a major component of the mixture, and therefore the peak for doubly-ionized CO_2, m/e 22, was used as the starting point for the analysis. (This peak is entirely due to CO_2 in these mixtures.) The resolved spectrum of each component was then used to calculate the partial pressure of that gas in the mixture, which was then divided by the sum of the partial pressures of all the components found in the sample to obtain the corresponding percentage figure. Since no NO_2 was visible in any of the samples, it was assumed that the concentration of NO_2 was negligible. A small amount of a Cl-containing compound was never positively identified and thus was included under the column labeled "Residual". It was probably vinyl chloride, and the sensitivity used to calculate its partial pressure was arrived at with this assumption.
>
> Duplicate analyses on given samples usually checked to within 5% of the quoted value for the major components (> 10%) and within 10% for the others; in most cases better agreement was attained. The values reported for H_2O do not have much significance because of the inherent difficulty of analyzing for H_2O with a mass spectrometer.

The analytical data obtained were combined with the gas-volume data and the filling data to provide the total ml STP of each molecular species produced or consumed at each interval.

III. RESULTS AND DISCUSSION

A. Radiographic Results

At 70 days transverse cracks were noted near the ends of the cylinders. At 331 days these ranged in severity from very slight to "relatively heavy".

B. Dimensional Changes

The results of the dimensional measurements are summarized in Table IV. The scatter is large compared to the changes observed, but clearly a) growth was most rapid early in the test, b) the charges became slightly barrel-shaped, and c) the length and the diameter at the center increased at about

TABLE IV

PHYSICAL CHANGES vs TIME

		Dimensional Changes (in.)							
		Diameter				Weight Loss		Density	Ultimate Comp Str
Days	Sample	Top	Middle	Botton	Length	(g)	(%)	(g/cm^3)	(psi)
70	Control							1.829	2240
	Air					0.019	0.027	1.813	1563
	Argon					0.025	0.035	1.813	1575
134	Control	+0.0005	+0.0001	+0.0003	+0.0010			1.827	2200
	Air	+0.0013	+0.0027	+0.0018	+0.0075	0.041	0.058	1.813	1490
	Argon	+0.0012	+0.0028	+0.0017	+0.0067	0.060	0.085	1.813	1490
149	Control	---------- Not Available ------------						1.827	2060
	Air	+0.0012	+0.0019	+0.0016	+0.0086			1.813	1327
	Argon	+0.0013	+0.0025	+0.0017	+0.0091			1.812	1433
205	Control	-0.0001	-0.0001	0.0000	0.0000			1.826	2080
	Air	+0.0017	+0.0027	+0.0021	+0.0071	0.064	0.091	1.812	1235
	Argon	+0.0017	+0.0028	+0.0020	+0.0082	0.078	0.111	1.811	1268
260	Control	0.0000	-0.0001	+0.0001	+0.0015			1.827	2155
	Air	+0.0021	+0.0029	+0.0022	+0.0108	0.095	0.134	1.810	1139
	Argon	+0.0018	+0.0031	+0.0031	+0.0125	0.105	0.149	1.807	1115
266	Control	0.0000	-0.0001	+0.0001	+0.0015				
	Air	+0.0017	+0.0026	+0.0016	+0.0088			-----	1115
	Argon	+0.0026	+0.0041	+0.0025	+0.0101			-----	1089
295	Control	0.0000	0.0000	-0.0001	+0.0002			1.827	2196
	Air	+0.0017	+0.0033	+0.0023	+0.0094	0.115	0.164	1.809	1039
	"	+0.0017	+0.0035	+0.0017	+0.0090				
	Argon	+0.0006	+0.0032	+0.0020	+0.0098	0.118	0.168	1.809	1090
	"	+0.0018	+0.0028	+010017	+0.0135				
331	Control	---------- Not Available ------------							
	Air	+0.0013	+0.0030	+0.0021	+0.0081	0.128	0.178	1.808	----
	"	+0.0024	+0.0035	+0.0021	+0.0120				
	"	+0.0023	+0.0038	+0.0024	+0.0097				
	Argon	+0.0024	+0.0036	+0.0028	+0.0106	0.142	0.202	1.805	----
	"	+0.0025	+0.0038	+0.0025	+0.0103				

the same relative rate (~ 0.36% at 331 days).

C. Weight Loss

Weight loss results primarily from the evolution of volatile decomposition products. The data are given in Table IV and are plotted in Fig 3. The Ar data are adequately fit by a single straight line through the origin; the air data can be fit by two straight lines with a change in slope at about the time the O_2 has been depleted (see below).

D. Density

The density data also are given in Table IV. The rapid growth that occurred early in the test is mainly responsible for the large initial decrease in density. The more gradual decrease that follows represents both continued growth and the loss of

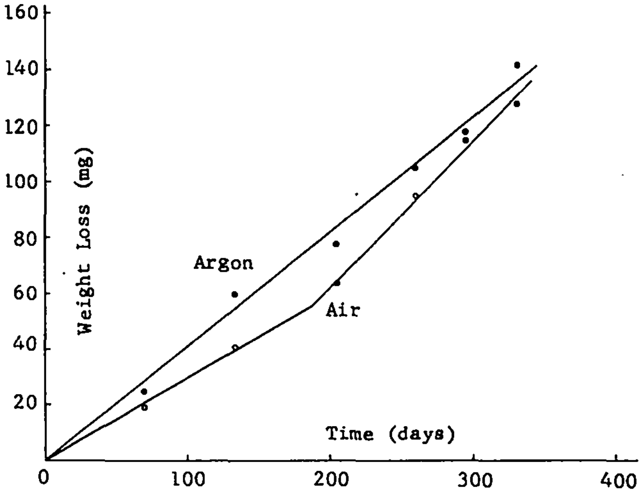


Fig 3. Weight Loss vs Time

volatile decomposition products.

E. Compressive Strength

The compressive strength results (Table IV) roughly parallel the density data, showing a large initial decrease followed by a slow steady decline.

F. Drop-Weight Impact Sensitivity

The data are given in Table V. Except for the 70-day figures, the results are remarkably constant.

G. Vacuum Thermal Stability

The available results are given in Table VI. A subsequent study indicated that large fluctuations in vacuum stability were characteristic of 9404, and we are unable to draw any significant conclusions from these data.

H. Stabilizer Content

Samples of the test specimens were analyzed at the end of the test to determine if any of the stabilizer was left. The powdered samples were extracted with trichloroethylene in a Soxhlet extractor, and paper chromatograms were made and analyzed by R. N. Rogers. The sample that had been stored in air contained mostly nitrodiphenylamines, with no diphenylamine or N-nitrosodiphenylamine present. The sample that had been stored in Ar contained mostly nitrodiphenylamines, a very little N-nitrosodiphenylamine, but no diphenylamine.

TABLE V

IMPACT SENSITIVITY - TYPE 12 MACHINE,

2.5 kg WEIGHT

	50% Point (cm)			
Days	Air	Argon	Control	RDX Std
70	45.2	43.3	42.4	22.2
134	37.2	38.4	37.2	21.7
	36.6	36.6	35.4	
205	37.3	39.1	38.0	23.3
260	37.8	38.7	36.5	22.4
295	38.9	39.3	36.5	22.4

TABLE VI

120°C VACUUM STABILITY (ml/g/48 h)

Days	Air	Argon	Control
70	1.66	2.03	1.53
	1.87	2.39	
134	1.73	2.35	3.06
	1.67	1.94	1.95
	1.87	2.98	2.08

Reaction of the stabilizer with the decomposition products causes a marked change in the appearance of the samples. The air sample turned orange-yellow and remained this color throughout the test. The Ar sample, a very pale brown at 70 days, later took on various shades of olive green.

I. Gas Evolution

The data are summarized in Table VII and are plotted in Figs 4 and 5. Several errors in the 70- and 134-day measurements were subsequently discovered, and some guesswork was involved in correcting the data. It is believed that the figures finally arrived at for the 134-day results are reasonably reliable, as can, perhaps, best be judged by comparing the 134- and 149-day data. We are less confident about the 70-day data, and we have given them little weight in drawing the curves shown in the figures.

About 1 ml (3 mg) of acetone was found in all the samples. This is presumed to be solvent occluded in the charges, and it was subtracted out in calculating the volume totals appearing at the bottom of the table. Water is strongly adsorbed by glass, and since the vacuum line and inlet system were both made of glass, we presume that most of the water formed was simply lost. Finally, NO_2 does not give a parent peak in our mass spectrometer and it will appear as NO in the analysis. However, it can be detected visually in quite small amounts, and none was ever observed in any of the samples.

With these comments and precautionary remarks, we proceed with the discussion of the data.

The major product in both sets of samples was CO_2, formed at a reasonably constant rate of 1.34×10^{-3} ml/g/day. Next in importance is N_2O, which is formed at a steadily increasing rate. Had the test continued, it may well have become the major product. CO was formed in smaller amounts, but its rate of formation also was accelerating near the end of the test.

The most notable difference in the two sets of data is that NO is found in significant amounts in the Ar samples, but is essentially absent in the air samples. Reaction of the NO with the O_2 in the air and scavenging of the NO_2 by the stabilizer can explain this during the early stages, but in most of the samples the O_2 has all been consumed by about 200 days. Small amounts of NO are indeed

TABLE VI

GAS VOLUMES AND COMPOSITIONS

	Argon Atmosphere							Air Atmosphere						
	70	134	149	205	260	295	331	70	134	149	205	260	295	331
N_2	2.4	4.3	4.3	7.5	11.7	15.0	16.5	6.1	6.2	6.4	10.1	13.7	16.0	16.0
N_2O	3.4	3.8	3.8	6.9	10.7	13.0	17.5	2.2	3.3	3.9	6.0	9.0	12.7	14.9
NO	1.3	1.7	2.1	2.5	2.7	2.6	3.6	0.15	0.15	0.08	0.00	0.09	0.94	0.00
CO	1.3	1.3	1.3	1.8	2.8	4.2	4.9	1.4	2.0	2.7	2.5	3.2	4.9	6.0
CO_2	11.2	12.5	13.2	18.6	24.1	27.0	31.4	10.4	14.2	14.9	19.8	23.6	26.7	28.3
H_2CO	0.02	0.04	0.01	0.05	0.05	0.07	0.07	0.01	0.04	0.03	0.06	0.02	0.04	0.06
$(CH_3)_2CO$	1.1	1.1	1.1	1.0	0.86	0.97	1.00	1.2	1.2	1.2	1.1	0.82	0.80	0.90
O_2	0.05	0.00	0.03	0.03	0.10	0.04	0.12	-3.0	-5.2	-6.2	-7.7	-7.8	-7.2	-8.9
H_2O	0.00	0.01	0.05	0.00	0.05	0.16	0.16	0.00	0.10	0.05	0.00	0.06	0.19	0.20
Residue	0.06	0.08	0.05	0.07	0.08	0.12	0.17	0.04	0.08	0.07	0.06	0.10	0.12	0.14
Total	19.7	23.7	24.8	37.4	52.3	62.2	74.4	17.3	20.9	21.9	30.8	42.0	54.4	56.7

Note: The surveillance time in days is given at the top of the columns. The volume data are in ml STP. The acetone was omitted in computing the total volumes produced.

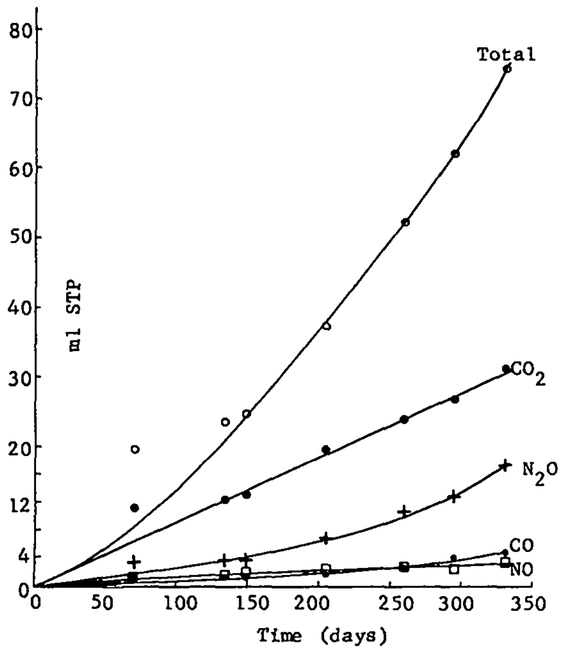


Fig. 4 - Gas Volumes vs Time, Argon Samples

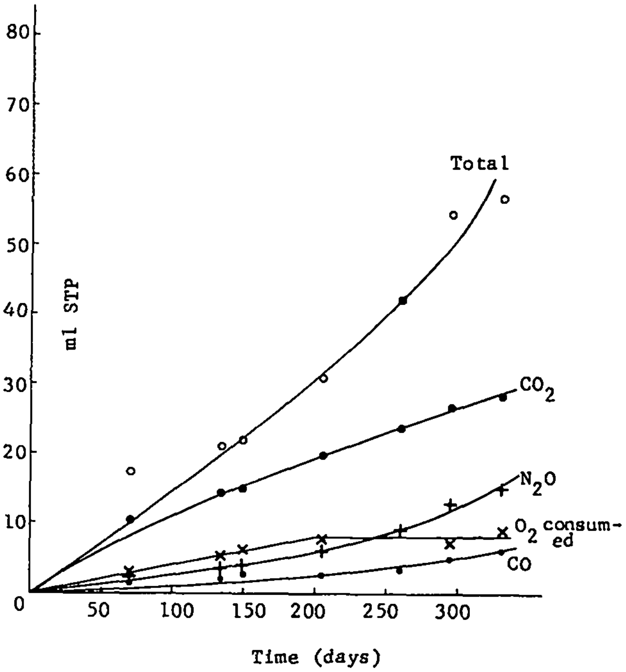


Fig. 5 - Gas Volumes vs Time, Air Samples

found in the 260- and 295-day air samples; its disappearance at 331 days may simply reflect the fact that that particular ampoule contained an exceptionally large volume of air.

The ampoules were, unfortunately, filled to constant pressure rather than constant volume, and, since the volumes varied somewhat, the amount of O_2 originally present also varied. The average value is 7.8 ml, but it ranged from 6.8 to 9.1 ml. So far as we can tell, it disappeared at a constant rate of 0.04 ml/day.

If the rate of disappearance of O_2 corresponds to the true rate of formation of NO, then NO is being formed at the rate of 3.7×10^{-6} moles/day. The 70-g charges originally contained 3.7×10^{-4} moles of DPA. If 1 mole of DPA can react with 3 moles of NO or NO_2, the stabilizer should be completely exhausted in 300 days. This is consistent with the apparent increase in the rate of gas evolution near the end of the test.

To put these results in perspective, in a closed, air-free system 10 kg of 9404, in 11 mo at 140°F, will evolve some 10 liters of gas, of which 3 liters will be nitrogen oxides. The latter can be expected to cause considerable mischief unless the system contains only highly corrosion-resistant components. Furthermore, if the system is really gas-tight and essentially void-free, it is obvious that a substantial increase in internal pressure will occur. These points must be kept in mind whenever 9404 is to be used in any such system.

ALT/mmj:144(100)