Acceptance Test for Tanks Used for Storage of Hydrazine

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A test has been developed based on the measurement over four days of the rates of pressure rise at 60°C of tanks filled with hydrazine with the objective of assessing the acceptability of these tanks for long-term sealed storage at normal ambient temperature. Rates of hydrazine decomposition in a number of tanks were measured over the temperature range 30-80°C in order to correlate rates of pressure rise measured during the acceptance test at 60°C with those occurring at normal storage temperatures. Results from a large number of stainless steel production tanks filled with various batches of hydrazine are presented, indicating the considerable range of rates of pressure rise that can result from tanks that are nominally identical and filled with hydrazine, which meets normal specification requirements. Data from tests carried out after extended storage show there was some decrease in rates of pressure rise with time, thus indicating that the acceptance test carried out shortly after filling underestimates life and errs on the side of safety for this type of tank.

Introduction

HYDRAZINE may decompose by homogeneous processes throughout the liquid phase or by heterogeneous processes at the surface of its container. The former is dependent on the purity of the hydrazine, while the latter depends on the purity and on the nature of the surface: its composition, true surface area, cleanliness and other factors that are not fully understood. The products of the decomposition at normal storage temperatures are mainly nitrogen and ammonia. While ammonia is very soluble in the liquid phase, nitrogen is not, which, therefore, produces a rise in the ullage pressure in a sealed container. The designer of a storage system will wish to limit the amount of ullage in a tank to a minimum that is consistent with an acceptable pressure rise. This may not be difficult to achieve for those systems that have short lives in service or consume the hydrazine steadily over longer times. However, for systems that must remain filled and sealed for many years before use, it is essential to demonstrate that the pressure will remain at a safe level throughout service life.

The primary task was filling several hundred hydrazine tanks that had to remain sealed and unused for a minimum of ten years. The literature values for rates of hydrazine decomposition when in contact with stainless steel show considerable variation and could not be used with confidence as a basis for calculating whether the pressure within the tanks would stay within acceptable limits.

To measure accurately the rate of pressure rise in each tank after filling with hydrazine would take a considerable time if the test was carried out at the normal storage temperature. This could produce unacceptable delays in the production program as well as logistical problems. In order to overcome these problems, an acceptance test of tanks filled with hydrazine was devised which involves measuring the rates of pressure rise over a few days at an elevated temperature and then relating these to the rates that would occur at normal storage temperatures.

Hydrazine Tanks

The type of tank used is illustrated in Figs. 1 and 2. Each tank consists of a stainless steel shell inside which is a stainless steel (304L) diaphragm and liner. The diaphragm is supported by stainless steel stabilization rings which are brazed to its outside surface. During expulsion of the hydrazine, these rings ensure that the diaphragm moves progressively and smoothly to the liquid end of the tank. Both the gas inlet and liquid outlets are sealed with stainless steel (347) burst discs. The smaller gas generator (GG) tank holds about 1.2 kg of hydrazine while the larger attitude control system (ACS) tank holds about 5.4 kg. Each set of tanks consists of two ACS tanks and one GG tank.

Hydrazine

All hydrazine used in this program was procured against the specification in Table 1.

Probably the most important item in the specification is the carbon dioxide content, which is known[1,2] to accelerate the rate of decomposition of hydrazine in contact with stainless steel surfaces and in addition causes some corrosion of the steel. The hydrazine was procured at intervals over a number of years in the form of batches each consisting of a few drums and each of which holds 440 lb of hydrazine.

Effect of Temperature on Rate of Hydrazine Decomposition

Experimental Procedure

In order to relate the rates of pressure rise measured at 60°C with those expected at normal storage temperature, it was necessary to make a series of determinations with several tanks (GG and ACS) of the rates of pressure rise over a range of temperature. Measurements of the rates of pressure rise were made by attaching pressure transducers to the liquid outlet that is normally closed by a burst disc. The transducers were

Table 1 Specification for hydrazine

Component	Units	Limits	
Hydrazine	% w/w	98.5	min
Water	% w/w	1.0	max
Aniline	% w/w	0.5	max
Ammonia	% w/w	0.4	max
Carbon dioxide	% w/w	0.005	max
Chloride	% w/w	0.0005	max
Particulate	mg/litre	1.0	max

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either Schaevitz Type P710 or P720 made of 17/4 PH stainless steel or Druck Type PDCR 110/D/W made of titanium. A short length (6 cm) of 18/8 stainless steel tubing was used to connect the transducers to the tank and to accommodate an 18/8 steel relief valve. It was necessary to measure the rate of gas generation at various temperatures due to the transducer assemblies in order to correct the rates later measured with tanks for the contributions due to the assemblies. To obtain this data, the volumes (6-8 cm^3) of the assemblies were first measured by filling them with water and weighing. Experiments were then carried out over a range of temperatures to determine the rate of hydrazine decomposition. This was done by introducing a weighed quantity (approximately 1 g) of hydrazine while the assembly was inside a nitrogen-filled glove box, inserting a plug, removing from the glove box, and monitoring the output of the transducer while maintaining a steady temperature.

The transducer assembly was then returned to the glove box, emptied of hydrazine, and attached to the liquid outlet of a hydrazine filled tank. The liquid outlet burst disc of the tank had previously been punctured to enable the internal pressure to be monitored. The tank was then placed in an oven at a set temperature and the transducer output recorded over a period of weeks until sufficient data had been obtained to calculate the mean rate of pressure rise. This was done at a number of temperatures in the range of 30 to 80°C using three GG tanks (one containing two different loads of hydrazine) and three ACS tanks (one with and without added carbon dioxide). One series of tests with a GG tank and one with an ACS tank were carried out using hydrazine that contained a level of carbon dioxide well above the specification limit of 50 ppm. Tank identification, hydrazine drum identification, ullage, and carbon dioxide content are given in Figs. 3 and 4 or Table 2.

Results

Hydrazine in contact with stainless steel produces[1] mainly nitrogen and ammonia as decomposition products in the temperature range of interest here, very little hydrogen being found by analysis. The decomposition reaction can, therefore, be represented by

$$3N_2H_4 \rightarrow 4NH_3 + N_2 \tag{1}$$

The rate of hydrazine decomposition is, therefore, directly related to the rate of nitrogen generation. The rates of pressure rise measured were converted into rates of nitrogen generation, expressed as standard cubic centimeters of nitrogen [scc (N_2) at 0°C and 760 mm pressure] from a knowledge of the volume of the tank ullage at the test temperature and the solubilities of nitrogen[3] and ammonia[4] in hydrazine. The way this is calculated to yield the quantity of nitrogen both released to the ullage and remaining dissolved in the liquid phase has been described elsewhere.[5] The calculated rates of nitrogen generation were corrected for the contributions due to the transducer assemblies by subtracting the values measured with the assemblies alone.

The effect of temperature on the rate of a chemical reaction is represented by the Arrhenius equation,

$$\text{Reaction rate} = Ae^{-E/RT} \tag{2}$$

where A is a constant, R the gas constant, T the absolute temperature, and E is a constant for the particular chemical reaction and is known as the activation energy.

A plot of log rate vs $1/T$ should, therefore, yield a straight line from the gradient of which the value of E can be calculated.

Figures 3 and 4 show these plots for tests carried out with GG and ACS tanks. The data form reasonably good straight lines. It is also of interest that with only one exception (ACS tank 015), and irrespective of whether the decomposition rate

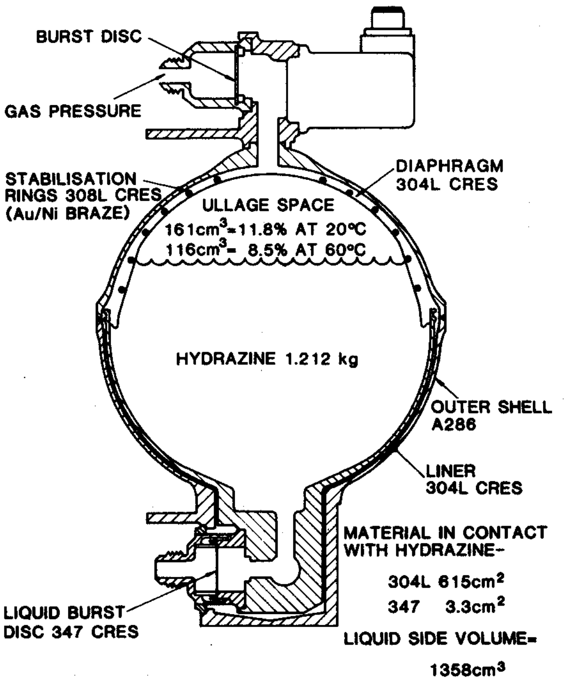

Fig. 1 Gas generator tank.

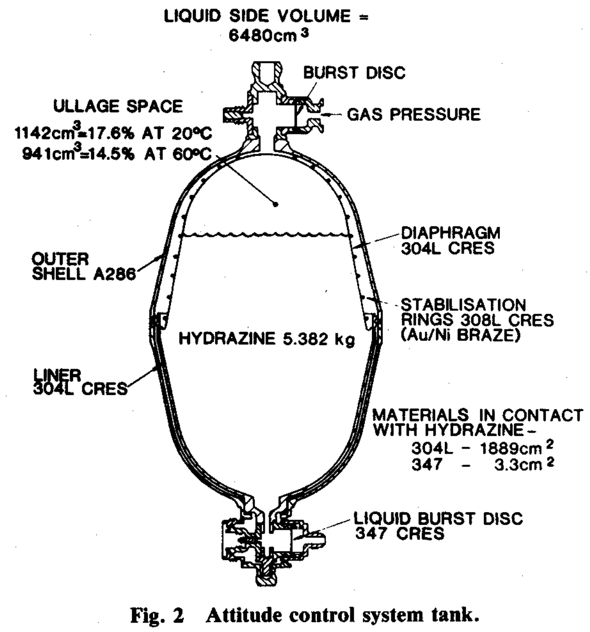

Fig. 2 Attitude control system tank.

Table 2 Calculated values of activation energy

Tank	Ullage, % at 20°C	CO_2, ppm	Rate of pressure rise at 60°C kPa/year (psi/year)	Activation energy, kJ/mole	kcal/mole
GG					
013	17.5	140	2550 (370)	61.4 ± 4.2	14.7 ± 1.0
013	17.5	30	690 (100)	62.6 ± 14.8	15.0 ± 3.6
501-25	11.0	13	410 (60)	62.4 ± 11.9	14.9 ± 2.9
011	16.8	24	205 (30)	60.8 ± 5.9	14.5 ± 1.4
ACS					
036	17.1	121	1310 (190)	61.6 ± 6.6	14.7 ± 1.6
036	17.1	41	205 (30)	69.5 ± 5.0	16.6 ± 1.2
015	14.1	34	140 (20)	81.1 ± 5.6	19.5 ± 1.3
023	14.1	29	70 (10)	67.5 ± 7.6	16.1 ± 1.8

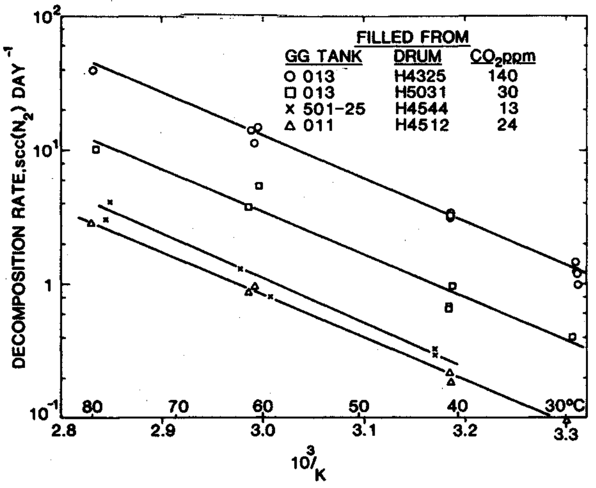

Fig. 3 The effect of temperature on decomposition rate in GG tanks.

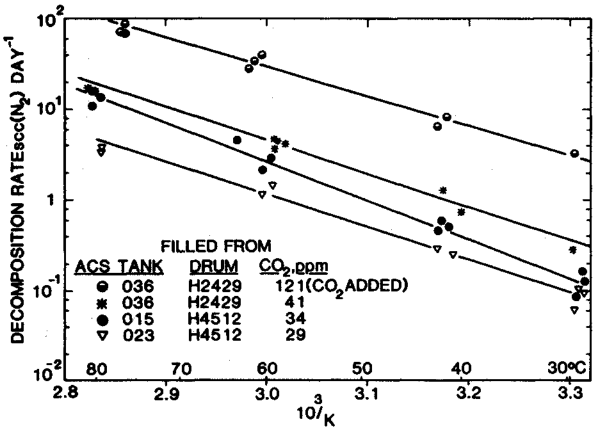

Fig. 4 The effect of temperature on decomposition rate in ACS tanks.

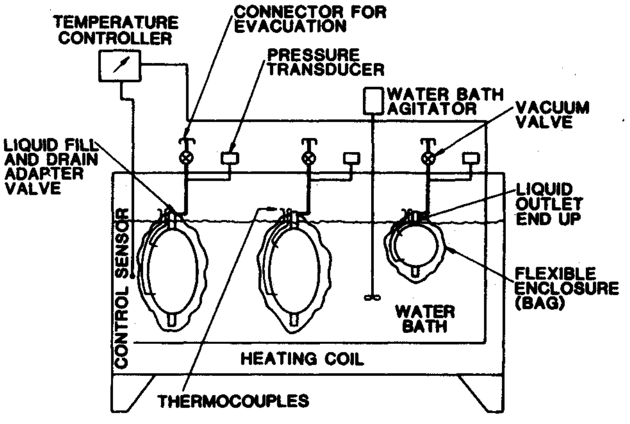

Fig. 5 Acceptance test equipment.

at a particular temperature is high or low, the gradients of the lines are very similar. The rate of decomposition at a higher temperature relative to that at a lower temperature is, therefore, the same regardless of the value of the rate. The rate at 60°C is about 14 times higher than the rate at 25°C. The highest rates were measured in each case from the tanks containing the highest concentrations of carbon dioxide impurity, and the correlation of rate with carbon dioxide content holds reasonably well for tests at the lower levels of carbon dioxide. The increase in rate with carbon dioxide content is in agreement with previous work[1,2] on this subject. The calculated values of activation energy together with 95% confidence limits and other data are given in Table 2.

Acceptance Test

Procedure

The hydrazine tanks were connected to a fill adaptor that included a valve through which the tanks were first evacuated, helium leak-checked, and then loaded with hydrazine. The quantities of hydrazine added and the remaining ullage are given in Fig. 1 and 2. Helium gas was then added to the ullage to give 41 to 45 kPa (6.0 to 6.5 psia) in a GG tank and 69 to 72 kPa (10.0 to 10.5 psia) in an ACS tank. A pressure measuring assembly (PMA) consisting of a stainless steel pressure transducer (Teledyne Taber, 0-172 kPa, 0-25 psia, 1 volt = 34 kPa, 5 psi), valve, and tubing was then connected to the fill adaptor. The PMA was then given a leak check by evacuating and leaving for 6 h during which time the pressure was monitored by the transducer. Limits were placed on the rates of pressure rise during this time; the limit for an ACS tank was 0.36 kPa/h (0.052 psi/h) and for a GG tank 0.12 kPa/h (0.017 psi/h). These maximum permitted leakage rates into the PMA were calculated on the basis of producing a negligible effect on the rate of pressure rise in the tanks during the acceptance test. The volume of the PMA was kept to a minimum (8 cm^3) and separate tests were carried out when filled with hydrazine to confirm that it contributed only small amounts of hydrazine decomposition in comparison to that produced by tanks that were close to the limit for acceptable life.

The valve connecting the tank to the PMA was then opened, and the tank was immersed in a water bath at 60°C for 48 h. It was found during initial tests that the rate of pressure rise in a tank sometimes decreased considerably during the first few days of an acceptance test at 60°C, and for 48 h prior to the acceptance test the "heat soak" was introduced to stabilize the rate. The tank was then removed from the water bath and allowed to cool to room temperature.

The acceptance test was then commenced by re-immersing the tank in the 60°C water bath. The duration of the test was 96 h: The first 24 h were allowed for the tank and its contents to reach temperature equilibrium and the remaining 72 h was the time during which the rate of pressure rise was assessed. Two thermocouples were attached to the outer skin of each tank, which was within a polyethylene bag and readings were taken each hour from these and the pressure transducer. The restrictions placed on temperature were that it should be between 59 and 61°C (usually found to be between 59.6 and 60.4°C), and not drift either up or down more than 0.2°C between the start and end of the final 72 h.

An outline drawing of a set of tanks under test is shown in Fig. 5. The type of pressure record obtained from a GG tank is shown in Fig. 6. The initial rise in pressure during the first few hours is due to the expansion of the liquid hydrazine, the rise in temperature of the helium gas in the ullage space and the increased vapor pressure of hydrazine. During the next period of 5-10 h, there is often a slight bulge in the pressure trace while the helium gas, now at higher pressure, re-establishes equilibrium with the liquid phase. Helium gas is more soluble in hydrazine[3] at 60°C than at 20°C, and, in the absence of nitrogen generation due to hydrazine decomposition, the pressure would actually fall from the peak value first established. This did occur with some of the ACS tanks where the rate of hydrazine decomposition was very low.

When gas/liquid equilibrium has been established, the pressure should then rise in a steady fashion provided that the rate of hydrazine decomposition over the next 72 h is reasonably constant. This was observed with most of the tanks tested that were given the prior 48 h "heat soak," though in some cases the rate would tend to decline a little with time. The general form of the pressure/time data for the GG tanks is shown in Fig. 6. Typical rises in pressure during the final 72 h were of the order of 3.4 to 11 kPa (0.5 to 1.6 psi) for GG

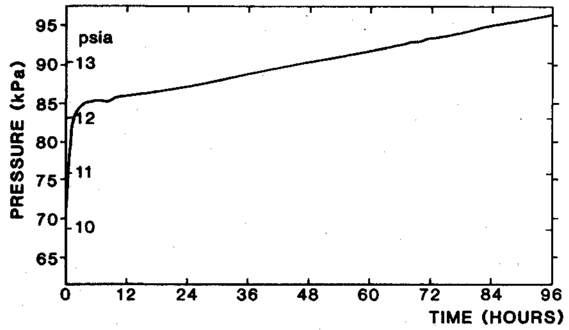

Fig. 6 Pressure record during the acceptance test of a GG tank.

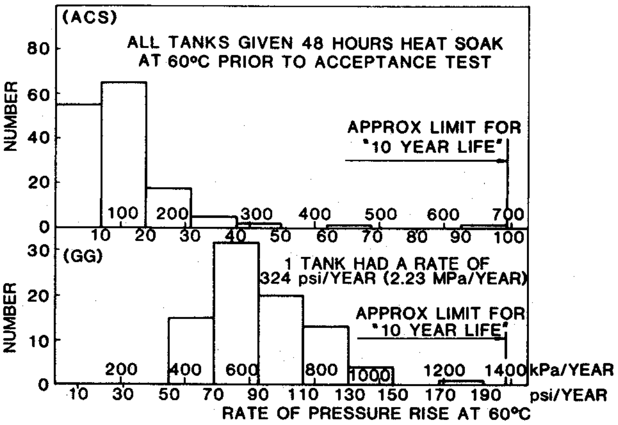

Fig. 7 Results of acceptance tests of tanks filled from seven drums.

Table 3 Hydrazine drums used and numbers of tanks filled

Production batch	Drum	Number of tanks filled ACS	GG
23-78	H3486	18	36
	H5079	10	—
34-79	H4358	11	21
	H5154	21	11
	H4893	21	16
265-81	H4544	2	2
267-81	H1473	16	10
16-83	H5300	30	—
	H5303	32	—
	Total	161	96

Table 4 Acceptance tests repeated after storage

GG tank	Rate of pressure rise during acceptance test, kPa/year (psi/year) Before storage	Storage interval, years	After storage
501	700 (102)	2.25	420 (61)
503	1050 (153)	2.25	730 (106)
504	620 (90)	2.17	360 (52)
505	920 (133)	2.00	280 (41)
507	790 (115)	1.42	760 (110)
508	1160 (168)	2.17	770 (111)
511	470 (68)	2.00	370 (54)
514	1110 (161)	2.00	360 (52)

tanks (Fig. 6) and of the order of 0.34 to 5.5 kPa (0.05 to 0.8 psi) for ACS tanks. The best straight line through the 72 pressure data points was evaluated to yield the mean rate of pressure rise together with the associated confidence limits.

At the end of the 96 h, the tank was taken from the water bath and allowed to cool to ambient, and the final pressure and temperature at ambient were recorded.

Results

Data obtained during the testing of 161 ACS and 96 GG tanks are given in this section. The hydrazine was obtained from nine drums which were part of five production batches. Drum and batch identification is given in Table 3.

The results of tests on GG and ACS tanks filled with hydrazine from seven of the drums from three production batches are given in Fig. 7; the results from drums H4544 and H1473 are given later.

The results are shown in terms of numbers of tanks within various ranges of rates of pressure rise. Also shown is the rate of pressure rise that is equivalent to a "10 year life." This value will depend on the pressure limit placed on a tank (in this case 793 kPa, 115 psia for ACS tanks and 1482 kPa, 215 psia for GG tanks; the weakest component is the outlet burst disc) and the temperature regime to which the tank will be subjected. Because of the priority placed on safety with this system, the temperature was assumed to be at the top end of the likely range (29°C) and to have a short term excursion to 60°C at any time during the life of the system. The rate of gas generation at 29°C is about one-tenth of that at 60°C; and because the final temperature in each case is 60°C, the rate of pressure rise at 29 and 60°C is also about one-tenth of that measured during the acceptance test. The relation (F) between the rate of pressure rise at 60°C and that at some other temperature T (e.g., 25°C) can be calculated using Eq. (2), the value of E from Table 1, the relative ullage volume at the two temperatures and the effect of temperature on gas solubilities.[5] The latter may be seen in most instances as being of minor importance. The predicted life of a tank can be expressed by the following general equation,

$$\text{Life} = (\text{years at temperature } T)\, \frac{F\,(PL - P)}{\mathrm{d}p/\mathrm{d}t\ (60^\circ\mathrm{C})} \tag{3}$$

where F is the thermal acceleration factor (see above), PL is the pressure limit for tank in kPa (psi) P the tank pressure at temperature T in kPa (psi) after acceptance test and $\mathrm{d}p/\mathrm{d}t$ (60°C) the rate of pressure rise during acceptance test in kPa/year (psi/year).

The most important aspect of the data in Fig. 7 is the wide spread of the rates of pressure rise both for GG and ACS tanks, even though they were manufactured and cleaned to the same standards and filled with hydrazine that conformed to a tight specification. The other interesting aspect of the data is the fact that the GG tanks approach the "10 year life" limit much more closely than the ACS tanks, even though they were designed and filled to give similar lives.

The internal surface area to ullage volume ratio for the GG tanks is about 2.7 times that for ACS tanks, but the pressure limit for GG tanks is about twice that for ACS tanks. Therefore, on the assumption that all the hydrazine decomposition occurs at the surface of the tank, then the life of an ACS tank should be about 1.4 times that for a GG tank. Similar calculations based on the mass of hydrazine, the ullage volume, and the assumption that all the decomposition occurs by homogeneous processes throughout the liquid phase give predicted lives that are almost equal for ACS and GG tanks.

One of the GG tanks had a rate of pressure rise sufficiently high to place it outside the acceptance limit while most of the ACS tanks were well away from that limit. Although there was some variation in the mean rates of pressure rise of tanks filled from different drums, the general spread of data from each drum was much larger than the difference in the means. This suggests that for these tanks filled from seven drums, the tank to tank variation was considerbly larger than the differences that could be attributed to hydrazine quality. Samples of

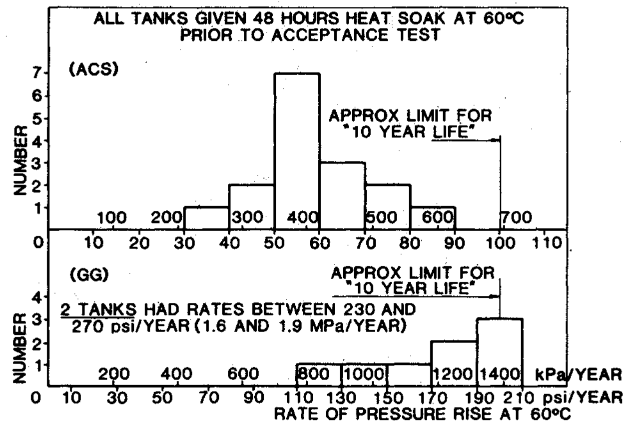

Fig. 8 Acceptance test results of tanks filled from drum H1473.

hydrazine were taken from the drums prior to use for full chemical analysis, and samples were also taken from the filling rig every 30 days for full analysis.

For drum H1473 the rates of pressure rise, especially for ACS tanks, were much higher even though the hydrazine conformed to the specification (e.g., carbon dioxide <50 ppm). These data are shown in Fig. 8 where it is seen that all the GG tanks approach or exceed the acceptance limit and some of the ACS tanks approach the limit. Two of the ten GG tanks failed the acceptance test and two others were right on the limit.

Two GG and two ACS tanks were filled from drum H4544. This drum was from batch 265-81 and was delivered at the same time as drum H1473 from batch 267-81. The two GG tanks had predicted lives of 11.6 and 11.8 years; the two ACS tanks gave 18.6 and 19.8 years. The hydrazine from drum H4544, therefore, behaved in a manner similar to the hydrazine from drum H1473, giving high rates of pressure rise and low predicted lives.

Investigations were carried out to determine the reason for this behavior when using hydrazine from two batches manufactured in 1981. Tests carried out using hydrazine from drum H1473 in a tank and drum H4544 in glassware indicated that they had a higher homogeneous rate of decomposition than normally observed. The rate of gas generation measured in glassware at 60°C using a sample from drum H4544 was 2.9×10^{-3} scc g^{-1} day^{-1}, while the rates with samples from nine other drums (four batches) were in the range 0.3 to 1.4×10^{-3} (mean 0.73×10^{-3}). A detailed chemical analysis of drum H4544, compared to the hydrazine from batch 34-79, showed higher concentrations of transition metal ions (Fe, Cr, Mn) and also the presence of alkyl phenols. The latter could catalyze the decomposition of hydrazine by behaving as acids and generating hydrazinium ions.

Longer Term Data

The reliability of an acceptance test for predicting safe tank life depends to a considerable degree on the way in which the rate of pressure rise changes during the life of a tank. If rates remained steady throughout life, then the prediction made on the basis of an acceptance test carried out shortly after a tank is filled would be accurate. If rates rose, however, then predictions of life would be too optimistic and the system would present a hazard in the later part of the predicted life. Rates that decreased would, on the other hand, increase the margin of safety. Eight GG tanks were given a repeat of the acceptance test after a storage interval of about two years and the results are compared with the data from the earlier tests in Table 4.

In every case, the rate of pressure rise has decreased after storage, but the size of the decrease is variable, ranging from only a modest decrease for tank 507 to decreases by a factor of three for tanks 505 and 514. Other tests with both ACS and GG tanks have shown the same trend: the rate decreases with time but to a variable extent. This information, therefore, strongly suggests that with this type of steel tank the acceptance test tends to underestimate the life to some degree, which, in a system where safety is of paramount importance, is a desirable feature.

Summary and Conclusions

An acceptance test has been described that enables predictions to be made regarding the safe life of tanks containing hydrazine, where tank life is limited by pressure rise. The test consists of monitoring the rise of pressure when the tank is maintained at 60°C for 96 h and relating this to the slower rate that applies at normal ambient temperature. In establishing the relationship between rates at 60°C and those at lower temperatures, it was found that the relative rate between two temperatures was independent of the actual values in any particular tank. There was a fairly strong correlation between rates of hydrazine decomposition and the concentration of the carbon dioxide impurity in the hydrazine for the stainless steel tanks used in this study.

The acceptance test has been applied to a large number of tanks and has revealed a large tank to tank variation, from tanks made and cleaned in an apparently identical manner. Variations due to hydrazine quality were, in general, smaller than tank to tank variations, though hydrazine from two drums gave markedly higher rates of pressure rise than those obtained from the other seven drums.

Tests on eight gas generator tanks after about two years of storage at ambient temperature showed that the rates of pressure rise had declined in each case, thus increasing the margin of safety compared with the predictions made from acceptance tests carried out shortly after they had been filled.

The type of acceptance test described can be applied to other designs of tanks/tank materials/propellants provided that sufficient data are obtained to establish the variation of decomposition rate with respect to temperature.

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