MHSMP-77-5D

EVALUATION OF GAS VOLUMES EVOLVED DURING VACUUM STABILITY TESTING OF HNS

Jacob Sandoval

DEVELOPMENT DIVISION

OCTOBER-DECEMBER 1976

Normal Process Development
Endeavor No. 107

Mason & Hanger-Silas Mason Co., Inc.
Pantex Plant
P. O. BOX 30020
AMARILLO, TEXAS 79177
806-335-1581

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ABSTRACT

This study was undertaken to determine the effect of dipicrylethane, a common impurity in HNS, on the volume of volatiles evolved during HNS vacuum stability measurements, and to evaluate the repeatability of results obtained during this testing.

DISCUSSION

The standard vacuum stability test apparatus is a one-piece all-glass unit comprising the sample tube and the mercury manometer well. Upon completion of the test the entire unit is discarded as it cannot be reconstructed.

As an economy measure and to facilitate the evacuation of the unit in preparation for testing, the all-glass apparatus was modified to consist of two sections (Fig. 1), which are held in place by a stainless steel union to which have been affixed an adapter and a Whitey valve (Fig. 2). On termination of the test only the sample tube section of the unit is discarded. Use of the modified test apparatus has reduced the cost of the all-glass unit by two-thirds.

HNS samples with a dipicrylethane content of 1, 5 and 10 percent were obtained and prepared for this study. To preclude sample contamination, special precautions were taken during specimen preparation. All test components with which HNS comes in contact during preparation and testing were cleaned thoroughly, rinsed, and dried. The vacuum stability testing was conducted as specified in Mason & Hanger "HNS Vacuum Stability Test," Standard Operating Procedure No. 6-1722.

Samples from the following lots of HNS were involved in these tests; Lot No. 02-76-0301-01 (DPE 10%), Lot No. 01-76-0312-01 (DPE 5%), and Lot No. 02-76-0421-02 and -04 (DPE 1%). Each test sample was run in triplicate and the ensuing volatile volumes measured at 20 and 140 minute periods. To further establish the repeatability of the test results, three of the samples, in duplicate, were reanalyzed. The evolved volatiles at 260 C for all samples are listed in Table I.

The primary objective of this study was to investigate what effect, if any, the presence of dipicrylethane in HNS has on the volume of evolved volatiles during vacuum stability testing; consequently all variables, except for the dipicrylethane (DPE) content in HNS, were kept constant. On termination of the vacuum stability testing, one sample from each of the HNS test lots (DPE 10, 5, 1%) was analyzed by liquid chromatography to reassess the sample composition. The results of these analyses, along with the composition of these samples, prior to vacuum stability testing, are listed in Table II. The test conditions and results for all samples are tabulated in Table III.

Thin-layer chromatography evaluation for each of the 3 HNS samples (DPE 10, 5, 1%) subjected to vacuum stability testing was conducted. One milligram samples were dissolved in 3 mℓ solvent (1 mℓ THF, 2 mℓ acetone) and spotted on a TLC plate. The resulting chromatogram (Fig. 3) reveals a slight trace of DPE as the only contaminant in the HNS samples.

The brevity of this study curtailed the generation of data; however, on the basis of the tabulated information a few observations can be made.

Five vacuum stability tests were made for each of 3 samples and the volumes of the evolved volatiles determined at 20 minutes and 140 minutes from introduction of the samples in the heating block. There is good agreement with the test values.

There is no substantiating evidence to suggest that DPE either enhances or abates the evolution of volatiles at 260 C (Table I).

Analysis of the samples by liquid chromatography indicates decomposition of the DPE (Table II) but since there is no increase in the volumes of evolved gases from the HNS samples (with higher DPE content), it must be assumed that the decomposition products are non-volatile.

Surveillance of the same samples by TLC procedures (Fig. 3) failed to reveal any extraneous product; thus one must suppose that the decomposition product is an insoluble carbonaceous material which defies solubility in the HNS solvents employed in TLC and LC techniques.

Close examination of the HNS solutions prepared for analysis by liquid chromatography reveals the presence of trace amounts of precipitated sediment. This sediment was not identified.

FUTURE WORK, COMMENTS

The scope of the investigation precluded isolation and characterization of the suspected insoluble decomposition products of DPE. These products may affect the sensitivity and performance of HNS and should be studied in the future.

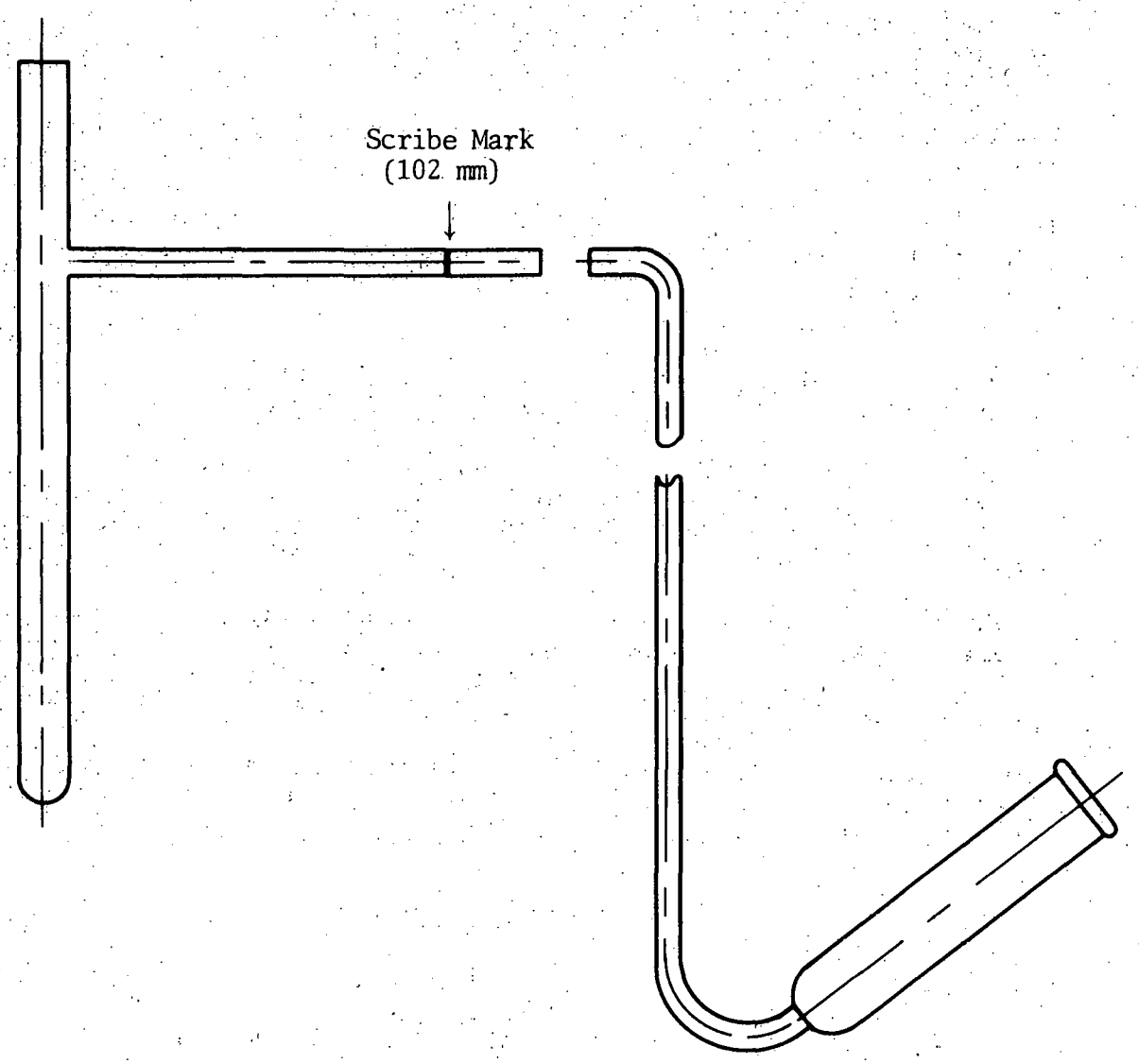
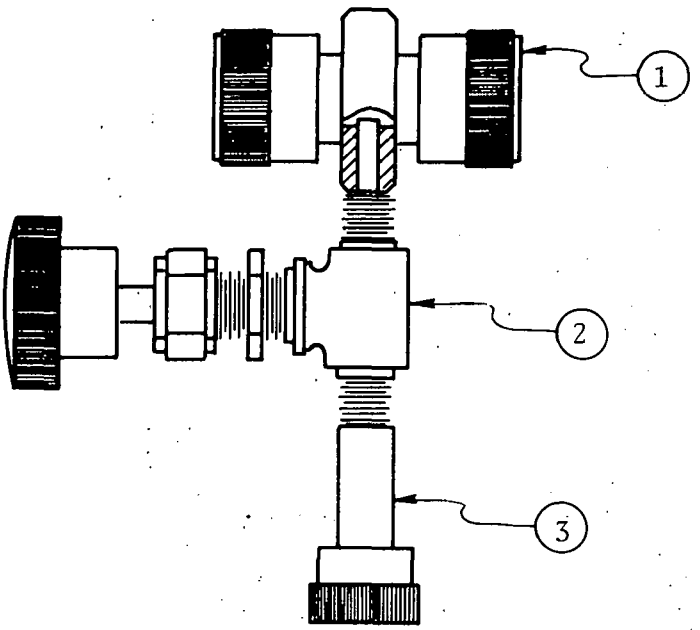


Fig. 1. Front and Rear Sections, All-Glass HNS Vacuum Stability Test Unit



1. Union
2. Whitey Valve
3. Adaptor

Fig. 2. Complementary Stainless Steel Hardware, HNS Vacuum Stability Test Unit

Table I. HNS Vacuum Stability Test

(Evolved volatiles at 260 C)

HNS Lot No.	Sample	Run	20 Min (mℓ/g)	60 Min (mℓ/g)
01-76-0301-01	1	1	4.44	1.88
	2	1	4.60	1.81
	3	1	4.51	1.53
01-76-0312-01	1	1	4.25	1.68
	2	1	4.40	1.55
	3	1	4.23	1.41
02-76-0421-04	1	1	2.66	1.14
	2	1	2.80	1.00
	3	1	2.70	1.08
02-76-0421-02	1	1	2.97	1.17
	2	1	2.90	1.22
	3	1	3.10	1.23
01-76-0301-01	1	2	4.59	2.02
	2	2	4.65	2.03
01-76-0312-01	1	2	4.60	1.98
	2	2	4.90	2.03
02-76-0421-04	1	2	2.82	1.20
	2	2	2.86	1.23

Table II. Liquid Chromatographic Analysis of HNS Before and After Vacuum Stability Testing

HNS Lot No.	Sample	Pre-Analysis, LC (%)				Post-Analysis, LC (%)			
		HNS	DPE*	TNB**	Other	HNS	DPE	TNB	Other
01-76-0301-01	1	85.6	10.4	4.0	-	99.3	0.6	0.1	-
01-76-0312-01	1	93.8	5.0	1.2	-	99.5	0.3	0.2	-
02-76-0421-04	4	98.1	1.3	0.6	-	99.5	0.3	0.1	-

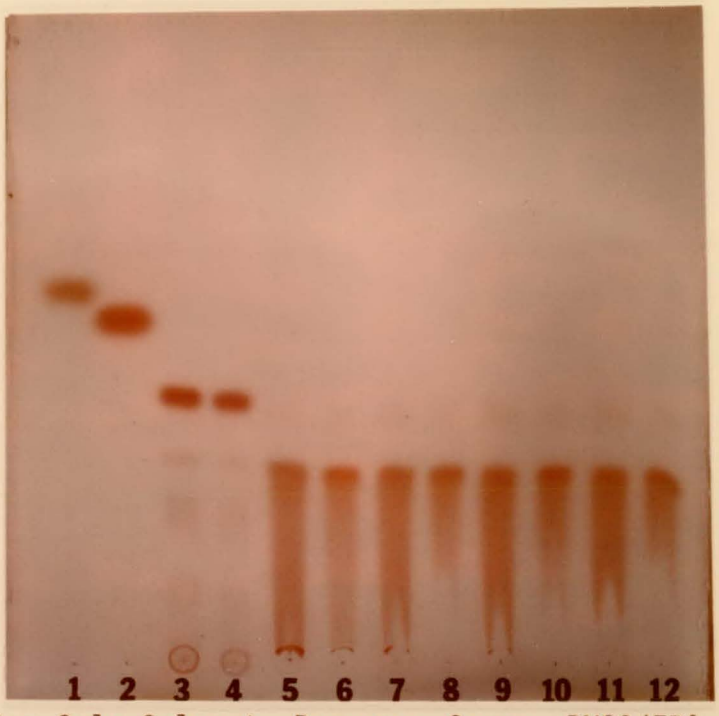
Dipicrylethane
**Trinitrobenzene*

Table III. Test Conditions and Evolved Volatiles

$$V = [(XY + X'Y')Z]/W$$

HNS Lot No.	Sample	Run	DTA Melting Point (C)	Mass (g)	Hot Zone X, (mm)	H^2 (mm)	H^3 (mm)	Room Temperature (C)	Barometer Pressure (mm) P^1	P^2	P^3	Z' (mm)	Z'' (mm)	Volatiles (mℓ/g) 20 Min	60 Min
01-76-0301-01	1	1	316.6	0.2009	10.92	103.0	87.0	22.2	674.0	674.6	674.0	103.0	87.0	4.44	1.86
	2	1		0.1991	10.64	108.0	85.0	22.2	674.0	674.0	674.0	108.0	85.0	4.60	1.81
	3	1		0.2003	10.25	110.0	74.5	22.2	674.0	674.0	674.0	110.0	74.5	4.51	1.53
01-76-0312-01	1	1	316.0	0.2016	10.30	104.0	82.0	22.2	674.0	674.0	674.0	104.0	82.0	4.25	1.68
	2	1			10.55	105.0	74.0	22.2	674.0	674.0	674.0	105.0	74.0	4.40	1.55
	3	1			10.32	102.5	68.5	22.2	674.0	674.0	674.0	102.5	68.5	4.23	1.41
02-76-0421-04	1	1	318.0	0.2007	10.30	65.0	54.0	22.0	679.2	679.2	681.0	65.0	55.8	2.66	1.14
	2	1		0.2013	10.67	66.5	49.0	24.0	680.4	480.4	679.0	66.5	47.6	2.80	1.00
	3	1		0.2011	10.50	65.0	50.0	22.0	679.2	679.2	681.0	65.0	51.8	2.70	1.08
02-76-0421-02	1	1	316.0	0.1996	10.30	72.0	55.0	22.0	679.2	679.2	681.0	72.0	56.8	2.97	1.17
	2	1		0.2001	10.15	71.5	58.5	22.0	679.2	679.2	681.0	71.5	60.3	2.90	1.22
	3	1		0.1993	10.50	74.0	57.0	22.0	679.2	679.2	681.0	74.0	58.8	3.10	1.23
01-76-0301-01	1	2	316.0	0.2016	10.35	112.0	101.0	23.7	670.0	670.0	668.0	112.0	99.0	4.59	2.02
	2	2		0.2000	10.35	112.5	100.5	23.7	670.0	670.0	668.0	112.5	98.5	4.65	2.03
01-76-0312-01	1	2	316.0	0.1996	10.48	110.0	97.0	23.7	670.0	670.0	668.0	110.0	95.0	4.60	1.98
	2	2		0.1998	10.50	117.0	99.0	23.7	670.0	670.0	668.0	117.0	97.0	4.90	2.03
02-76-0421-04	1	2	318.0	0.1997	10.40	68.0	60.0	23.7	670.0	670.0	668.0	68.0	58.0	2.82	1.20
	2	2		0.1998	10.40	69.0	61.5	23.7	670.0	670.0	668.0	69.0	59.5	2.86	1.23

H^1 = Manometer pressure (mm), start of test = 0
H^2 = Manometer pressure (mm), at 20 minutes = $H^2 - H^1$
H^3 = Manometer pressure (mm), at 140 minutes = $H^3 - H^1$
Z' = Corrected Pressure at 20 minutes = $(P^2 - P^1) + H^2$
Z'' = Corrected pressure at end of test = $(P^3 - P^1) + H^3$
X' = External unit volume (mℓ), room temperature $\simeq$ 1.07
Y = 273/[(260 + 273) x 760] = 0.000674
Y' = 273/[(t + 273) x 760)] $\simeq$ 0.0013



Silica Gel; Solvent, Benzene; Spray, DMSO/EDA (1:1)

		µg
1.	TNT	25
2.	Trinitrobenzene	25
3.	Dipicrylethane	25
4.	Dipicrylethane	15
5.	HNS 02-76-0421-04	25
6.	HNS 02-76-0421-04	15
7.	HNS 02-76-0421-02	25
8.	HNS 02-76-0421-02	15
9.	HNS 01-76-0312-01	25
10.	HNS 01-76-0312-01	15
11.	HNS 01-76-0301-01	25
12.	HNS 01-76-0301-01	15

Fig. 3. Chromatogram of HNS Subjected to Vacuum Stability Testing