Lawrence Livermore Laboratory

HALTHANE POLYOL ROUND ROBIN TEST RESULTS

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FROM: F.N. Larsen

SUBJECT: HALTHANE POLYOL ROUND ROBIN TEST RESULTS

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SUMMARY

A ROUND ROBIN CHEMICAL ANALYSIS OF TWO HALTHANE ADHESIVE POLYOL CURE AGENTS FOR HYDROXYL NUMBER, ACID NUMBER, AND WATER CONTENT HAS BEEN CONDUCTED BETWEEN ANALYTICAL LABORATORIES AT LLL, PANTEX, BENDIX, AND UNION CARBIDE (Y-12). THE REPORTED DATA SHOW SUFFICIENT SCATTER AS TO RECOMMEND THAT SPECIFIC TEST PROCEDURES BE CALLED OUT. DIFFERENT METHODS WERE USED IN THE VARIOUS LABS, SOME WITH SLIGHT MODIFICATIONS, OTHERS WERE ENTIRELY DIFFERENT. ALSO, SOME ASTM PROCEDURES WERE MISAPPLIED AND OTHERS WERE INCORRECTLY CALLED OUT. FOR THESE POLYETHER MATERIALS, ASTM E-222-73 (ACETYLATION REFLUX) SHOULD BE ADOPTED FOR THE HYDROXYL NUMBER DETERMINATION. THE ASTM 2849-69 METHOD FOR ACID NUMBER SHOULD BE DISCONTINUED AND THE 'QUAKER OATS' PROCEDURE BE ADOPTED. WATER DETERMINATION BY KARL FISCHER TITRATION IS ACCEPTABLE WITH THE RECOMMENDATION THAT THE 'AQUATEST II' INSTRUMENTATION BE CALLED OUT (USED BY THREE OF THE FOUR LAB PARTICIPANTS).

THE TEST DATA REPORTED GAVE THE FOLLOWING NOMINAL VALUES FOR THE TWO POLYOL CURE AGENTS:

	<u>OH NO.</u>	<u>EQUIV. WT.</u>	<u>ACID NO.</u>	<u>WATER, %</u>
HGH 14	218 - 220	255 - 257	0.02	0.02
HGH 18	250	224	0.02	0.04

THIS ROUND ROBIN TEST PROGRAM PROVED TO BE VERY USEFUL FOR THESE MATERIALS WHICH WILL BE USED IN VARIOUS WEAPONS PROGRAMS. MATERIALS SPECIFICATIONS, MATERIALS HANDLING, TEST PROCEDURE AWARENESS, AND PRODUCTION PLANNING ARE A FEW OF THE BENEFITS OF SUCH A PROGRAM.

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OBJECTIVES

To gain better confidence in the analytical determinations of hydroxyl, water and acid number of the polyol components for the HALTHANE adhesives which have been developed at LLL.

To provide the production agencies experience in handling and analyzing these materials which will be required in certification and shelf life testing.

To provide data for specifications, including test methods.

REFERENCE

Attached to this report is a copy of the request for participation in the test program. It is entitled: "ROUND ROBIN TESTING OF HALTHANE POLYOL HARDENERS," TO: DISTRIBUTION, FROM: F. N. LARSEN, FEBRUARY 2, 1976. This memorandum gives details of the materials, tests requested, handling instructions, etc. It is suggested that the reader refer to that document to better understand the results of the Round Robin.

MATERIALS

HALTHANE (HGH) 14, Lot MCII-31

HALTHANE (HGH) 18, Lot MCII-32

METHODS

The test methods were not specified but left up to the individual laboratories to use their current methods or select a method of their choice for the analysis. As can be seen from Table I, several different methods were used.

TABLE I
METHODS OF ANALYSIS FOR HALTHANE POLYOLS

	<u>Hydroxyl No.</u>	<u>Acid No.</u>	<u>Water</u>
BKC	Acetylation (D-1638)	D-2849-69	Aquatest II
Pantex	(1) Phthalation (D-2849-C)	D-2849-69	Aquatest II
	(2) Acetylation (9981017)		
Y-12	Acetylation E-222-67(B)	Quaker Oats Procedure	Aquatest II
LLL	PMDA	Acetone/.02N NaOH recording titrator	Beckman Aquameter

Both techniques for the water analysis involve Karl Fischer reagent, a long used standard technique for water determinations.

For the acid number determination PX and BKC used ASTM D-2849-69, which uses 5 - 8 grams sample in 50 ml. ethanol and titration with 0.1N base. Y-12 used the Quaker Oats (POLYMEG) procedure calling for

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30 g. sample in 100 ml. chloroform and titration with 0.05N base. LLL uses acetone as a solvent and titrates with 0.02N base.

For the hydroxyl determination, PX, Y-12 and BKC employed the reflux acetylation procedure, correctly designated ASTM E-222-67, Method B. Currently, ASTM 2849-69 allows only pressure bottle acetylation, phthalation, and reflux phthalation. ASTM D-1638 applies only to isocyanate raw materials in the current (1974) ASTM methods. LLL uses a micro pyromellitic dianhydride esterification procedure, which on a macro scale is designated ASTM E-335-69.

DATE OF TESTING

A report of the date of testing was requested to determine if aging of the material or exposure to ambient conditions was related to the analytical values, particularly water. The dates of testing for the four laboratories were as follows:

Pantex	2/24 to 3/5/76
Y-12	3/8 - 10/76
Bendix	1/20, 21/76
LLL	2/6/76 (OH No.), 2/11/76 (AN), 2/24/76 (H ₂ O)

RESULTS

The results are given here in three tables.

TABLE II
WATER DETERMINATION IN HALTHANE POLYOL HARDENERS

HGH 14				HGH 18			
<u>PX</u>	<u>BKC</u>	<u>Y-12</u>	<u>LLL</u>	<u>PX</u>	<u>BKC</u>	<u>Y-12</u>	<u>LLL</u>
-	0.049	0.09	0.051	-	0.054	0.031	0.067
-	0.042	0.09	0.039	-	0.053	0.031	0.069
_____	_____	_____	0.050	_____	_____	_____	0.054
0.015	0.046	0.09	0.046	0.034	0.054	0.031	0.072
			0.051				0.059
			<u>0.048</u>				<u>0.068</u>
			0.048				0.065

Pantex reported no replicates; but did run such, BKC and Y-12 both reported duplicates and LLL requested six replicates. It was determined that PX and Y-12 handled the samples very carefully regarding exposure to ambient moisture and were tested for moisture prior to any other analyses and immediately after opening. These laboratories reported the lowest water contents and it is apparent that sample handling does strongly affect water analyses at these low levels. Standard deviations of the test method were not calculated for this determination. It would appear that the true moisture value is lower than 0.05 weight percent and is probably close to 0.02%.

TABLE III
ACID NUMBER DETERMINATION OF HALTHANE POLYOLS

HGH 14				HGH 18			
<u>PX</u>	<u>BKC</u>	<u>Y-12</u>	<u>LLL</u>	<u>PX</u>	<u>BKC</u>	<u>Y-12</u>	<u>LLL</u>
-	0.03	0.019	0.023	-	0.08	0.029	<0.01
-	0.05	0.020	0.025	-	0.07	0.025	<0.01
_____	_____	_____	_____	_____	_____	<u>0.026</u>	_____
0.02	0.04	0.020	0.024	0.02	0.08	0.027	0.01

Once again standard deviations were not calculated in such small sample sets, and it is apparent the true value is very close to 0.02 acid number. The 0.08 BKC value for HGH 18 appears to be out of line and the < 0.01 value reported by LLL perhaps reflects a potentiometric end-point using very dilute base (0.02N). (The HGH 18 does contain 5% of a weak base, Quadrol.)

TABLE IV
HYDROXYL NUMBER DETERMINATION OF HALTHANE POLYOLS

HGH 14				HGH 18			
<u>PX</u>	<u>BKC</u>	<u>Y-12</u>	<u>LLL</u>	<u>PX</u>	<u>BKC</u>	<u>Y-12</u>	<u>LLL</u>
216.6	222.0	223	208.9	248.4	251.3	250	242.6
219.1	220.3	225	210.8	251.8	251.0	253	244.2
213.7	219.9	225	213.5	254.6	252.5	250	247.4
<u>216.9</u>	_____	_____	_____	<u>246.4</u>	_____	_____	_____
$\bar{X}$ 216.6	220.7	224.3	211.1	250.3	251.6	251.0	244.7
S.D. 2.22	1.12	1.15	2.31	3.63	0.79	1.73	2.44

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These data reveal that intralaboratory repeatability as reflected in the standard deviation (S.D.) for each laboratory is equal to or less than ± 2.3 hydroxyl number. This is comparable to the ASTM procedure limits of repeatability (single analyst) of $\pm 1\%$ (± 2.25) for the HGH 14. The data for the HGH 18 are somewhat more scattered with the standard deviation varying from 0.79 to 3.63 with the higher value being outside the 1% level of ± 2.6 hydroxyl numbers.

The interlaboratory reproducibility is the reverse situation where the HGH 14 test data yield a S.D. of ± 5.67 compared to the acceptable ASTM level of $\pm 1.5\%$ (± 3.4 OH No.). The S.D. for the HGH 18 data is ± 3.18 compared to the ± 3.87 acceptable level.

QUADROL AND 1,4-butanediol CONTENT

Aside from the round robin tests, Bendix was asked to provide quantitative analysis of the 1,4-butanediol content of HGH 14 and 18 and the Quadrol content of HGH 18. The Quadrol was determined by titration of the tertiary amine moiety with perchloric acid in acetic acid. The 1,4-butanediol was determined by gas-liquid chromatography. The data are:

	<u>1,4-butanediol, %</u>	<u>Quadrol, %</u>
HGH 14, Lot MC II-31	9.68	-
HGH 18, Lot MC II-32	9.89	4.96

These data agree quite well with the nominal values of 10.0% and 5.0% for the BDO and Quadrol in the formulations.

CONCLUSIONS AND RECOMMENDATIONS

It is apparent that each laboratory has its own test methods for hydroxyl and acid number and water content in reasonable control, but the use of different test methods obviously is causing unacceptable inter-laboratory variations. The data are summarized in Table V.

TABLE V
SUMMARY OF POLYOL ROUND ROBIN TEST DATA

	HGH 14			HGH 18		
	OH No.	Acid No.	Water	OH No.	Acid No.	Water
Pantex	217	0.01	0.015	250	0.02	0.034
Bendix	221	0.04	0.046	252	0.08	0.054
Y-12	224	0.02	0.009	251	0.03	0.031
LLL	211	0.02	0.048	245	<0.01	0.065

These data are rounded off. Particularly, the hydroxyl number is rounded off, where the ASTM procedure suggests reporting OH No. to the nearest whole number for values above 100. The LLL PMDA procedure is giving low values for hydroxyls compared to the other laboratories. Otherwise, the data in general are not too bad. However, it is recommended that for the HALTHANE polyols a single procedure be adopted for the hydroxyl number determination.

The methods recommended are as follows:

HYDROXYL NUMBER - ASTM E-222-73, Method B

This method is the most widely used procedure for OH No. (See attachment). Current ASTM D-2849 does not allow a reflux acetylation, only pressure bottle techniques and reflux phthalation, none of which seem to be used to any extent in our laboratories.

ACID NUMBER - ASTM D-2849-69

ASTM D-2849-69 is not recommended for use with polyethers as noted in paragraph 20.1 of the Scope and Application (See attached copy of portions of 2849-69). It is suggested that the Quaker Oats procedure used at Y-12 be used for the acid number determination of HALTHANE polyols, since they incorporate the POLYMEG 1000 and 2000 (poly tetramethylene ether glycols). The method essentially uses a 30 gram sample dissolved in 100 ml chloroform and titration with dilute (0.01 to 0.05 N) methanolic KOH and phenolphthalein indicator. Further details of the procedure can be obtained from Quaker Oats or George Dorsey, Y-12 Development Group.

WATER

Any of the standard Karl Fischer techniques are applicable. It is suggested that a final procedure could be written around the PHOTOVOLT CORP.,* AQUATEST II coulometric instrument, which is the most popular,

* Photovolt Corporation, 1115 Broadway, New York, N.Y. 10010
(212) 989-2900 Cost approx. \$2,000

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widely used instrument for KF titrations of water today. Sample handling is the most important part of this technique and from this test data would appear to require a standardization of procedure.

Finally, it should be noted that the HGH 18 lot of material used in this round robin has a value for hydroxyl number of 250 ± 2 which compares to the calculated value of 258, assuming formulation from pure components. This is certainly not the case and the 250 value seems quite reasonable using commercially available materials. This also points out the need for adequate specifications on the POLYMEG (poly tetramethylene ether glycols), butanediol and Quadrol components. The HGH 14 material even with a wide spread on the analysis is certainly in the range of 218 - 220 which also compares favorably with the calculated value for pure components of 225 hydroxyl number.

ACCOMPLISHMENTS

It would appear that this round robin test program has been extremely useful. It has accomplished the following:

- Brought cognizant agency laboratory personnel in contact with each other.
- Pointed out some long standing errors in methods call-out and applications to polyether analysis.

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- Provided information for specification preparation.
- Allowed pre-production handling and analysis problems to be solved early in program applications.
- Emphasized a need for additional and continual awareness of the chemical analysis problems of polymeric materials.

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