

THE PDI REAL WORLD TEST

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PDI REAL WORLD TEST

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Institute of Packaging Professionals *
Chemical Packaging Committee (CPC)
Petroleum Packaging Committee (PPC)

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EXECUTIVE SUMMARY

INTRODUCTION

In 1983 the Plastic Drum Institute (PDI) issued a report entitled "The 55-Gallon All Plastic Drum Reuse Study." That report concluded:

- Ladings did not affect the structural integrity of the plastic drums.
- Reconditioning did not affect the structural integrity of the plastic drums.
- Minimal residue from previous ladings packaged remained in the reconditioned drums.

The significance of this residue to the chemical and petroleum packaging industry was broadly discussed within the PDI.

As a result of these discussions, the PDI proposed a task force in conjunction with the Petroleum Packaging Committee (PPC) and the Chemical Packaging Committee (CPC) of the Institute of Packaging Professionals and the National Barrel and Drum Association (NABADA) to develop a second study to include the evaluation of shippers responsible for the purity of packaged ladings. The task force recommended a program outline which the PDI agreed to coordinate. This program has become known as the "Real World Test."

OBJECTIVES

The primary objective of the "Real World Test" was to establish the suitability of 55-gallon all-plastic drums, which had previously seen service with another lading, for the storage and shipping of a second lading.

The criteria for acceptability were the quality control analyses performed by the shippers upon their ladings following three months storage in the used containers.

A secondary objective was to reconfirm the results of the 1983 study regarding the integrity of all-plastic drums following service and reconditioning. The test criterion was a water-filled drop test.

A further objective was the determination of the residual second lading absorbed into the polyethylene drum wall and remaining after reconditioning. Five testing laboratories produced and performed analytical procedures on sections cut from walls of the test drums.

CONCLUSIONS

The results of the "Real World Test" reconfirmed:

- Ladings did not affect the structural integrity of plastic drums.
- Reconditioning did not affect the structural integrity of the plastic drums.
- Minimal residue from previous ladings packaged remained in the reconditioned drums.

And finally it was determined that:

- Most shippers concluded that reconditioned plastic drums were acceptable for the ladings used in the study.

SUMMARY

The "Real World Test" involved the filling and storage of seventy-two 55-gallon high density polyethylene containers with six selected ladings. The ladings were chosen by the joint Task Force as representative of classes of products currently shipped in all-plastic containers. The six ladings chosen by the joint Task Force were:

Methanol
Mineral Spirits
Acrylic Acid
Acetic Acid
Sulfuric Acid
Motor Oil

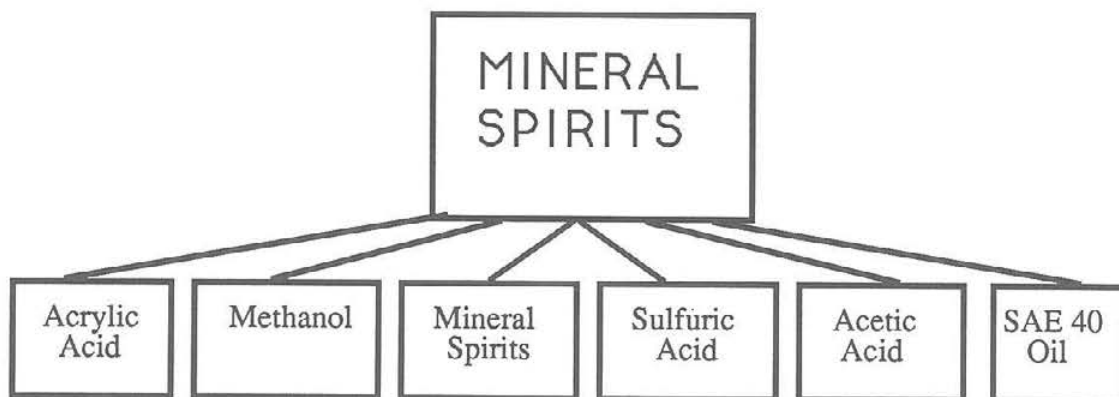
For the first phase of this test, twelve containers were filled with the ladings.

Before storage, the ladings were analyzed as a base reference. After the storage period of three months, the ladings would again be analyzed to determine what effect, if any, the storage in plastic containers had on the product in question.

After three months storage at the shippers'/fillers' facilities, the drums were emptied and sent to the reconditioner where the drums were cleaned using normal procedures for plastic drum interior, exterior and closure and, were submitted to final inspection.

The next step involved twelve drums from each product being disbursed to the various other products and filled.

The chart below illustrates the 12 drums with Mineral Spirits being apportioned to the other chemicals in the test program



The following chart illustrates the apportionment of Acrylic Acid. This same procedure would be conducted with the remaining 4 chemicals until all 72 drums were in their proper categories.



After filling, the drums were stored by shippers/fillers for a period of three months. Before and after the three month storage period, the ladings were again analyzed for possible contaminates. Comments of the shippers/fillers concerning these assay results determined the suitability of reused drums for service with each lading.

After emptying the second lading, the drums were returned to the reconditioner and were again cleaned following normal procedures for plastic drums.

The drums were subjected to flat-side drop at an ambient temperature from a height of six feet. The drums were divided into sets pertaining to the second lading and forwarded to five laboratories while they developed techniques for quantifying the residual second lading absorbed into HPDE. The laboratories were asked to determine the residual second lading in sections cut from the drum walls. Lading concentrations were reported as an average value for each lading and as a function of the first lading.

Further, for drums that contained the same lading in both fillings, the laboratories determined a residual lading gradient by dividing the drum wall crosssection into thirds (inner, middle, and outer) and performing the analysis on these sections.

PART I

LADING QUALITY: Shippers' Results

OBJECTIVE:

The primary objective of the "Real World Test" was the determination of the quality of the second lading.

FILLING & STORAGE

The six groups of twelve new drums each were shipped by the drum fabricators to the chemical shippers who had agreed to participate in the program. Each group of 12 drums included 6 blue and 6 black to establish differences in drum performance as a function of color. The shippers filled the drums using their normal filling equipment and procedures, drawing, during the filling sequence, samples for later assay. This assay, made by the shipper, established the purity levels of his lading at the test start.

Each shipper held the filled drums in his normal warehouse storage for three months, exposing them to the actual conditions his commercial products experienced. At the end of the three months storage, he emptied the drums, again drawing samples for his assay to determine the changes, if any, which had occurred from storage in new drums.

In all cases, these assays made after three months storage showed that no changes had occurred. In addition, drum color was found to have no effect on this or any aspect of the "Real World Test"

The shippers then sent the empty drums to one reconditioning facility for cleaning. The reconditioning procedure involved alternate hot water, steam and ambient temperature water rinses, but no chemical neutralization.

The reconditioner sent the drums back to the original shippers for filling with the second loadings. The second lading pattern, shown in Table 1, has first lading drum sets filled with a different lading. Out of each drum set there is one pair of drums which has the same lading in the second filling as in the first filling.

Again the shipper sampled and assayed each lading during the second filling, and again the shipper stored the drums in his warehouse for three months, then emptied the drums and assayed the contents. Finally, the empty drums were returned to the same reconditioner for cleaning, testing and preparation for analysis.

The second lading assays are shown in Tables 2 thru 8.

Acetic Acid (Table 2)

The acetic acid assay showed no significant differences from the control and the acetic acid shipper concluded that the reconditioned drums were acceptable for use with his lading.

Sulfuric Acid (Table 3)

The sulfuric acid assay showed no significant differences from the specification except for the 77 vs. 50 ppm sulfur dioxide in the acrylic acid drum. The sulfuric acid shipper stated that sulfur dioxide at that level was of no concern.

Methanol (Table 4)

The methanol assay showed contamination which the shipper identified as mineral spirits, introduced during the drum filling. The shipper concluded that the reconditioned drums were acceptable for use with methanol.

Mineral Spirits (Table 5)

The mineral spirits assay showed contamination which the shipper could not identify as methanol; he suggested it may have been introduced before filling. On this basis, the shipper concluded that the reconditioned drums may cause contamination problems with non-alcohol solvents.

Motor Oil (Table 6)

The motor oil assays showed no significant differences from the control, and the motor oil shipper concluded that the reconditioned drums were acceptable for use with motor oil.

This shipper chose, in addition, to test the reconditioned drums for use with specialized, high performance transformer oil, and concluded he would continue to use only new drums in this service.

Acrylic Acid (Tables 7-8)

Acrylic acid is a reactive chemical which tends to react with itself during storage to form an acrylic acid dimer. The reaction can be controlled to some degree by the addition of an inhibitor, in this test methylethyl hydroquinone (MEHQ). The progress of the dimerization (and the loss of reactive acrylic acid) can be followed by a measurement of the increase in dimer level and decrease in inhibitor level during the storage period. During the three month storage period, the shipper sampled all drums (as well as a control) four times at well spaced intervals to follow the progress of the dimer formation. The resulting 28 analyses showed the rate of dimer formation and inhibitor disappearance were the same as the control regardless of the previous lading.

Controlled polymerization is critical in the efficient use of acrylic acid, and impurities can either inhibit or accelerate polymerization. Sulfur is known as an inhibitor. The acrylic acid shipper found 6 ppm sulfur in the acrylic acid stored in the drum which had previously held sulfuric acid. Based on this potential, the acrylic acid shipper chose not to use the reconditioned drums for his product.

TABLE 1

PDI REAL WORLD TEST

DRUM LADING KEY ¹

SECOND LADING:	<u>Acrylic Acid</u> ²	<u>Methanol</u>	<u>Mineral Spirits</u>	<u>Sulfuric Acid</u>	<u>Acetic Acid</u>	<u>Motor Oil</u>
FIRST LADING:						
Acrylic Acid	01, 02	03, 04	05, 06	07, 08	09, 10	11, 12
Methanol	13, 14	15, 16	17, 18	19, 20	21, 22	23, 24
Mineral Spirits	25, 26	27, 28	29, 30	31, 32	33, 34	35, 36
Sulfuric Acid	37, 38	39, 40	41, 42	43, 44	45, 46	47, 48
Acetic Acid	49, 50	51, 52	53, 54	55, 56	57, 58	59, 60
Motor Oil	61, 62	63, 64	65, 66	67, 68	69, 70	71, 72

1. Numbers refer to the numbered drum sets.
2. One drum set, which had contained acrylic acid as the second lading, was lost.

TABLE 2

PDI REAL WORLD TEST PROGRAMACETIC ACID

<u>FIRST LADING</u>	<u>ACRYLIC ACID</u>	<u>SULFURIC ACID</u>	<u>METHANOL</u>	<u>MINERAL SPIRITS</u>	<u>ACETIC ACID</u>	<u>MOTOR OIL</u>
% ACETIC ACID 99.5% MIN	99.98	99.98	99.98	99.98	99.98	99.93
COLOR	WATER WHITE	WW	WW	WW	WW	WW
5 APHA UNITS						
IRON, 2 PPM MAX	0.25	0.25	0.2	0.2	0.25	0.25
LEAD, 3 PPM MAX	0.8	0.5	1.2	1.0	0.4	0.5
RESIDUE AFTER EVAP 100 PPM MAX	8	4	5	10	5	7
CHLORIDES, 15 PPM MAX	4	1	2	4	1	1
ACETIC ANHYDRIDE	<100	<100	<100	<100	<100	<100
SULFATES 15 PPM MAX	8	4	4.5	8	3.5	4
2701E						

TABLE 3

PDI REAL WORLD TEST PROGRAMSULFURIC ACID

<u>FIRST LADING</u>	<u>ACRYLIC ACID</u>	<u>SULFURIC ACID</u>	<u>METHANOL</u>	<u>MINERAL SPIRITS</u>	<u>ACETIC ACID</u>	<u>MOTOR OIL</u>
% SULFURIC ACID, 93.19% MIN	93.54	93.46	93.55	93.56	93.50	93.45
SPECIFIC GRAVITY	1.835	1.835	1.835	1.835	1.835	1.835
HAZEN COLOR, 40 UNITS MAX	20	25	25	25	20	20
IRON, 50 PPM MAX	8	8	11	11	11	8
SULFUR DIOXIDE, 50 PPM MAX	77	23	22	32	19	20
TRANSMITTANCE, 60% MIN	92	90	90	73	91	86

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TABLE 4

PDI REAL WORLD TEST PROGRAM

METHANOL

<u>FIRST LADING</u>	<u>CONTAMINATION, % BY VOLUME</u>
ACRYLIC ACID	0.4
ACRYLIC ACID	.1
SULFURIC ACID	.1
SULFURIC ACID	.1
METHANOL	.1
METHANOL	.1
MINERAL SPIRITS	.2
MINERAL SPIRITS	.1
ACETIC ACID	.1
ACETIC ACID	.1
MOTOR OIL	.04
MOTOR OIL	.2

TABLE 5

PDI REAL WORLD TEST PROGRAM

MINERAL SPIRITS

<u>FIRST LADING</u>	<u>CONTAMINATION, % BY VOLUME</u>
ACRYLIC ACID	0.01
ACRYLIC ACID	.01
SULFURIC ACID	.01
SULFURIC ACID	.01
METHANOL	.01
METHANOL	.01
MINERAL SPIRITS	.001
MINERAL SPIRITS	.02
ACETIC ACID	.001
ACETIC ACID	.01
MOTOR OIL	.01
MOTOR OIL	.01

TABLE 6

PDI REAL WORLD TEST PROGRAM

<u>FIRST LADING</u>	<u>MOTOR OIL</u>	<u>SECOND LADING</u>	<u>CONTAMINATION FROM FIRST LADING</u>
ACRYLIC ACID		TRANSFORMER OIL	192 PPM
ACETIC ACID		MOTOR OIL	<30 PPM
ACETIC ACID		TRANSFORMER OIL	<30 PPM
SULFURIC ACID		MOTOR OIL	<80 PPM
SULFURIC ACID		TRANSFORMER OIL	<100 PPM
METHANOL		MOTOR OIL	<100 PPM
METHANOL		TRANSFORMER OIL	<100 PPM
MINERAL SPIRITS		MOTOR OIL	<1%
MINERAL SPIRITS		TRANSFORMER OIL	<1%
MOTOR OIL		MOTOR OIL	<100 PPM
MOTOR OIL		TRANSFORMER OIL	<100 PPM

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TABLE 7

PDI REAL WORLD TEST PROGRAM

ACRYLIC ACID

	CONTROL	ACRYLIC ACID	ACETIC ACID	METHANOL	SULFURIC ACID	MOTOR OIL	MINERAL SPIRITS
START (8/28/87)							
DIMER, WT.%	0.10	-	-	-	-	-	-
MEHQ, PPM	211						
9/16/87							
DIMER, WT.%	0.73	0.73	0.70	0.70	0.68	0.69	0.71
MEHQ, PPM	205	208	197	216	197	209	215
10/01/87							
DIMER, WT.%	1.08	1.16	1.11	1.12	1.09	1.07	1.14
MEHQ, PPM	205	211	209	208	207	207	208
11/05/87							
DIMER, WT.%	1.78	1.77	1.73	1.77	1.78	1.75	1.79
MEHQ, PPM	191	189	191	189	193	192	188
12/02/87							
DIMER, WT.%	1.94	2.01	1.92	1.86	1.93	1.95	1.93
MEHQ, PPM	186	190	189	189	185	187	190

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TABLE 8

PDI REAL WORLD TEST PROGRAM

ACRYLIC ACID

CONTAMINATION DETERMINATIONS

<u>PREVIOUS LADINGS</u>	<u>CONTAMINATION BY GC</u>	<u>SULFUR BY MICROCOULOMETRY</u>
-------------------------	----------------------------	----------------------------------

ACRYLIC ACID	N/A	N/A
METHANOL	ND	N/A
MINERAL SPIRITS	50-100 PPM	N/A
SULFURIC ACID	N/A	5.8 PPM
ACETIC ACID	N/A	N/A
MOTOR OIL SAE 40	ND	1.4 PPM

N/A - TESTING NOT MEANINGFUL/OR APPLICABLE

ND - NOT DETECTED

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PART II

STRUCTURAL INTEGRITY: Analytical Procedures And Results

TESTING & DISCUSSION

OBJECTIVE:

A secondary objective was to analyze the results of the "Real World Test" to reconfirm the structural integrity of all-plastic drums after fillings and reconditionings.

The 1983 Reuse Study had indicated good retention of structural integrity in the HDPE drums after service with most loadings and subsequent reconditioning. A random sampling of the drums was also drop tested to determine if the storage of two different loading had an effect on structural integrity.

The DOT -34 specified drop test for 55-gallon all-plastic drums currently involves filling the drums with an ethylene glycol solution, cooling the filled drums to 0 deg. F. and dropping the drums from a height of four feet. In this test, however, ethylene glycol solution was not used because of the necessity for subsequent chemical analysis of the drum walls. Instead, the drums were filled with water at ambient temperature and dropped from an increased height of six feet. The drums were then examined for signs of leakage. Table 9 shows the drums that were dropped, their paired loadings, and the results of the drop tests.

CONCLUSIONS

All drums successfully passed the drop test. Temporary distortion of some drums did occur. The drums' shapes returned to normal within a short time. The results show that the multiple loadings, reconditionings and the drum color used in the study had no effect on the structural integrity of the all-plastic drums.

ANALYTICAL TESTING

OBJECTIVE:

Another objective of the "Real World Test" was to analyze and quantify the residual second loading absorbed into the drum wall and remaining after reconditioning.

TESTING PROCEDURES

Six test laboratories volunteered to develop and make available a testing procedure for determining the level of a residual loading in high density polyethylene. These same laboratories agreed to perform testing on the drum walls as provided by the "Real World Test". Only five procedures were produced because one set of drums which had contained acrylic acid as the second loading was lost. The procedures, as written by the testing laboratories, appears in Appendix B.

A summary of the test techniques used is as follows:

<u>LADING</u>	<u>TEST METHOD</u>	<u>LABORATORY</u>
Methanol	G. C. Headspace	Hoechst Celanese
Acetic Acid	Extraction G.C.	Quantum Chemical, USI Div.
Sulfuric Acid	X-Ray Fluorescence	The Dow Chemical Company
Mineral Spirits	Loss of Heating	Container Corp. of America
Motor Oil	Extraction G.C.	Phillips Petroleum

RESULTS & DISCUSSION

Table 10 summarizes the results of the analytical testing for the residual second lading. These results are averages of all tests without separating the possible effects of the first lading. Results are reported in parts per million residual in the drum wall except for sulfuric acid.

Sulfuric acid reacts with the inside surface of the polyethylene drum, forming a surface barrier layer in a process called sulfonation. Deeper penetration of the sulfuric acid was not expected.

Mineral spirits and motor oil showed the highest levels of residual of the five tested ladings. This is not unexpected as hydrocarbon permeation of polyethylene is well known.

Methanol tested the lowest. One theory is that the methanol volatility causes it to migrate out of the drum wall with time.

Tables 11 thru 15 separate the analytical results according to first lading. For the majority of cases, the level of second lading residual was not significantly affected by the nature of the first lading. Certain exceptions were noted: a higher level of motor oil was absorbed into drums that previously contained mineral spirits. Conversely, higher levels of mineral spirits were found in drums that had previously contained motor oil.

PARTITIONING

For drums that contained the same lading twice, four of the analytical testing laboratories agreed to partition a section of the drum wall.

The wall was partitioned into thirds in an attempt to determine a concentration gradient for the lading. Each third (inner, middle and outer) was analyzed for the residual lading. The results, determined for methanol, acetic acid, mineral spirits and motor oil, appear on Table 16.

With the exception of acetic acid, the ladings show highest concentration of residual in the inner third of the drum wall. This is expected as this is the point of direct contact with the lading.

Acetic acid showed the middle third of the drum wall to contain the highest level of residual. As acetic acid is quite soluble in water, it is speculated that the reconditioning process might have extracted some acetic acid from the inner third of the drum wall.

TABLE 9

PDI REAL WORLD TEST

DROP TEST RESULTS

<u>DRUM NUMBER</u>	<u>FIRST LADING</u>	<u>SECOND LADING</u>	<u>PASS/FAIL</u>
4	Acrylic Acid	Methanol	P
5	Acrylic Acid	Mineral Spirits	P
6	Acrylic Acid	Mineral Spirits	P
7	Acrylic Acid	Sulfuric Acid	P
8	Acrylic Acid	Sulfuric Acid	P
9	Acrylic Acid	Acetic Acid	P
10	Acrylic Acid	Acetic Acid	P
15	Methanol	Methanol	P
19	Methanol	Sulfuric Acid	P
20	Methanol	Sulfuric Acid	P
21	Methanol	Acetic Acid	P
22	Methanol	Acetic Acid	P
27	Mineral Spirits	Methanol	P
28	Mineral Spirits	Methanol	P
29	Mineral Spirits	Mineral Spirits	P
30	Mineral Spirits	Mineral Spirits	P
31	Mineral Spirits	Sulfuric Acid	P
32	Mineral Spirits	Sulfuric Acid	P
33	Mineral Spirits	Acetic Acid	P
34	Mineral Spirits	Acetic Acid	P
39	Sulfuric Acid	Methanol	P
43	Sulfuric Acid	Sulfuric Acid	P
44	Sulfuric Acid	Sulfuric Acid	P
45	Sulfuric Acid	Acetic Acid	P
46	Sulfuric Acid	Acetic Acid	P
51	Acetic Acid	Methanol	P
54	Acetic Acid	Mineral Spirits	P
55	Acetic Acid	Sulfuric Acid	P
56	Acetic Acid	Sulfuric Acid	P
58	Acetic Acid	Acetic Acid	P
64	Motor Oil	Methanol	P
66	Motor Oil	Mineral Spirits	P
67	Motor Oil	Sulfuric Acid	P
68	Motor Oil	Sulfuric Acid	P
69	Motor Oil	Acetic Acid	P
70	Motor Oil	Acetic Acid	P

TABLE 10

PDI REAL WORLD TEST

ANALYTICAL RESULTS; RESIDUAL LADING IN DRUM SIDEWALL

<u>LADING</u>	<u>TEST METHOD</u>	<u>AVG. RESULT</u>	<u>UNITS</u>	<u>RANGE</u>
Methanol	G.C.-Headspace	2.4	ppm	1.5-4.6
Acetic Acid	Extraction/G.C.	56.5	ppm	5.0-97
Sulfuric Acid	X-Ray Fluoresc.	26.2	mg S/sq. in.	16-44
Mineral Spirits	Loss on Heating	9000	ppm	1600-12100
Motor Oil	Extraction/G.C.	5300	ppm	2600-11500

TABLE 11

PDI REAL WORLD TEST

RESIDUAL SECOND LADING AS A FUNCTION OF FIRST LADING

SECOND LADING: SULFURIC ACID

<u>FIRST LADING</u>	<u>RESIDUAL SECOND LADING</u>
ACRYLIC ACID	36 mg S/sq. in.
ACETIC ACID	20 mg S/sq. in.
MOTOR OIL	27 mg S/sq. in.
MINERAL SPIRITS	36 mg S/sq. in.
SULFURIC ACID	17 mg S/sq. in.
METHANOL	22 mg S/sq. in.

TABLE 12

PDI REAL WORLD TEST

RESIDUAL SECOND LADING AS A FUNCTION OF FIRST LADING

SECOND LADING: METHANOL

<u>FIRST LADING</u>	<u>RESIDUAL SECOND LADING</u>
ACRYLIC ACID	4.6 ppm
ACETIC ACID	2.8 ppm
MOTOR OIL	1.5 ppm
MINERAL SPIRITS	1.9 ppm
SULFURIC ACID	1.6 ppm

TABLE 13

PDI REAL WORLD TEST

RESIDUAL SECOND LADING AS A FUNCTION OF FIRST LADING

SECOND LADING: MINERAL SPIRITS

FIRST LADING

RESIDUAL SECOND LADING

ACRYLIC ACID

6500 ppm

ACETIC ACID

8700 ppm

MOTOR OIL

12100 ppm

MINERAL SPIRITS

10000 ppm

TABLE 14

PDI REAL WORLD TEST

RESIDUAL SECOND LADING AS A FUNCTION OF FIRST LADING

SECOND LADING: ACETIC ACID

<u>FIRST LADING</u>	<u>RESIDUAL SECOND LADING</u>
ACRYLIC ACID	50 ppm
ACETIC ACID	97 ppm
MOTOR OIL	32 ppm
MINERAL SPIRITS	37 ppm
SULFURIC ACID	78 ppm
METHANOL	40 ppm

TABLE 15

PDI REAL WORLD TEST

RESIDUAL SECOND LADING AS A FUNCTION OF FIRST LADING

SECOND LADING: MOTOR OIL

<u>FIRST LADING</u>	<u>RESIDUAL SECOND LADING</u>
ACRYLIC ACID	7800 ppm
ACETIC ACID	3400 ppm
MOTOR OIL	3800 ppm
MINERAL SPIRITS	9100 ppm
SULFURIC ACID	2600 ppm
METHANOL	5200 ppm

TABLE 16

PDI REAL WORLD TEST

ANALYTICAL RESULTS:RESIDUAL LADING, PARTITIONED SIDEWALL

DUPLICATE LADINGS

<u>LADING</u>	<u>UNITS</u>	<u>INNER</u>	<u>MIDDLE</u>	<u>OUTER</u>
Methanol	ppm	3.79	0.95	0.67
Acetic Acid	ppm	147	231	95
Mineral Spirits	ppm	18600	14700	8800
Motor Oil	ppm	9900	300	1100

APPENDIX A

PART I LADING QUALITY: Shippers' Results

Report on Real-World Test

Hunter Drums Ltd.

We provided C.I.L. in Cornwall, Ontario with 12 drums permanently branded S.A. 1 - 12 for Sulfuric Acid filling and 12 drums permanently branded A.A. 1 - 12 for Acetic Acid filling.

These drums were filled on July 31, 1986 and stored for three months. ✓

The following chart illustrates the C.I.L. criteria for commercial grade Acetic Acid and commercial grade Sulfuric Acid.

<u>ACETIC ACID</u>		<u>SULFURIC ACID</u>	
<u>TEST</u>	<u>COMMERCIAL SPEC.</u>	<u>TEST</u>	<u>COMMERCIAL SPEC.</u>
ASSAY	99.5% Min.	ASSAY	93.19% Min.
COLOR	5 APHA Units	COLOR	40 HAZEN Units
IRON	2.00 ppm Max.	IRON	50 ppm Max.
LEAD	3.00 ppm Max.	SO ₂	50 ppm Max.
RESIDUE AFTER EVAPORATION	100 ppm Max.	TRANSMITTANCE	60% Min.
CHLORIDES	15 ppm Max.		
ACETIC ANHYDRIDE	0.03% Max.		
SULPHATES	15.0 ppm Max.		

On Oct. 30, 1986 C.I.L. compared the samples taken from the 24 drums with their commercial specifications for acetic and sulfuric acid.

All samples met their criteria for commercial grade acids.

The drums were then emptied and forwarded to Bakerstown Containers for reconditioning and subsequently distributed for refilling with the other loadings outlined in the test.

On May the 25th Hunter Drums received from Bakerstown 24 drums which had been reconditioned and numbered as follows:

Metacrylic Acid	- 7, 8, 9, 10
Methanol	- 19, 20, 21, 22
Mineral Spirits	- 31, 32, 33, 34
Sulfuric Acid	- 43, 44, 45, 46
Acetic Acid	- 55, 56, 57, 58
S.A.E. 30 Motor Oil	- 67, 68, 69, 70

These 24 drums were forwarded to C.I.L. and two drums from each previous loading were filled with acetic acid and two drums from each previous loading were filled with sulfuric acid.

The following chart illustrates the specifications of each loading when filled on July 10, 1987 and the results of the tests on the acids removed from the drums Nov. 8, 1987.

Commercial Grade Sulfuric Acid

Drum previously filled with:	<u>Metacrylic Acid</u>	<u>S.A.E. 30 Motor Oil</u>	<u>Acetic Acid</u>	<u>Sulfuric Acid</u>	<u>Mineral Spirits</u>	<u>Methan</u>
Sample #	613	614	615	616	617	618
Drum #	7, 8	67, 68	55, 56	43, 44	31, 32	19, 20
Specific Gravity	1.835	1.835	1.835	1.835	1.835	1.835
Assay % Sulfuric 93.19% Min.	93.54	93.45	93.50	93.46	93.56	93.55
Color 40 Hazen Units Max.	20	20	20	25	25	25
Iron 50 ppm. Max.	8.174	8.174	10.899	8.164	10.899	10.899
Sulfur Dioxide 50 ppm. Max.	76.80	20.25	18.85	23.04	32.12	21.64
Transmittance 60% Min.	92	85.5	91	90	73	90

Commercial Acetic Acid

Drum previously filled with:	<u>Metacrylic Acid</u>	<u>S.A.E. 30 Motor Oil</u>	<u>Acetic Acid</u>	<u>Sulfuric Acid</u>	<u>Mineral Spirits</u>	<u>Methan</u>
Sample #	619	620	621	622	623	624
Drum #	9, 10	69, 70	57, 58	45, 46	33, 34	21, 22
Assay % Acetic 99.5% Min.	99.98	99.93	99.98	99.98	99.98	99.98
Color 5 APHA Units	Water White	W.W.	W.W.	W.W.	W.W.	W.W.
Iron 2.0 ppm Max.	0.25	0.25	0.25	0.25	0.20	0.20
Lead 3.0 ppm Max.	0.80	0.50	0.40	0.50	1.00	1.20
Residue After Evaporation 10 ppm Max.	8	7	5	4	10	5
Chlorides 15 ppm Max.	3.75	1.00	0.75	1.00	3.75	2.00
Acetic Anhydride 0.03% Max.	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Sulfates 15.0 ppm Max.	8.0	4.0	3.5	4.0	8.0	4.5



Industrial Chemicals and Solvents Division
Customer Service Laboratory

LABORATORY REPORT

TO: Dan Brown	LOCATION: Dublin	DATE: August 21, 1987
FROM: Rick Layman	SUBJECT: Service	
CUSTOMER: Internal	SAMPLE: Methanol/Mineral Spirits	LAB NO.: 87-1687-1710

Analysis:

<u>Drum #</u>	<u>Product</u>	<u>% by Vol. Contamination</u>
3	Methanol	0.4
4	Methanol	0.1
5	Mineral Spirits	0.01
6	Mineral Spirits	0.01
39	Methanol	0.1
15	Methanol	0.1
16	Methanol	0.1
17	Mineral Spirits	0.01
27	Methanol	0.2
28	Methanol	0.1
29	Mineral Spirits	0.001
30	Mineral Spirits	0.02
40	Methanol	0.1
41	Mineral Spirits	0.01
42	Mineral Spirits	0.01
51	Methanol	0.1
52	Methanol	0.1
53	Mineral Spirits	0.001
54	Mineral Spirits	0.01
63	Methanol	0.04
64	Methanol	0.2
65	Mineral Spirits	0.01
	Mineral Spirits	0.01
66	Mineral Spirits	0.01

Comment:

The contamination in the Methanol drums was Mineral Spirits.

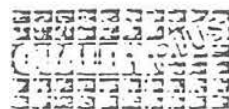
The contamination in the Mineral Spirits could not be identified, but is not Methanol.

The contamination in the Mineral Spirits might have been introduced before the product was put into the drums.

The plastic drums appear to be useable with alcohol solvents, but may cause contamination problems with other solvents.

RL/pjn *Rick Layman*

COPIES TO: B. Whitlock



The information contained herein is correct to the best of our knowledge. If an unknown sample was submitted for analysis, we cannot guarantee duplication of the original formulation.

Prospective customers for a product based on this analysis must determine suitability for its intended use, and should consult with us for any considerations before the order is taken. Ashland makes no guarantee or representation as to results.

MEMORANDUM

ESSO PETROLEUM CANADA
- RESEARCH DEPARTMENT

To: R.A. Miller
From: B.A. Osborne

89 01 09
R 40051

PLASTIC DRUM INSTITUTE TEST PROGRAM

Last summer, Esso Petroleum Canada agreed to participate in the Plastic Drum Institute Real World Test Program, a study to measure the practicality of reusing plastic drums in non-dedicated service. EPC's role in the program was to test the drums in a petroleum oil environment.

In all, eleven drums were submitted for tests. They had previously been filled with one of the following products - methacrylic acid (Drum #11), acetic acid (#59 and #60), sulphuric acid (#47 and #48), methanol (#23 and #24), mineral spirits (#35 and #36), and SAE 30 oil (#71 and #72) - stored for 3 months, reconditioned, and then shipped to EPC for testing with oil fills. One drum from each of the 5 sets of reconditioned drums was filled with Voltesso 35 transformer oil, which is very sensitive to low levels of contamination. The remaining drum from each of the 5 sets was filled with Esolube XD-3 10W engine oil, a low SAE viscosity grade product. The final drum, formerly containing methacrylic acid, was filled with Voltesso 35. The 11 drums were stored on pallets outside in a covered area from August to November, then sampled and returned to Bakerstown for reconditioning a second time and further testing.

Oil samples from each drum were analyzed after the 3 month storage period to determine any contamination present in the oils from the initial fills. Base-case samples of both Esso products were taken from the filling line before the drums were filled for comparison to the drum samples. These two oil samples were stored in amber glass bottles and kept in the laboratory away from any source of light.

Fourier Transform Infrared (FTIR) difference spectra were obtained for base-case and drum-stored oils to detect any contamination. In addition, Power Factors (ASTM D924), Interfacial Tensions (ASTM D971), and Karl Fischer water contents were run on all Voltesso 35 samples. The samples from the drums with an initial acid fill were tested for Total Acid Numbers (ASTM D974) and the samples from the drums with an initial SAE 30 oil fill were tested for additive metal contents. Also, sulphur contents were obtained on the samples with an initial sulphuric acid fill.

The FTIR spectrum, high Power Factor, low Interfacial Tension and high Total Acid Number on the oil from Drum 11, indicates contamination with methacrylic acid. The total acid number value points to a contamination level of approximately 192 ppm methacrylic acid in the oil or 34 g methacrylic acid in 178 kg oil. The remaining Voltesso 35 samples and the Essolube XD-3 10W samples showed no indication of the initial fill products in the oil.

In conclusion, 10 of the 11 reconditioned plastic drums submitted for EPC tests were satisfactory for at least 3 months storage with EPC lubricants. Drum No. 11 appeared to contain a small amount of the initial methacrylic acid fill. The EPC test results and technical information for this test program will be on file at the Esso Research Center in Sarnia.

cc: H.V. Tilley
R.S. Kartzmark
W.D. Hewson
D.A. Slack
P.J. Kozak
B.A. Graham

Attachment
1104mlw.bao

APPENDIX B

PART II

STRUCTURAL INTEGRITY:

Analytical Procedures



CONTAINER CORPORATION OF AMERICA

AN AFFILIATE OF JEFFERSON SMURFIT CORPORATION

Plastics Division

1004 EAST 10TH STREET
WILMINGTON, DE 19802

SUBJECT: Determination of volatile organic compounds in high molecular weight, high density polyethylene by thermogravimetry.

SCOPE: This procedure will measure the total volatile components present in high molecular weight, high density polyethylene (HMWHDPE) that are retrained by the material after exposure to chemicals and any cleaning procedures.

INTRODUCTION:

HMWHDPE is used in the manufacture of all-plastic drums intended for the storage and transport of hazardous chemicals. These drums may be cleaned for reuse in chemical service or ground up in 1/2"-1/4" particles for re-manufacture into other articles.

In order to safely reuse drums or reprocess ground drum material, it is necessary to determine the amount and/or identification of any residual material retained by the HMWHDPE.

Several procedures may be used to make this determination, including extraction and analysis of extractable materials and devolatilization with collection of volatile components for analysis.

The current procedure is based on devolatilization of the HMWHDPE by the technique of thermogravimetry (TG). "Thermogravimetry is a technique in which the mass of a substance is measured as a function of temperature while the substance is subjected to a controlled temperature program". (ASTM E473)

Since the loadings of the drums from which the test samples were taken for this data are known, no attempt will be made to identify volatile components and results will be given as percent based on weight loss.

This procedure can also be extended to determine the decomposition point of the HMWHDPE to evaluate any changes which may have occurred due to exposure to the chemicals contained or cleaning procedures used.

EXPERIMENTAL:

A. Samples. HMWHDPE samples are taken from sidewall sections of drums which have contained various chemicals as defined in the Plastic Drum Institute's Reuse Study: The Real World Test.

1. Black pigmented HMWHDPE - 11 samples.
2. Blue pigmented HMWHDPE - 11 samples.

B. Sample Size.

1. A 25 mg sample representative of the entire cross section is cut from the sidewall sample. Three separate samples are to be tested.
2. 25 mg samples taken from inner 1/3, middle 1/3 and outer 1/3 of drum thickness are cut from sidewall section to determine concentration gradient. Three samples each are to be analyzed.

C. Apparatus.

1. Thermogravimetric Analyzer. Consisting of an autobalance to record weight change while being tested at a controlled rate in an inert (nitrogen) atmosphere. The balance sensitivity should be ± 0.05 mg.
2. Nitrogen gas supply.

D. Procedure:

1. Place 25 mg sample (accurately weighed) in balance pan. Set range to 2 mg/full scale, each charge division equals 0.02 mg, approximately 0.1% of sample weight.
2. Place furnace into position around sample pan.
3. Start nitrogen purge gas at 50-100 ml/min., wait 5 minutes.
4. Set temperature program for range 50°C to 600°C.
5. Set program rate at 20°C/min.
6. Start temperature program and chart recorder.
7. Repeat for each sample.

E. Data Recorded.

1. Weight loss at 250°C, mg.
2. Decomposition Temperature of HMWHDPE. Taken as intersection of lines tangent to curve of loss vs. temperature before and after onset of rapid weight loss.
3. Weight loss at 250°C for inner 1/3, middle 1/3 and outer 1/3 (if done).

RESULTS:

The results are given as follows:

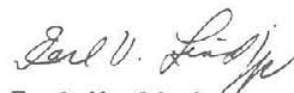
- A. W250 (%) - Weight loss up to 250°C. Average of 3 determinations. W250 (%) = $\frac{\text{Loss (avg.)}}{\text{Sample Wt.}} \times 100$
- B. T_D (°C) - Decomposition temperature for sample. Average of 3 determinations.
- C. W250 (%) fraction - Percent weight loss for inner 1/3, middle 1/3 and outer 1/3 of thickness.
- D. Grams/Drum - Calculate total volatile material possible in standard weight drum (20-24 lbs.).

DISCUSSION:

A discussion of the results is presented to explain results and describe any other observations made during the test such as presence of steps in the weight-temperature curve indicating possibility of multiple products being volatilized.

CONCLUSIONS:

Assessment of level of contamination and suitability of drum for reuse or recycle programs.



Earl V. Lind
Manager
Materials & Systems Engineering
Container Corporation of America
Plastics Division

EVL:jr
8022C-3

TECHNICAL INFORMATION

The following is the procedure which was used in the determination of the degree to which the drum samples, supplied by the PDI, had absorbed any amounts of the sulphuric acid lading which it contained.

The procedure may involve hazardous materials, operations, and equipment. This procedure is not implying that it addresses all of the safety issues associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to its use.

MEASUREMENT OF SURFACE-SULFONATION USING X-RAY FLUORESCENCE

The analyst is referred to ASTM B 568-85, vol. 02.05, "Standard Test Method for Measurement of Coating Thickness by X-ray Spectrometry" and/or ASTM A 754-79, vol. 01.06, "Standard Test Method for Coating Thickness by X-ray Fluorescence" as a guide to testing using x-ray fluorescence.

Much of the surface-sulfonation testing can be accomplished in a manner similar to that described in ASTM C 810-75, vol. 02.05, "Standard Test Method for Nickel on Steel for Porcelain Enameling by X-ray Emission Spectrometry". Following the form of ASTM C 810-75, the necessary additions and corrections are given below for measuring surface-sulfonation using ASTM C 810-75:

1. Scope

- 1.1 This test method covers the measurement of the amount of total sulfur deposited upon or reacted with the surface of high-density polyethylene.

2. Applicable Document

- 2.1 Omit

3. Summary of Method

- 3.1 Surface-sulfonated high-density polyethylene samples are inserted into a sample holder and irradiated with either an x-ray tube or a radio-isotope source. The resulting emission characteristic of sulfur (S K-alpha) is recorded for intensity using a period sufficient to give the desired counting statistics (see ASTM A 754-79, section 3.5). The intensity count is converted by a calibration curve to micrograms of sulfur per square inch.

See reverse side

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TECHNICAL INFORMATION

MEASUREMENT OF SURFACE-SULFONATION USING X-RAY FLUORESCENCE (cont'd)

4. Significance

- 4.1 This test method is a highly accurate and rapid means for measuring surface-sulfur levels on high-density polyethylene.

5. Interferences

- 5.1 No interferences are expected for the S K-alpha emission. Suspicions of interferences should be checked by scanning about the S K-alpha emission line. However, low values can be obtained if overlaying material, for example, moisture or grease, is present. It is also possible to obtain incorrect values for sulfur concentration if the sulfonation depth is much different from that of the calibration materials. This is not usually a problem for the concentration range at or below that indicated in 8.1.

6. Apparatus

- 6.1 Suitable x-ray emission spectrometer complete with x-ray tube or radioisotope source (see manufacturer's instructions in the proper use of the spectrometer). Sulfur K-alpha emission may be measured using either energy- or wave-dispersive x-ray fluorescence (see ASTM B 568-85, sections 4.3.1 and 4.3.2) systems.
- 6.2 A sample holder will be required in moving the sample to the x-ray source area. This holder is usually designed for samples in the range of 1-2 inches in diameter.
- 6.3 High-density polyethylene discs with various levels of sulfur-coating are required for calibration and standardization.

7. Safety Precautions

- 7.1 Equipment should be periodically checked for radiation leaks to ensure against exposure to X-radiation.

8. Calibration and Standardization

- 8.1 Preparation of Standard Calibration Curve:

See reverse side

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MEASUREMENT OF SURFACE-SULFONATION USING X-RAY FLUORESCENCE (cont'd)

- 8.1.1 Prepare sufficient samples to obtain an average of at least six (6) determinations (the number of determinations will be judged by the variability found for the samples and the area measured). Prepare standard samples by surface-sulfinating high-density polyethylene for varying treatment times to provide a range of surface-sulfonation values (this range is typically 50-500 micrograms of sulfur per square inch). Prepare a minimum of three (3) samples at each sulfonation level.
- 8.1.2 After determining the S K-alpha emission intensity versus specimen number, determine, for at least one specimen for each sulfonation level, the sulfur per square inch using an appropriate "wet-chemical" analysis.
- 8.1.3 Plot the sulfur emission intensity versus sulfur concentration as determined in 8.1.1 and 8.1.2, above.

9. Procedure

9.1 Standardization of Equipment

The surface-sulfonated discs, provided in 8.1, may be used for peaking response for S K-alpha emission and for calibrating the response of the x-ray emission spectrometer.

9.2 Sulfur Determination

- 9.2.1 Insert a sample disc into the sample holder, place the sample holder in the x-ray beam and measure the S K-alpha emission intensity. Repeat the sulfur-emission measurement. Average the counts so measured and read the sulfur concentration from the standard curve.
- 9.2.2 Specific details of operation of the x-ray apparatus are not included herein due to the various types of systems which may be applicable to this procedure. These details may be provided by the manufacturer.

10. Report

- 10.1 Convert x-ray counts to micrograms sulfur per square inch by using the calibration curve.

See reverse side

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TECHNICAL INFORMATION

MEASUREMENT OF SURFACE-SULFONATION USING X-RAY FLUORESCENCE (cont'd)

11. Precision and Accuracy

- 11.1 Precision will be determined by the counting statistics and the drift associated with each spectrometer. Accuracy will be defined by the preparation and wet-chemical analysis of the surface-sulfonated discs used for calibration.

JMT:chg
1/5/89

See reverse side

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DETERMINATION OF RESIDUAL ACETIC ACID
IN HIGH DENSITY POLYETHYLENE DRUM SAMPLES
GAS CHROMATOGRAPHIC METHOD

Key Words: Acetic Acid, Drum, GC, HDPE, Polyethylene

I. PRINCIPLE

The concentration of residual acetic acid in high density polyethylene drum samples is determined quantitatively by extracting pellet-sized pieces of the sample with methylene chloride then analyzing the extract by gas chromatography using a Carbowax 20M column and flame ionization detector. The chromatograph is calibrated with a standard solution of acetic acid in methylene chloride and the peak area method of calculation is used.

II. SCOPE

This method was developed to determine residual acetic acid concentrations within the range of 5 ppm to 1 percent by weight in high density polyethylene (HDPE) drum samples.

III. SAFETY PRECAUTIONS

- A. Acetic Acid: Strong acid. Avoid exposure to vapor or contact of skin with liquid.
- B. Methylene Chloride: Avoid prolonged or repeated exposure to vapor or excessive contact of skin with liquid.

IV. APPARATUS AND EQUIPMENT

- A. Hewlett-Packard Model 5880A Gas Chromatograph equipped with a 1/4 inch packed column vaporizing injector and flame ionization detector, or equivalent
- B. Hewlett-Packard Model 5880A GC Terminal with integrator option or other equivalent integrating data system capability
- C. Hamilton 10µl Syringe Model #701 or #1701
- D. 6 ml capacity Hypo vials with crimp-on caps, teflon-lined septa, and crimping tool

V. REAGENTS

- A. Acetic Acid: Reagent grade for standards preparation
- B. Methylene Chloride: Chromatographic quality (Burdick and Jackson Lot #AP111 or equivalent)

VI. REQUIREMENTS

Approximately 3 g of sample is required per analysis. Preparation of HDPE drum samples includes cutting them into pellet-sized pieces, approximately 1/4 inch square, and extracting them overnight. The analysis time for one sample is approximately 3 hours, which includes GC setup time and analyses of both the sample and standard. The analysis time for 6 samples is approximately 6 hours.

VII. PROCEDURE

A. Instrument Conditions

1. Column

Material: Glass
Length: 10 ft.
Diameter: 6 mm o.d. x 2 mm i.d.
Liquid Phase: 4% Carbowax 20M
Solid Support: Carbopack B-DA, 80/120 Mesh

2. Gas Flows

Helium Carrier: 30 cc/min
Hydrogen: 30 cc/min
Air: 300 cc/min

3. Temperatures

Injector: 210°C
Detector: 230°C
Column Temperature Program: (See Note 1)
Initial Temp.: 80°C
Initial Hold Time: 2 mins
Program Rate: 10°C/min
Final Temp.: 200°C
Final Hold Time: 6 mins

B. Preparation of Sample Extract

1. Weigh 3 g of pellet-sized pieces of the HDPE drum sample to the nearest 0.1 mg into a 6 ml Hypo vial.
2. Using a volumetric pipet, add 4 ml of methylene chloride to the vial. Seal it tightly with a cap and septum, teflon side toward the sample, using the crimping tool.
3. Agitate the mixture several minutes. Allow the sample to extract overnight.

C. Preparation of Standards

1. Weigh 0.38 g of acetic acid to the nearest 0.1 mg into a 50 ml volumetric flask.
2. Dilute to volume with methylene chloride.
3. This standard contains 7600 mg/l acetic acid in methylene chloride, equivalent to the concentration found in the extract of a HDPE drum sample containing approximately 1% by weight acetic acid.
4. Further dilutions should be made, if necessary, to obtain a standard that closely matches the acetic acid concentration in the sample extract.

D. Calibration of the Gas Chromatograph

1. Inject 1 μ l of the appropriate standard into the gas chromatograph.
2. Record the chromatogram and measure the area of the acetic acid peak which elutes at approximately 9.5 mins.
3. Figure 1 is a chromatogram and area report of a standard containing 4360 mg/l acetic acid in methylene chloride.

E. Analysis of a Sample Extract

1. Inject 1 μ l of the sample extract into the gas chromatograph.
2. Record the chromatogram and measure the area of the acetic acid peak which elutes at approximately 9.5 mins.

3. Figure 2 is a chromatogram and area report of a sample extract.

VIII. CALCULATIONS

A. Calibration Standard

The response factor is the peak area obtained per unit of concentration and is calculated by dividing the concentration of acetic acid in the standard into the acetic acid peak area.

$$\text{Response Factor of Acetic Acid} = A / C$$

Where:

A = Acetic Acid Peak Area of the Standard

C = Acetic Acid Concentration of Standard in mg/l

B. Sample

The concentration of acetic acid in the sample extract is calculated by dividing the response factor of the standard into the acetic acid peak area of the sample extract. The concentration of acetic acid in the original HDPE drum sample is calculated by dividing the extracted sample weight into the product of the extract acetic acid concentration and the extract volume, converting to the appropriate units.

$$\text{Weight\% Acetic Acid} = \frac{A}{RF} \times \frac{V}{W} \times \frac{1}{1000000} \times 100$$

Where:

A = Acetic Acid Peak Area of the Sample Extract

RF = Response Factor of Acetic Acid Standard

V = Volume used for Sample Extract = 4 ml

W = Weight of HDPE Sample Extracted in g

1000000 = Conversion Factor 1000 mg/g x 1000 ml/l

And:

$$\text{ppm by Weight} = \text{Weight\%} \times 10000$$

IX. REPORT

Report the residual acetic acid content of the HDPE drum sample in either weight% or ppm by weight to three significant figures.

X. PRECISION AND ACCURACY

Precision data was obtained by analyzing five replicate extracts of a HDPE plaque sample containing approximately 0.6% by weight acetic acid. Five manual injections were made for each of the extracts and the standard. This analysis was repeated injecting the extracts with an autosampler. Table I is a summary of the precision data obtained in this study. The RSD was calculated for the five replicate injections of each extract and injection technique. The RSD average and range for each injection technique characterize its precision. The weight% acetic acid in each sample was calculated using the average of the five replicate injections. The method RSD for each injection technique is the variability of the resulting acetic acid concentrations.

Accuracy data for the method is not currently available. However, due to the moderately high volatility of acetic acid, the accuracy of this analysis will largely depend upon the sample history and timeliness of sample preparation and analysis.

XI. NOTES

1. As stated, the column temperature program requires a run time of 20 mins. However, presence of late-eluting compounds such as catalyst carrier hydrocarbons in the extract may require extending the final column temperature hold time and thus the overall run time.

XII. REFERENCES

Research Notebook No.: 2454
Pages: 163, 185

Author: William R. Behymer
Location: CRL

Table I

<u>Injection</u> <u>Technique</u>	<u>Inj. Technique</u> <u>Avg. RSD and Range</u>	<u>Avg. Wt.%</u> <u>Acetic Acid</u>	<u>Method</u> <u>Precision(RSD)</u>
Manual	.85%(.32-1.2%)	.605%	1.79%
Auto	.57%(.40-.79%)	.618%	1.19%

Figure 1

```

***** EXTERNAL STANDARD TABLE *****
***** 07-28-1988 16:19:28 Version 4.1 *****
* Sample Name: 5-12 #1 4360 mg/l          Data File: W:HOAC2
* Date: 07-15-1988 15:46:37 Method: W:ACETIC 07-15-1988 15:56:42 # 4
* Interface: 4 Cycle#: 2 Operator WRB Channel#: 0 Vial#: N.A.
* Starting Peak Width: 10 Threshold: .02 Area Threshold: 10
*****
* Instrument Type: HP 5880A GC          Column Type: 10ft 4% CRBW 20M DA
* Solvent Description: 30 cc/min Helium
* Conditions: Column Prog. 80C for 2 mins + 10C/min to 200C
* Detector 0: FID 230C          Detector 1: N/A
* Misc. Information: Inj. 210C, 1ul(#1701), %OFF=1, 2^0
*****
Starting Delay: 0.00          Ending retention time: 20.00
Area reject: 0          One sample per 0.500 sec.
Amount injected: 1.00          Dilution factor: 1.00
Sample Weight: 1.000000

```

PEAK NUM	RET TIME	PEAK NAME	CONCENTRATION in mg/l	NORMALIZED CONC	AREA	HEIGHT	AREA/ HEIGHT	REF PEAK	% DELTA RET TIME	CONC/AREA
1	6.288		0.0000	0.0000%	17906	2346	7.6 1			0.0000E+00
2	6.933		0.0000	0.0000%	129615	18157	7.1 1			0.0000E+00
3	9.567	Acetic Acid	4360.0000	100.0000%	2826899	481483	7.0 1	0	-3.472	1.5423E-03
4	11.588		0.0000	0.0000%	7444	1277	5.8 1			0.0000E+00

TOTAL AMOUNT = 4360.0000

Data File = W:HOAC2.PTS Printed on 07-28-1988 at 16:20:00
 Start time: 0.00 min. Stop time: 20.01 min. Offset: -80 mv.
 Full Range: 100 millivolts

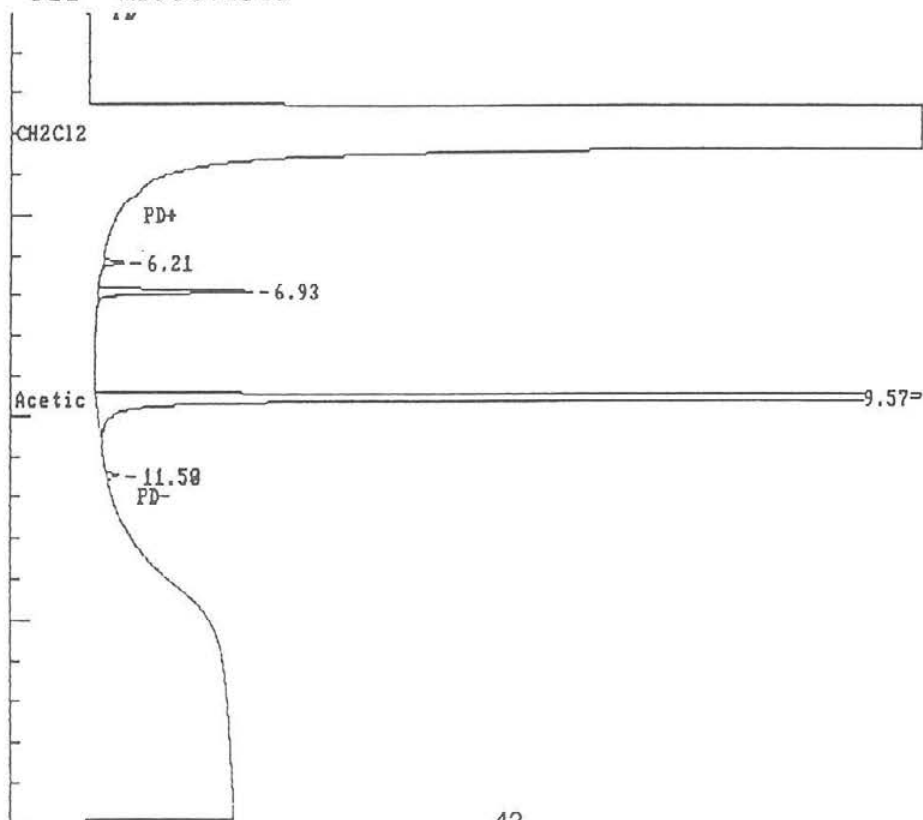


Figure 2

```

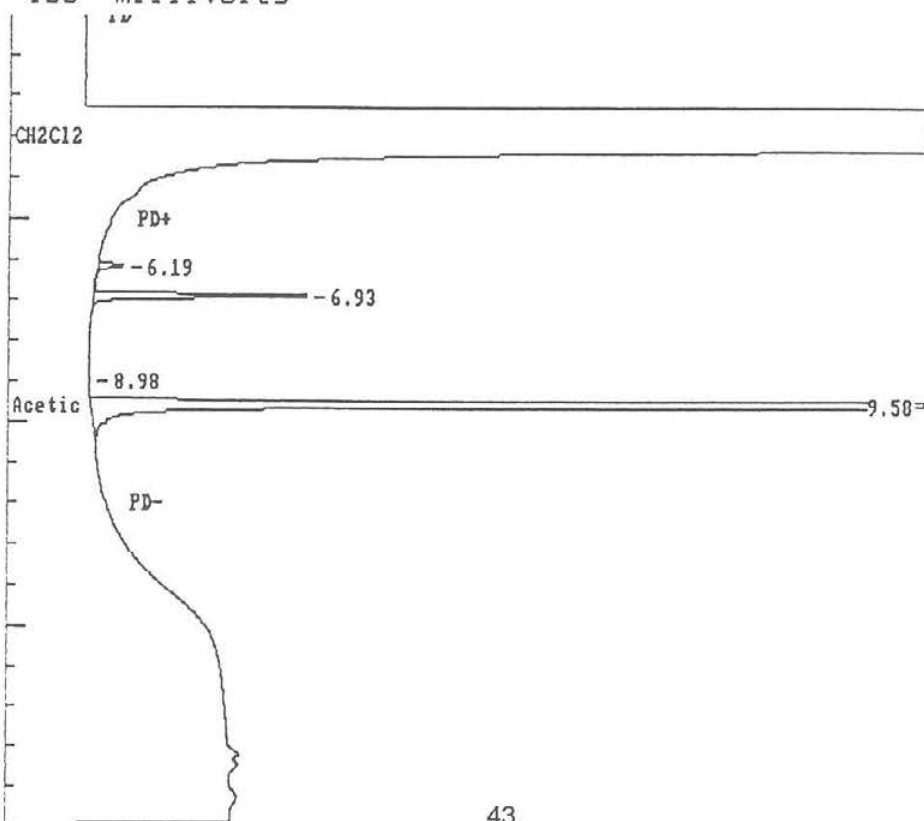
***** EXTERNAL STANDARD TABLE *****
***** 07-28-1988 16:21:59 Version 4.1 *****
* Sample Name: 2454-163-5 3.0283g          Data File: W:HOAC3
* Date: 07-15-1988 16:19:34 Method: W:ACETIC 07-15-1988 15:56:42 # 4
* Interface: 4 Cycle#: 3 Operator WRB Channel#: 0 Vial#: N.A.
* Starting Peak Width: 10 Threshold: .02 Area Threshold: 10
*****
* Instrument Type: HP 5880A GC          Column Type: 10ft 4% CRBW 20M DA
* Solvent Description: 30 cc/min Helium
* Conditions: Column Prog. 80C for 2 mins + 10C/min to 200C
* Detector 0: FID 230C          Detector 1: N/A
* Misc. Information: Inj. 210C, 1ul (#1701), %OFF=1, 2^0
*****
Starting Delay: 0.00          Ending retention time: 20.00
Area reject: 0          One sample per 0.500 sec.
Amount injected: 1.00          Dilution factor: 1.00
Sample Weight: 1.000000

```

PEAK NUM	RET TIME	PEAK NAME	CONCENTRATION in ug/l	NORMALIZED CONC	AREA	HEIGHT	AREA/ HEIGHT BL	REF PEAK	% DELTA RET TIME	CONC/AREA
1	6.192		0.0000	0.0000%	22026	3021	7.6 1			0.0000E+00
2	6.925		0.0000	0.0000%	182270	25090	7.3 1			0.0000E+00
3	8.975		0.0000	0.0000%	875	55	15.9 1			0.0000E+00
4	9.575	Acetic Acid	3906.4026	100.0000%	2532800	357943	7.1 1	0	-.2604	1.5423E-03

TOTAL AMOUNT = 3906.4026

Data File = W:HOAC3.PTS Printed on 07-28-1988 at 16:22:22
 Start time: 0.00 min. Stop time: 20.01 min. Offset: -80 mv.
 Full Range: 100 millivolts



HOECHST CELANESE CORPORATION
Technical Center
Corpus Christi, Texas

To: J. P. Parr - Bayport Works

November 29, 1988

From: N. M. Lamon
K. A. Fritch

ASR-77-88/NML
KAF-215-88

**Methanol Analysis Scheme for
High Density Polyethylene Samples from Bayport Works**

A Gas Chromatography-Headspace method has been developed for the analysis of trace level concentrations of methanol in high density polyethylene samples. The method can detect methanol down to a 1 ppm concentration level. The Appendix contains the analysis procedure for this method.

The linearity and the repeatability evaluation studies of this method were performed on a Hewlett-Packard 5890A Gas Chromatography instrument equipped with a flame ionization detector and a Hewlett-Packard 19395A Headspace sampler unit. The data integration is performed on a Hewlett-Packard 3357 Laboratory Automation System computer.

Norma M. Lamon
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gl
Attachment

Keywords

Bayport Works
Methanol
Analysis
PPM
High
Density
Polyethylene
Gas Chromatography
Hewlett-Packard
Laboratory Automation System
S-1492

Instrument
Headspace
Method
Sampler
Linearity
Repeatability
Data

"QUALITY AND TEAMWORK—A WINNING COMBINATION"

ANALYSIS SCHEME

OBJECTIVE: Determine trace levels of methanol (MEOH) in high density polyethylene (HDPE) samples derived from drum containers used to store methanol. Detection limits down to 5 ppm are desired.

INSTRUMENT: Hewlett-Packard 5890A Gas Chromatograph (GC) equipped with a flame ionization detector, and a Hewlett-Packard 19395A Headspace sampler unit.

I. **Hewlett-Packard 5890A Gas Chromatograph Parameters:**

Column: 30 meter x 0.25 mm I.D. DX-4 capillary column, 0.25 micron film thickness.

Temperature Program: Initial temperature: 40°C for 3 minutes.
 Ramp rate: 10°C/minute.
 Final temperature: 200°C for 10 minutes.

Equilibrium time: 0.5 minutes.

Injector temperature: 210°C.

Detector temperature: 280°C.

Carrier Gas: Helium, 0.74 ml/minute.

Split vent flow: 60 ml/minute.

Split ratio: 82:1

Auxillary gas: Nitrogen, 30 ml/minute.

Septum purge: Helium, 6 ml/minute.

Detector gases: Air: 300 ml/minute.
 Hydrogen: 30 ml/minute.

Range: 2

Attenuation: 2

II. Hewlett-Packard 19395A Headspace Sampler Unit Parameters:

Equilibrium time: 30 minutes or more. The samples are equilibrated for 30 minutes and then the first sample is injected. The subsequent samples are equilibrated for 30 minutes plus the analysis time of the previous samples.

Bath temperature: 120°C.

Valve/loop temperature: 120°C.

Sample size: 1 ml sample loop.

Vial size: 10 ml.

Valve timing:

Probe: 0:01 seconds.

Press: 0:03 seconds.

Press: 0:33 seconds.

Vent: 0:38 seconds.

Vent: 0:43 seconds.

Inj: 0:44 seconds.

Inj: 37:00 minutes.

Probe: 37:01 minutes.

Carrier gas: Helium, 0.9 bar.

Auxillary gas: Helium, 1.5 bar.

Servo air: 3.5 bar.

III. Sample Preparation:

The HDPE samples are cut into small sample blocks (~5 mm x 5 mm x 7 mm).

1. Place ~0.5 gm HDPE sample and ~0.5 gm of decalin solvent (0.5 ml as measured from a 20 ml glass syringe) into a glass headspace vial.
2. Seal the headspace vial with a silicone septum and an aluminum crimp-style cap.
3. Place the sample vial into the headspace sampler tray unit. (The sampler tray is immersed into a silicone oil bath which is maintained at a temperature of 120°C. The sample will melt in the presence of decalin solvent at a temperature of 100°C.)
4. Allow the samples to sit for 30 minutes to allow for the equilibration of the methanol between the molten solid, the liquid, and the gas phases.
5. After equilibration, the headspace sampler unit pierces the septum of the sample vial and fills a 1.0 ml sample loop with the vapor phase which is transferred into the gas chromatography (GC) instrument via a heated transfer line (120°C).

IV. Method Evaluation:

The calibration standards will be conditioned in the same fashion as the test samples.

1. Prepare a control sample by combining decalin solvent with a blank HDPE sample which has not been exposed to methanol (~0.5 gm of blank HDPE sx and ~0.5 gm of decalin).
2. Make headspace injections of the control sample to determine if there are any interferences present that may elute at the same retention time as methanol. This area will be subtracted from the methanol area of all test samples and calibration standards.
3. Prepare a solution containing 11.6 ppm methanol in decalin solvent.
4. Make up five separate vials of a 50:50 mixture of the 11.6 ppm methanol solution and the blank HDPE sample to evaluate the repeatability of the method (~0.5 gm of the 11.6 ppm MECH solution and ~0.5 gm of the blank HDPE sample in each vial). Table I shows the repeatability of these results. Figure 1 is the GC chromatogram of a 50:50 mixture sample.
5. Prepare methanol solutions at concentration levels of 1.2, 7.0, 11.6, and 15.4 ppm in decalin solvent.

6. Combine the solutions from Step IV.5. with blank HDPE sample to generate the calibration curve. Approximately 0.5 gm of each solution and ~0.5 gm of blank HDPE sample is placed in each vial. Prepare a total of 5 vials for each of the different methanol calibration standards. Table II contains the raw data obtained from this study. Figure 2 is the methanol linearity curve.

V. Statistical Evaluation of the Method:

1. The repeatability for five individual preparations of four different concentrations of blend is contained in Figure 2. The data of concentration versus area for nineteen points has been plotted and regressed as shown in Figure 2.
2. In Table III, the ratio of the concentrations versus areas have been determined for nineteen points. The standard deviation for the response factors or ratio is multiplied by the appropriate T factor (for $df = n - 1 = 19 - 1 = 18$) to arrive at the best approximation of the error in a sample result at the 95% confidence limits.

Calculations:

The sample result will be determined 5 times and each corrected area for methanol will be related to its concentration via the regression equation:

$$\text{conc ppm} = 0.544 + 0.00246 \text{ Area}$$

TABLE I
METHANOL REPEATABILITY STUDY
(11.6 PPM)

COMPONENT METHANOL
11
9.8
10.8
10.2
10

68% CONFIDENCE LEVEL.
AVERAGE 10.36

STD. DEV. .517687
COEFF. VAR. 4.99698

95% CONFIDENCE LEVEL
AVERAGE 10.36

STD. DEV. 1.4371
COEFF. VAR. 13.8716

STANDARD DEVIATION (STDV)
AT 68% CONFIDENCE LEVEL:

$$s = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n-1}}$$

Where:

Σ = the summation of all the values 1 thru n.

n = the number of data points evaluated.

\bar{x} = average (mean) of the N values.

x_i = represents each value.

%RSDV = % relative standard deviation of the mean.
(Coefficient of variation)

$$\text{COEFFICIENT OF VARIATION (\%RSDV)} = \frac{\text{Standard Deviation}}{\text{Mean}} \times 100$$

STDV (95% Conf. level) = STDV (68% Conf. level) x T value (n-1) from
the table below

COEFF. VAR. (95% Conf. level) = COEFF. VAR. (68% Conf. level) x T value (n-1)
from the table
below

T Table for calculating the probability of data occurring
at the 95% Confidence level

N degrees of freedom	T
1	12.71
2	4.30
3	3.18
4	2.78
5	2.57
6	2.45
7	2.37
8	2.31
9	2.26
10	2.23

TABLE II

LINEARITY STUDY OF MEOH IN DECALIN SOLVENT IN THE PRESENCE OF HDPE CONTROL SAMPLE

MEOH CONC.	MEOH SOLN.	HDPE WT.	MEOH AREA*	CORRECTED MEOH AREA**
1.2 ppm	1	0.5722 gm	408	355
	2	0.5424 gm	405	352
	3	0.5458 gm	410	357
	4	0.5293 gm	396	343
	5	0.5121 gm	389	336
AVERAGE		0.5404 gm	402	349
7.0 ppm	1	0.5877 gm	3120	3067
	2	0.5142 gm	2657	2604
	3	0.5601 gm	2972	2819
	4	0.5205 gm	2705	2652
	5	0.5856 gm	2998	2945
AVERAGE		0.5536 gm	2890	2837
11.6 ppm	1	0.5551 gm	4292	4239
	2	0.5191 gm	3822	3769
	3	0.5590 gm	4236	4173
	4	0.5146 gm	3986	3933
	5	0.5071 gm	3889	3846
AVERAGE		0.5310 gm	4045	3992
15.4 ppm	1	0.5332 gm	6616	6563
	2	0.5063 gm	6335	6182
	3	0.5097 gm	6302	6269
	4	0.6113 gm	7490	7437
	5	0.5173 gm	6197	6144
AVERAGE		0.5356 gm	6568	6515

* The control sample impurity has not been subtracted from the methanol area.

** The methanol area is corrected by subtracting out the control sample impurity (average of four injections = 53).

TABLE III
RATIO OF THE CONCENTRATIONS VERSUS AREAS

ROW	Conc ppm	Area	Ratio	Conc ppm	Area	Ratio	Conc ppm	Area	Ratio	Conc ppm	Area	Ratio
1	1.2	355	0.0033803	7.0	3067	0.0022824	11.6	4239	0.0027365	15.6	6563	0.0023465
2	1.2	352	0.0034091	7.0	2604	0.0026882	11.6	3769	0.0030777	15.6	6182	0.0024911
3	1.2	357	0.0033613	7.0	2919	0.0025981	11.6	4173	0.0027798	15.6	6249	0.0024644
4	1.2	343	0.0034985	7.0	2652	0.0026395	11.6	3933	0.0029494	15.6	6144	0.0025065
5	1.2	336	0.0035714	7.0	2945	0.0023769	11.6	3846	0.0030161	---	---	---
				N	19							
				MEAN	0.00284							
				STDEV *	0.00090							
				WRSDEV *	31.7							

* At the 95% confidence level.

FIGURE 1

GC CHROMATOGRAM OF A 11.6 PPM MEOH STANDARD

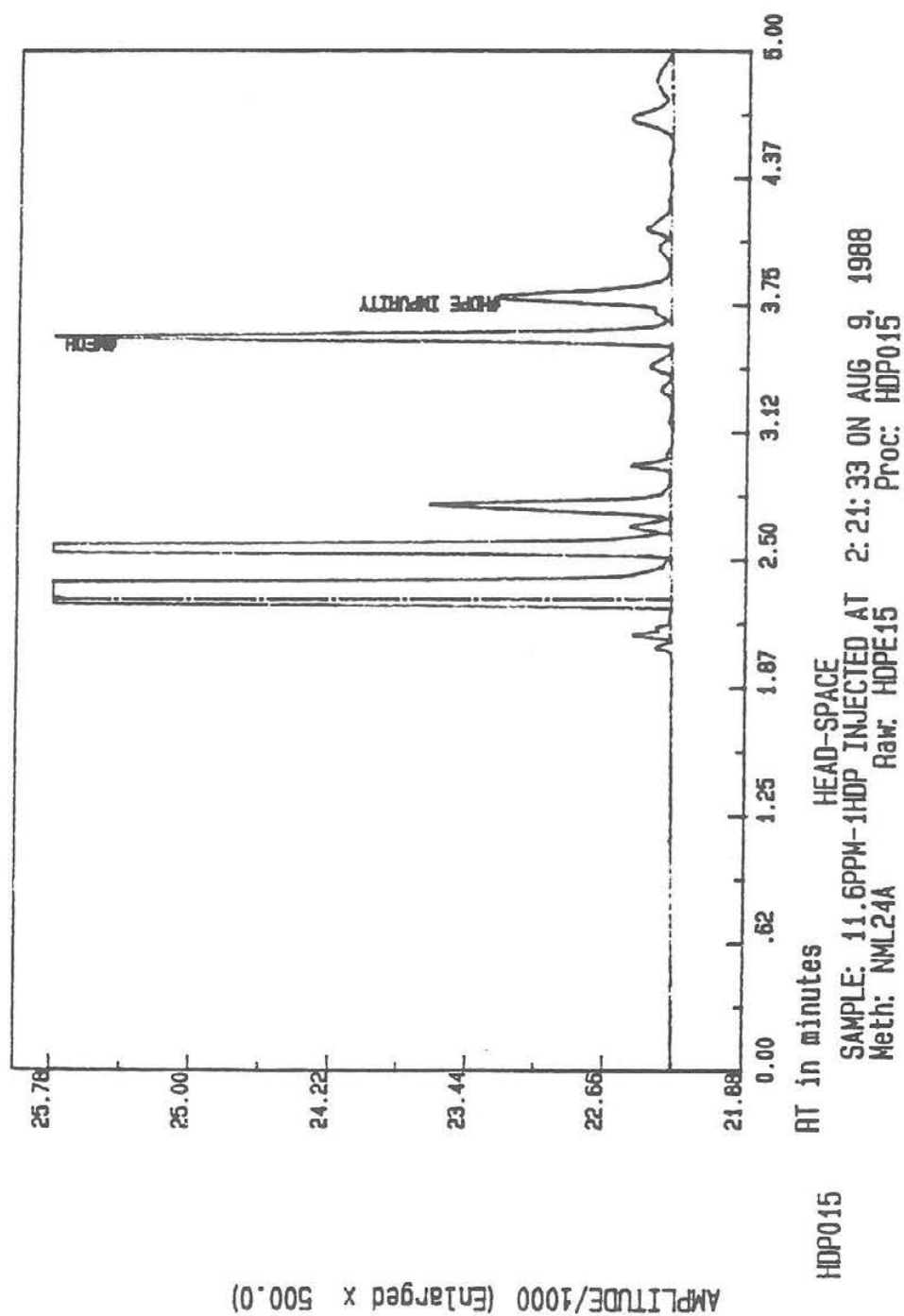


FIGURE 2
METHANOL LINEARITY STUDY
METHANOL STATISTICAL EVALUATION AT THE 95% CONFIDENCE LEVEL

ROW	1.2 ppm	area 1.2	7.0 ppm	area 7.0	11.6 ppm	area 11.6	15.4 ppm	area 15.4
1	1.2	355	7.0	3067	11.6	4239	15.4	6563
2	1.2	352	7.0	2604	11.6	3769	15.4	6182
3	1.2	357	7.0	2919	11.6	4173	15.4	6249
4	1.2	343	7.0	2852	11.6	3933	15.6	6146
5	1.2	336	7.0	2945	11.6	3846	---	---
N	5	5	5	5	5	5	4	4
MEAN	1.2	348.6	7.0	2837.4	11.6	3992.0	15.4	6286.5
STDEV	0.0	24.6	0.0	555.7	0.0	570.2	0.0	606.4
SRSDV	7.0		19.6		14.3			9.6

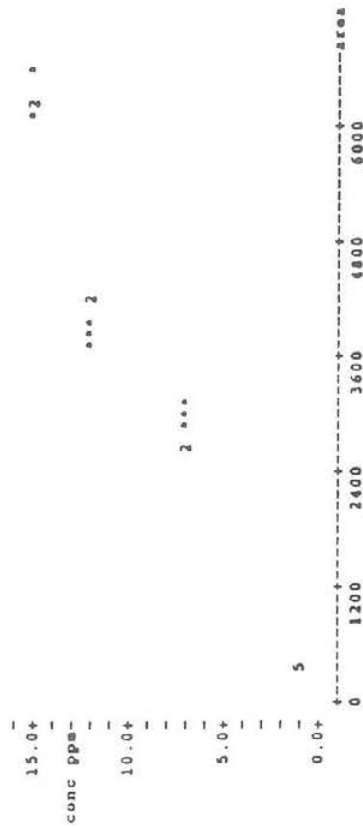


Fig. 2 Methanol linearity study

The regression equation is conc ppm = 0.544 + 0.00246 area

Predictor	Coef	Stdev	t-ratio	p
Constant	0.5438	0.3724	1.46	0.162
area	0.00246227	0.00009718	25.34	0.000

n = 0.8850 R-sq = 97.4% R-sq(adj) = 97.3%

Analysis of Variance

SOURCE	DF	SS	MS	F	p
Regression	1	502.83	502.83	641.98	0.000
Error	17	13.32	0.78		
Total	18	516.15			

Unusual Observations

Obs.	area	conc ppm	Fit	Stdev.Fit	Residual	St.Resid
12	3769	11.600	9.824	0.210	1.776	2.078

R denotes an obs. with a large st. resid.

PROCEDURE FOR ANALYZING LADINGS ABSORBED IN POLYETHYLENE DRUMS

- 1.) Place 1 gram of ground polymer in a suitable container for solvent extraction. Place 20 ml of the extraction solvent, in this case methylene chloride, in the container and place on a shaker for one hour.
- 2.) Analyze the extraction solvent by gas chromatography. In this study a gas chromatograph with a 25 meter capillary column with methyl silicone as the stationary phase was used. The GC conditions were:

Initial temperature:	10 deg. C
Final temperature:	325 deg. C
Program rate:	15 deg./min.
Injector temperature:	325 deg. C
Detector Temperature:	350 deg. C
- 3.) The extraction runs are compared to standards. The standards used in this study were dilutions in methylene chloride of the engine oil and transformer oil type that was used in the second lading.

APPENDIX C

PART II

STRUCTRUAL INTEGRITY:

Analytical Results

To: L. E. Wade

From: N. M. Lamon
K. A. Fritch

April 18, 1989

ASR-83-89/NML
KAF-219-89

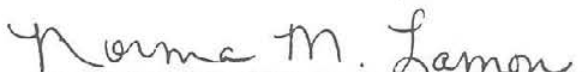
**Methanol Analysis Scheme and Sample Data Results
for High Density Polyethylene Samples from Bayport Works**

A round-robin testing program was initiated to determine the compatibility of high density polyethylene drum liners with various solvents. The program was supported with analytical labs from multiple companies. The CCTC provided the analytical support for Bayport Works during this program.

A Gas Chromatographic-Headspace method was used for the determination of trace level concentrations of methanol in high density polyethylene samples. The methanol detection limit for this method is ~0.8 ppm. The appendix contains the analysis procedure and the sample analysis results obtained with this method.

The linearity and the repeatability evaluation studies of this method were performed on a Hewlett-Packard 5890A Gas Chromatography instrument equipped with a flame ionization detector and a Hewlett-Packard 19395A Headspace sampler unit. The data integration is performed on a Hewlett-Packard 3357 Laboratory Automation System computer.

The six samples received from Bayport Works each contained less than 5 ppm methanol as shown in Table V.


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K. A. Fritch

gl
Attachment

Keywords

Bayport Works
Methanol
Headspace
Gas Chromatography
Hewlett-Packard
Laboratory Automation System
S-1492

Density
Polyethylene
Analysis
Sampler
PPM
High

Instrument
Data
Method
Linearity
Repeatability

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APPENDIX

METHANOL ANALYSIS SCHEME AND SAMPLE DATA RESULTS

ANALYSIS SCHEME

Objective: Determine trace levels of methanol (MEOH) in high density polyethylene (HDPE) samples derived from drum containers used to store methanol. Detection limits down to 5 ppm are desired.

Instrument: Hewlett-Packard 5890A Gas Chromatograph (GC) equipped with a flame ionization detector, and a Hewlett-Packard 19395A Headspace sampler unit.

I. Hewlett-Packard 5890A Gas Chromatograph parameters:

Column: 30 meter x 0.25 mm I.D. DX-4 capillary column, 0.25 micron film thickness.

Temperature program:

Initial temperature: 40°C for 3 minutes.

Ramp rate: 10°C/minute.

Final temperature: 200°C for 10 minutes.

Equilibrium time: 0.5 minutes.

Injector temperature: 210°C.

Detector temperature: 280°C.

Carrier Gas: Helium, 0.74 ml/minute.

Split vent flow: 51 ml/minute.

Split ratio: 69:1

Auxillary gas: Nitrogen, 30 ml/minute.

Septum purge: Helium, 6 ml/minute.

Detector gases:

Air: 300 ml/minute.

Hydrogen: 30 ml/minute.

Range: 2

Attenuation: 2

II. Hewlett-Packard 19395A Headspace Sampler Unit Parameters:

Equilibrium time: 30 minutes or more. The samples are equilibrated for 30 minutes and then the first sample is injected. The subsequent samples are equilibrated for 30 minutes plus the analysis time of the previous sample.

Bath temperature: 120°C.

Valve/loop temperature: 120°C.

Sample size: 1 ml sample loop.

Vial size: 10 ml.

Valve timing:

Probe: 0:01 seconds.

Press: 0:03 seconds.

Press: 0:33 seconds.

Vent: 0:38 seconds.

Vent: 0:48 seconds.

Inj: 0:49 seconds.

Inj: 1:49 seconds.

Probe: 1:50 seconds.

Carrier gas: Helium, 0.9 bar.

Auxillary gas: Helium, 1.5 bar.

Servo air: 3.5 bar.

III. Sample preparation: The HDPE samples are cut into small sample blocks (~5 mm x 5 mm x 7 mm)

1. Place ~0.5 gm HDPE sample and ~0.5 gm of decalin solvent (0.5 ml as measured from a 20 ml glass syringe) into a glass headspace vial.
2. Seal the headspace vial with a silicone septum and an aluminum crimp-style cap.
3. Place the sample vial into the headspace sampler tray unit. (The sampler tray is immersed into a silicone oil bath which is maintained at a temperature of 120°C. The sample will melt in the presence of decalin solvent at a temperature of 100°C.)
4. Allow the samples to sit for 30 minutes to allow for the equilibration of the methanol between the molten solid, the liquid, and the gas phases.
5. After equilibration, the headspace sampler unit pierces the septum of the sample vial and fills a 1.0 ml sample loop with the vapor phase which is transferred into the gas chromatography (GC) instrument via a heated transfer line (120°C).

IV. Method evaluation:

The calibration standards will be conditioned in the same fashion as the test samples.

1. Prepare a control sample by combining decalin solvent with a blank HDPE sample which has not been exposed to methanol. (~0.5 gm of blank HDPE sample and ~0.5 gm of decalin)
2. Make headspace injections of the control sample to determine if there are any interferences present that may elute at the same retention time as methanol. This area will be subtracted from the methanol area of all test samples and calibration standards.
3. Prepare a solution containing 9.8 ppm methanol in decalin solvent.
4. Make up five separate vials of a 50:50 mixture of the 9.8 ppm methanol solution and the blank HDPE sample to evaluate the repeatability of the method (~0.5 gm of the 9.8 ppm MEOH solution and ~0.5 gm of the blank HDPE sample in each vial). Table I shows the repeatability of these results. Figure 1 is the GC chromatogram of a 50:50 mixture sample.

5. Prepare methanol solutions at concentration levels of 0.768, 6.3, 9.8, and 17.6 ppm in decalin solvent.
6. Combine the solutions from Step IV.5 with blank HDPE sample to generate the calibration curve. Approximately 0.5 gm of each solution and ~0.5 gm of blank HDPE sample is placed in each vial. Prepare a total of five vials for each of the different methanol calibration standards. Table II contains the raw data obtained from this study. Figure 2 is the methanol linearity curve.

V. Statistical evaluation of the method:

1. The repeatability for five individual preparations of four different concentrations of blend is contained in Table II. The data of concentration versus area for 20 points has been plotted and regressed as shown in Figure 2.
2. In Table III, the ratio of the concentrations versus areas have been determined for 20 points. The standard deviation for the response factors or ratio is multiplied by the appropriate T factor (for $df = n - 1 = 20 - 1 = 19$) to arrive at the best approximation of the error in a sample result at the 95% confidence limits.

VI. Calculations:

The sample result will be determined five times and each corrected area for methanol will be related to its concentration via the regression equation:

$$\text{conc ppm} = 1.08 + 0.00187 \text{ AREA}$$

VII. Sample analysis results:

Table IV contains the HDPE sample analysis raw data. The analysis results are statistically evaluated at the 95% confidence level in Table V.

TABLE I
METHANOL REPEATABILITY STUDY
(9.8 PPM)

COMPONENT	METHANOL
9.9	
9.9	
10.2	
10.4	
9.6	
	68% CONFIDENCE LEVEL.
	AVERAGE 10
STD. DEV.	.308221
COEFF. VAR.	3.08221
	95% CONFIDENCE LEVEL
	AVERAGE 10
STD. DEV.	.855621
COEFF. VAR.	8.55621

TABLE II
LINEARITY STUDY OF MEOH IN DECALIN SOLVENT
IN THE PRESENCE OF HDPE CONTROL SAMPLE

MEOH conc.	MEOH soln. wt.	HDPE wt.	MEOH AREA*	CORRECTED MEOH AREA**
0.768 ppm - 1	0.4917 gm	0.5102 gm	365	326
- 2	0.4932 gm	0.5179 gm	329	290
- 3	0.5039 gm	0.4971 gm	374	335
- 4	0.4839 gm	0.5210 gm	395	356
- 5	0.4999 gm	0.5144 gm	354	315
AVERAGE	0.4945 gm	0.5121 gm	363	324
6.3 ppm - 1	0.5111 gm	0.5271 gm	2222	2183
- 2	0.5052 gm	0.4966 gm	2185	2146
- 3	0.5123 gm	0.4966 gm	2035	1996
- 4	0.5586 gm	0.5150 gm	2311	2272
- 5	0.5016 gm	0.4994 gm	2125	2086
AVERAGE	0.5178 gm	0.5069 gm	2176	2137
9.8 ppm - 1	0.5024 gm	0.5052 gm	4743	4704
- 2	0.5112 gm	0.5135 gm	4737	4698
- 3	0.5357 gm	0.5092 gm	4926	4887
- 4	0.5378 gm	0.5103 gm	5035	4996
- 5	0.4953 gm	0.5165 gm	4598	4559
AVERAGE	0.5165 gm	0.5109 gm	4808	4769
17.6 ppm - 1	0.5468 gm	0.5115 gm	9648	9609
- 2	0.5150 gm	0.4945 gm	8514	8475
- 3	0.5111 gm	0.5268 gm	9055	9016
- 4	0.5146 gm	0.5119 gm	9034	8995
- 5	0.4949 gm	0.5199 gm	8285	8246
AVERAGE	0.5165 gm	0.5129 gm	8907	8868

* The control sample impurity has not been subtracted from the methanol area.

** The methanol area is corrected by subtracting off the control sample impurity (average of five injections = 39).

TABLE III
RATIO OF THE CONCENTRATIONS VERSUS AREA

ROW	PPM conc	Area	Ratio	PPM conc	Area	Ratio	PPM conc	Area	Ratio	PPM conc	Area	Ratio
1	0.768	326	0.0023558	6.3	2183	0.0028859	9.8	4704	0.0020833	17.6	9609	0.0018316
2	0.768	290	0.0026483	6.3	2146	0.0029357	9.8	4698	0.0020860	17.6	8475	0.0020767
3	0.768	335	0.0022925	6.3	1996	0.0031563	9.8	4887	0.0020053	17.6	9016	0.0019521
4	0.768	356	0.0021573	6.3	2272	0.0027729	9.8	4996	0.0019616	17.6	8995	0.0019566
5	0.768	315	0.0024381	6.3	2086	0.0030201	9.8	4559	0.0021496	17.6	8246	0.0021344
				N	20							
				MEAN	0.00235							
				STDEV *	0.00086							
				%RSDDEV *	36.6							

* At the 95% confidence level.

TABLE IV
HDPE SAMPLE ANALYSIS RAW DATA

Sample no.	HDPE wt.	Decalin wt.	MEOH area *	Corrected MEOH area **	PPM MEOH
#4 - 1	0.5090 gm	0.5572 gm	1343	1304	3.5 ***
- 2	0.5037 gm	0.5380 gm	1690	1651	4.2
- 3	0.5176 gm	0.5189 gm	1929	1890	4.6
- 4	0.5137 gm	0.5059 gm	1974	1935	4.7
- 5	0.5060 gm	0.5071 gm	2097	2058	4.9
AVERAGE	0.5100 gm	0.5254 gm	1806.6	1767.6	4.6
#27 - 1	0.4961 gm	0.5102 gm	577	538	2.1
- 2	0.5110 gm	0.4895 gm	608	569	2.1
- 3	0.4952 gm	0.5088 gm	613	574	2.2
- 4	0.5150 gm	0.5396 gm	680	641	2.3
- 5	0.5099 gm	0.4928 gm	677	638	2.3
AVERAGE	0.5054 gm	0.5082 gm	631	592	2.2
#28 - 1	0.5170 gm	0.4976 gm	286	247	1.5
- 2	0.4983 gm	0.5072 gm	274	235	1.5
- 3	0.5137 gm	0.4921 gm	381	342	1.7 ***
- 4	0.5098 gm	0.5175 gm	300	261	1.6
- 5	0.5062 gm	0.4987 gm	318	279	1.6
AVERAGE	0.5090 gm	0.5026 gm	311.8	272.8	1.6
#39 - 1	0.5085 gm	0.5001 gm	366	327	1.7
- 2	0.5068 gm	0.5593 gm	314	275	1.6
- 3	0.5172 gm	0.4937 gm	318	279	1.6
- 4	0.4967 gm	0.5207 gm	348	309	1.6
- 5	0.5036 gm	0.5061 gm	305	266	1.6
AVERAGE	0.5066 gm	0.5160 gm	330.2	291.2	1.6
#51 - 1	0.5006 gm	0.5041 gm	867	828	2.6
- 2	0.5022 gm	0.5665 gm	891	852	2.7
- 3	0.5031 gm	0.5032 gm	943	904	2.8
- 4	0.5112 gm	0.5073 gm	988	949	2.8
- 5	0.5153 gm	0.4929 gm	1003	964	2.9
AVERAGE	0.5065 gm	0.5148 gm	938.4	899.4	2.8
#64 - 1	0.5125 gm	0.4933 gm	186	147	1.4 ***
- 2	0.5038 gm	0.5634 gm	232	193	1.4
- 3	0.4956 gm	0.5261 gm	257	218	1.5
- 4	0.5239 gm	0.5111 gm	257	218	1.5
- 5	0.5085 gm	0.5354 gm	281	242	1.5
AVERAGE	0.5089 gm	0.5259 gm	242.6	203.6	1.5

* The control sample impurity has not been subtracted from the methanol area.

** The methanol area is corrected by subtracting out the control sample impurity (average of 5 injections = 39).

*** These results were not included in the average.

TABLE V
STATISTICAL EVALUATION OF THE
HDPE SAMPLE RESULTS AT THE 95% CONFIDENCE LEVEL

ROW	04 Area	04 ppm MEON	027 Area	027 ppm MEON	028 Area	028 ppm MEON	039 Area	039 ppm MEON	051 Area	051 ppm MEON	064 Area	064 ppm MEON
1	-----	-----	538	2.1	247	1.5	327	1.7	828	2.6	-----	-----
2	1651	4.2	569	2.1	235	1.5	275	1.6	852	2.7	193	1.4
3	1890	4.6	574	2.2	-----	-----	279	1.6	904	2.8	218	1.5
4	1935	4.7	641	2.3	261	1.6	309	1.6	949	2.8	218	1.5
5	2058	4.9	638	2.3	279	1.6	266	1.6	964	2.9	242	1.5
N	4	4	5	5	4	4	5	5	5	5	4	4
MEAN	1883.5	4.6	592	2.2	255.5	1.6	291.2	1.6	899.4	2.8	217.75	1.5
STDEV	542.5	0.937	126.3	0.278	60.2	0.183	71.4	0.124	164.2	0.316	63.6	0.159
TRSDDEV	28.8	20.4	21.3	12.6	23.6	11.8	24.5	7.7	18.2	11.5	29.2	10.8

FIGURE 1

GC CHROMATOGRAM OF A 9.8 PPM MEOH STANDARD

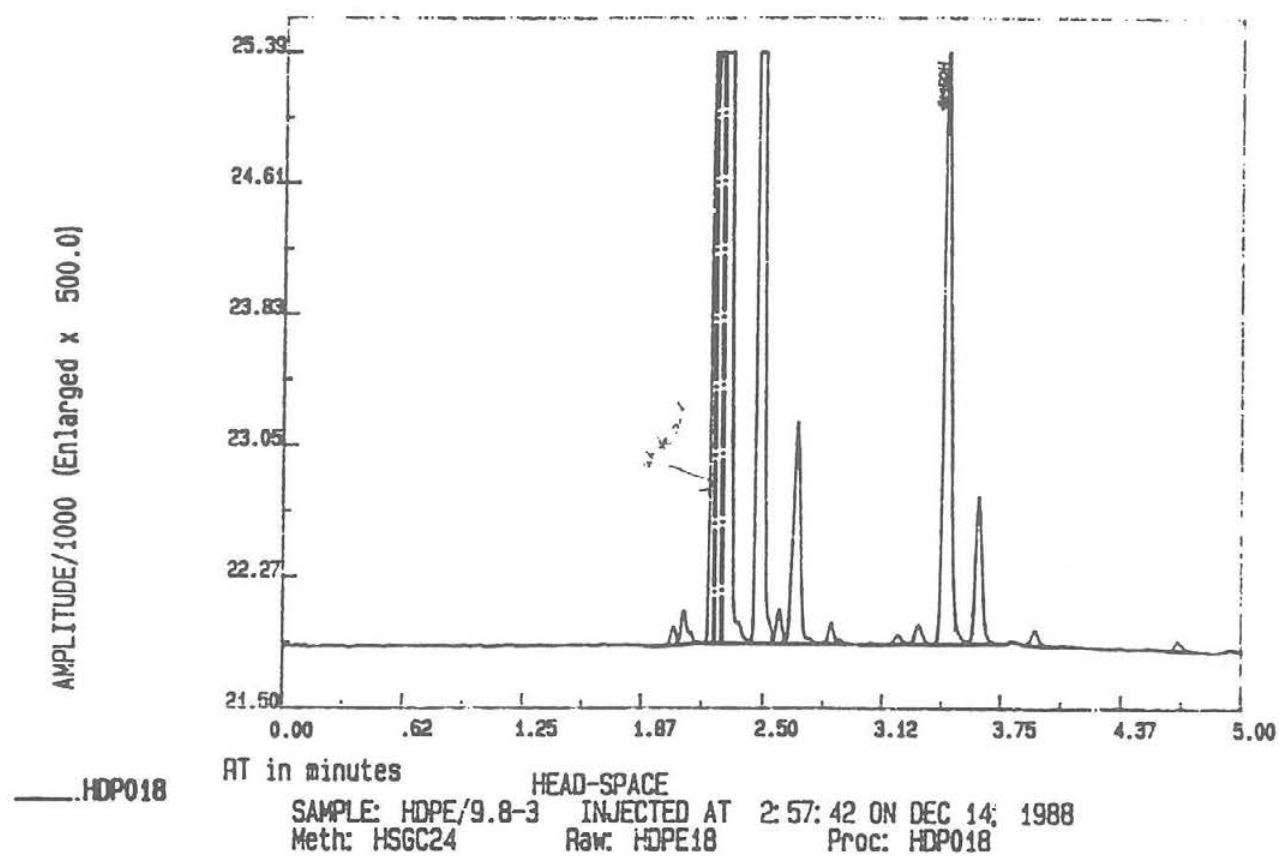


FIGURE 2

METHANOL LINEARITY STUDY

METHANOL STATISTICAL EVALUATION AT THE 95% CONFIDENCE LEVEL

ROW	0.768 ppm	area 0.768	6.3 ppm	area 6.3	9.8 ppm	area 9.8	17.6 ppm	area 17.6
1	0.768	326	6.3	2183	9.8	4784	17.6	9889
2	0.768	290	6.3	2146	9.8	4698	17.6	8475
3	0.768	335	6.3	1996	9.8	4887	17.6	9016
4	0.768	356	6.3	2272	9.8	4996	17.6	8995
5	0.768	315	6.3	2086	9.8	4559	17.6	8246
N	5	5	5	5	5	5	5	5
MEAN	0.768	326.4	6.3	2136.6	9.8	4768.8	17.6	8868.2
STDEV	0.0	67.8	0.0	287.5	0.0	478.4	0.0	1474.4
VARSEV		20.9		13.4		10.0		16.6

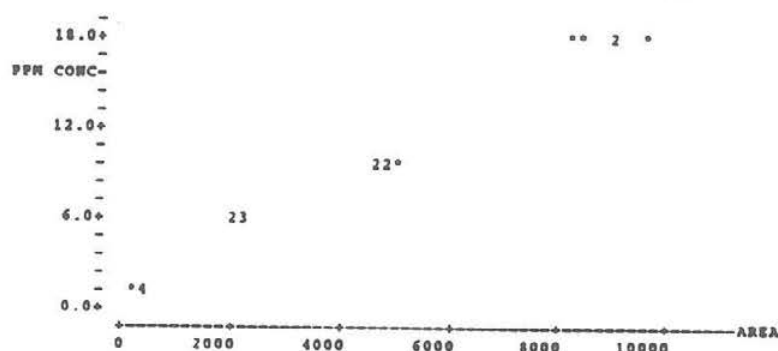


Fig. 2 Methanol linearity study

The regression equation is PPM CONC = 1.08 + 0.00187 AREA

Predictor	Coef	Stdev	t-ratio	P
Constant	1.0768	0.3420	3.15	0.006
AREA	0.00187359	0.00006634	28.24	0.000

s = 0.9559 R-sq = 97.8% R-sq(adj) = 97.7%

Analysis of Variance

SOURCE	DF	SS	MS	F	P
Regression	1	728.98	728.98	797.71	0.000
Error	18	16.45	0.91		
Total	19	745.35			

QUANTUM CHEMICAL CORPORATION
USI DIVISION

INTEROFFICE CORRESPONDENCE

To: John Bergerhouse (RML)

Date: December 15, 1988

cc: William Behymer (CRL)

File: BERG1215

Subject: Analysis of PDI Drum
Samples for Residual
Acetic Acid

Copies: P. Hanik (RML)
R. Henkel (RML)
I. Peat (CRL)
R. Vordenberg (CRL)

The analysis of the eleven drum samples received in November for residual acetic acid is complete. Approximately 1/8 to 1/4 in. cubes cut from each of the drum wall samples were extracted overnight in methylene chloride. The acetic acid concentration in the extracts, determined by Gas Chromatography, was then related by weight to the original drum samples.

The first of the eleven samples was labelled #6 or #9 whose second lading was acetic acid or mineral spirits. The chromatogram of this sample contained a large group of peaks whose overall pattern was nearly identical to those of samples #33 and #34, both of which had been laden with mineral spirits. From this information, it was concluded that the sample sent to us was actually #6, which had been laden with mineral spirits, and not #9.

The following is a summary of the results obtained from the analysis of the eleven drum wall samples:

<u>Sample</u>	<u>First Lading</u>	<u>Second Lading</u>	<u>ppm Acetic Acid</u>
# 6	Methacrylic Acid	Mineral Spirits	3 ppm
#10	Methacrylic Acid	Acetic Acid	96 ppm
#21	Methanol	Acetic Acid	5 ppm
#22	Methanol	Acetic Acid	74 ppm
#33	Mineral Spirits	Acetic Acid	70 ppm
#34	Mineral Spirits	Acetic Acid	5 ppm
#45	Sulfuric Acid	Acetic Acid	83 ppm
#46	Sulfuric Acid	Acetic Acid	72 ppm
#58	Acetic Acid	Acetic Acid	97 ppm
#69	SAE 30 Motor Oil	Acetic Acid	49 ppm
#70	SAE 30 Motor Oil	Acetic Acid	14 ppm

As requested, a migration or concentration gradient study was also conducted using sample #58 whose first and second loadings were acetic acid. The sample was milled in such a way as to obtain sections of the outer, middle and inner thirds of the approximately 1/4 in. thick drum wall. Due

to the curvature and stiffness of the sample, however, it was difficult to obtain a uniform cut across the sample and overlap between the thirds was unavoidable. Each of the three sections was cut into approximately 1/8 in. cubes. These pieces were then extracted overnight in methylene chloride and analyzed by Gas Chromatography for residual acetic acid.

The following is a summary of the results obtained from this study:

<u>Sample</u>	<u>ppm Acetic Acid</u>
#58 Outer Third	95 ppm
#58 Middle Third	231 ppm
#58 Inner Third	147 ppm

William R. Behymer

William R. Behymer

WRB/mfb



Building B-1607
January 10, 1989

TEXAS OPERATIONS
FREEPORT, TEXAS 77541

J. E. Bergerhouse
Quantum
USI Division
3100 Golf Road
Rolling Meadows, IL 60008

Dear Mr. Bergerhouse:

Upon request by the Reuse Committee of The Plastic Drum Institute, twelve (12) 55-gallon drums were analyzed for residual traces of sulphuric acid. When high density polyethylene is exposed to sulphuric acid, a chemical reaction takes place in which sulphur atoms are incorporated in the chemical structure of the polyethylene. The reaction is commonly called sulfonation.

Three coupons were cut from the side walls of each drum. Each coupon was analyzed for the amount of surface sulfonation using x-ray fluorescence. The unit of measure is micrograms of sulphur per square inch of sample and the accuracy of the test is $\pm 10\%$ of the measured value. For reference purposes, an average automotive gas tank that has been properly sulphonated will contain a barrier layer that contains approximately 250 to 300 micrograms of sulphur per square inch.

Regards,

Joseph M. Tanner
Polyethylene TS&D
Plastics Department

chg/Attachment



TECHNICAL INFORMATION

CONCENTRATION OF SULPHUR IN THE WALLS OF 55-GALLON DRUMS

<u>DRUM NUMBER</u>	<u>SULPHUR LEVEL</u> (Micrograms/sq. in.)			<u>AVERAGE SULPHUR LEVEL</u> (Micrograms/sq. in.)
	<u>SAMPLE #1</u>	<u>#2</u>	<u>#3</u>	
7	18	26	41	28
8	41	34	58	44
19	21	18	20	20
20	24	25	24	24
31	42	33	45	40
32	31	32	33	32
43	16	17	16	16
44	17	18	19	18
55	16	16	16	16
56	21	21	26	23
67	29	27	35	30
68	22	24	24	23

JMT:chg

1/89

See reverse side

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OLEFIN AND STYRENE PLASTICS DEPARTMENT
THE DOW CHEMICAL COMPANY • MIDLAND, MICHIGAN 48674





CONTAINER CORPORATION OF AMERICA

AN AFFILIATE OF JEFFERSON SMURFIT CORPORATION

Plastics Division

1204 EAST 12TH STREET
WILMINGTON, DE 19802

February 3, 1989

Mr. John Bergerhouse
USI Division
Quantum Chemical Corp.
3100 Golf Rd.
Rolling Meadows, IL 60008

Dear John:

I have attached the results of our analysis of the drums returned to us after the reconditioning and drop testing that was carried out at Bakerstown Container.

We did not use the test procedure using the TGA that I sent to you in March, 1988. The reason is that we first ran a quick loss-on-heating test in a standard lab hot air oven and found a significant level of volatile materials which indicated we did not need the added sensitivity available by using TGA.

We used a two stage procedure as follows:

1. A sample approximately 3" x 3" was taken from each drum and weighed. The weights ranged from 40-60 grams.
2. The sample was placed in a 100°C hot air oven for one hour.
3. After one hour, the sample was removed, cooled and re-weighed.
4. Percent loss at 100°C was calculated.
5. The oven temperature was raised to 130°C and the samples heated for an additional hour at this temperature.
6. The samples were again cooled and re-weighed with the additional percent loss calculated.
7. Total hours was obtained by adding the loss at 100°C and 130°C.

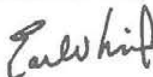
The results we obtained are consistent with previous values we have found for hydrocarbons stored in polyethylene containers.

Mr. John Bergerhouse
Quantum Chemical Corp.
February 3, 1989
Page 2

If you have any questions regarding the attached results, please give me a call.

Very truly yours,

CONTAINER CORPORATION OF AMERICA/
PLASTICS DIVISION



Earl V. Lind
Manager
Materials & Systems Engineering

EVL: jr
8889C

cc: J. A. Geyer

Attachment

LOSS-ON-HEATING TEST RESULTS
PDI REUSE PROGRAM

<u>DRUM #</u>	<u>MANUFACTURER</u>	<u>COLOR</u>	<u>LADING 1</u>	<u>LADING 2</u>	<u>% - 100°C</u>	<u>% - 130°C</u>	<u>TOTAL</u>
5	Sonoco Plstics Drum	Blue Blue	Acrylic Acid	Mineral Spirits	0.45	0.68	1.13
6					0.06	0.10	0.16
29	CCA CCA	Black Blue	Mineral Spirits	Mineral Spirits	0.25	0.43	0.68
30					0.51	0.82	1.33
54	Hunter	Blue	Acetic Acid	Mineral Spirits	0.29	0.58	0.87
66	Eastern	Black	SAE 40	Mineral Spirits	0.48	0.73	1.21

74.

These are the only drums that we received. The results appear to be consistent with previous data we have obtained using hydrocarbons with FMWHDPE, except for Drum #6.

We have not tried to determine the reason for the lower value found for this drum.

EVL:jr
8889C

<u>SAMPLE DESCRIPTION</u>	<u>INNER OIL IN POLYMER WT%</u>	<u>MIDDLE OIL IN POLYMER WT%</u>	<u>OUTER OIL IN POLYMER WT%</u>
#11 Blue PE	transformer oil 1.86%	transformer oil 0.31%	transformer oil 0.18%
#23 Black PE	transformer oil 1.39%	transformer oil 0.29%	transformer oi 0.16%
#24 Black PE	engine oil 0.86%	engine oil 0.22%	transformer oil 0.48%
#35 Black PE	transformer oil 2.06%	transformer oil 1.21%	transformer oil 0.18%
	(mineral spirits)	(has bigger area	(has mineral spirits)
#36 Blue PE	engine oil 1.86%	mineral spirits)	transformer oil 0.51%
	(mineral spirits)	engine oil 0.37%	(has mineral spirits)
#47 Dk Blue PE	engine oil 0.66%	engine oil 0.01%	transformer oil 0.11%
#48 Dk Blue PE	transformer oil 1.39%	transformer oil 0.40%	transformer oil 0.04%
#59 Dk Blue PE	transformer oil 0.80%	transformer oil 0.14%	transformer oil 0.05%
#60 Dk Blue PE	engine oil 0.93%	engine oil 0.02%	transformer oil 0.06%
#71 Black PE	engine oil 0.99%	engine oil 0.03%	transformer oil 0.11%
#72 Blue PE	transformer oil 1.32%	transformer oil 0.19%	transformer oil 0.03%

Data from Phillips Petroleum