Inter-organization Correspondence

B.F.Goodrich

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FROM	**FIELD POINT OR DEPT. & BLDG. NO.**	**DATE THIS LETTER**
P. M. Zakriski	Brecksville R & D Center, D/8506	Dec. 13, 1976

SUBJECT

Personal Protection from Vinyl Chloride During Source Testing

To the best of my knowledge, no one has measured the vinyl chloride concentrations on the roof tops where source measurement are to be made. It is probable that if a source is in compliance its vinyl chloride concentration will be no greater than 10 ppm. Then, with dilution by the outside air the roof top concentration can not be greater than 10 ppm. However, in lieu of measurements to prove that roof top concentrations are below 1 ppm we will follow the following procedure. We will amend this procedure as our roof top measurements indicate we can safely do so.

PROCEDURE

The source testing team will always take to the roof the following equipment:

a) Organic vapor analyzer or H-NU organic vapor analyzer.

b) NIOSH approved carbon cannisters for vinyl chloride and face masks.

c) Bendix PMCC tubes for vinyl chloride and micron air pumps.

The following procedure will be followed:

a) Personnel sampling tubes and pumps will be worn and the tubes analyzed upon return to the lab.

b) Measurements with the OVA or H-NU will be made often. When these measurements indicate average levels in excess of 1 ppm the masks with carbon cannisters will be worn. Work will be permitted with face mask and cannister as long as the apparent average pollution level is below 25 ppm.

c) When the OVA or H-NU measurements show the pollutant level (vinyl chloride and/or all others) to be greater than 25 ppm (on the average), then work will be carried on only with either a Scot air pack or an air line respirator from the building. In the event that neither of these protections can be used, then no further work will be carried on until the average pollutant level falls below 25 ppm. When the levels retreat below 25 ppm, then testing may be resumed.

We see the very strong possibility that our OVA or H-NU and PMCC tube measurements will show that roof top levels of vinyl chloride are below 1 ppm. When this situation has been documented, we will dispense with the requirement to take masks and cannisters.

Paul Zakriski

Paul M. Zakriski

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Introduction

Geon CPVC compounds contain residues of chloroform and carbon tetrachloride which originate in the resin chlorination process. Sometime ago analysis of a water sample which had been in a section of CPVC pipe for 4 years showed that carbon tetrachloride had migrated from the compound[1]. There is concern that migration may occur over shorter time intervals. Consequently, there have been extraction studies to determine the amount of chloroform and carbon tetrachloride transferred into water after exposure to CPVC pipe. In each of four investigations unexpected sampling and analytical problems were encountered. Therefore, the data are somewhat uncertain. This report describes each of the studies and thus provides a basis for planning future extraction programs which will hopefully answer the existing questions.

First Extraction Study

Purpose

In this initial study we wanted to determine if unacceptable amounts of residual "solvent" migrated from CPVC pipe into water in relatively short time intervals. It was decided, arbitrarily, that an acceptable level should be a maximum of 50 ppb.

Materials

In previous work[2], analysis of pipe made from various production lots showed that the carbon tetrachloride content varied from about 3500 to 6000 ppm. Three of these materials were selected for the extraction study.

There has been a research effort to devise a process to reduce the amount of residual "solvents" in CPVC resin prior to compounding. A sample of this "stripped" resin, identified as 603 X 560 #8940, was compounded (at ALTC) into the 3007 recipe and extruded into pipe (reference 163-17-50-2). Corresponding pipe made with standard CPVC resin was also prepared (163-17-50-1). These two materials were included in the extraction study.

The residual "solvent" levels in the pipe samples are listed below:

Compound (pipe)	$CHCl_3$ (ppm)	CCl_4 (ppm)
3007-309 #265	66	4894
3007-309 #286	107	7884
3007-309 #374	56	4119
163-17-50-1	21	4885
163-17-50-2	3	466

Procedure

The migration of a component is influenced by the surface-to-volume ratio, temperature, time and the extractant. Usually extraction studies are carried out at more severe conditions than those encountered in actual use so that the migration will be accelerated. Obviously the choice of these conditions is subjective. Although the outline of the program has been reported[3], the essential details will be repeated.

Since CPVC pipe is used primarily in potable water applications, the surface-to-volume ratio is relatively high. In this study 3/4 inch CPVC pipe was cut into 6 inch lengths and 18 pieces were immersed in 1400 ml of water contained in a 1/2 gal. jar. The calculated surface-to-volume ratio was 6.3 $in.^2/in.^3$. It was assumed that migration occurred from all surfaces of the immersed pieces.

Most residential hot water systems operate near 140°F and the water flow is intermittent. Consequently, it is unlikely that the CPVC pipe is at a temperature of even 140°F for an extended time. Nevertheless in certification testing of CPVC, the National Sanitation Foundation (NSF) extracts the material at 180°F. It was decided that 180°F would be used for this initial extraction study. Presumably any migration detected at this temperature would be greater than that expected in normal use.

Of course the intermittent use of hot water means that there is limited contact time with the pipe, at least at elevated temperatures. Conceivably under certain circumstances water could be stagnant in the pipe at ambient temperature for perhaps 2 or 3 weeks. It was decided that the extraction conditions would be exaggerated by holding the samples for 2 weeks (at 180°F). Duplicate samples of two of the materials were stored for 4 weeks at 180°F to determine if substantial amounts of "solvent" continued to migrate with further exposure.

Since tap water may contain some chlorinated hydrocarbons, it was decided to use distilled water as the extractant. Nevertheless two of the materials were also extracted with tap water to obtain comparative data.

After the prescribed storage period at elevated temperature, the jars containing the pipe samples immersed in water were submitted to the analytical group for determination of the chloroform and carbon tetrachloride content in the water. The analyses were made with a gas chromatograph equipped with an electron capture detector. The output from the detector was fed to a computer which was programmed to make the necessary calculations.

Discussion

The results of the analyses have been reported previously[4] but are repeated in Table I for convenience. The data suggests that if the residual carbon tetrachloride in the pipe is less than 0.4%, migration into water will not be a problem. However,

TABLE I

Migration of Residual "Solvent" from CPVC

	$CHCl_3$ (ppb)			CCl_4 (ppb)		
Extractant	Dist.	Dist.	Tap	Dist.	Dist.	Tap
Time (wk.)	2	4	2	2	4	2
Materials						
163-17-50-1	<10	104	54	<10	371	90
163-17-50-2	<10	<10	<10	<10	<10	<10
3007-309						
#236	<20			<20		
#385	212			28,600		
#374	29			<20		

Discussion - (Continued)

at higher levels of residual "solvent" (one data point) unacceptable amounts migrated into tap water (during a 2 week exposure at 180°F). The results indicate that continued exposure would cause further migration (no equilibration at least over 4 week interval). There is also an indication that tap water is more aggressive than distilled water in removing the residual "solvents".

The data in Table I should be viewed with some skepticism. The jars containing the water and pipe were not sealed. Any residual "solvent" in the headspace escaped. Furthermore there was a long delay between the time the jars were removed from the oven and the time the analyses were completed. Thus, there was an opportunity for the "solvents" to be readsorbed or to react. Finally, the analytical procedure is subject to some uncertainty. Comparison of values obtained at Avon Lake and Brecksville have shown inconsistencies. When the concentrations of residual solvents are high, the comparison is good[5]. However, as shown below, when the concentration is low the discrepancies are large.

	CCl_4 (ppm)	
Sample	ALTC	Brecksville
4111306	1,810	151,218
4111307	2,886	296,485
4100803	1,638	346,281
4100806	95	22,181
4121901 #8	1,197	386,387,418 387,388,389
4121901 #10	1,180	197,275

If the results in Table I are correct, it can be concluded that the resin manufacturing process must be modified to provide additional stripping. It is apparent that further work is needed to establish an acceptable level of residual "solvent" in the pipe. Of course, additional extraction work should also confirm the results obtained in the initial study.

Second Extraction Study

Purpose

It was hoped that this study would establish the relationship between the amount of residual "solvent" in the sample and the quantity which migrated into water under prescribed conditions.

Second Extraction Study - (Continued)

Materials

Some of the compounds used in the first extraction study were also used in this investigation. These included the two materials prepared at Avon Lake, as well as 4 lots of standard production compound from Louisville. In addition, 4 lots of special compound prepared at Louisville were added to the extraction study. These special materials were based on resins which had been made with the UPS-1 dispersant system. After chlorination, they were stripped for various periods of time. At the time the materials were selected not all of the analyses were available. However, the data subsequently obtained are tabulated below.

	Brooksville		Avon Lake	
	CCl_4 (ppm)	$CHCl_3$ (ppm)	CCl_4 (ppm)	$CHCl_3$ (ppm)
163-17-50-1	4,270	0	5,179	172
163-17-50-2	0	0	570	138
3007-309				
#355	8,430	0	8,927	214
#375			6,791	278
#349			7,484	175
#374			6,943	235
3007-250				
#393	10,500	0	10,090	244
#394	1,230, 2,360	0	2,414	135
#395	300	0	2,010	131
#396	1,440	0	1,519	127

Comparison of the analytical results from 2 laboratories again demonstrates the discrepancies [illegible] the concentrations are low.

Procedure

In the previous study relatively large quantities (1400 ml) of water was used in the extraction. Since analyses for the migrating "solvents" requires only a very small amount of water, it was decided that the extractions should be scaled down. Consequently, glass vials (approximately 1/2" diam. X 4" long) were used as containers. They were equipped with polyethylene lined phenolic screw tops. A hole was drilled through the phenolic top so that the water could be sampled (by puncturing the polyethylene liner) without unscrapping the container. The pipe samples consisted of 4 strips obtained by making longitudinal cuts of short sections of 3/4 inch pipe.

Procedure - (Continued)

In most cases the calculated surface-to-volume ratio was about 9 ($in.^2/in.^3$). However, for a few materials shorter lengths were used so that the surface-to-volume ratio was reduced (about 6.4 $in.^2/in.^3$).

In most cases the vials were filled with tap water but a few samples were also extracted with distilled water. The filled vials were stored in heating blocks. The majority of the extractions were made at 180°F but several were held at 100°F to provide data showing the influence of temperature.

The first extraction study showed that unacceptable amounts of residual "solvent" could migrate in 2 weeks at 180°F. There was some concern that high levels of migration might occur in even shorter times. Consequently in this study a couple of extractions were made for only 3 days. Most of the samples were stored for 14 days, but a few were extracted for 28 days. An outline of the samples and extraction conditions is shown in Table II.

After the prescribed storage period the vials were submitted to the analytical group. Hypodermic syringes were used to puncture the polyethylene seals and remove water. The analytical procedure was the same as that used in the previous study.

Discussion

Analysis of the first series of extraction samples showed that the water contained unexpectedly large amounts of residual solvents. For example, some of the water extracts contained more than 1000 ppb of carbon tetrachloride. Visual comparison of the chromatograms and the analyses from the Poco computer showed some inconsistencies. Consequently the areas from the chromatograms were measured manually and then converted to the corresponding concentrations. Table III compares the computer values with those determined manually. It will be noted that in some cases there were large discrepancies while in other instances the agreement was good. The values determined manually should be reliable so there was speculation about the source of error in the computed results. It was suggested that perhaps the sloping baseline led to inaccurate [illegible] combinations. (Subsequently other possible explanations have been offered.) In any event, another computer (Hewlett-Packard) was pressed into service. Analysis of known standards demonstrated that reliable data could be obtained with this computer. Therefore, the water samples from the first set of extractions were reanalyzed. These values are shown in Table IV along with the manually determined results of the original analyses. In nearly every case the second analysis is less than the original value. There was a delay of 6 days between the two analyses. It was assumed that the analytical results were correct and, therefore, there was conjecture that the losses must be due to readsorption of the "solvents" by the strips of pipe during the storage period between analysis. Alternatively it can be speculated that although the vials were uncapped the seals were faulty and some of the solvent escaped. Additionally,

TABLE II

Second Extraction Study of CPVC Pipe

(Sample Identification)

S/V ($in.^2/in.^3$)	6.4	6.4	9	9	9	9	9
Extractant *	D	D	T	T	T	D	T
Temp. (°F)	180	180	180	180	180	100	100
Time (day)	14	28	3	14	28	14	14
Materials							
163-17-30-1	1	2		5		19	20
163-17-30-2				6		21	
3007-309							
#385	3			7			
#375				8			
#369				9			
#374	4			10			
3007-250							
#393			11	12	13	22	23
#394				14			
#395			15	16	17	24	25
#396				18			

* D — distilled water, T — tap water