4-21-2013

Effects of Glycerin Antifreeze on CPVC

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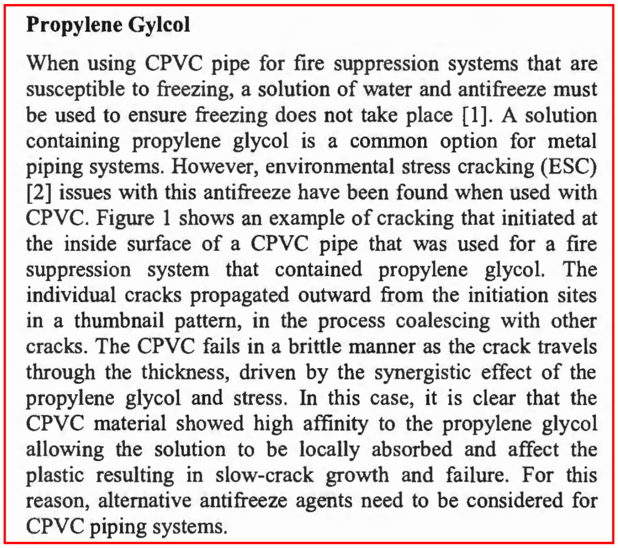

Propylene Gylcol

When using CPVC pipe for fire suppression systems that are susceptible to freezing, a solution of water and antifreeze must be used to ensure freezing does not take place [1]. A solution containing propylene glycol is a common option for metal piping systems. However, environmental stress cracking (ESC) [2] issues with this antifreeze have been found when used with CPVC. Figure 1 shows an example of cracking that initiated at the inside surface of a CPVC pipe that was used for a fire suppression system that contained propylene glycol. The individual cracks propagated outward from the initiation sites in a thumbnail pattern, in the process coalescing with other cracks. The CPVC fails in a brittle manner as the crack travels through the thickness, driven by the synergistic effect of the propylene glycol and stress. In this case, it is clear that the CPVC material showed high affinity to the propylene glycol allowing the solution to be locally absorbed and affect the plastic resulting in slow-crack growth and failure. For this reason, alternative antifreeze agents need to be considered for CPVC piping systems.

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There are multiple applications where chlorinated poly(vinyl chloride) (CPVC) may come in contact with glycerin. One common application is in fire suppression systems that could be subjected to subfreezing temperatures. Chlorinated poly(vinyl chloride) is increasingly being used for these systems in place of metal because of its many advantages, including the ease of installation, weight reduction, cost benefits and chemical resistance. When CPVC piping is used in an area that has the potential to freeze, an antifreeze solution must be used in the fire suppression systems to suppress the freezing temperature of the water and reduce possibility of failure of the piping system. Glycerin is a commonly used antifreeze for this application. The following article discusses the effects of using glycerin with CPVC piping and presents a case study of the use of bio-derived glycerin as an antifreeze agent. In general, it was found that glycerin from the bio-diesel industry had adverse effects on the CPVC.

Disciplines

Food Science | Human and Clinical Nutrition | Molecular, Genetic, and Biochemical Nutrition | Other Nutrition

Comments

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Effects of Glycerin Antifreeze on CPVC

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Abstract

There are multiple applications where chlorinated poly(vinyl chloride) (CPVC) may come in contact with glycerin. One common application is in fire suppression systems that could be subjected to subfreezing temperatures. Chlorinated poly(vinyl chloride) is increasingly being used for these systems in place of metal because of its many advantages, including the ease of installation, weight reduction, cost benefits and chemical resistance. When CPVC piping is used in an area that has the potential to freeze, an antifreeze solution must be used in the fire suppression systems to suppress the freezing temperature of the water and reduce possibility of failure of the piping system. Glycerin is a commonly used antifreeze for this application. The following article discusses the effects of using glycerin with CPVC piping and presents a case study of the use of bio-derived glycerin as an antifreeze agent. In general, it was found that glycerin from the bio-diesel industry had adverse effects on the CPVC.

Introduction

A common application where CPVC may come into contact with glycerin is in fire suppression systems. It has been proven that one of the most effective techniques to prevent a fire from spreading is the use of ceiling mounted fire sprinklers. Their use in new commercial construction has been required for many years. In addition, requirements of their use in multi-family and even single family residence has become increasing popular. A proper sprinkler layout requires the connection of numerous pipe sections routed throughout the building's ceiling and walls.

Chlorinated poly(vinyl chloride) piping is increasingly being used in place of metal piping because of its many advantageous, including the ease of installation, weight reduction, cost benefits and chemical resistance. However, when used as part of a fire suppression system in an area that has the potential to freeze, an antifreeze solution must be used to ensure freezing water does not cause failure of the plastic piping. Water freezing and expanding in a piping system can create excessively high pressures that can lead to a pipe or component failure. Freeze can cause water leakage from a pipe rupture or make the system ineffective in the event of a fire as well as cause water damage if left unattended.

Common antifreeze agents used for fire suppression systems include chemicals such as propylene glycol and glycerin. These chemicals are used as antifreeze agents because their chemical structure forms strong hydrogen bonds with water molecules that prevent the formation of ice crystals at normal water freeze temperature which suppresses the freezing temperature of the water. These chemicals are preferred over other antifreeze agents such as ethylene glycol because of their low toxicity. However, certain solutions of these chemicals can negatively affect CPVC piping [1]. Additionally, the specific method to produce these chemicals can result in various residual components. For example, glycerin can be produced through different methods, i.e. from propylene, as a byproduct of making soap, or as a co-product of biodiesel. Each process can yield various residual components within the glycerin. It is important to consider all these individual components present in an antifreeze solution that may come into contact with CPVC piping to assure that the integrity of the piping will be maintained during the intended service life.

CPVC Piping

Chlorinated poly(vinyl chloride) is a material with relatively high chemical resistance. However, certain specific chemicals such as aromatic solvents, esters, and ketones can readily affect CPVC. Chlorinated poly(vinyl chloride) is very similar to its better known cousin poly(vinyl chloride) (PVC). However, CPVC possesses a higher degree of chlorination which provides increased thermal stability and in general, better chemical resistance. Most buildings and residences have some type of PVC piping installed. Most of this piping is non-pressurized and associated with the transport of waste water. Because of the higher thermal stability, CPVC piping is commonly used for hot and cold water distribution systems including fire suppression systems.

The advantages of using CPVC over metal for fire suppression systems are numerous. Perhaps one of the most favorable is the material costs. However, another significant cost savings is realized with installation. The typical installation methods for metal fire suppression pipes are threaded and grooved joints. Both require trained pipe fitters with complex equipment that commonly need to cut pipe threads or perform the grooving at the job site. Chlorinated poly(vinyl chloride) pipe is easy to cut and typically uses a solvent bonding procedure to join pipes and connectors which do not require any special equipment. However, it is known that the solvent bonding procedure can be a source of problems if not completed correctly. Another significant advantage of CPVC over metal is corrosion resistance. Corrosion of metal when exposed to water and bacteria is well known. Although CPVC does not have the same corrosion issues as metal and has relatively good chemical resistance, it has been found to suffer from attack by a number of chemicals that may be present in piping systems. In many instances, CPVC piping is connected to metal piping. In these configurations, cutting oils and lubricants used for metal pipes have been detected inside of CPVC pipes. Some of these oils and lubricants have been found to chemically affect CPVC leading to failures [1]. Likewise, insecticides, antibacterial additives and coatings, caulks, and cables or wires that may contact the exterior surface of the pipe can be incompatible with CPVC.

Propylene Gylcol

When using CPVC pipe for fire suppression systems that are susceptible to freezing, a solution of water and antifreeze must be used to ensure freezing does not take place [1]. A solution containing propylene glycol is a common option for metal piping systems. However, environmental stress cracking (ESC) [2] issues with this antifreeze have been found when used with CPVC. Figure 1 shows an example of cracking that initiated at the inside surface of a CPVC pipe that was used for a fire suppression system that contained propylene glycol. The individual cracks propagated outward from the initiation sites in a thumbnail pattern, in the process coalescing with other cracks. The CPVC fails in a brittle manner as the crack travels through the thickness, driven by the synergistic effect of the propylene glycol and stress. In this case, it is clear that the CPVC material showed high affinity to the propylene glycol allowing the solution to be locally absorbed and affect the plastic resulting in slow-crack growth and failure. For this reason, alternative antifreeze agents need to be considered for CPVC piping systems.

Glycerin

Glycerin is another common choice of antifreeze solution for fire suppression piping systems. Chemically pure or USP[1] grade glycerin mixed at a concentration of up to 48% by volume [1] has been approved to be used with CPVC piping for fire suppression systems. This solution of glycerin can lower the freezing point to approximately -25°C (-13°F) [3].

Glycerin is a colorless, odorless and viscous liquid that when mixed in solution with water, is visually undetectable. The molecular structure of glycerin is that of a polyol that consists of three carbons and three hydroxyl groups. Its chemical representation is shown in Figure 2. As expected, with three hydroxyl groups, glycerin is readily soluble in water. Glycerin is essentially the backbone structure of a triglyceride. Therefore, a common production method for glycerin consists of the reactions of triglycerides that generate glycerin as one of the reaction products. Because biodiesel fuel is made from a reaction of triglycerides and methanol, glycerin will be one of the reaction products.

Bio-Derived Glycerin

A growing source of glycerin is the biodiesel industry where 0.66 lbs of crude glycerin is made from every gallon of biodiesel [4], an industry that produced over a billion gallons of diesel fuel in 2011 [5]. As biodiesel production continues to increase, crude glycerin production is projected to reach approximately 5.8 billion pounds/annum globally by 2020 [6]. Because of the massive resource of glycerin from the biodiesel industries, some end-user manufacturers are choosing to use this glycerin over USP grade glycerin. It is a very promising resource because it is abundant and significantly lower price compared to USP grade glycerin. However, because it is not refined, it is expected that it may contain impurities. Depending on the feedstock used, the majority of the crude glycerin from the biodiesel industry will contain impurities such as methanol, water, soap, and residual biodiesel or fatty acid methyl esters (FAME). Figure 3 shows the chemical reaction that takes place when producing biodiesel and the glycerin co-product. In this case triglycerides are reacted with methanol yielding fatty acid methyl esters and glycerin. As the figure shows, the biodiesel is an ester-based compound. Biodiesel, in general, refers to fuel produced from vegetable oil or animal fat consisting of methyl, propyl, or ethyl esters of fatty acids. It is important to note that biodiesel can be produced from a range of feedstocks, but the most common are soy bean oil or animal fat (tallow) and the various feedstocks produce varying chemical stuctures of FAME molecules.

It is known that many plastics including CPVC will have incompatibility issues with ester-based chemicals [7, 8]. Therefore, incompatibilities with bio-derived glycerin on CPVC can be expected. The following details a case where a significant loss of properties occurred when bio-glycerin was used in place of USP grade glycerin as antifreeze in a fire suppression system [9].

Failure of a CPVC Fire Suppression System

This case involves the failure of numerous CPVC pipes used for a fire suppression systems in 45 townhouses. The fire suppression systems in these townhouses were recharged after it was discovered that the freeze rating did not meet code. The contractor that was hired to perform the recharge mixed the liquid solution from the existing system with glycerin at a 50% by volume ratio. Approximately six months after the recharge took place leaking water from the fire suppression systems was reported by owners of the townhouses. Because the water was coming from the fire suppression systems the home owners were unable to simply turn off the flow of water. To shut down the systems the fire marshal ordered 24 hour surveillance of all the townhomes in the complex adding to the costs of this failure beyond the water damage.

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[1] United States Pharmacopeia

Visual/Microscopy Analysis

The homeowners described the leaking pipes as having striated areas of softness with regions of bulging and sagging between supports. Figure 4 shows a bulged section of pipe. Figure 5 shows striations in one of the failed pipes. The striations were evident as a lighter orange color that ran axially along the pipe. The striations were much softer than the non-striated regions of the pipe to the degree that one could press a fingernail into CPVC in these regions. During inspection of the piping system in an attic area, significant sagging of a pipe between supports was observed, see Figure 6. The pipe, which should have had maximum sag of less than 1 inch, was found to be sagging over four inches. The sagging is an indication of softening and creep of the pipe under the force of gravity.

Cross-Sectional Analysis

One of the failed pipes was cross-sectioned through a region that contained striations. Figure 7 shows the striations at the inside of the pipe and Figure 8 shows the striations through the cross-section. It was clear from Figure 8 that the striations had originated at the inner surface of the pipe and propagated outward. That is to say, there are limited evidence of striations on the outer wall while the there are numerous striations on the inner wall.

Flattening Test

Two-inch sections were removed from failed pipes to perform flattening tests following ASTM D 442 [10], Section 8.6 to determine if the pipe had been structurally compromised. In this test, the pipe is flattened to 40% of its original diameter over a specified time period. During and after the test, the section was examined for any cracks at the outside and inside surfaces. As defined by the standard, the section passes the test if no cracking is observed. In this case, all sections that were tested cracked catastrophically at four locations approximately 90 degrees apart, see Figure 9. One of the cracks was opened and examined using a Keyence digital microscope, see Figure 10. The fracture surface showed a smooth surface immediately adjacent to the inner diameter of the pipe. The majority of the fracture surface appeared to be softened with long ductile flaps. The CPVC at the fracture was soft and material was easily displaced. It was clear that the material had been solvated, which reduced the mechanical properties of the pipe.

Fourier Transformation Infrared Spectroscopy (FTIR)

It was seen that a significant foreign mass was present at the inner surfaces of some of the pipes examined, see Figure 11. This material was greenish and had the consistency of petroleum jelly. This material was foreign to the system and could pose a problem by clogging the sprinkler head in the event of a fire. The chemical structure of this material was examined using FTIR in attenuated total reflectance (ATR) mode. A small amount of the substance was placed on the ATR unit giving the spectra shown in Figure 12. The closest library match for this material was glycerol, or glycerin (also presented in Figure 12). Furthermore, ester functionality was observed in the spectra at approximately 1700 cm^{-1}. It should be noted that the library match shown is for pure glycerin.

Gas Chromatography/Mass Spectroscopy (GC/MS)

Three fluid samples and two pipe samples were analyzed by GC/MS to detect the presence of incompatible substances. In this procedure a portion of each sample was weighed into a clean new glass vial. GC/MS grade ethanol solvent was prepared to contain 76.3 micrograms per gram of dodecane internal standard was added to each sample to allow for a semi-quantitative calculation of the detected analytics. The GC/MS analysis was carried out on a PE Clarus 600/600D GC-MS, using a 30 m x 0.25 mm I.D. fused silica capillary column. The mass spectrometer was operated in full scan mode with a mass range of 33 m/z to 500 m/z. The mass spectra for each peak was compared against a NIST mass spectral library and the compounds were identified based on the best library match and technician assisted interpretation. The components of the fluid samples were all nearly identical with the primary components being ester-based chemical groups, Table 1.

Conclusions

A known application where CPVC may come in contact with glycerin is in fire suppression systems as these normally need to be filled with antifreeze solutions to protect the system from freezing. The most common method for antifreeze protection is to use a solution of water and antifreeze that is present inside the system at all times. The only NFPA (National Fire Protection Association) approved antifreeze that can currently be used with CPVC is USP grade glycerin since other common antifreeze agents can be incompatible and cause latent failures to occur.

A relatively new source of glycerin is the bio-diesel industry. Glycerin is a byproduct from the production of bio-diesel, a fuel created from biological-based products such as soy, tallow, and cooking oils, among others. A key difference between USP grade glycerin and bio-glycerin is the residual ester-based compounds that can be present in bio-glycerin. Many plastics are incompatible with compounds that have ester functionality, including CPVC. This paper showed a case where massive leaking took place in a complex of 45 townhomes that were charged with a solution of water and bio-glycerin. The pipes were found to soften over time, which eventually led to cracking.

References

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[7] IPEX, CPVC Chemical Resistance Guide, 2009
[8] D. Grewell, T. Wong, Melissa Montalbo-Lomboy, Linxing Yao, P. Gramann and J. Cruz, "Effects of Biodiesel on Plastics," to be published in the proceedings Annual Technical Conference Society of Plastic Engineers, Cincinnati (2013).
[9] Approval to publish facts and photographs of this case was given by Keith Ray of Lathrop & Gage, LLP of Denver, CO.
[10] ASTM F 442, "Standard Specification for Chlorinated Poly(Vinyl Chloride) (CPVC) Plastic Pipe (SDR–PR)," (1999).

Figures

Figure 1 – Cracking through the thickness of a CPVC pipe that contained propylene glycol.

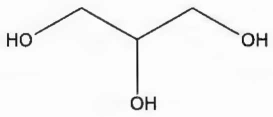

Figure 2 – Chemical representation of pure glycerin.

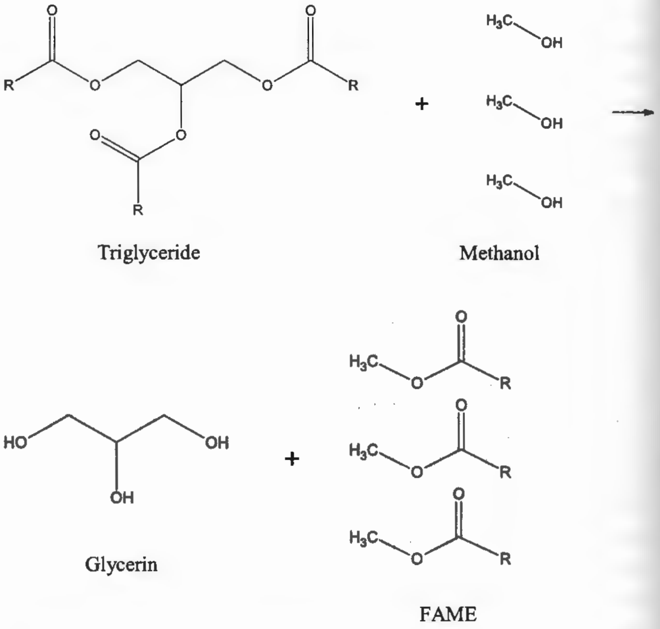

Figure 3 – Chemical representation of the production of biodiesel and glycerin byproduct.

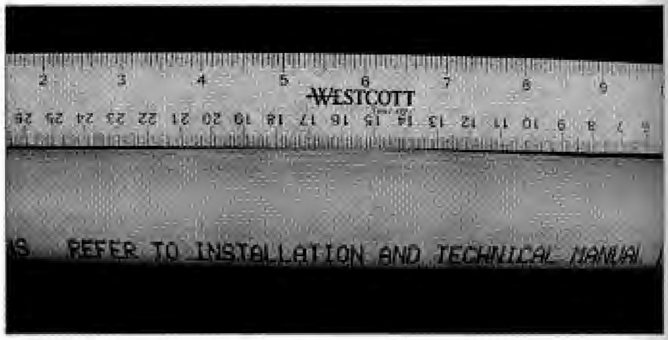

Figure 4 – Bulging of a failed CPVC pipe exposed to a mixture of water and bio-glycerin.

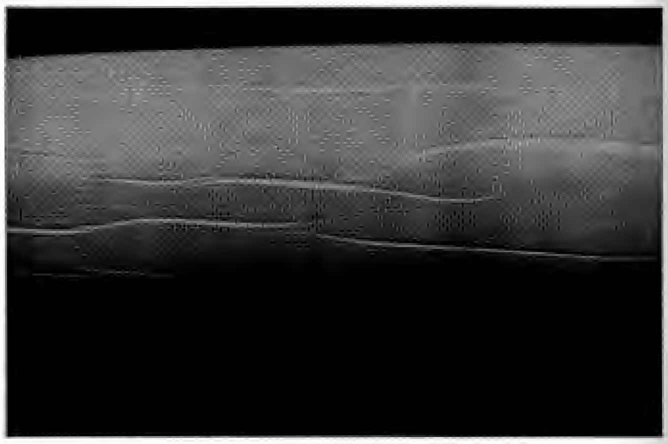

Figure 5 – Axial striations on the outside a failed CPVC pipe exposed to a mixture of water and bio-glycerin.

Figure 6 – Sagging of an installed CPVC pipe exposed to a mixture of water and bio-glycerin.

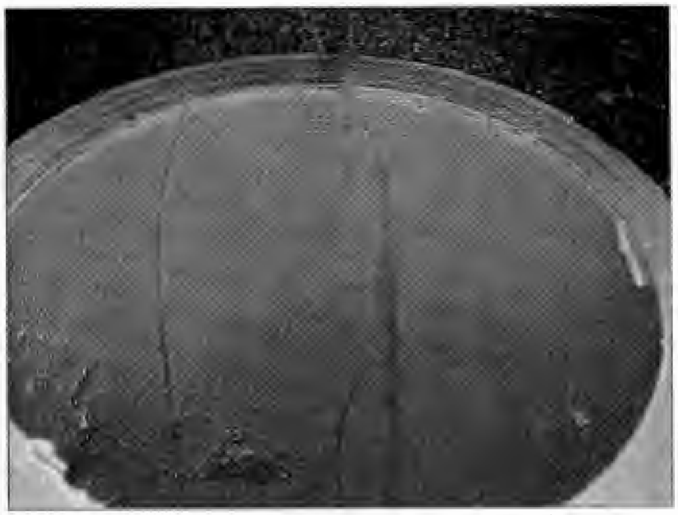

Figure 7 – Striations evident at the inside of a failed CPVC pipe exposed to a mixture of water and bio-glycerin.

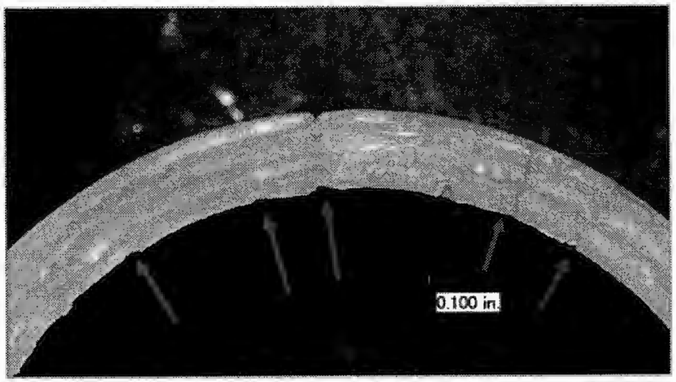

Figure 8 – Striations initiating at the inner diameter of the CPVC pipe exposed to a mixture of water and bio-glycerin.

Figure 9 – Result of flattening test [8] of a CPVC section that was exposed to a mixture of water and bio-glycerin.

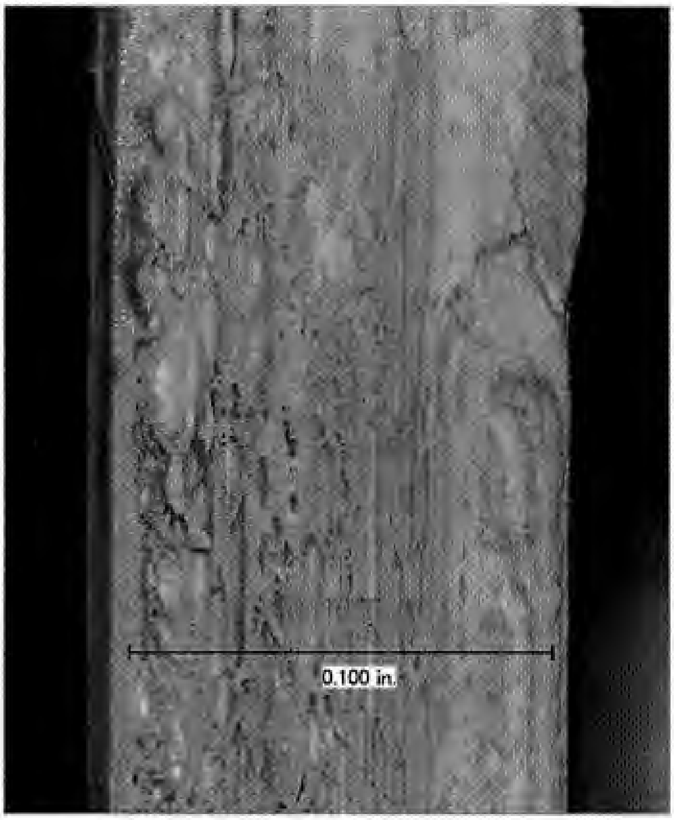

Figure 10 – A fracture surface of the pipe section shown in Figure 9.

Figure 11 – Material observed at inner surface of failed CPVC pipe exposed to a mixture of water and bio-glycerin.

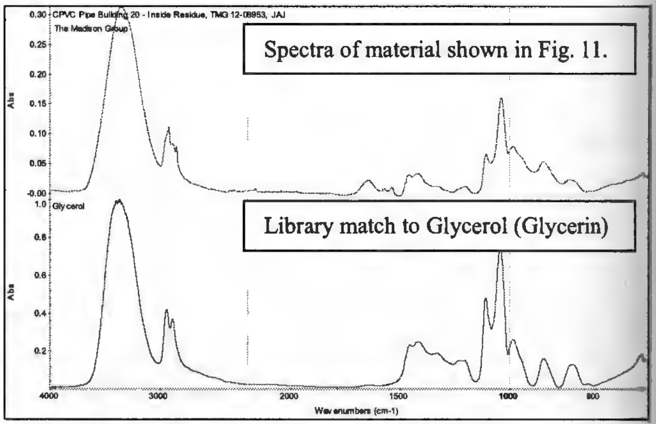

Figure 12 – FTIR spectra of material shown in Figure 11.

Table 1 – Major components detected in liquid contained in the CPVC pipes of the fire suppression system.

Compound	Concentration, micrograms per gram				
	Barrel 4 Liquid	Barrel 28 Liquid	Bldg 35 Liquid	Bldg 20 CPVC	Bldg 35 CPVC
Siloxane from Propylene Glycol	100	80	--	11	7
Tetradecyloxirane	20	40	40	2	< 1
Methyl tetradecanoate	20	100	60	17	< 1
9-Hexadecenoic acid, methyl ester, (Z)-	30	60	90	34	6
Hexadecanoic acid, methyl ester	920	3200	6800	900	260
Hexadecenoic acid, Z-11-	100	280	370	< 1	< 1
n-Hexadecanoic acid	2800	8900	16,000	<1	< 1
Hexadecanoic acid, 14-methyl-, methyl ester	20	20	60	6	3
9,12-Octadecadienoic acid (Z,Z)-, methyl ester	1900	11,500	24,200	1700	870
9-Octadecenoic acid (Z)-, methyl ester	2700	9100	25,100	2800	860
Octadecanoic acid, methyl ester	450	1300	4400	520	140
Oleic acid	18,300	64,700	236,000	6	< 1
Octadecanoic acid	240	1800	2000	7	5
Phthalate Trace?	100	110	530	< 1	< 1
9-Octadecenoic acid (Z)-, 2-hydroxy-1-(hydroxymethyl)ethyl ester	380	3600	11,100	8	2