MATERIALS

A SCIENTIFIC LOOK AT LAB QUALITY DEIONIZED WATER PIPING MATERIALS

Six conditions are known to make up the requirements of components found in water piping systems used in the various high tech industries (1, 2). They include concerns about the contribution of particulates, total organic carbon or oxidizable carbon (TOC), metallic or ionic contamination as well as surface conditions, and the safe and reliable nature of the material once installed.

Safe and reliable not only includes achieving the expected life of a properly installed system, but also the efficacy of the system and that it is suited for the application from a standpoint of any health, hygiene, or environmental issues. These high tech industries, which include life sciences, biotech, food and beverage, and electronics have a variety of applications and needs in their usage of water, and hence, a variety of restrictions on the assortment of allowable contaminants.

Despite the maturity of these industries, much confusion still exists concerning the multitudes of water qualities available. The water qualities are typically grouped into categories such as deionized (DI) or high-purity water. For example, the electronics industry lists a range of allowable contaminants (3) because of the variety of products being produced there. The SEMI F063 effort has been the best activity to date to give a usable definition for high-purity water in the electronics industry. However, for other industrial applications, the requirements for high-purity water might differ completely. For the life science industry, *United States Pharmacopeia 23* (*USP* 23) is well defined and has been the regulative directive (4). (It should be noted that while *USP 23* is the basis for the current pharmaceutical water quality standards, that the document itself has been replaced by *USP 26-National Formulary 21*.) Meanwhile, SEMATECH still lists high-purity water as "deionized and filtered water" (5). Other attempts, such as the American Society for Testing and Materials (ASTM) (6), have also tried to find more concrete definitions for the different water qualities and reduce the portfolio of water regimes.

It is widely known that polyvinylidene fluoride (PVDF) has been the material of choice for high-purity water systems in the electronics industry of years (7) because it offers the lowest contamination risk and other favorable factors. Likewise, stainless steel has dominated the life science industry. However, PVDF is finding its way into these industries (8) as well because of a number of advantages such as weight, absence of corrosion, ease of installation, and costs.

Still, a variety of lesser-demanding applications exist that do not require exacting high-purity water standards such as SEMI F063 and *USP 23*. Therefore, this study is intended to investigate the applicability of alternative polymer materials in these applications. Besides commercial aspects, it is especially focused on technical and performance aspects.

Since cost reasons often do not allow the use of the best performing materials and not every application requires highest high-purity water, there are choices that fill the requirements for these other DI arenas.

Background

Nowadays, an often-discussed topic is how to economize the constructing of a manufacturing facility. Due to economical constraints, cost reduction and searching out cheaper materials or lower installation costs is a common practice. However, among cost considerations should be the applicability, and equal or better performance as well as possible consequential costs like increased maintenance, less lifetime, or costs for later disposal. Consequently, the main goal is to find the best compromise between cost considerations, and the best performance for a given application.

In the past, leach-out data for some polyvinyl chloride (PVC) clean materials have been published, but the tests were not always performed according to recognized test requirements. Also, the connecting technique by cementing was usually disregarded. Likewise, polypropylene (PP) is only periodically considered as an alternative. Therefore, this study takes into account not only the leach out of components as supplied from the manufacturer, but also the influence of the connecting technique it-

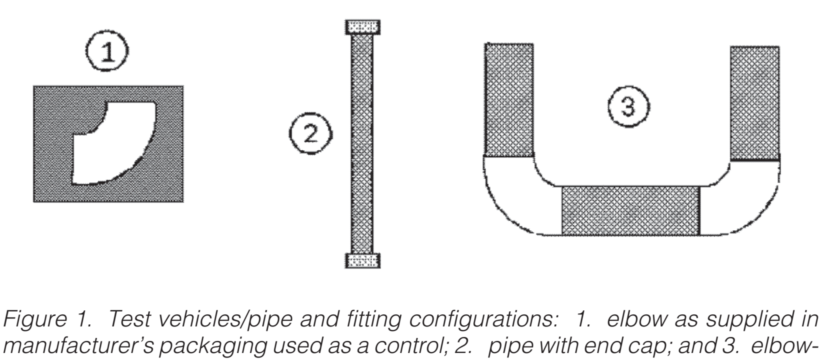

Figure 1. Test vehicles/pipe and fitting configurations: 1. elbow as supplied in manufacturer's packaging used as a control; 2. pipe with end cap; and 3. elbow-pipe-elbow "system".

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self. That is, assembling a small piping system to give the reader the information needed for informed decisions.

For discussion purposes, we refer to the investigated clean type of PVC as "PVC-X". The cleanliness of PVC-X solvent cemented piping systems were compared to IR® thermally welded systems[a] made of natural PP (PP n) and beta nucleated PP homopolymer that is cleaned and double bagged (henceforth referred to as "PP cdb").

Target applications for this report include the water used in hospital and university labs, as well as some lesser demanding applications in the life sciences and electronics industries.

In assembling a system, elbows and pipes were constructed into a "piping system" (see Figure 1, Item 3). Thus, the leach out of TOC, metals and anions, and the influence of the connection procedure itself were investigated. The glue to assemble the PVC-X system was included in this investigation as well.

To create a baseline the leach out for solvent, cemented PVC-X or thermally welded PPn and PP cdb pipes with end caps (see Figure 1, Item 2), and elbow-pipe-elbow systems (see Figure 1, Item 3) were compared to "as supplied" elbows (see Figure 1, Item 1). That is, elbows delivered to us in the original manufacturer's packaging. All test vehicles were statically leached.

Experimental

Reagents and chemicals. Aqueous solutions for sample and standard preparation were prepared using only acids of high-purity quality (Merck), and high–purity water (18.2 megohm-cm). The water was prepared by a lab-quality treatment system[b]. Standards were prepared from single and multi-element standards recommended for use with inductively coupled plasma mass spectrometer (ICP-MS) provided by Merck and Alfa Aesar.

Instrumentation

The spectrometer used in metal determinations of the aqueous leach out solutions was a magnetic sector field ICP-MS *ELEMENT II* (Thermo-Finnigan) operated under standard plasma conditions (see Table A). All anions were determined using ion chromatography (IC) Metrohm Series 700 installed in a Skan-Clean-Bench. The system is operated with chemical suppression. The automated sample introduction system works with individual pre-concentration.

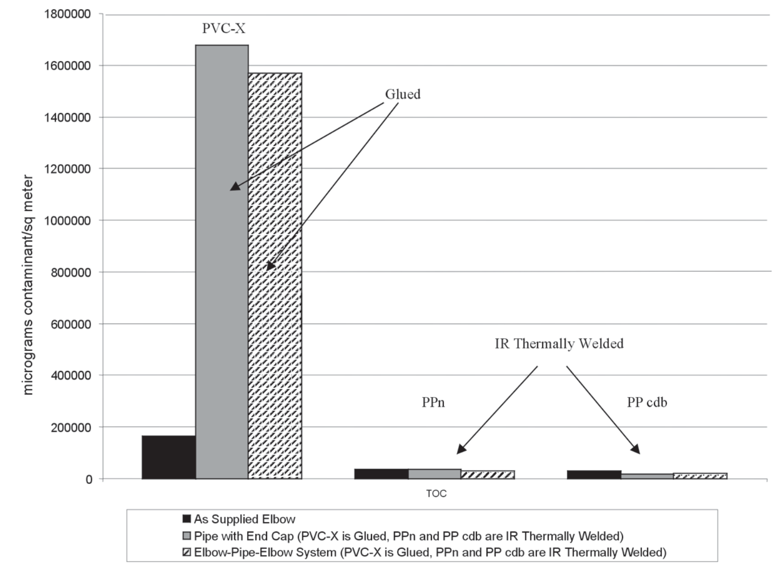

Figure 2. TOC leac hout data > PVC-X versus PPn versus PP cdb.

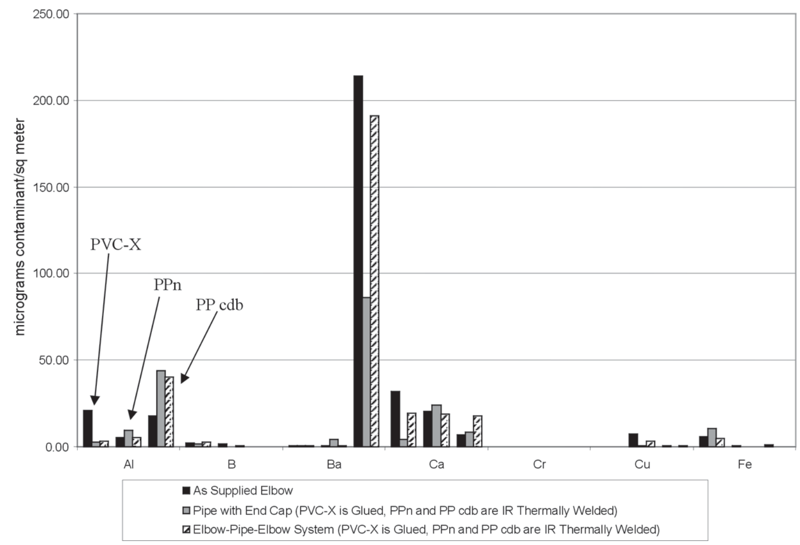

Figure 3. Metallic leach out data > PVC-X versus PPn versus PP cdb.

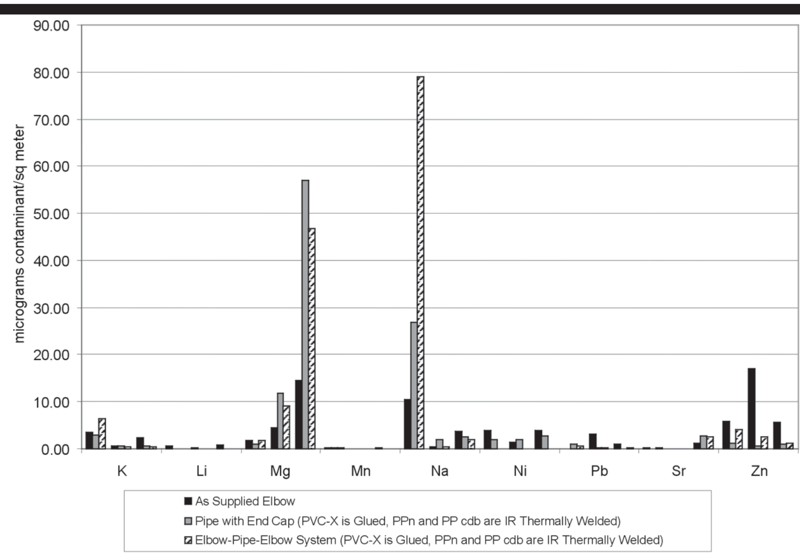

Figure 4. Metallic leach out data (continued) > PVC-X versus PPn versus PP cdb.

TABLE A
Operating Conditions for the ICP-MS

Parameter	*Thermo-Finnigan ELEMENT II*
Power [W]	1,100
Plasma gas flow [L/min]	15
RF generator [MHz]	40 (free-running)
Aux. gas flow [L/min]	1
Nebulizer gas flow [L/min]	0.89
Nebulizer	PFA Nebulizer
Spray chamber	PFA spray chamber
Resolution	Low ≈ 300
	Medium ≈ 4,000
	High ≈ 10,000
Dynamic range	10^9 (Dual-Mode ETP)

A conductivity-measuring cell performs the detection of the following anions: fluoride (F), chlorine (Cl), nitrate (NO_3), bromine (Br), phosphate (PO_4), and sulfate (SO_4). Typical detection limits are approximately 0.1 micrograms per liter (µg/L). When needed, nitrite (NO_2) can be determined more sensitively with a detection limit of < 0.01µg/L via an electrochemical detector. Total organic carbon was determined using a Shimadzu TOC Analyzer TOC-5000A. The instrument can separate different carbon species (e.g., in aqueous samples down to a TOC-content of 1 µg/L).

Sample Preparation

Samples of 1 inch (in) or 32-millimeters (mm) outside diameter products were obtained through normal distribution channels and in their original factory packaging. All elbows were tested as supplied (see again Figure 1, Item 1) and were submitted to the laboratory in their originally packaging. As for pipes, they were cut to lengths of 0.9 meter each and a cap was affixed to the bottom using the manufacturer's prescribed connection method (either glue or thermal welding). A specially designed O-ring seal end cap made of the same material closed the top of the pipe. This O-ring seal technique offers the ability to seal the contained high-purity water from extraneous contamination during the test duration, while at the same time offering a means of opening the vessel to decant the high-purity water once the leach out is complete. It has been used in our leach out studies since 1993 and found not to contribute contamination since it is not in contact with the high-purity water. The same special cap was used to close off the elbow-pipe-elbow samples. For the elbow-pipe-elbow systems, PVC-X was solvent cemented according to manufacturer's instructions and using the glue recommended for high-purity applications. PPn and PP cdb elbow-pipe-elbow systems were thermally welded, according to manufacturer's requirements. The assembly was performed under clean conditions, according to good installation practice.

The pipes with end caps and elbow-pipe-elbow systems were bagged into special high purity PA/PE packing foils after assembly. All samples were delivered to and tested by the Swiss Federal Laboratories for Materials Testing and Research (EMPA) in Duebendorf, Switzerland. The EMPA (9) is known worldwide for its trace analytical capabilities.

Leach-out tests were carried out according to the instructions given by SEMI F40-0699 (10). This industry recognized document, along with SEMI F057, uses a temperature of 85°C, which is required to compare limits given by SEMI F057. However, a leach out temperature of 60°C had to be used in this study because this is the maximum application temperature for PVC-X. Research of available literature revealed that only SEMI offers a method for comparing components used in piping systems. There is no equivalent for the life science industry that could be found.

Following the prescribed 10x pre-wash with 18.2 megohm-cm high-purity water to simulate the flushing process of a newly installed piping system, all items were leached for seven days at 60°C. Elbows were immersed in pre-leached perfluoroalkoxy (PFA) vessels with high-purity water. Pipes and elbow-pipe-elbow samples were filled with high-purity water and capped.

All lab ware used for samples and blanks were high purity, lab quality PFA vessels prepared and checked for conformance to SEMI requirements before use by the following procedure:

1. All new vessels are pre-leached at 85°C for several days while changing the high-purity water every 2 or 3 days.

2. After about 3 weeks, the suitability for use in SEMI tests is verified.

3. Background is periodically checked to confirm that the levels are still appropriate throughout the life of the vessel.

A set of five blanks is prepared (in the vessel type of use for that particular test) to determine the detection limits and the preparation procedure. For example, the leach out of elbows and blanks all takes place in identical 500-milliliter (mL) vessels for determination of anions, metals, and TOC. That is, blanks and sample vessels always match in size and type. Samples were run in triplicate. Results are shown as averages of those samples.

After leaching, the metallic contamination was determined using high resolution ICP-MS. IC was used for anions and the TOC analyzer for the "non purgable" total organic carbon (NPOC). The detection limits for the elements are defined as three times the standard deviation of the blank solutions using a 3-sigma method. Blank values were subtracted from the sample results and the concentrations were calculated as micrograms of contaminant per square meter based on the total volume of solution and component surface area.

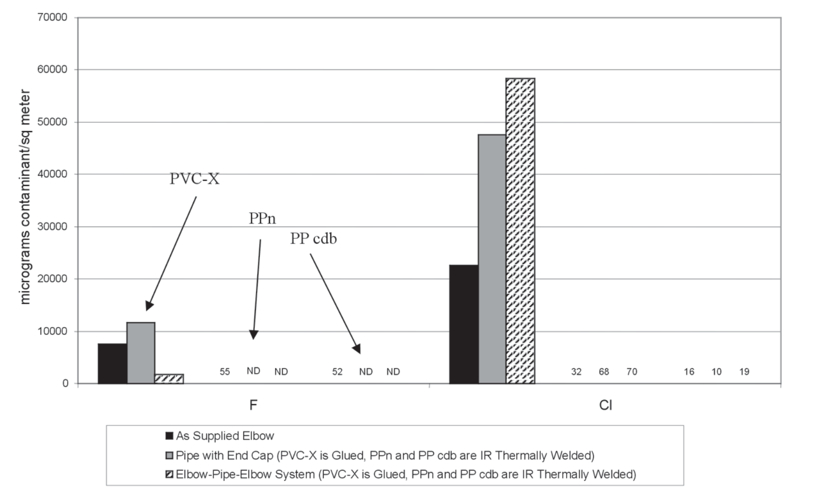

Figure 5. Fluoride and chloride leach out data > PVC-X versus PPn versus PP cdb.

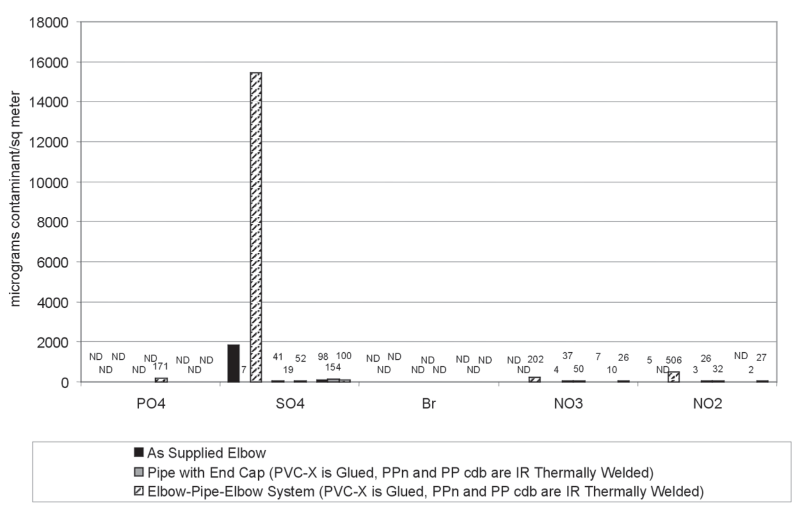

Figure 6. Remaining anion leach out data > PVC-X versus PPn versus PP cdb.

Results and Discussion

Each contaminate is represented with 9 bars on the corresponding graph (see Figures 2 through 6). For each contaminant the first 3 bars belong to PVC-X, the next three belong to PPn and the last three belong to PP cdb. Bars 1 through 3 of each material type represent the leach out from the "as supplied" elbow, the pipe with end cap, and the elbow-pipe-elbow system, respectively.

The SEMI F040 methodology uses a static leach-out procedure, whereby the component to be tested is pre-washed to simulate flushing following installation, and then exposed to high-purity water for seven days at elevated temperatures. Finally, the high-purity water is analyzed for the contaminants that have gone into solution. Since the topic in this report is DI water and not high-purity water, we will not compare the outcome of the testing to the requirements of SEMI F057. But, remarkably, the PPn tested fairly well against these stringent limits for such contaminants as TOC and anions. Of course, PVDF meets all aspects of SEMI F057 without question.

The reasons for using SEMI static test methods and such high temperature testing when the actual usage of the material might be much lower is a result of years of debate in the high purity industry and optimization by a team of industry partners, suppliers, and chemists. The procedure has been optimized to give a reliable result in a short period of time (seven days, only one preparation step). The high temperature supports the leach out of contaminants so that the time could be limited to seven days. These static and accelerated tests speed the leaching process that will eventually happen over time.

The goal of this SEMI standard was to develop a reproducible and reliable routine procedure to assess the contamination hazard for high-purity water and liquid distribution systems due to the leach out of piping system material only and independent of extraneous equipment.

Dynamic tests depend too much on the test set up and parameters used (flowrate, and component diameter, among others). Dynamic values (µg/L, nanograms per liter [ng/L], and others) are useful ways of maintaining control over process fluid purity within the manufacturing environment. However, for processes sensitive to atomic or trace molecular level impurities, dynamic values fail to show the true picture of the contamination present, and are often seven orders of magnitude *less sensitive* than the values that are derived from a static test (µg/m^2, ng/m^2, and others).

For this reason, SEMI F057 offers a theoretical dynamic concentration (TDC) value, based on the results of a static test, the diameter of the pipe or component, the velocity of the fluid, and other factors. When viewing the TDC or dynamic results, it is very important to realize that a leached species could be escaping detection during dynamic measuring but still be polluting the process with trillions of atoms or molecules of unwanted contaminants.

Total Organic Carbon

The PVC-X elbows (as supplied from the manufacturer) were approximately five to six times higher for TOC than the values found in PPn and PP cdb (see Figure 2). If it is taken into account that contamination leach out from piping system surfaces is temperature dependent (11), even more TOC should be expected if the tests had been performed at the SEMI F57 recommended temperature of 85°C.

Figure 2 represents also the TOC leach out results of the pipe with end cap and elbow-pipe-elbow assembly (as described in the Experimental section and Figure 1). This arrangement encompasses the component as well as the connection technique. In the case of the PVC-X, most likely the glue is contributing a large TOC amount because the leach out has increased about ten times for solvent-cemented parts in comparison to the original supplied unconnected parts. On the contrary, the thermally welded materials (PP n, PP cdb) did not appear to change in TOC level. The assumption that the glue is the main reason for the increasing TOC levels can be proved by analysis of the glue components (see Table B). The glue consists mainly of organic ingredients, which are predominantly or partly soluble in water.

Solvent introduction into a high-purity water stream provides another potential nutrient source for microbial growth. Technical literature states a positive correlation between TOC concentrations and viable bacterial numbers (12). As well, one source states, "Microbial contamination in analytical-grade water can negatively affect the results of critical laboratory research" (13).

Metals

As for metals (see Figures 3 and 4), a variety of contaminants were found in all three materials. Table B lists in tabular form the total of the 16 key elements leaching from the three materials and three different sample configurations. Pipe usually comprises more than 85% of the total surface area in a piping system. For comparison purposes, PVDF pipe is typically less than 9 μg per square meter (μg /m^2).

Anions

The most remarkable differences for anions is shown in the fluoride, chloride, and sulfate results (see Figures 5 and 6). The fluoride values for the studied elbows of PVC-X were more that 100 times greater than the PPn and PP cdb.

As expected, the chloride leach out for the PVC-X was almost 1,000 times higher than either PP types. Chloride is a notorious corrosive agent to the atomic size interconnects of semiconductor devices. In life sciences, saline solutions are common. Therefore, a low content is not so important. When an as supplied elbow is compared to the constructed "system" a dramatic jump in chloride was observed in the glued PVC-X. The lack of sulfate presence in the PVC-X pipe followed by the abnormally high increase in the elbow-pipe-elbow and supplied elbow value cannot be explained. Anions that were not detected are marked with the label "ND". Those situations where the bar is not visible, due to the scale, are data labeled.

Solvent Cement

When considering the influence of welding procedure, the most important problem with a solvent-cemented system is, of course, the glue. The glue consists mainly of tetrahydrofurane (THF) and other organic solvents (see Table C). This involves a high risk of TOC contamination as is suspected in Figure 2. A variety of other potential contaminants can also come from the ingredients of the glue, such as solids and ash, which are typically PVC stabilizers, modifiers and thickening agents. The ash usually consists mainly of SiO_2.

TABLE B
Total Metallic Contamination Found per Sample Type (mg/m^2)

Sample Material	*Elbow*	*Pipe with End Cap*	*Elbow-Pipe-Elbow*
PVC-X	87.8	54.8	121.9
PPn	62.6	55.8	41.0
PP cdb	272.8	205.2	302.0

Conclusions

An overall performance summary that encompasses the leach out derived from this study is shown in Table D. However it should be expressly mentioned that our study shows only a "snap-shot" because no regular leach out monitoring of PP or PVC components is performed. And, these raw materials were never intended for consistent high-purity piping system destinations. Additionally, the reader may find that his or her process can tolerate certain contaminants better than other contaminants.

No proper procedure exists which gives reliable and comparable results when considering lower temperature materials like PVC. SEMI F057 requires 85°C. So, the test procedure was modified to reduce the leach out temperature.

The increasing concentrations of TOC seen in the solvent-cemented system (PVC-X) are possibly caused by water solubility of the cement ingredients as well as by a swelling at the contact surface of the PVC material itself. That is, due to the influence of the aggressive organic materials of the solvent cement. This hypothesis is supported by the fact that with the thermal welding systems, no TOC increase could be seen in either the PP cdb or PPn samples. The glue needs these organic ingredients to archive the properties that are necessary to cement the pipes together.

One source quotes the effect of increased TOC from glue lasting for 1 to 2 months in running streams (14). Another source reports the presumable aggressive nature of DI water itself on PVC. In this situation, an 8- to 10-year old system of PVC conveying DI water shattered upon decommissioning and removal. The interior of the material was white and the PVC was overall very brittle. The system had been hydrogen peroxide sterilized upon commissioning (15).

A comparison of the compositions of the high-purity glue to other common PVC glues showed no big differences in the component mixture except for the ash and the cyclohexanone content, which were both less than 0.1%. Another disadvantage of the high-purity grade glue was that an exposure time (the time that the container can be open without loss of vital ingredients) of the glue is stated at less than 2 minutes. This could become critical when assembling larger dimensions.

There was some metal leach out increases seen in all results. These might be introduced by the components themselves, meaning material, and/or manufacturing processes. Or, they could come from the connection technique - welding or solvent cementing, or by the human factor. Most remarkable is Na in the PVC-X elbow-pipe-elbow. Sodium is an omnipresent metal for which contamination happens very easy.

PP cdb showed a relatively high barium concentration in both original and welded parts.

It is very likely that raw material ingredients are responsible for the high Ba content. Oxides of barium are usually added to PP gray as pigments or optical brighteners. Both of the PPs performed much better than the PVC-X for anion leach out.

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TABLE C
Chemical and Precautionary Properties of Different PVC Glues

	Solubility in Water	*Tangit® Stated Values*	*Typical Glues Stated Values*	*PVC-X Measured Values*
Tetrahydrofuran	soluble	25%-30%	20%-50%	52.7%
Methyl Ethyl Ketone	292 g/L (20°C)	25%-30%	5%-40%	32.7%
Cyclohexanone	90 g/L (20°C)	<25%	10%-30%	<0.1%
Solid content		20%	10%-25%	14.6%
Ash		2%	1%-3%	<0.1
Maximum recommended time that container can be open to air (minutes)		4	4	2
Safety Symbols – Flammable Marking		Yes	Yes	No

Fischer for sample preparation as well as a list of people involved in the analysis at EMPA Laboratories.■

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Endnotes

[a] The thermally welded technique, known as IR®, is a patented technology from George Fischer.
[b] The lab-quality water treatment system referred to was a Milli-Q Gradient A10 System from Millipore, Bedford, Mass.

Keywords: MATERIALS OF CONTRUCTION, PHARMACEUTICALS, PVDF, SEMICONDUCTORS, USP

TABLE D
Overall Performance Summary – Leach Outs Only

Sample Material	*Contaminant*		
	TOC	*Metals*	*Anions*
PVC-X	Several orders of magnitude worse than either PP	Slightly worse than PPn	Much worse than either PP
PPn	Equal to PP cdb than PVC-X	Slightly better cdb	
PP cdb	Equal to PPn	Pigments detected	Equal to PPn