Degreasing with Trichloroethylene

A look at the latest developments around degreasing with chlorinated solvents

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Recently, one of our members asked if we could recommend an alternative option to trichloroethylene (TCE or Trike) degreasing. In our attempts to be of service, it became clear that what seemed like a simple inquiry was opening up many avenues of research and debate. It was also clear that there are lots of differing opinions. On the one hand we have keen environmental legislators who'd prefer to clear it off the planet and on the other we have users of the product that have not been convinced that there are any viable alternatives for their specific applications.

David Elliott, CEO of the Surface Engineering Association of the UK comments as follows: “Many aerospace/ministry of defence specifications call for the use of TCE and the companies are unwilling to change as they will have to go through the whole process of certification again.”

Metal Finishers in South Africa who have used TCE solvent vapour degreasing know that it is a hard act to follow, and ideally suited to specific situations where alternatives just don't work as well.

What exactly is TCE? For a start it is what is known as a VOC or volatile organic compound. It is a chlorinated hydrocarbon and one of a family of chlorinated solvents of which the most well known are Trichloroethylene, Perchloroethylene and Methylene Chloride. All three of these are used in metal cleaning. Perchloroethylene is used extensively in dry cleaning and Methylene Chloride has many additional uses from paint stripping to pharmaceuticals, chemical processing and more.

Some may recall the ascendancy of another chlorinated solvent 1,1,1 trichloroethane which was also extensively used in metal cleaning but was banned during 1996 when it was discovered that it was responsible for ozone depletion (which is said not to be the case with TCE, Perc or Methylene Chloride) With the banning of trichloroethane, TCE came back into fashion and remains a preferred choice in many areas of metal cleaning and pre-treatment.

With the banning of trichloroethane TCE came back into fashion.

Why TCE?

In Barbara Kanegsberg's excellent manual “Handbook for Critical Cleaning”[1] TCE is described as follows:

TCE has long been recognised for its cleaning power. TCE is a heavy substance, (1.46

Kg per litre) with a high vapour density (4.53 times that of air) that allows for relatively easy recovery from vapour degreasing systems. It's high solvency dissolves soils faster, providing high output.

TCE is used extensively for degreasing zinc, brass, bronze and steel parts during fabrication and assembly. It is especially suited for degreasing aluminium without staining or pitting the work, because it's stabiliser system protects the solvent against decomposition. For cleaning sheet and strip steel prior to galvanizing, TCE degreases more thoroughly and several times faster than alkaline cleaning, and it requires smaller equipment that consumes less energy.

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Producers of the product believe that flawed research has resulted in it's "R45" status in the EU that effectively declares that it "may cause cancer" even though this conclusion is no longer being contested. There have been several large studies conducted on thousands of people that have worked with trichloroethylene compared to those who have not and apparently these studies failed to prove a connection between exposure to TCE and an increase in cancer.[2] There are many people and pressure groups that disagree with this finding and firmly believe that it is a definite carcinogen.

It doesn't seem to be contested that exposure to the vapour can cause all sorts of undesirable health effects such as eye irritation, dizziness, headache, slowed reaction time, and drowsiness.

There are some powerful backers behind the lobby that is working to keep chlorinated

***Label Markings for TCE that have been Legislated*[3]**

T
R: 36/38,45,67,52/53
S: (2-)45-53-61
Carcinogenicity Cat. 2; Mutagenicity Cat. 3
T: Toxic
R45: May cause cancer
R36/38: Irritating to eyes and skin
R67: Vapours may cause drowsiness
R52/53: Harmful to aquatic organisms, may cause long term adverse effects in the aquatic environment
S2: Keep out of the reach of children
S45: In case of accident or if you feel unwell, seek medical advice immediately
S53: Avoid exposure - obtain special instructions before use
S61: Avoid release to the environment. Refer to special instructions/Safety data sheets

solvents firmly on the map. These include companies that believe it to be absolutely necessary for their production processes and the producers. On the Eurochlor website you will find the following statement:

"The interests of European chlorinated solvent producers and consumers are represented by ECSA (European Chlorinated Solvent Association), part of Euro Chlor.[4] ECSA works to support the long-term sustainability of the chlorinated solvent industry. The association defines and promotes safe practice as well as commissions toxicological studies to further increase our knowledge of the products. ECSA's goal is to ensure that hazards are identified and that proper risk management is applied by users of chlorinated solvents."

The Association defines and promotes safe practice

ECSA members include Arekema (France), Dow-Europe – producing in Germany, Ecros (Spain), LII Europe (Germany), INEOS Chlor (U.K.) and Solway (Belgium – producing in France & Italy, also representing its subsidiary Solvay Solexis of Italy.)

The result of efforts by this group has been the development of new-generation TCE degreasers that don't allow the escape of any vapour and are consequently seen as absolutely safe to work with. There have also been significant changes to the way that the chemistry of the cleaning is managed in the factory, as well as control over the way fresh solvent is delivered and spent solvent returned for recovery.

Commenting on new generation technology, Richard Starkey, Sales Manager for SAFECHEM UK/Ireland said "In a nutshell more and more companies are either choosing or switching back to chlorinated solvents. This is because of enclosed, compliant technology, mainly developed in Germany on the back of legislation."

Others have taken the route of looking for the so-called "drop in" replacement, a product that works virtually as well, but without the "may cause cancer" label. One that appears to be promising is a product based on n-propyl bromide (nPB) which has a boiling point of 70° C compared to that of TCE at 87°C. The commercial stabilized solvents are sold under several brand names with one advertising prominently that it has been approved by Boeing[5] as a replacement for TCE and other chlorinated solvents in aerospace vapour degreasing.

...looking for the so-called "drop in" replacement...

From available information it seems that the price of this product is steeply higher than that of TCE and that in itself is enough to cause people to have another look at TCE given the new developments.

In addition, an R60 risk phrase [May impair fertility] has been slapped on nPB in the EU.

Whilst this ruling has been appealed, the R60 tag remains for now.

The US EPA notes that the following effects have been reported amongst workers who have been exposed to high levels of nPB:[6]

- *Leg weakness and pain leading to a difficulty with standing and walking (stumbling)*
- *Numbness, tingling, and prickling in legs*
- *Headache, dizziness, nausea, memory and concentration difficulties*

Studies on animals indicate a range of effects on the liver, nervous system, and the male and female reproductive systems.

Obviously, if you must stay with solvent degreasing, the trick is to use the solvent in a manner that prevents workers being exposed to dangerous levels, in which case, except for price considerations, it seems academic whether one prefers to use TCE or nPB.

New-generation TCE degreasers are very different from the basic open-top vapour degreasers of yesteryear. Then it was quite common to enter a metal finishing factory and be able to smell the strong TCE vapours wafting across the room as you entered the workshop.

It should be noted that a distinction should be made between vapour degreasing and solvent degreasing. In the simplest form of vapour degreasing, cool metal parts are suspended above a reservoir of boiling solvent. The hot solvent vapour condenses on the parts dissolving the oils and soils, carrying them to the reservoir below as it drains. A set of refrigerated coils is fixed above this work area creating a cool zone that is designed to condense any vapours rising beyond this point, theoretically containing the TCE in the plant.

Strictly speaking, when using the term “solvent degreasing” we should be referring to actual immersion of the parts in liquid solvent. Making use of vapour degreasing alone, it is possible that the vapour may not penetrate sufficiently into all areas of parts that have blind or threaded holes, slots, deep channels and the like. Direct immersion into the solvent is more likely to ensure contact with the more difficult-to-access areas. The downside of using the solvent as an immersion bath is that the oils and greases that are dissolved remain in solution and traces are likely to cling to the parts as they are drawn out of the tank. In the case of vapour degreasing the removed oil remains in the reservoir and (at least in theory) is not transported up to the parts in the vapour.

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Because of this different designs of plant were available. If, due to the configuration of the parts, vapour degreasing on it's own could do the job perfectly, the plant required

was simpler, with only a heated reservoir and a cool zone above. Where the parts were more complex and required both solvent and solvent vapour degreasing, machines were provided that included a pre-dipping tank in which parts were initially degreased by plunging into cool TCE. They were then moved into position in a second compartment situated above a heated tank of TCE, where the vapour degreasing step was completed. In some machines, the cool solvent tank was fitted with an ultrasonic transducer to enhance the action.

Some operators didn't understand the distinction between vapour and solvent vapour degreasing and it was not uncommon to see workers plunging the parts into the hot TCE reservoir, effectively using a vapour degreasing machine as a hot solvent degreaser.

For various reasons, a good deal of TCE escaped from these older plants. The piston like effect of work being moved in and out of the tank displaced vapour into the surrounding atmosphere. Parts were removed before they had dried properly. Drafts in the factory could also draw vapour out of the tank. In some cases, the poor design of the plant exacerbated these losses. There were also the inevitable spills when removing contaminated solvent and recharging with fresh solvent.

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Worse yet, there was a cavalier attitude to the use and disposal of TCE in earlier times. TCE has been picked up in groundwater samples in many locations in the USA. During 2003 inhabitants of the village of Endicott in Broome County, New York experienced a scary phenomenon. In the Winter 2004 edition of the Sierra Atlantic newsletter, Scott Lauffer, chair of the Susquehanna Group reported "……early in 2003 traces of chemicals, including TCE, were found entering homes and businesses through a process called vapour intrusion. This is a phenomenon that was little understood by the scientific community. At least 480 properties in a 300-acre plume area between the IBM facility and the Susquehanna River are affected by toxic vapor."

Endicott was not the only village to experience this. There are accounts of this type of ground water contamination from other locations as well.

TCE showed up above acceptable limits in 40% of boreholes sampled

And at least one study in the industrial and metal finishing heartland of the UK, carried out by University of Birmingham and the Water Research Centre (WRc) showed that contamination by chlorinated solvents was extensive.[7] Trichloroethylene contamination showed up above acceptable limits in 40% of the boreholes sampled in the Birmingham aquifer.

It became clear that if TCE cleaning was to survive as an acceptable process in today's environmentally concerned society, some significant improvements would have to be engineered.

That is exactly what has happened. Today's machines are very different. In one sophisticated example the parts are initially loaded into a totally sealed “treatment chamber”. Solvent from a reservoir is pumped through this chamber to achieve an initial solvent soak clean that gets rid of any particulate matter. The solvent is filtered and distilled and then in a second treatment cycle the chamber may be refilled for an ultrasonic immersion treatment or jet cleaning as an option. Following this phase, the chamber is drained, the TCE is filtered and returned to the tank, and the chamber is filled with hot solvent vapour to complete the degreasing phase. A vacuum rapid drying phase then begins and this is followed by an adsorption phase that removes all solvent vapours from the chamber before the work is removed. The machine then goes into regeneration mode, setting itself up for a new cycle with refreshed solvent.[8]

An adsorption phase removes all the solvent vapours from the chamber

It goes without saying that such a machine carries a hefty price tag. In the circumstances, only those manufacturers who really need to rely on TCE degreasing and who have the order volumes to justify it, would find such an investment feasible. Clearly there are a large number of such clients in Europe and around the world or the manufacturers of this type of machine would not have bothered to develop and market it.

The management of TCE goes beyond what happens in the machine however. To prevent the loss of TCE during the transport, as well during charging of the machinery with fresh solvent, a special container system has been developed. The system involves the use of two similar separate containers, one for handling the fresh solvent, and another for conveying contaminated solvent from the machine for transport back to the regeneration facility.

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Each dedicated container is equipped with a pump, and a purpose built coupling system that totally prevents emissions or spills. The used solvent container also features an overfill protection device. [9]

Finally, an important element of modern management of chlorinated solvent systems is the control of the stabiliser component of the solvent. Maintaining the stabilizer concentration at specification levels assures optimum cleaning power, it prevents acidification and contributes to a smooth-running process. To simplify this for the operator, solvent analysis test kits are provided that consist of the test instruments,

tools and instructions for use.

Using the "SAFE-TAINER™" system and new generation plant with methylene chloride as the solvent, one case study reveals that savings of 90% over the volumes of solvent originally consumed were achieved. This particular plant consumed only 200 litres of solvent in almost a year of operation at increased production rates. [10]

All of this demonstrates that if it is necessary to use solvent degreasing, it can be done much more safely and with virtually no impact on the environment.

TCE and the Future

Following negotiations, a voluntary agreement "Charter for the safe use of trichloroethylene in metal cleaning" has been signed by all European producers of TCE. The effect of this charter is that from January 2011 all existing open-topped vapour degreasing machines using TCE will need to be totally enclosed, even where the solvent consumption is below 1 ton a year. [11] Where consumption exceeds 1 ton per year, the end user will still be policed by the authorities under the SED. [Solvents Emission Directive]

From January 2011 all existing TCE machines will need to be totally enclosed

Consequently many engineering companies currently using open-topped degreasing tanks are looking for alternatives to TCE for degreasing. These could include alternative organic solvents or aqueous degreasing methods. Lower risk solvents should preferably be used. Any operator proposing to use specified risk phrase solvents as a substitute would be expected to provide strong justification.

As South Africa tends to follow informed world opinion on these matters, and will be affected by the charter, we can assume that the same rules will be applied here.

Degreasing precision parts and assemblies that have to be 100% clean, bone dry and guaranteed free of any entrapped solution before the next stage is always going to be a task where solvent/vapour degreasing must be an option to consider.

However, for the average metal finisher solvent/vapour degreasing is usually not indicated. For general requirements, an appropriately formulated soak cleaner is more than adequate. Electroplating, for instance, is a wet process throughout. There is no necessity to introduce dry parts into the acid pickle. If the alkaline cleaner on it's own doesn't pack enough punch, one can introduce agitation by pump or stirrer action, or with an eductor system. In certain cases, one can consider ultrasonic cleaning.

For general requirements an appropriately formulated soak cleaner is all that is required

Some sophisticated soak cleaners are available in South

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Africa today. One system worth considering is a system called bioremediation that relies on naturally occurring microorganisms that have the ability to convert organic molecules into less complex innocuous substances such as carbon dioxide and water. The system utilizes microorganism bioremediation combined with emulsifying surfactants to consume and metabolize a wide range of oils and other complex organics from the working cleaner. An economical, steady state, never-dump schedule is thus possible.[12]

There are circumstances where parts must be dry after degreasing – particularly where the next operation is not a wet process like electroplating. The part may need to be painted or perhaps coated with an adhesive. In such cases vapour degreasing offers an ideal solution. However, even in this event, if one wants to steer away from solvents, it is possible to use a wet cleaner, and then dry off in a very hot rinse and/or a drying tank with blowers. The pro-chlorinated-solvents lobby will point out that if you do the math, the additional cost of tanks, heaters and the space needed can end up costing more than a vapour/solvent degreasing process. [13]

Vapour degreasing also has the advantage of not attacking a galvanized surface, so that parts that are stamped from galvanized plate can be degreased safely. It's also wonderful for removing hardened polishes out of engraved or pressed patterns on items like jewellery or any fancy goods that require polishing.

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When evaluating degreasing requirements, one should always start at source. That is – ask what type of oil or grease we are removing and where it came from. And then consider whether a different more easily removable oil or grease can be substituted. In a factory in Denmark that the writer visited, the oil that had been used in the stamping process was substituted for a product that was based on a type of soap. The finished product required a nickel chrome finish. When it arrived at the plating line the degreasing process could be performed in a mild neutral solution.

1 *googlebooks.co.za*
2 & 3 *http://www.eurochlor.org/qandatrienglish*
4 *http://www.eurochlor.org/solvents*
5 *http://www.ensolv.com/P_ensolv5408.htm*
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7 *Chlorinated Solvents in UK Aquifers*
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Acknowledgements