Solving Acidic Solvent

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Dear Advice & Counsel,
I suppose my company is in the minority, but we continue to use vapor degreasing with trichloroethylene, and find it to be the most effective way to clean the type of parts we are processing. I can't say that I have had a great amount of expertise using vapor degreasing, so I have what you will probably call a few "basic" questions.

I have heard that the solvent can go acidic. I thought that solvents had no pH - just water-based solutions, so I'm not sure how this can happen, how to avoid it from happening and what to do if it does happen. Please enlighten me.

Signed,
Trent Charles Edward (TCE)

Dear TCE,
I will try to provide an answer to each of your questions, but your best source for detailed guidance on the issue of acidic degreasers is the supplier of your vapor degreasing equipment and solvent, since both may have an impact on the tendency towards forming acid.

History

Trichloroethylene (a.k.a. TCE, $ClCH=CCl_2$) was first mass produced in the 1920s for the extraction of oils from various food-stuff plants such as coconut. It was used for dry cleaning clothes until perchloroethylene was proven to be superior in that application around 1950. From the early 1950s to the late 1980s, TCE was a popular vapor degreasing solvent, and it is still used in numerous metal finishing facilities today (although the military has essentially stopped using it).

Early users of TCE for vapor degreasing found that, under certain conditions, unstabilized or ineffectively stabilized TCE can decompose producing hydrochloric and or trichloroacetic acids.

The solvent vapor degreasing operation exposed the solvent to many heating-cooling cycles. Condensation of the solvent and atmospheric moisture on the cooling coils produced unstable solvent-water mixes if not efficiently separated. The solvent was also exposed to metals (especially problematical are fine metal chips and power), oxygen and UV light, each of which degraded the solvent to varying degrees.

Therefore, as early as 1960, manufacturers of chlorinated solvents for vapor degreasers offered stabilizer packages that acted to resist/prevent decomposition of the solvent. These TCE stabilizer packages may contain three or more stabilizers, for acid neutralization, to prevent oxidation and for UV stability. Most important, in regard to your question, is the acid acceptance stabilizer.

The acid acceptor stabilizer reacts with any acid produced by decomposition of the solvent producing insoluble compounds which yield sludge in the solvent sump (and are removed during maintenance).

Signs of trouble

The following are signs that indicate the possibility of acidic conditions in a vapor degreaser:

- A dense, white cloud under and in the vapor zone,
- A burning odor,
- A darker than normal solvent or visible tar like materials on degreaser components
- Spotting on processed aluminum parts and or rust on steel parts shortly after degreasing,
- Chemical attack (corrosion) of condensing coils and or stainless steel components.

Causes of acidic conditions in degreaser solvent

Some of the conditions (in no special order of importance) that act to destabilize a chlorinated solvent (in some cases, even if a stabilizer is present) are:

1. Excess water in the solvent

TCE can chemically degrade in the presence of excessive amounts of water, producing acids. Water can contaminate the solvent due to condensation, introduction of wet parts, damaged or cooling coils and introduction of parts machined with water-based cutting fluids.

Visible spotting of work as it leaves the degreaser, corrosion of tank walls near the cooling coils or at the solvent-air interface, or a deep, dense white cloud in the vapor zone of the degreaser are indications that the solvent contains a significant amount of water and has turned corrosive.

Modern vapor degreasers employ gravity separators, to remove water contamination continuously. These need to be inspected and serviced regularly. To separate the water from the solvent properly, a five-minute retention time is a typical design parameter for a water separator. The solvent temperature (for TCE) in the water separator should be below 100∞F (38∞C). The stabilizers have some solubility in the water portion of the separator and are therefore continuously removed by the process.

The water layer in the separator typically overflows into a receptacle. A periodic (weekly) flushing of the separator with fresh water is a good idea. The pH of the water in the water separator should not be below 7. If it does go below 7, it may be time to replace the solvent. A solution of 84 g/L of sodium bicarbonate (fully dissolved - never dry) in water can be used to flush the water separator and eliminate the acidic condition. Never add sodium hydroxide to the water separator, as this can result in a violent reaction that can produce dichloroacetylene which is toxic spontaneously combustible.

2. Contact with metals

Aluminum and other metals such as zinc appear to either catalyze or accelerate the decomposition of chlorinated solvents to produce acidity. Therefore, never allow non-ferrous metals such as these to soak for long periods of time in the solvent. When continuously degreasing these metals, make a daily effort at removing any metal fines that may be present.

3. Excessive heat

At least 1.5 inches of liquid should always be above the heating elements exposed to solvent. If the solvent is exposed to high temperatures, thermal decomposition can produce acidity. If the solvent contains a large amount of light oil, a fire may result. The solvent sump should have a shutdown system, based on sump temperature. Thermostats should shut off heat at 195°F (91°C) for TCE. Frequent inspection of all temperature controls and visual confirmation of solvent level is highly recommended.

Avoid installing vapor degreasers near any operation that may combine solvent and excessive heat and or UV radiation (welding, ovens, furnaces etc.). Stray solvent not captured by the ventilation system may decompose on these hot surfaces, or may decompose upon exposure to strong UV rays.

4. Certain oils

Some chlorinated oils are unstable at temperatures above 150°F (65°C), breaking down to produce acids. Also, newer cutting and machining lubricants may contain additives that are incompatible with TCE or any chlorinated solvent.

5. Excessive oil-solvent concentration

High oil/grease content in the solvent sump can cause solvent decomposition, insufficient vapor generation and sludge/scale formation. The higher boiling temperature may thermally break down the solvent as well. Maximum recommended still temperatures are typically around 193°F (89°C) for TCE, which corresponds to around 25 to 30% oil.

6. Mixed degreasing solvents

If various chlorinated solvents are blended, the stabilizers may be at the wrong concentration or may be inadequate for stabilizing the solvent mixture. The end result is decomposition of the mixed solvent, producing acids. Also, the varying boiling temperatures of various solvents may produce decomposition. For example perchloroethylene (PCE) boils at about 250°F (121°C). If mixed with TCE, which decomposes at this temperature, acid is produced by thermal decomposition of the TCE.

7. Introduction of acidic matter

Some brazing and soldering fluxes contain acidic compounds. When introduced into a vapor degreaser, these compounds may overwhelm the stabilizer(s) in the TCE or, in small amounts, they may lower the acid acceptance value of the solvent.

Preventive action

Some operations change the solvent in the vapor degreaser frequently enough to avoid acidic conditions. According to the *Electroplating Engineering Handbook* (3rd edition): “With modern well-stabilized solvents, the need for chemical control is virtually eliminated.”

However, when the bulk of the workload is aluminum and or other light metals, and when the above indicated conditions for producing acidity can not be readily controlled or prevented, a periodic acid acceptance test can verify that the solvent is sufficiently stabilized.

Most solvent suppliers provide kits or procedures to determine the acid acceptance value, but their procedures will vary. The simplest test is described in the above mentioned handbook. Vigorously mix equal portions of distilled neutral water and test solvent under a fume hood. Allow the solvent and water to separate. Next, measure the pH of the water portion. A reading of 6 to 8 is normal, while 5 to 9 is on the edge and any pH less than 5 confirms an acidic condition. Other procedures involve acid-base titrations which can provide acid acceptance values in equivalent sodium hydroxide concentrations.

According to one major solvent supplier (Dow Chemical), acid acceptance values should normally be above 0.1 wt% sodium hydroxide (NaOH). When it drops to 0.08 wt% NaOH, it should be monitored daily. Below 0.04 wt%, NaOH, corrective action should be taken.

Corrective action may involve adjusting the stabilizer concentration in the solvent or blending the affected solvent with fresh solvent. Vapor degreasers containing solvent with very high acidity need to be specially treated. The following guidance for cleaning such an acidic vapor degreaser comes from Reference 1:

1. Turn off heat.
2. Add soda ash to sump in a solution of one pound of soda ash (sodium carbonate) dissolved in five gallons of water (no solids!), and agitate as much as possible while the solvent is cooling.
3. When the solvent is cool, remove it from the degreaser.
4. Following approved confined space procedures and wearing all recommended safety gear, remove as much sludge as possible from inside and outside of the degreaser.
5. Fill the degreaser with water to a depth of 4 to 6 inches above the heating elements, and add soda ash at the rate of one pound per five gallons of water in the sump.
6. Heat the soda ash solution and boil if possible. Wash all parts of the degreaser that were in contact with the acid solvent.
7. Drain the degreaser and dry completely.
8. Add fresh solvent.
9. Determine the cause of acid generation and take action to prevent future occurrences. *P&SF*

References

1. Roderick P. Murphy, *How a Vapor Degreaser Works*, Degreasing Devices Co., Southbridge, MA, 2000; http://www.degreasingdevices.com/ebook.htm.

2. *Trichloroethylene Stabilization and Maintenance*, Detrex Technical Bulletin, Detrex Corporation, Southfield, MI.

3. *Electroplating Engineering Handbook*, 3rd Edition, A.K. Graham, Ed., and 4th Edition, L.J. Durney, Ed., Van Nostrand Reinhold, New York, NY, 1984.

4. *Economical & Efficient Degreasing with Chlorinated Solvents from Dow*, Form No. 100-6096-485, Dow Chemical Corporation, Midland, MI, 1985, 49 pp.

DOLLARS & SENSE

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For an organization with a number of different plating processes, it is reasonable to set up each process or line as a separate profit center with indirect costs allocated according to some reasonable model. Models such as these are effective and widely used.

Generally though, surface finishers do not take into account the surface area of the parts they are plating, despite the fact that they are in the surface finishing business, and, generally speaking, within a given process, the costs are proportional to the surface area and the plating thickness. Articles in future issues will discuss surface area - how it is calculated and how it can be used profitably by the practicing surface finisher. *P&SF*