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# HCFC-225 Phaseout—What Now?

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**Abstract**
On January 1, 2015, nine months from APEX 2014, the production and use restrictions on HCFC-225 will be in effect throughout the United States. This phase out is encompassing in scope. This phase out will have significant technical, performance, and economic implications for the electronics industry. The regulatory situation remains fluid. A number of alternative solvents have been or are in the process of being developed. We discuss the options for assemblers and component manufacturers.

## The Message for Electronic Assembly

As of January 1, 2015, the production of the cleaning solvent HCFC-225 will cease and its continued use will be severely restricted. Manufacturers who currently use HCFC-225 may not find an easily adoptable replacement. Despite the claims of some cleaning chemical suppliers, there is no drop-in replacement. Planning and testing will be required and both take time.

Although the time of the HCFC-225 phase out has been known for many years, significant details associated with its implementation have changed several times (1). The question of what will happen to stocks of HCFC-225 has not yet been fully resolved although recent action by the EPA may answer this question by the time of the 2014 APEX conference.

Even if you do not use HCFC-225, the phase out may affect you. Some in your supply change may rely on HCFC-225 for cleaning the products they ship up the chain to you. A cleaning process change may affect the quality of those products, perhaps "passing-the-buck" up the chain.

Whether or not you or your suppliers use HCFC-225, this is a good opportunity to reap the benefits. Re-evaluate all your cleaning processes and look at the alternatives that are available or are being developed. Electronic assemblers and suppliers of electronic components face many challenges. There is always the pressure to reduce costs while maintaining or improving product quality. Performance requirements, including expected product lifetime, continue to grow while design squeezes components into smaller and smaller spaces and lower standoff. The need for effective cleaning increases while it becomes more challenging to get cleaning agents to the location where they are needed and to subsequently remove the flux residue or other soils along with the cleaning agents themselves. Many of the chemical replacements for HCFC-225 have their own regulatory baggage and may or may not therefore be feasible for your applications.

## Why we like HCFC-225

HCFC-225 has been favored by many manufacturers, not only in electronics assembly but for aerospace, military and medical device cleaning as well.

*HCFC-225 Attributes*

- Is exempt as a VOC, making it one of the few acceptable solvents in areas with poor air quality.
- Has moderate solvency, similar to CFC-113 (2)
    - The solvency has been increased in a number of azeotropic blends.
- Suitable for vapor degreasing as well as immersion and spray applications
- Dries residue-free.
- Is not a Hazardous Air Pollutant (HAP)
- Is non-flammable
- Is non-aqueous
    - Has high wetting capability
    - Has low corrosion potential

*Specific attributes for electronic assembly*

Electronic assembly poses specific challenges. HCFC-225 has addressed some of these.

As boards become more densely packed and as standoffs have decreased to less than 5 mils, the wetting capability of cleaning agents becomes a more important attribute. As we will outline in a section later in this paper, HCFC-225 has a very high wetting capability compared to water or even water with surfactants.

Higher temperatures associated with lead-free solders can make the flux residues more adherent. A more aggressive solvent than water or chemically enhanced water is frequently a better choice.

HCFC-225 is an organic solvent. The principal of "like dissolves like" is applicable for dissolving and removing organic soils. Fluxes are a combination of organic and inorganic materials.

**HCFC-225 Phaseout**

So why and how is HCFC-225 going away? It is a Class II Ozone Depleting Substance (ODS). The US phaseout is mandated by the modifications of the Clean Air Act which were passed as a response to the global Montreal Protocol agreement of 1987. The EPA is responsible for implementing and enforcing the phaseout in the US.

Although the phaseout date is less than a year away, the phaseout rules remain fluid. Before 2012, the EPA position had been that manufacturers would be able to use up existing stock of HCFC-225. Then the interpretation changed. The revised position of EPA spokespeople was that production, sale and **use** of virgin-225 would be prohibited after the end of 2014 (3). Continued use would be allowed only for recycled solvent or where the solvent had already been packaged into a product such as an aerosol or pre-packaged wipes.

However, in December, 2013, the position changed again back to one close to the earlier one (4). A new proposed rule includes a provision that while production and sale would be prohibited, the use of existing stock of virgin solvent already in the possession of users could continue.

The exception allowing continued use of HCFC-225 already in inventory is based a *de minimus* doctrine. This doctrine, stemming from several court cases from the 1960's to 1980, allows government regulators to provide exemptions when the "burdens of regulation yield a gain of trivial or no value."

Also, after Jan. 1, 2015, any product that contains or is manufactured with HCFC-225 whether virgin, recycled or already incorporated into a product such as an aerosol, will be subject to labeling requirements. Products that will be shipped inter-state will need to have a label stating, "Warning: Contains [or Manufactured with, if applicable] HCFC-225, a substance which harms public health and environment by destroying ozone in the upper atmosphere."

The proposed rule was published in the Federal Register on December 24, 2013. There is a comment period that ends March 10, 2014. If the comments do not cause a further delay, it is expected that the final rule will be in effect shortly thereafter.

**How does HCFC-225 clean?**

In order to have a perspective on the options available for replacing HCFC-225, it is useful to review a few of the primary tenets of critical cleaning.

Cleaning action is accomplished by a combination of *force*, *chemistry*, *temperature*, and *time*. Forces and chemistry are the mechanisms by which soils are dislodged from surfaces. Temperature is a measure of kinetic energy of the system. Higher energy generally makes soil removal easier, although thermally induced chemical changes, such as oxidation and caramelization sometimes make soil removal more difficult. Also, in general, the longer the clean time, the more soil is removed. Again there can be too much of a good thing if the cleaning action occurs over so long a time that the surface becomes damaged.

A cleaning process has three basic phases (5). A *wash* phase delivers a cleaning agent to the vicinity of the soil where it acts to remove the soil from the surface. The removal action may be due to a momentum process, knocking the soil loose by the kinetic energy of the agent. Momentum processes include spray and agitation, including agitation from ultrasonic cavitation. The removal action might also be chemical, dissolving the bonds that hold the soil to the surface. In most cases, the removal actions are combinations of both physical momentum and chemical solvency.

HCFC-225 has properties that make it effective both for physical and chemical cleaning. The physical, momentum, aspects make it effective for particle removal while the chemical solvency makes it useful for cleaning non-polar soils such as oil, grease, or rosin flux.

The second phase of a cleaning process is the *rinse*. The purpose of the rinse is to purge the area to be cleaned of the cleaning agent, carrying away the soils at the same time. In many instances, a rinse also continues to remove soil by physical or chemical action. One advantage of a solvent such as HCFC-225 is that when the cleaning is accomplished in a vapor degreaser, the cleaning agent is also the rinse agent. Solvent condenses on the part suspended in the vapor, providing a self-rinsing action.

The third phase is the *dry*. The rinse agent is removed from the surface by evaporation, usually heat enhanced, and/or by physical displacement such as an air blower. Drying can sometimes be accomplished by chemical displacement such as when an alcohol is used to displace residual water. An organic solvent like HCFC-225 leaves no residue when dry.

The ability of a liquid to penetrate into small spaces is called wetting. The late Bill Kenyon developed a guideline that is a useful "teaching tool" which he called the "Wetting Index."

**Wetting index = density x 1000/(surface tension x viscosity)**

The density is a measure of the momentum capability to knock soils off surfaces. Think of the comparison between a ping pong ball and a golf ball. Both the surface tension and the viscosity impede the ability of a molecule to get into tight spaces, such as under low-standoff components.

The higher the Wetting Index, the more effective a fluid should be as a cleaner by its ability to penetrate to where the soils are and to then be removed. Table 1 contains the parameters that compose the Wetting Index for a number of commonly used chemicals (including a few that are no longer available). Note especially that water and alcohol have much lower wetting capability than HCFC-225 and other organic solvents.

**Table 1 Physical parameters and Wetting Index**

| **Cleaning Agents** | **Density g/ cm3 (25 deg C)** | **Surface Tension Dynes/cm3 (25 deg C)** | **Viscosity Centipoises (25 deg C)** | **Wetting Index** |
|---|---|---|---|---|
| HCFC-225 | 1.55 | 16.2 | 0.59 | 162 |
| n-propyl bromide | 1.35. | 25.9 | 0.49 | 106 |
| 1,1,1-trichloroethane | 1.32 | 25.6 | 0.79 | 65 |
| HCFC-141b | 1.24 | 19.3 | 0.43 | 149 |
| Trichloroethylene | 1.46 | 26.4 | 0.54 | 102 |
| CFC-113 | 1.57 | 17.3 | 0.65 | 140 |
| HFC-43-10 (6) | 1.58 | 14.1 | 0.67 | 167 |
| HFE 7200 (7) | 1.43 | 13.6 | 0.61 | 172 |
| **1233zd(E) (8)** | 1.3 | 13.3 | 0.489 | 200 |
| Isopropyl alcohol | 0.78 | 21.8 (15 deg C) | 2.4 (20 deg C) | 15 |
| Acetone | 0.79 (20 deg C) | 23.3 (20 deg C) | 0.36 (20 deg C) | 94 |
| Hexane | 0.66 (20 deg C) | 18 (25 deg C) | 0.31 (20 deg C) | 118 |
| Volatile methyl siloxane (9) | 0.82 | 16.5 | .82 | 61 |
| d-limonene | 0.84 | 25 | 1.28 | 26 |
| Water | 1.00 | 72.8 | 1.00 | 14 |
| Water with 6% ethanolamine-based saponifier | 1.00 | 29.7 | 1.08 | 31 |

**What are your options?**
So, as a user of HCFC-225 for a cleaning process, what can you do?

You can act like a proverbial ostrich and deny that the phaseout will happen, but that outcome is not likely to occur. There is no indication, either from chemical suppliers, users or government officials, that the phaseout will be canceled or delayed.

You can acquire a stockpile of HCFC-225 either to buy some additional time to develop other options or with the intent of recycling it to keep it in use. Keep in mind that there are chemical losses with any process so eventually the supply will diminish. Also, under the proposed rule, you will not be able to acquire virgin HCFC-225 from anyone if it is not already in your inventory by January 1, 2015. So, unless your application is a relatively short term one, continuing to use HCFC-225 is best considered as a short-term option to allow more development time for a replacement process.

*Change the process*
There are many avenues open for changing a process. You can stay with a solvent process or switch to an aqueous or "non-chemical" process, such as by CO2 or steam.

There have been some recent innovations in aqueous processes. Spray cleaning can be replaced or augmented by an immersion flooding technology that improves agitation and penetration. Increased agitation can also be achieved by a technique that exploits liquid and vapor action near the boiling point of the liquid.

*Change the flux*
Another process choice is to change cleaning requirements by changing the flux. Many applications have adopted "no-clean" fluxes. These fluxes do leave residues, but because the residues are non-ionic, they may not interfere with product performance. However, most high-value applications need to clean "no clean". Non-ionic residues can interfere with adhesion of conformal coating. The residues may also trap ionic contaminants or distort high frequency performance due to dielectric properties. "No-clean" fluxes also vary in the ease of being cleaned. The efficacy of cleaning can depend on the cleaning mechanism (e.g. in-line vs. batch, or spray vs. immersion) as well as the choice of cleaning chemistry (water alone or chemically assisted).

Another flux choice is organic acid (OA). OA fluxes are water soluble and therefore can be cleaned with in aqueous systems. However, any residues are conductive so cleaning must be very thorough. Densely populated boards or components with low standoff pose particular challenges when it comes to cleaning OA fluxes.

*Change the solvent*
Finding a replacement solvent for an HCFC-225 process can be difficult. Most other solvents are VOCs and have restricted use in areas with low air quality. Many solvents also pose worker safety concerns either through toxicity or flammability. Flammability can sometimes be inerted by blending with a non-flammable solvent. It is important to remember that, for any blend, the blend constituent ratios may change over time unless the blend is an azeotrope. Even with azeotropes, the condition of constituent stability is valid over a finite range of temperatures, so process vigilance is required.

There are a number of solvents or solvent blends that can be considered for replacement. These include hydrofluorocarbons (HFCs), hydrofluoroethers (HFEs), and hydrofluoro-olefins (HFOs). Although HFC and HFE solvents have been available for quite a while, HFO solvents for cleaning are relatively new and may not have been approved by all regulatory agencies that affect your operation.

One example of a recently introduced HFO is trans-1-chloro-3,3,3-trifluoropropene ( **1233zd(E))(8)**. It has passed the Federal EPA hurdles of "Significant New Alternatives Policy" (SNAP) and VOC-exempt acceptance. It has a very high Wetting Index (Table 1) and has similar solvency parameters as HCFC-225.

Is trans-1-chloro-3,3,3-trifluoropropene a drop-in replacement for HCFC-225? The jury is still out. It has a low boiling point (19C), and many vapor degreasers would need modification to operate at such a low temperature. Concerns that it would rapidly boil off under room temperature conditions are mitigated by a high heat of vaporization that slows evaporation.

Some companies that have tried the **1233zd(E) (8)** report successful cleaning, but some others have not been as satisfied. Also, although approval for use and VOC-exemption have been granted at the Federal level, local or state agencies may not yet have approved it. The South Coast Air Quality Management District (SCAQMD) in southern California is encouraging small scale testing but has not yet acted on the rule change that would permit its use in production (10).

Other companies are also offering existing or recently formulated replacement solvents or solvent blends.

**What should you do?**

The time to plan is NOW! The deadline is rapidly approaching and is unlikely to be deferred. Planning should consist of examining your whole process. Chemistry and equipment work as a team.

It is important to know your local regulatory situation. Local and state agencies might be open to changes on alternatives but you must **ask** for them.

As with any process, test before you buy. Most suppliers have applications labs and will help you to conduct testing but it is important to work closely with the lab (11).

Stockpiling or obtaining the ability to recycle HCFC-225 may buy a little time to accomplish a cost effective process change. This option should not be considered to be a good long-term solution.

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