

SMT



Alternatives Replace Older Cleaners

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Existing product choices for cleaning lead-free assemblies are being phased out, providing weak results, or are overly expensive. New research in chemicals indicates that scientists may have cracked the code in developing a class of solvents for defluxing lead-free electronics.

The electronics industry well understands the problems of transitioning to lead-free soldering processes. Lead-free solders and pastes typically require higher temperatures during reflow. This ripples back through the engineering chain to different fluxes, different assembly processes, different components, and even different specifications for the bare boards.

One persistent problem with lead-free has been cleaning. Lead-free soldering materials are prone to unsightly white residues, especially when using no-clean lead-free products. These residues can cause premature failure of the boards and cosmetic concerns during assembly inspection.

Reworking lead-free boards adds another layer of complexity, due to issues such as operator skills, temperature variations (both to the high and low sides of the specification), and the lack of proper equipment. These exacerbate the need to clean. Meanwhile, evolving environmental and safety regulatory pressures (particularly in California) are making the problems and processes of cleaning more complex and expensive.

Beginning in 2004, product development specialists* became aware of the evolving requirements associated with cleaning lead-free electronics and developed a research program to determine if any of the existing or foreseeable solvent options might resolve them. When they compared customer requirements to current solvent cleaning capabilities, it became apparent that there were shortcomings in the offerings available. Customer feedback on existing products suggested that most of the current choices were suboptimal or overly expensive. HCFCs on the market were ozone-depleting materials and subject to phase-out over the next few years. Existing solvents could not

consistently and reliably handle the extra cleaning burden imposed by lead-free processes. This left engineers with few acceptable choices.

Looking back at older technologies, perchlorethylene and trichloroethylene, two popular chlorinated solvents, never have been popular in the electronics industry due to poor materials compatibility. Another powerful cleaner, nPB, is worrisome due to health and safety concerns. Among the aqueous options, water-based cleaners have difficulty achieving acceptable results at reasonable throughput, and increasing energy costs continue to be a source of concern to many users. There is room in the market for a safe, fast, reliable, and inexpensive cleaning system for lead-free electronics.

The Research Design

Engineers seek formulations that have four crucial characteristics. First, the product must be a highly activated solvent, that is, sufficiently aggressive to clean “no-clean” and lead-free materials. The Kb value – a standardized measure of solvent strength – of the solvent must be greater than 70 (Table 1). The product also must be nonflammable and exhibit no flashpoint. It needs to exhibit stable, azeotrope-like behavior to fit into normal vapor degreaser operations and be recycled easily. Users demanded a drop-in replacement for the solvents currently in use so that few, if any, equipment changes are needed.



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Figures 1A & B. Poor cleaning can result in white residues (B) that detrimentally affect inspection and PCB performance.

Research began with a comprehensive review of all the chemicals and ingredients in proprietary labs and at partner companies, looking at both those products on the market and “orphan” ingredients that never made it out of the lab. Scientists asked, What did we assume wouldn’t work in the old days that may work today? They set out to find a low-boiling, nonflammable, azeotropic ingredient that would work in an existing vapor degreaser and be aggressive sufficiently to clean lead-free materials. After multi-tiered field trials and reformulations, a chemical designated K17351** was developed for this problem.

Formulation Characteristics

The search for orphan materials paid off with the discovery of a hydrofluorocarbon (HFC) material that had never been commercialized successfully as a solvent, due to its high cost. This ingredient became the key that unlocked the new solvent formula for lead-free electronics cleaning.

Three of the ingredients in K17351 are well-known to industry today: nonflammable decafluoropentane, the flammable solvent trans-1,2-dichloroethylene, and methanol. The methanol helps lift polar contaminants off PCBs. These three ingredients form a ternary azeotrope, which helps make the final mixture easy to handle, ship, and use.

The innovation came with a proprietary HFC, which mixed with trans-1,2-dichloroethylene and formed a second azeotrope. When the two azeotropes combined, they formed a blend of azeotropes that gave the product aggressive cleaning strength while keeping it nonflammable. This was achieved even though approximately 70% of the ingredients in the mixture were flammable. In effect, the proprietary HFC had the unexpected side effect of completely suppressing the flammability of the trans and methanol components.

In addition to the safety factor provided by nonflammable nature of the mixture, the material demonstrates an acceptable exposure limit (AEL) of 187 ppm (8-hour TWA), within the safe operating parameters of today's cleaning machines. Table 1 lists the operating parameters of the proposed solvent.

Field Trials

The rubber meets the road, of course, in real-world circuit board production. Testing was performed to confirm that the solvent remained a stable, nonflammable azeotrope even after contamination with flux residues. The mixture exhibited stability in three customers' degreasers. Even with solvent losses and during solvent recovery operations, the mixture showed little change and maintained its performance levels. In general, K17351 remained unchanged as measured by specific gravity and gas chromatography.

A field trial took place at a company experiencing problems with white residues, after hand soldering during rework-and-repair, when using a popular lead-free no-clean flux. The customer's solvent cleaner was insufficiently strong to clean the hand-soldered PCBs. Visual inspection and ionic measurements performed after implementing the new azeotropic solvent found that all of the reworked boards passed cleanliness inspection during four months of continuous use. Even difficult assemblies that were developing severe residues were found to be acceptably clean after using the K17351 formulation.

A more complex trial involved a massive 2,000-liter vapor degreaser. The prior solvent worked fine for leaded soldering materials but, as the customer began to switch to a lead-free process, the older solvent was not sustaining the required performance as measured by throughput and cleanliness levels. To meet requirements, the system was being slowed and cleaning cycles extended from an initial level of 9 min./cycle to 29 min./cycle, impacting throughput significantly. Also, the company was under environmental pressure to switch from HCFCs due to their ozone impact.



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Figure 2. *The board, being relatively cold, causes the vapors to condense onto its surface, dissolving contamination and allowing it to drip down into the liquid solvent.*

For the initial test, a lengthy series of production boards were produced with both hand-soldered components and reflow-soldered devices. The biggest board was a large backplane with 24 connectors. Both RMA and leaded no-clean solder pastes were used for the automatic soldering systems, and the hand-soldered work was performed with a lead-free material. Unable to disturb the giant degreaser, testers temporarily deployed a smaller Branson vapor degreaser, with a 20-liter capacity. An ionograph with a threshold of 2 mega Ω of resistance in the test fluid provided cleanliness measurement. In this test, all boards passed for cleanliness, even when cycle times were reduced to the original standard of 9 min./cycle.

Further testing brought the formula to an established user of a large aqueous cleaning system. The company hoped to eliminate the cost of running the aqueous system. According to the production engineer, there were unexpectedly high costs to maintain and operate the system. There was an environmental footprint problem, as well as a floor space constraint, and the system inflicted high energy costs. Products for the test were large military two-sided PCBs, processed with a no-clean flux for automated soldering and secondary flux for hand-soldering touchups. Depending upon the design of the board, each could be reflowed/wave soldered as many as three times during the production process.

TABLE 1. Characteristics of K17351 compared to other popular cleaners.

Property	K17351	HFC-43-10	nPB	Perc	Water
Boiling point (°C)	41	55	71	121	100
Liquid density (g/cc @ 25°C)	1.28	1.580	1.322	1.631	1.00
Surface tension (dyn/cm @ 25°C)	19.9	14.1	25.9	32.0	72.80
Viscosity (cPs @ 25°C)	0.58	0.67	0.49	0.89	1.00
Heat of vaporization (cal/g)	68	31.0	58.8	51	543.0
KB value	101	17	125	90	0

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In this case, the boards were shipped overnight to the lab for testing. This inflicted approximately four days of aging on the fluxes, making them harder to clean. However, with cycle times of between 12 and 16 min., all of the boards were successfully cleaned, and all ionograph tests were positive.

Conclusion

The technology developed for K17351 appears to make it reliable and cost-effective to clean advanced circuit boards made with lead-free soldering materials, including those made with no-clean lead-free materials, in vapor degreasers. This breakthrough, using a blend of azeotropes, enables companies to achieve high throughput, brief cycle times, and high-quality cleaning with minimal economic and environmental issues. The azeotropic blend can replace energy-intensive aqueous cleaning systems as well as materials like HCFCs, TCEs, and nPB.

*R&D took place at DuPont Fluoroproducts.

**DuPont and MicroCare will commercialize K17351 as Vertrel SFR.

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Azeotropes for Cleaning

An azeotrope technically is a mixture of liquids that are "a constant boiling blend," which means that the both the liquid and vapor compositions of a mixture remain identical. There is a bit of magic to making azeotropes. Not all liquids form azeotropes because the pressure, density, boiling point, and surface tension all must be exactly right. But azeotropes are attractive because they allow engineers to tailor a mixture of chemicals to obtain specific properties and performance.

This "tailoring" is important. As with chemical composition K17351, azeotropes allow mixing of flammable and nonflammable ingredients to produce a stable nonflammable mixture. Another benefit is that azeotropes are easy to distill and recover, making them ideal for use in a vapor degreaser. Lastly, azeotropes permit tweaking of a blend to obtain unique physical properties such as drying speed or cleaning strength, which extends the usefulness of the ingredients across a broad range of applications.

Not all azeotropes are created equal. To a finicky chemist, a perfect true azeotrope only exists at a single temperature and specific pressure where the azeotropic behavior is observed. Many successful products today are not perfect azeotropes but near-azeotropes that exhibit stable behavior across all normal operating temperatures and pressures even though they don't fit the classic chemical definition of a perfect azeotrope. These products have been tested thoroughly and are so close to being true azeotropes that they can be used without problems in vapor degreasing applications.

What Is Vapor Degreasing?

Many younger engineers may never have seen a vapor degreaser, so a review is worthwhile. Vapor degreasers are cleaning systems based on low-boiling solvents. Typically, these solvents boil from 90° to 170°F and, unlike water, these solvents also have low viscosities, low surface tension ratings, high densities, low specific heat, and low latent heat. When they are used in a properly configured cleaning machine, results are affordable, fast, reliable, safe, and environmentally acceptable cleaning.

To begin, a low-boiling solvent is placed in the boil sump of a degreaser and heated. Parts to be cleaned are inserted into the boil sump and subsequently into the rinse sump, after which they are removed for further processing.

In the meantime, in addition to cleaning the parts, the boiling solvent produces a clear, dense vapor that is heavier than air. These vapors fill the inside of the machine and eventually rise up to refrigeration coils. The coils chill the vapors and condense them back into a liquid state. This condensation is recaptured, moved through a water separator, and reintroduced into the cleaning system. In short, a vapor degreaser is an automatic, continuously recycling, closed-loop cleaning environment. The concentrated waste is trapped in the boil sump for removal and maintenance, while the solvent is constantly refreshed and repurified in the distillation process in the machine.

Vapor degreasing is a simple, safe, reliable, and elegant technology that uses the inherent chemical characteristics of the solvent to perform both the cleaning task and recycling. It's relatively benign environmentally, with low energy consumption, no water requirements, and nominal waste treatment issues. Degreasers easily clean complex shapes and the parts come out cool and dry. Cycle times are fast, keeping productivity high. Systems are scalable from small benchtop machines to units longer than eighteen-wheel trucks.

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