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Synergy 3000 CCS™: A New Precision Cleaning Agent

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Synergy 3000 CCS™: A New Precision Cleaning Agent

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Abstract

It has been found that a synergistic solution of terpene and heterocyclic alcohol solvents acts as an efficient non-ozone depleting, biodegradable cleaning agent for application to critical cleaning of components used in the electronics industry. Results of testing and evaluation are presented as well as current and potential applications.

Introduction

As a result of scientific studies indicating an alarming depletion of the stratospheric ozone layer, the international community ratified a series of agreements, starting with the Montreal Protocol in 1987, to completely phase out the use of chlorofluorocarbons (CFCs) by the year 2000. As the millennium approaches, the legal and ethical issues associated with these materials serve to act as a driving force for investigations into suitable alternatives. This provides a unique opportunity for us to reevaluate the technological approach that traditionally, has been employed for solvent cleaning processes.

Environmental considerations, coupled with recent advances in solvent chemistries, have led to increased application of low-volatility cleaning agents for use with water rinses, commonly referred to as semiaqueous cleaners. The primary advantage of these low-volatility cleaners is the reduction in the amount of chemicals vaporized during the cleaning process. However, because these chemicals do not evaporate rapidly, rinses are typically required to remove the solvent from the substrate being cleaned.

Some of the semiaqueous cleaners in use employ terpenes as the cleaning agent, usually followed by a water rinse to remove the cleaner. Because terpenes are not miscible in water, these cleaners require the addition of a surfactant to facilitate the water rinsing step. The surfactants are generally nonvolatile materials, some of which can be left behind on the substrate being cleaned in areas which tend to trap contaminants. Further, terpene/surfactant cleaning agents generally are not distillable because of the nonvolatile nature of the surfactants, complicating recycling of the cleaner for reuse. Finally, although terpenes have been found to be satisfactory for a variety of cleaning applications, they are not fully effective in removing polar contaminants.

A collaboration between engineers at the Hewlett-Packard Company, Microwave Technology Division, and AlliedSignal Aerospace, Kansas City Division, has resulted in the development of a new critical cleaning solvent (CCS) that has been named Synergy 3000 CCS™ (patent application pending). This material is a proprietary blend of terpene and heterocyclic alcohol solvents formulated to remove polar and nonpolar contaminants such as rosin fluxes, machining oils, greases, waxes, tape adhesive residue and handling soils from electrical and mechanical components and assemblies. It is a high

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purity, low odor solvent that does not require surfactants for water rinsing, and is derived from naturally and annually renewable resources. It demonstrates a high loading capacity for soils, grease, and contaminants and is compatible with a wide range of engineering materials commonly used in electronics applications. All of its components are biodegradable, are approved as food additives, and have no known human health effects. It has been formulated to have a higher flash point than citrus terpenes and flammable alcohols, and can be recycled via distillation. This paper presents some of the tests and evaluations that were performed during the development of Synergy 3000 CCS™, hereinafter referred to as CCS, as well as current and potential applications for the solvent.

Experimental Procedure

An accepted cleanliness test method used in military electronics soldering specifications is an ionic cleanliness test, designated as MIL-P-28809, "Military Specification for Circuit Card Assemblies Rigid, Flexible, and Rigid-Flex." This test measures the change in resistivity of an isopropyl alcohol and water rinse solution due to ionic contamination dissolved and removed from the test sample. In order to verify the effectiveness of this new cleaning agent, samples were prepared and tested according to the ionic cleanliness test specification.

Test samples were prepared by depositing a measured amount of rosin-activated flux on printed wiring assemblies (PWA) and drag soldering the samples in a 490-degree F solder pot for approximately seven seconds. The test samples were then cleaned in either CCS, a terpene component alone, or an alcohol component alone by immersing them in a 40 kHz ultrasonic cleaning tank for one minute and then blow drying the samples with nitrogen. The ionic cleanliness of each sample was determined using an Alpha Metals Omegameter Model 600.

Another method for measuring organic contamination is the residual rosin test, as described in the Institute for Interconnection and Packaging Electronic Circuits (IPC) document IPC-TR-580, "Cleaning and Cleanliness Test Program Phase 1 Test Results." This test is performed by measuring the change in absorbency of a test sample extract solution (99% IPA/1% phosphoric acid, agitated in extract for one hour) by using an ultraviolet/visible spectrophotometer. The change in absorbency can then be correlated to micrograms of residual rosin per square inch of test sample surface area.

Test samples for this study were prepared by wave soldering of PWAs using a mildly activated rosin flux. Test samples were cleaned for four minutes, either in CCS or a terpene component alone, using a production batch-type spray cleaner. The samples cleaned in CCS were spray rinsed for four minutes in 140-degree F deionized water (>1MΩ-cm resistivity). Sample groups cleaned in the terpene component alone were spray rinsed either in straight DI water, as with the CCS group, or a one-minute and 30-second IPA spray rinse followed by a four minute warm DI-water rinse.

In another investigation, two identical sample sets were prepared by electroplating 2 microns of gold over 2 microns of nickel on 12.5 x 12.5 x 0.7 mm ASTM F-15 blanks, that were exposed to three different solvents using the processes outlined in Table 1.

Table 1. Sample Set Specimens/Processes

Specimen #1 - control, as plated blanks
Specimen #2 - cleaned in Solvent "A", rinsed in Fluorinert®
Specimen #3 - soiled-paraffin grease, cleaned in Solvent "A", rinsed in Fluorinert®
Specimen #4 - soiled-RMA flux, cleaned in Solvent "A", rinsed in Fluorinert®
Specimen #5 - cleaned with DBM in vapor degreaser
Specimen #6 - soiled-paraffin grease, cleaned with DBM in vapor degreaser
Specimen #7 - soiled-RMA flux, cleaned with DBM in vapor degreaser
Specimen #8 - cleaned in CCS, rinsed in IPA
Specimen #9 - soiled-paraffin grease, cleaned in CCS, rinsed in IPA
Specimen #10 - soiled-RMA flux, cleaned in CCS, rinsed in IPA
Specimen #11 - soiled-RMA flux, cleaned in CCS, rinsed in warm water

The first specimen in each set was the experimental control reference standard. It was not exposed to any cleaning agents or processes other than the electroplating process. The rest of the specimens were exposed to each of three cleaning agents (and their associated processes), with and without exposure to intentional contaminants. The contaminant was either a mildly activated rosin flux that was baked on the specimen at 465-degrees F for three minutes or a thin film of paraffin based vacuum leak test grease that has been found to be notoriously difficult to clean.

The next three specimens in each set were cleaned in a commercially available organic solvent formulation (referred to as Solvent "A" in Table 1) in each of two identical production systems employed for cleaning of hybrid microelectronic package assemblies. The systems operate essentially as vapor degreasers and employ a perfluorocarbon rinsing agent. Specimens were baked in a 300-degree F drying oven for fifteen minutes after the cleaning step.

For specimens cleaned in dibromomethane (DBM), the solvent was boiled in a conventional vapor degreaser and the samples were lowered into the vapor for one minute, then immersed in the solvent with 40 kHz ultrasonics for three minutes (separate sump). The samples were allowed to dry by holding them in the proximity of the degreaser cooling coils for several minutes until no solvent was observed condensing on the samples or cleaning basket.

The cleaning process used for the CCS specimen group was immersion in the solvent for five minutes with swept frequency ultrasonics (20-40 kHz) and mechanical agitation, rinse in IPA (or warm DI water) with hand agitation for one minute, and dry in a solvent drying oven for ten minutes at 300-degrees F.

One sample set was analyzed for contamination using Fourier Transform Infrared (FTIR) Spectroscopy on a Nicolet Model 44 with a grazing angle sample stage. This analytical technique is very useful for the study of organic contaminants on surfaces because it provides specific information about molecular structure and chemical bonding from films as thin as twenty angstroms.

are called clean in this matrix returned either FTIR or GC/MS results that were below their respective instrument detection limit. Those labeled dirty had some detectable contaminant and in cases where this occurred, the contaminant was found to be consistent with residue of the soil originally applied.

Table 4. FTIR-GC/MS Surface Analysis

Specimen	Contaminant	Cleaning Agent	FTIR	GC/MS
1	none (control)	as plated	Clean	Clean
2	none	Solvent "A"	Clean	Clean
3	paraffin grease	Solvent "A"	Dirty	Dirty
4	RMA flux	Solvent "A"	Clean	Dirty
5	none	DBM	Clean	Clean
6	paraffin grease	DBM	Clean	Clean
7	RMA flux	DBM	Clean	Dirty
8	none	CCS/IPA rinse	Clean	Clean
9	paraffin grease	CCS/IPA rinse	Clean	Clean
10	RMA flux	CCS/IPA rinse	Clean	Clean
11	RMA flux	CCS/water rinse	Clean	Clean

The results in Table 4 indicate that Solvent "A" (with system cycle times of about thirty plus minutes) was not capable of removing the paraffin based vacuum leak test grease and, as evidenced by the GC results, was only marginally successful at removing all of the flux related contaminant. The process using dibromomethane in a vapor degreaser was successful in removing the paraffin grease, but was found to leave behind some of the nonpolar constituents of the flux contamination.

It is clear from these results that whether rinsed with IPA or water, the specimens cleaned in CCS display surfaces that can be characterized as microscopically clean. This material is capable of removing flux and vacuum grease from metallic alloy surfaces using inexpensive equipment and short cleaning process cycle times to a level deemed suitable for any critical cleaning application.

Conclusions

Synergy 3000 CCS™ is an environmentally friendly precision cleaning agent that has been developed to be a safe, effective, distillable, and long-term alternative to regulated chlorinated and fluorinated cleaning solvents. Testing and evaluation at AlliedSignal and Hewlett-Packard has demonstrated that this material is trenchant for the removal of both polar and nonpolar contaminants commonly encountered in the electronics industry.

Since its implementation for production use at various divisions of Hewlett-Packard,

The other sample set was analyzed using gas chromatography with mass spectrometry detection (GC/MS) on a Finnigan Model MAT-TSQ-70. GC samples were prepared by extraction using high purity methylene chloride. This analytical technique is a very sensitive method for finding trace hydrocarbon residue.

Results and Discussion

The ionic cleanliness test data indicate that the CCS formulation demonstrates a pronounced synergistic effect of combining the terpene and alcohol components. When compared with the terpene or alcohol component alone, the CCS results show a factor of three improvement in ionic cleanliness. The data are presented in Table 2 where the ionic cleanliness values (average of three runs) are given in units of micrograms NaCl equivalent per square inch of sample.

Table 2. Ionic Cleanliness, MIL-P-28809

Cleaning Agent	Ionic Cleanliness ($\mu gm/in^2$)
terpene component alone	9.3
alcohol component alone	6.6
CCS formulation	2.4

The results of the residual rosin test again demonstrate the improved cleaning efficacy of the CCS formulation for removing both the polar and nonpolar contaminants associated with rosin flux soldering processes. The results of the residual rosin testing are presented in Table 3 with the residual rosin values given in units of micrograms rosin per square inch of sample.

Table 3. Residual Rosin Testing

Cleaning Agent	Rinse	Residual Rosin ($\mu gm/in^2$)
terpene component	IPA	148
terpene component	IPA/water	161
CCS formulation	water	90

It is interesting to note that for the case of the terpene agent clean, the thirty-second IPA spray rinse followed by a four-minute water rinse was not as effective as the straight four-minute IPA spray rinse. It is also apparent that the CCS formulation returns acceptable cleaning results with a water rinse and does not necessarily depend on an IPA rinse for success.

The results of the combined FTIR-GC/MS surface analysis investigation are presented in Table 4. In each case the results are indicated as either "clean" or "dirty." Samples that

CCS has found applications in a number of different areas including wafer processing, hybrid microelectronic package assembly, plating and surface finishing operations as well as metalworking and fabrication shops. It is employed for hand wiping, bench top cleaning, immersion with and without agitation/ultrasonics, and spray under immersion. It has been used to replace a number of traditional cleaning solvents including acetone, toluene, xylene, 1,1,1-trichloroethane, trichloroethylene and CFC-113.

In other divisions of Hewlett-Packard, AlliedSignal, and selected companies, CCS has been beta tested for cleaning of printed circuit boards and printed wiring assemblies, as well as surface mount assemblies using linear and batch spray-cleaning systems. The solvent also shows promise for bench top cleaning using direct brushing followed by air drying.

What started as a government-industry collaboration to eliminate toxic and environmentally damaging solvents ultimately resulted in an elegant and practical solution for a number of critical cleaning applications.

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