Crown ethers added to non-polar solvents have been found to improve cleaning, alleviate expense, and appease environmental concerns.

Crown Ethers Enhance Ionic Residue Removal

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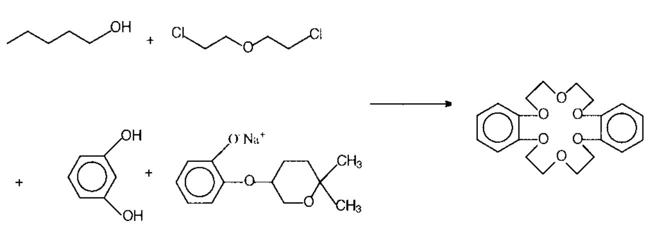
Post-solvent/solvent-blend defluxing of printed circuit assemblies, after the soldering process, has become a well-established branch of chemistry. Blends usually consist of a non-polar solvent and various moderately polar to polar solvents. Well-known examples include Freon™ TMS (CFC-113 and methanol) as well as hydrocarbon-alcohol and straight alcohol blends.

All systems to be discussed contain a non-polar solvent which exhibits solvency for the flux, as well as a polar solvent to enhance the removal of residues (i.e., salts formed during the soldering process by activators, etc.). The non-polar solvents by themselves are poor defluxers, thus requiring a flammable co-solvent to be blended with them in order to cover the broad polarity spectrum encountered with flux residues.

We have recently been able to dramatically enhance the defluxing capabilities of a large number of non-polar solvents without the use of flammable alcohols. This has been done by incorporating small amounts of a class of compounds known as "coronands" (i.e., crown ethers) into the non-polar solvent systems.

Crown ethers were first characterized in 1967 by Charles Pederson at DuPont. This occurred during a serendipitous reaction attempting to modify properties of vanadium catalysts used for olefin polymerization (i.e., to find a complexor for the vanadyl ion). The first crown ether was developed in the preparation of bis[2-(o-hydroxyphenoxy)ethyl]ether by reacting in an aqueous solution of 1-butanol bis(2-chloro-ethyl)ether with the sodium salt of 2-(o-hydroxyphenoxy)tetrahydropyran.

Figure 1
Dibenzo-18-Crown-6



The original product that Pederson was searching for had the consistency of a black, tarry, sticky substance. What he actually found was a fine, white fibrous powder, the structure of which was determined to be commonly known as dibenzo-18crown-6 (Figure 1[1]). Further evaluation revealed contaminated catechol in the reaction tube.

The work done by Pederson is important. In fact, Pederson, along with two researchers who carried his work into host-guest chemistry, won the Nobel Prize for chemistry in 1988.

Host-Guest Complexes

Crown ethers maintain the characteristics of being capable of forming stable complexes with many salts of the alkali and alkaline earth metals. One of the unique features of crown ethers is that they can chelate metal ions. Different sized cyclic ethers chelate different sized metal ions. In these particular complexes, the crown ether is referred to as the host, while the metal ion is called the guest.[2]

One advantage of having an ionic compound dissolved in a non-polar solvent is fairly evident: an ionic reagent can be dissolved in an organic phase, where it can then react with a water-insoluble organic compound.

A second advantage is that the nucleophilicity of the anions is greatly enhanced in non-polar solvents where, normally, the anion is poorly solvated. The electron donating atoms are arranged such that the electron pairs (orbitals) point inside the center of the macrocyclic ring. The highly hydrophilic cation is soluble inside the ring structure because of its size.[3]

There is a very specific host-guest relationship with respect to macrocyclic ring size and cation size. The outside of the macrocyclic ring (the part exposed to the solvent system) is relatively water insoluble, thus making the whole host-guest complex soluble in a non-polar solvent.[4]

Table 1[5] presents examples of the host-guest specificity for the listed cations, with each cation diameter being large enough to fit precisely into the corresponding crown ether cavity.

Observations of the influence of solvation and ion pairing on the behavior of ions have led to the development of a particularly effective method of removing inorganic materials, known as phase transfer catalysis.

For carrying out reactions rapidly and in high yield between organic molecules and ionic reagents, the organic substrate is

Table 1
Host-Guest Specificities Relative to Cation Size

CATION	CATION [A] DIAMETER	CROWN ETHER	CAVITY [A] DIAMETER
Li+	1.36	12-crown-4	1.2-1.5
		benzo-12-crown-4	1.2-1.5
Na+	1.90	15-crown-5	1.7-2.2
		cyclohexano-15-crown-5	1.7-2.2
		benzo-15-crown-5	1.7-2.2
		dicyclohexano-15-crown-5	1.7-2.2
		dibenzo-15-crown-5	1.7-2.2
K+	2.66	18-crown-6	2.6-3.2
		dicyclohexano-18-crown-6	2.6-3.2
		dibenzo-18-crown-6	2.6-3.2

dissolved in a non-polar organic solvent when the reagent - an ionic substance which the anion is to act upon - is dissolved in an aqueous phase.

A phase transfer catalyst is added, forming ion pairs with the reagent anion, and these pairs move into the organic layer due to the large hydrocarbon substituents on the cation. In the organic phase, the anion is solvated only very weakly by the non-polar solvent molecules and is paired with a large cation. It is consequently highly reactive.

The phase transfer cations can continue to migrate back and forth between the phases, bringing the more anionic reagent to the reacting system. Crown ethers function as phase transfer catalysts by complexing a cation and then bringing the complexed-cation-anion pair into the non-polar phase.[6-8] By complexing the cation in the cavity of the crown ether, these compounds act as solubilizing agents.

Two-Phase Dissolving

Many salts that are insoluble in organic solvents dissolve in the presence of crown ethers. Once dissolved in solvents, the anions are highly reactive since they are weakly solvated, and tight ion-pairing is precluded by the complexation of the cation by the crown ether.

As a result, the bonding ability reaches or exceeds that observed in polar solvents. Being natural ionophores, crown ethers can form a stable complex with a positively charged species [Na+, K+, Li+).[4]

The conditions for phase transfer processes involve use of a two-phase system. The organic substrate is dissolved in a water-insoluble organic solvent, such as a hydrocarbon or halogenated hydrocarbon; the ion is dissolved in water.

Even with vigorous mixing, such systems show little tendency to react since the compound reacting with the organic material and substrate remains separated in the aqueous and organic phases, respectively. This situation changes with the addition of a phase transfer catalyst[9]

When the catalyst groups are sufficiently large to solubilize the crown ether in the organic phase, the cations carry anions from the water phase into the organic phase to maintain electroneutrality. As a result, the anions are not strongly solvated in the organic phase. Consequently, crown ethers may be retrieved from a two-phase system and reused without damage to the initial structure.

By adding an aqueous phase, the crown ether will align itself between the organic and aqueous phases, release its captured cation into the aqueous phase, and then remove another cation from the organic phase.

Benefits Formulated

The evolution of circuit board cleaning has been influenced by many factors, in eluding cost, the degree of cleanliness required, and environmental ramifications.

The high cost of many solvent systems can be minimized through use of crown ethers in the cleaning system. Because the crown ether analogs will increase the cleaning properties of the solvent, less solvent will be required and less expense incurred. Over a period of time, expense for waste removal will also be minimized. Even if the cleaning capabilities of the crown ether are spent, the non-polar solvent will still clean without modification.

The addition of crown ethers into the non-polar solvent system promises cleaning ability beyond the defluxing of printed circuit boards. Whenever removal of ionic contamination is necessary - potassium or sodium, for example - crown ether/non-polar solvent mixtures will clean effectively.

Crown ethers are considered environmentally "friendly." They contain no chlorines, are biodegradable, have minimal atmospheric emissions due to low vapor pressure, and are non-volatile and non-flammable. Thus, ozone depletion potentials (ODP) and greenhouse warming potentials (GWP) are zero.

Crown ethers can be easily recovered and recharged. One hundred percent recyclable, they are a renewable and reusable cleaning material. The solvent itself can be "recharged" by being passed through a water bath which will relieve the crown ether of its ion, allowing the solvent to be used until saturated with lipophilic contaminates rather than be disposed of because the hydrophilic component is saturated with ionic contaminates.

When the solvent is saturated with material, the crown ethers can be recovered before the spent solvent is sent to the recycler. The crown ethers are then put into the next solvent batch. This means that active solvent could be used for longer periods of time, which would be beneficial for EPA-mandated waste minimization plans going into effect.

Experimental Procedure

The following method of testing is a modified form of the Phase 2 type tests designed by the EPA/DOD/IPC Ad Hoc Solvents Working Group to evaluate alternatives for reducing the level of chlorofluorocarbons used in electronics manufacturing cleaning processes.[10]

FR-4 laminate (epoxy-glass) test boards had a surface area of 36 square inches. The appropriate flux was applied, saturating the non-traced side of the board for one minute, and then the boards were allowed to dry at room temperature.

Using Chromolox heaters, the fluxed side of the test boards were exposed to temperatures of 1200°F to 1500°F, passing one-sixteenth inch below the heaters for 30 to 40 seconds, and then allowed to cool to room temperature.

The boards were then placed, for six minutes, in a Branson 5200 ultrasonic cleaner containing the appropriate solvent formula. Then, for another six minutes, boards were subjected to an ultrasonic rinse of the same solvent. After the rinse and drying at room temperature, the boards were placed in an Alpha 500 M ionograph.

Three fluxes were used in the cleaning evaluation, each from AlphaMetals: rosin mildly activated (RMA Flux), rosin (R Flux), and synthetically activated (SA Flux).

The solvents used for experimental data include Freon 113 (DuPont), a CFC; hexane (Aldrich reagent grade), an aliphatic hydrocarbon: toluene (Aldrich reagent grade), an aromatic hydrocarbon; and BioAct EC-7 (AlphaMetals), a terpene. Each of the solvents was chosen for its chemical properties among a wide spectrum of solvents.

The first set of experiments was performed using each of the solvents in their "virgin" states of 100 percent solution. The second series of experiments included compositions consisting of 99.4 percent solvent solution, 0.1 percent 12-crown4, 0.4 percent 15.crown-5, and 0.1 percent 18-crown-6 crown ethers (Aldrich reagent grade).

The third series of experiments included a composition consisting of 96.54 percent solvent, 0.1 percent 12-crown-4, 0.4 percent benzo- 15-crown 5,0.1 percent dibenzo-18-crown-6 crown ethers, and 2.86 percent dichloromethane (Aldrich reagent grade) for solubility purposes.

Results

Table 2 outlines results of the ionograph testing. Comparing all percentages not of the pure nature with the pure solvent shows that, in all cases, the crown ethers, even at low percentages, increased the cleaning ability of the solvent. In some cases, the

Table2

PCB Cleaning Performance with Various Mixtures of Crown Ethers and Straight Solvents

CROWN ETHERS (%)

SOLVENT	%	12C4	15C5	BENZO 15C5	18C6	DIBENZO 18C6	DCM	RMA vglsq	R FLUX pg/sq	SA FLUX pg/sq
Freon 113	100	-	-	-	-	-	-	54.26	22.13	90.71
Freon 113	99.4	0.1	0.4	-	0.1	-	-	47.98	9.21	32.63
Freon 113	96.5	0.1	-	0.4	-	0.1	2.86	21.25	6.09	26.74
Hexane	100	-	-	-	-	-	-	33.96	11.14	76.31
Hexane	99.4	0.1	0.4	-	0.1	-	-	10.30	6.31	22.96
Hexane	96.5	0.1	-	0.4	-	0.1	2.86	19.03	7.85	33.69
Toluene	100	-	-	-	-	-	-	51.39	30.95	129.11
Toluene	99.4	0.1	0.4	-	0.1	-	-	37.52	4.25	12.16
Toluene	96.5	0.1	-	0.4	-	0.1	2.86	8.23	5.99	24.76
BioAct EC7	100	-	-	-	-	-	-	22.92	22.47	32.36
BioAct EC7	99.4	0.1	0.4		0.1	-	-	13.99	21.07	28.84
BioAct EC7	96.5	0.1	-	0.4	-	0.1	2.86	18.97	5.27	25.34

solution cleaned better by as much as 90.57 percent.

The percentage of crown ethers never went beyond 0.6 percent by weight. The difference between the boards cleaned with straight solvent - as opposed to solvent mixed with differing percentages of crown ethers - is fairly evident.

In all of 36 tests performed, the solvent with the crown ethers cleaned better than the original solvent. By breaking down the results even further, averages of cleaning ability compared to the first series of 100 percent solvent can be taken to determine the overall effectiveness of crown ethers as cleaners.

For the RMA flux, the second series consisting of 0.1 percent 12-crown-4, 0.4 percent 15-crown-5, and 0.1 percent l8-crown-6 cleaned 36.80 percent better than did the original 100 percent solvent. The third series consisting of 0.1 percent 12-crown-4. 0.4 percent benzo-15-crown-5, and 0.1 percent dibenzo-l8-crown-6 cleaned 51.51 percent better than did the first series with 100 percent solvent.

For the R flux, the second series cleaned 48.55 percent better than the straight solvent, while the third series increased cleaning ability by 64.80 percent. For the SA flux, the usual pattern is followed, where the second series cleaned 58.85 percent better, while the third series cleaned better by 57.22 percent.

Continuing Research

It is apparent from the data that crown ethers would increase the ability of all non-polar solvent cleaning systems. In cases where “ultra” clean (i.e., relatively free of all ionic contamination) substrates are required, ion-specific coronands may be incorporated into existing solvent systems to achieve this most desirable effect.

While the experiments presented were performed with a crown ether percentage of 0.6 percent by weight, continuing research focuses on creating concentrations with greater than 1 percent. How well these solutions clean will be most interesting. The greater the crown ether percentages, the greater the cleaning ability of the solvent.

As has been demonstrated, crown ethers enhance the cleaning ability of nonpolar solvents by a minimum of nearly 50 percent. The limit to how well a solution can clean by adding enhancement factors will soon be determtned.

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