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Room temp, 23°C

SEMIQUANTITATIVE GAS CHROMATOGRAPHY-MASS SPECTROMETRY ANALYSIS OF ORGANIC COMPOUNDS OUTGASSING FROM A POLYURETHANE SAMPLE.

EXPERIMENTAL

Two glass bottles containing the components for a two part urethane sealant were received at Balazs. One bottle was labeled urethane, Softseal A, 90-0701, and contained a viscous blue liquid. The other bottle was labeled urethane, Softseal B, 90-0702, and contained a yellow liquid.

The mixing instructions from W.M. Plastics were as follows: Add the blue component to the clear component, 1:1 by volume. Mix with a glass rod for five minutes.

The densities of the two components were measured and it was found that the two components had similar densities. Since the densities of the two components were equivalent they were mixed 1:1 by weight . The exact weights used were Softseal B (yellow) 24.88 g and Softseal A (blue) 24.87 g.

The mixed gel was transferred to an aluminum channel. The dimensions of the channel were 6" long x 3/4" wide x 1/2" deep to simulate a "HEPA" grid. The channel was filled 1/2" with the gel. The gel sample was cured in a glass chamber at room temperature (23±1°C) with 40% relative humidity purified air, at a flow rate of 200 mL/min for 1 week. At the end of the 1 week cure a stainless steel sample tube packed with a proprietary adsorbent was used to collect the outgassing from the sample for 1 hour.

GC-MS ANALYSIS

The sample tube was thermally desorbed using an automated thermal desorption system, followed by GC-MS (Gas Chromatography - Mass Spectrometry) analysis for identification

and quantitation of the trapped organic compounds. The method has been described in a recent publication (Contamination Control Proceedings of the IES Annual Technical Meeting, May 7, 1997 "Organic Outgassing from Cleanroom Materials Including HEPA/ULPA Filter Components: Standardized Testing Proposal" by M. Camenzind and A. Kumar).

A Perkin-Elmer ATD-400 automated thermal desorption system connected to a HP 6890 GC (gas chromatograph) and HP 5972 MSD (Mass Selective Detector) were used for sample tube analyses. The sample tube was purged with helium then thermally desorbed at 350°C for 30 minutes using an automated thermal desorption system. During this time, all outgassing organic compounds were passed into a helium carrier gas and were cryofocused onto a secondary adsorbent trap containing activated carbon (the secondary trap improves the peak shapes for the chromatography, allowing better identification, quantitation, lower detection limits, and improved recovery for low-boiling compounds). This secondary trap was then desorbed at 350°C, and trapped organic compounds were passed onto a GC-MS system. An internal standard of d8-toluene was added to each sample during the analysis. A non-polar poly(dimethylsiloxane) phase capillary GC column was used for separating compounds. The initial column temperature was held at 35°C for 3.5 minutes, ramped at a rate of 10°C/minute to 280°C, then held at this temperature for 10 minutes. Each compound passed down the column at a characteristic rate. As each compound exited the gas chromatograph, it entered the mass spectrometer where compounds were ionized using electron impact ionization (70 eV). Mass spectra (10-700 amu) were recorded using a quadrapole mass spectrometer. A full mass spectrum was collected and stored approximately once per second. Identification of each compound detected was first attempted by searching a Wiley library of 275,000 mass spectra. In cases that no matches were found, mass spectra were interpreted manually to give our best estimate of the most probable compound or class of compounds.

A hydrocarbon standard was analyzed using a separate tube. This tube contained a proprietary adsorbent to adsorb the standard. A hydrocarbon mixture containing 500 ng each of a series of n-alkanes, from n-hexane to n-octacosane ($C_{28}H_{58}$), was added to the tube, and the tube was purged with nitrogen to remove the carrier solvent. This tube was desorbed in the same manner as the other tubes mentioned above. The standard was used to calibrate the instrument only, and gives not only an assessment of the sensitivity of the GC-MS, but also the boiling point of compounds that could be detected by the instrument. Note that the surface area, sample thickness, cure time, gas flow rate, and the outgassing time period are variables that can affect the amount of outgassing detected.

RESULTS & DISCUSSION

The data from the outgassing analysis of the polyurethane sample are summarized in two different ways:

1) By boiling point ranges. Semiquantitative analyses of the amounts of organic compounds were calculated by using the TIC (Total Ion Count) response factor for an n-decane standard. The organic compounds were classified into low-boiling (>C6-C10), medium-boiling (>C10-C20) and high-boiling (>C20) ranges, based on comparisons with the retention times of a C6-C28 n-hydrocarbon external standard. The total organic compounds falling into each of these three ranges, and the sum of all organics detected for the dynamic headspace outgassing of the polyurethane sample are summarized in Table I in units of ppmw (parts per million by weight or µg/g) and Table II in units of µg/12' HEPA perimeter/hour (this corresponds to one 2' X 4' HEPA filter).

2) Individual compounds. The semiquantitative analyses of individually identified compounds was carried out using the TIC area response factor for an n-decane standard. These results for the dynamic headspace outgassing from the polyurethane sample are presented in Table III in units of ppmw in Table IV in units of µg/12' HEPA perimeter/hour.

TABLE I. Total organics outgassed from a polyurethane sample at room temperature for one hour by boiling ranges after a 1 week cure. Cure conditions: 200 ml/min 40% relative humidity air, room temperature (23±1°C). Results are reported in units of ppmw.

Sample ID	Low boilers >C6-C10	Medium boilers >C10-C20	High boilers >C20	Sum >C6
Softseal urethane 1 week cure, RT	<0.5	0.5	<0.5	0.5

TABLE II. Total organics outgassed from a polyurethane sample at room temperature for one hour by boiling ranges after a 1 week cure. Cure conditions: 200 ml/min 40% relative humidity air, room temperature (23±1°C). Results are reported in units of µg/12' HEPA perimeter/hour.

Sample ID	Low boilers >C6-C10	Medium boilers >C10-C20	High boilers >C20	Sum >C6
Softseal urethane 1 week cure, RT	<200	226	<200	, 226

TABLE III. Calculated levels of identified organic compounds outgassed at room temperature from a polyurethane sample after a 1 week cure. Cure conditions: 200 ml/min 40% relative humidity air at room temperature (23±1°C). Results are reported in units of ppmw.

Identified Compounds	Softseal urethane 1 week cure, RT
Semiquantitated Compounds	
C8-C9 Hydrocarbons	<0.5
Medium-boiling esters	0.5

TABLE IV. Calculated levels of identified organic compounds outgassed at room temperature from a polyurethane sample after a 1 week cure. Cure conditions: 200 ml/min 40% relative humidity air at room temperature (23±1°C). Results are reported in units of µg/12' HEPA perimeter/hour.

Identified Compounds	Softseal urethane 1 week cure, RT
Semiquantitated Compounds	
C8-C9 Hydrocarbons	<200
Medium-boiling esters	224

Note: The detection limit for each component from this sample was 0.5 ppmw or 200 µg/12' HEPA perimeter/hour. Lower detection limits are possible for selected compounds. Semiquantitated compound concentrations were calculated based on the n-decane external standard TIC response factor. d8-Toluene was used as an internal standard.

The labeled chromatogram is given in Figure 1. The retention times for each compound are given on the bottom of the chromatograms and the relative abundance on the left, vertical scales. The ion chromatograms plotted represent the sum of all ions within the mass range 33-700 amu. Mass spectra were collected for the time range of 1-38 minutes but only the range of 3-35 minutes was plotted since all peaks of interest fall within this range. The mass spectrometer detector becomes partially saturated at abundance's over 2×10^7 (not observed for this set of samples). In general, for similar classes of compounds, longer retention times correspond to higher boiling compounds. The area under the chromatogram roughly correlates with the amount of each compound present.

This test method was designed to trap semivolatile compounds only. Some polar organic compounds with lower boiling points may not be trapped effectively by this method (e.g. methanol, IPA). Hydrocarbons with boiling points significantly lower than hexane (bp 69°C),

or other low-boiling compounds may not be recovered well. Some high-boiling or unstable compounds may not have good recoveries.

Analysis of the hydrocarbon standard demonstrated that the analytical instrument can readily detect ppm levels of semivolatile compounds outgassed from polymers. Outgassing compounds could be detected with boiling points from that of hexane (bp 69°C), to at least octacosane (bp 432°C, retention time 34.1 minutes). Since the chromatogram was collected to 38 minutes, it is likely that compounds with boiling points of up to ≈ 450°C (C30 hydrocarbons) could be detected by this method. For compounds within this boiling-point range estimated detection limits were about 0.5 ppmw or 200 µg/12' HEPA perimeter/hour for any single component.

The C8-C9 hydrocarbons are common solvents used in the manufacture of polymers.

The medium-boiling esters were probably added as plasticizers.

CONCLUSIONS

In general medium boiling compounds could deposit onto a wafer and cause problems with wetting, etching or other processes.

Please call if you have any questions regarding this report.

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CJC
Enclosure: 1 Chromatogram

Figure 1: Dynamic headspace gas chromatography-mass spectrometry analysis of compounds outgassed from Softseal urethane after 1 week cure. Cure conditions: room temperature (23°C) with flow rate 200 mL/min, 40% RH air. Sample collection time was 1 hour. d8-Toluene is an internal standard.