Chapter II

Outgasing of Adhesives & Dynamic Headspace Analysis

During drive operation, the spindle motor rotates the disk at a designed speed. As a result of the operation, heat is generated and it volatilizes the organic compounds within the HDD components. The outgassed compounds will then condense on the disk. These compounds will smear the head when it 'flies' on the disk during read-write operation. Consequently, the head will not be able to read/ write data. Outgassing test plays an important role in capturing volatile organic compounds that outgas from the HDD components. In the following sections, the outgas phenomena of adhesives compounds will be discussed.

2.1 Outgassing of Adhesives

Generally, 'outgas' is a term used to describe the phenomena of 'release of chemical compounds' to the environment from a component/ material. The IDEMA defines outgas as 'entrainment of volatile species in surrounding fluid medium such as air stream in head disk enclosure'.

In the recent years, a large percentage of the outgassed compounds detected in HDD originates from the adhesives. Adhesives used in the HDD are the structural adhesives and pressure sensitive adhesives (PSA) [5].

Pressure Sensitive Adhesive (PSA) is widely used as seals and labels in the HDD industry. They are permanent tacky polymers or polymer blends where the bonding mechanism is based on Van Der Waals forces. Nearly all PSA used in HDD are solution acrylic polymers. The polymers are based upon monomer selection, molecular weight and cross-linking chemistry. Primary monomers used in PSA are 2-ethyl hexyl acrylate, butyl acrylate, vinyl acetate, methyl acrylate and acrylic acid. These compounds can cause corrosion to the pole and disk and can be detected via GCMS. Over the years, the PSA industry has gone through significant improvements in bonding applications technology that reduce the outgassing level [6]. These include:

- Reducing volatile organic compound by weight
- Eliminating acrylic acid which causes head corrosion and media fogging
- Developing organo-tin free and silicone free release liner

Structural adhesives are found in many forms and they are used in the assembly of HDD sub components. These adhesive can be classified according to their curing process. Anaerobic curing reaction happens in the absence of oxygen and the presence of active metal surface. In this condition, free radicals initiate the polymerization process. It may also be cured by heat. Some adhesive cured when they are exposed to ultraviolet (UV) radiation at the correct wavelength and intensity. In the UV radiation, the photoinitiators are split to produce free radicals, which then

start the polymerization. Cyanoacrylates cured rapidly on contact with slightly alkaline surfaces. In general, the ambient humidity in the air is sufficient to initiate the curing process. Adhesive cured with activator systems (modified acrylics) requires the application of an activator.

The acrylates/ methacrylates, being the major compounds of the adhesives are found outgas at a very significant level from HDD components such as motor. Figure 4 shows examples of HDD motors.

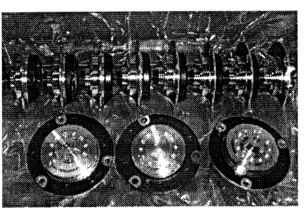

Figure 4. Examples of HDD motors

The HDD motor is assembled from various sub components such as stator wire coil, the motor bracket, hub, magnet, shaft, bearing and labyrinth seal. These sub components are assembled by the application of various types of adhesives. The outgas level of a spindle motor adhesive depends on type of adhesive, amount used and curing process. The application of adhesive on the assembly of the spindle motor is indicated in Figure 5 [7].

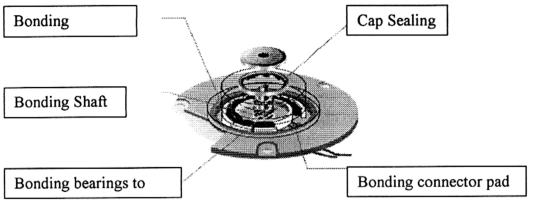

Figure 5. Adhesive Application in HDD Motor (Source: Ref. 7)

An example of the cap sealing adhesive is the Threebond 3061H, which is a UV cured adhesive. It cures in not more than a few tens of seconds where the curing process will change the adhesive color. The adhesive is claimed to have very little adverse effects on HDD media as very little outgassing occurs during thermal aging after curing under UV irradiation. Adhesive used for bonding the magnets is a type of cynoacrylate whilst the for bonding shaft, the anaerobic curing adhesive is being used [7]. As the technology for spindle speed increase (10,000 rpm at current technology), the spindle motor cleanliness has become more challenging. The control in the area of lower outgassing is of particular concern.

Evaluation on the HDD motor adhesive curing process is carried out by comparison of curing time to its outgas amount. One of the methods applied to outgassing of adhesives is the dynamic headspace (DHS) outgassing test procedure. In the following section, a general DHS test will be discussed.

2.2 Headspace Analysis

2.2.1 Static Headspace vs. Dynamic Headspace

Headspace sampling method and GCMS are used for outgasing test in HDD industry. Headspace analysis relies totally on volatization to extract the analytes from a solid matrix and injected into the GC as a vapour. There are two types of outgassing analysis applied in HDD industries, i.e. Static headspace (SHS) and dynamic headspace (DHS).

In SHS analysis, samples are sealed in the sample vials and introduced into an oven where the vapor sample equilibrium is established. The vials are heated at a constant temperature for a sufficient period of time. After a pre-programmed time, the vial is pressurized to column head pressure by the sampling needle and the valves are switched so that sample vapors from the vial pass directly onto the GC column. Examples of the SHS analyzer are the HP7694 and Perkin Elmer HS40 that has auto-sampler devices.

In the recent years, most of the HDD manufacturers have adopted the DHS technique. DHS analysis uses a different sampling technique than SHS, instead of the 'static' equilibrium vapor sampling, the DHS apply a 'dynamic' vapor non-equilibrium sampling method. Samples are heated at elecvated temperatures in an inert sampling container to drive the volatile compounds from the sample matrix into the atmosphere above the sample, called headspace. A measured flow of dry nitrogen gas is used to purge the outgassed compounds continuously to an adsorbent for a period of time. The adsorbent is then subjected to thermal desorption in reverse flow and the

compounds are trapped into the inlet of a GC. In order to concentrate the desorbed compounds, the cryogenic injection system is used, where the inlet temperature is cooled down to –30 °C or lower during concentrating process and flash heated to injection temperature during injection process. The GC separate the compounds and the mass spectrometer analyze them.

The comparison of SHS and DHS analysis techniques was reported [8]. Six common plastic additives: four plasticizers (di-octyl adipate, di-ethyl, butyl, otctyl phthalate), an antioxidant (Butylated hydroxy toluene) and a flame retardant, tris-chloroethyl phosphate were analyzed. It was reported that the total quantity of material outgassed at a given temperature is the function of both its equilibrium vapor pressure and the diffusivity of the sample matrix. SHS was reported to have less efficient at recovery than the DHS for high boiling point compounds. Comparison of SHS and DHS parameters is shown in Table 1.

Parameter	SHS	DHS
Sampling technique	Equilibrium Static sampling	Non-equilibrium Dynamic sampling
Sampling Container	10 mL/ 20 mL vials	Must be <4 inches diameter
High Boilers	Less Recovery	More Recovery
Volatile Compounds	Yes	No
Solvent Use	No	Yes
Limit of Detection	Higher	Lower

Table 1. Comparison of SHS and DHS techniques (Source: Ref 8)

2.2.2 Dynamic Headspace/ GCMS analysis

2.2.2.1 Sampling

Sampling containers are usually custom made for required volume and size. The containers are made of inert materials that do not react with the chemical compounds or solvent and at the same time can stand the operating temperature. Common materials used are the Teflon and stainless steel fittings. These containers are placed in an oven that has a built in timer and temperature controller. All tubing that connects from the gas source to the containers and from containers to the adsorbent should be made of inert material.

The adsorbent material plays an important role in trapping, retaining and releasing the compounds of interest during the thermal desorption without thermal decomposition. The rate of release will be as rapid as possible to minimize analysis time. Solid adsorbent is characterized by a high specific mass/ volume surface area. The pore size classification by their average diameter (d_{pr}) is as follows [9]:

Macropore : $d_{pr} > 50$ nm

Mesopore : $50 > d_{pr} > 20$nm

Micropore : $2 > d_{pr} > 0.4$ nm

Submicropore : $d_{pr} < 0.4$ nm

Common adsorbents used for DHS application are the graphatized carbon blacks. Graphitisation reduces both polarity and microporosity to give an adsorbent with a highly homogeneous surface. Thus, graphitized carbon blacks are non-porous, non-polar, inert materials suitable for analysis of gases sample. Carbotrap B and Carbotrap C are non-porous graphatized carbon blacks that trap a wide range of organic compounds. Carbotrap B has a larger surface area than the Carbotrap C (100 m^2/g vs. 10 m^2/g) and thus it is used for trapping lighter compounds, from C5 to C12. Carbotrap C traps larger air borne molecules, in the range of C12 to C20. Another example of adsorbent used in DHS is Tenax TA, a porous material based on 2,6-diphenylene oxide polymer. Tenax TA has a surface area of 35-40 m^2/g and pore size of approximately 200 nm.

The purge gas used to bring the vapor from the headspace of sampling container to the adsorbent should be inert. Nitrogen gas (99.99%) or helium gas (99.99%) can be used but the former is usually preferred due to lower cost. The purge gas is connected to each sampling chamber and controlled by fine needle valves to ensure delicate flow control.

Two types of outgas temperature are being used in most of the HDD industries, i.e. low temperature outgas at 85 °C and high temperature outgas at 120 °C. The sampling duration specified is 3

hours. This is adopted in almost all suppliers and drive manufacturing companies.

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2.2.2.2 Thermal Desorption System (TDS)

The compounds adsorbed on the adsorbent are desorbed at a suitable temperature by a TDS. TDS extraction method is advantageous over the other solvent extraction method as it does not dilute the samples. The desorption temperature for graphitized carbon can be as high as 350 °C. The desorbed compounds, purged by dry helium gas (99.999%) will flow through a transfer line to the cryogenic trap. Cryogenic trap is maintained at a very low temperature, for example – 30 or –100 °C, depending on the cooling device. It serves to concentrate the solutes to a small volume. When desorption process is completed, the cryogenic trap is flash heated. Within a few seconds, the temperature change to reach the injection temperature and the desorbed samples are injected into a GC column. The TDS is coupled to an auto sampler (from 20 to 50 samples run).

There are various makes of the TDS systems available in the market. Gerstel (Figure 6) offers highly sensitive thermal desorption device that utilize a short inert transfer line (14 to 15 cm) and the cryogenic trapping of analytes during desorption. The lowest cryogenic trapping temperature can be at –150 °C by using liquid nitrogen as the cyrogenic medium.

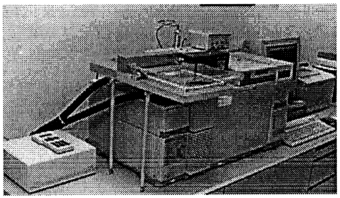

Figure 6. Gerstel TDS2/CIS4 coupled to Agilent GCMS

A Perkin Elmer ATD400 is shown in Figure 7. The unit has a long transfer line (~1 m) that is connected to the GC column. The GC column itself can be connected directly to the TDS outlet. This will increase the sensitivity of detection. The instrument uses electrical Peltier cooling system and liquid nitrogen cooling system where the latter is optional. ATD400 has a 50 tubes autosampler.

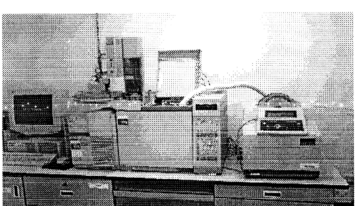

Figure 7. ATD400 coupled to Agilent GCMS

There are TDS with built-in sampling containers. These TDS offers advantages as the errors in manual sampling procedure can be avoided. The sample is placed in each chamber and the inlet flow path is directly connected to a built-in adsorbent. Thus, desorption process can immediately take place when the sampling process ends. However, the very significant draw back in these type of instruments are the significantly low throughput as only one built-in adsorbent is available and this cause longer total analysis time.

2.2.2.3 Gas Chromatography-Mass Spectrometer

Figure 8 shows a schematic diagram of a GCMS. The invention of mass spectroscopic technique has brought traditional chromatographic technique compound identification to another stage. GC was the first technique to be interfaced to a mass spectrometer and development of capillary columns enable direct interface to the mass spectrometer.

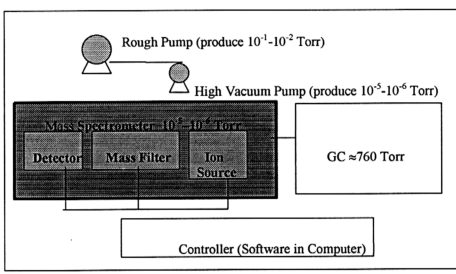

Figure 8. Schematic diagram of a GCMS

MSD functions in high vacuum as it provides adequate mean free path and collision-free ion trajectories, reduces ion-molecular reactions and background interference at the same time increases filament lifetime, sensitivity and avoid electrical discharge. Helium is used as the mobile phase as it is an inert gas, with a high ionisation potential of 24.6 eV.

When the gaseous sample is injected into the GC column, separation of compounds occurs. The separated compounds will enter the mass spectrometer and undergo mechanism as illustrated in Figure 9.

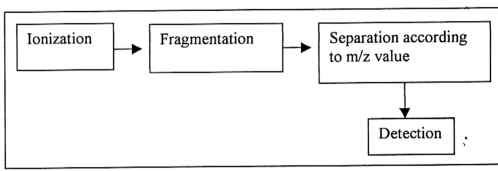

Figure 9. Basic Mechanism In Mass Spectrometer Detection

The ionization and fragmentation steps take place in the ion source. Once the analytes enter the ion source, they are ionized. Electron Ionization (EI) or hard ionization mode is commonly used for HDD industry application. In EI mode, molecules are bombarded by high-energy electron hence producing fragments of ion in different abundance. The fragments of molecular ions (usually positive charge) will then be accelerated and directed to the mass analyzer.

A quadrupole mass analyser scans sufficiently rapid for 'on the fly' analysis, ie. spectrum is obtained in a fraction of a second as the sample emerges from the chromatograph. Fragments of ions with different mass to charge (m/z) ratio and abundance are separated according to their m/z values.

Detector in the mass spectrometer usually consists of a high-energy dynode (HED) and an electron multiplier (EM). The HED attracts the positively charged ions exit from the mass analyzer. When the ion beam hits the HED, electrons are emitted. The electrons are attracted to the EM, which will amplify the signal. The computational software controller records the signal output. With the aid of the microprocessor in computer, large amounts of data can be sensibly and rapidly analysed and compared with reference spectra. Based on the principal of ion fragments separating according to their mass-to-charge ratio (m/z), the mass spectrometer may be set up to detect compounds range from $10^{-7}$to 10^{-13} g.

The TDS coupled to GC has the TDS cryogenic trap serves as the GC injection port. Flash heating of the cryogenic trap will inject the analytes into the GC column. For most of the HDD companies, the mass spectrometer used is the quadrupole analyzer with Electron Impact ionization mode. Mass spectrum produced in total ion current mode enable the compound identification via matching with mass spectrum library. Common commercial mass spectrum libraries are the Wiley275 and the NIST98. To make the identification of compounds easier, the GC-MS is equipped with software for users to set up their own mass spectrum library. This is carried out by injecting known standard compounds to the GCMS and the mass spectrum obtained is input to the library database.

2.3 Objective of Project

The primary objective of this project is to apply the DHS/GCMS technique to study the outgassing compounds of four types of motors semi quantitatively. Due to proprietary concern, the names of the companies are confidential and thus withheld. Motors will be labeled as supplier A, B, C and D

After identifying the compounds that outgassed from the motors, the secondary objective is to establish a full quantification method to determine the acrylate/methacrylates that commonly outgassed at a significant amount across the motors. Calibration curves for these compounds will be established for accurate quantification purpose.