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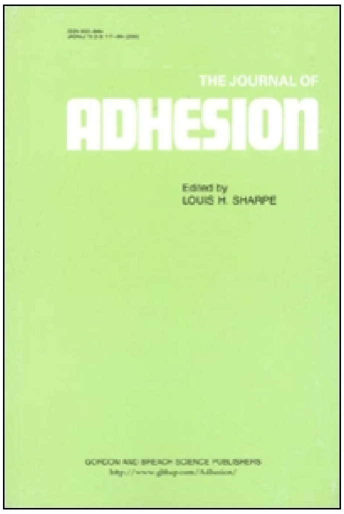

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Elimination of Outgassing from UV Curable Adhesives

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Outgassing of volatile compounds from UV curable adhesives was shown to corrode thin film magnetic disks. Volatility of the corrosive species was dependent on the adhesive's glass transition temperature, which varied linearly with flexibilizer concentration. Thermogravimetric analysis revealed that outgassing was reduced an order of magnitude in adhesives containing reduced concentrations of a polycaprolactone-based flexibilizer.

KEY WORDS: UV curable adhesives; outgassing; corrosion; glass transition temperature; hard disk drives; thermogravimetry.

INTRODUCTION

In hard disk drives, the read/write head flies over the disk on a load-bearing film of air. In order to achieve higher recording densities, the read/write head-to-disk gap, currently $\leq 0.1\,\mu m$, is constantly being reduced. Any material that adsorbs onto the thin film disk and alters the flying height of the head can cause the disk drive to malfunction and, in extreme cases, to crash. Mass transfer of volatile contaminants within the disk drive leads to liquid-like condensation at the head/disk interface.[1] Upon exposure to localized high temperatures or humidity, these adsorbed species can induce corrosion or chemical degradation which affects the flying height of the head over the disk.[2] Intense effort has been focused on minimizing or eliminating volatile organic components from disk drive materials. Since UV curable adhesives are typically used in very close proximity to the disk, elimination of outgassing from these materials is of paramount importance.

Due to a combination of several attractive features, UV curable adhesives have been used in sundry operations in the fabrication of hard disk drives. Typical requirements for any UV curable adhesive slated for use within a disk drive include:

- Pseudoplastic behavior (shear thinning)
- Rapid cure (tack time < 15–30 sec)
- 100% solids formulation (no volatile solvent)
- Low volatility

The adhesive must exhibit pseudoplastic, or shear thinning, behavior in order to facilitate dispensing as well as to prevent adhesive sag. Rapid cure is essential to ensure adequate throughput as well as to minimize tooling and fixture costs. The material should preferably be 100% reactive, devoid of solvent, and comprised of non-volatile components in order to curtail outgassing into the disk drive.

Elimination of outgassing from UV curable adhesives can be accomplished in either one of two ways: removal of the volatile component from the material, or trapping the volatile species within the adhesive. Experience has shown that removal of a component from an adhesive formulation can deleteriously affect the properties of the adhesive. Therefore, this paper focuses on trapping the volatile species within the adhesive in order to minimize outgassing into the disk drive.

EXPERIMENTAL

Commercially available, UV curable adhesives (not identified for proprietary reasons) were purchased from various vendors and used as received. The adhesives were cured according to the manufacturer's recommendations using a Fusion® Systems Model F300 UV exposure unit. The F300 was equipped with an electrodeless Hg D bulb set to deliver 4.5–5.0 J/cm^2 at the sample surface, measured *via* an International Light IL 1700 radiometer.

Union Carbide ERL 4221 (a cycloaliphatic epoxide), Dow DER 361 (a bisphenol A epoxide), Dow Voranol 2070 (a polyether triol), Union Carbide UVI 6974H (a 50 wt% solution of mixed triarylsulfonium salt photoinitiators in propylene carbonate), and Cabot Cab-O-Sil M-5 (amorphous, fumed silica) were kindly provided by the respective vendors and used as-received. Formulations were prepared based on weight percent of the total epoxy resin weight and cured as previously described.

Functional corrosion testing of novel adhesive formulations was performed by dispensing the adhesive onto a stainless steel substrate, photochemically curing the adhesive, then fixturing the adhesive 1 mm above the surface of the disk in such a fashion to ensure that the adhesive was in direct line-of-sight with the disk surface. Stainless steel substrates without adhesive served as controls. The entire fixture was then subjected to temperature and humidity aging for a period not exceeding 21 days. Accelerated aging was conducted at 60 C/80% RH; storage aging was carried out at 32 C/85% RH. Following temperature and humidity exposure, the disk surface was visually inspected for evidence of corrosion *via* optical examination. The severity of disk corrosion was qualitatively assessed by means of a figure of merit scale:

- 3 = gross corrosion evident under ambient light conditions
- 2 = corrosion evident under bright light illumination
- 1 = corrosion evident at 5–10X magnification
- 0 = no corrosion observed under magnification (5–10X)

In all cases, no evidence of corrosion was observed for the control samples. In those cases where corrosion was observed, surface analysis (AES) was utilized to determine the corrosion products. Depth profiling was accomplished using a Physical Electronics Model 670 Nanoprobe spectrometer. The sample was bombarded with 3.5 KeV Ar$^+$ ions to achieve an etch rate of 40–50 Å/min.

Glass transition temperatures were determined by preparing test bars of the appropriate dimensions and fixturing them within the furnace of a Perkin Elmer DMA 7 dynamic-mechanical analyzer. For all cases, the frequency was held constant at 1 Hz and the temperature ramped at 5 C/min. The T_g was taken as the peak in the loss modulus *vs* T scan.

Isothermal outgassing analysis was performed on Perkin Elmer TGA 7 thermogravimetric analyzer. The isothermal temperature was selected based on the operating temperature of current hard disk drives.

RESULTS AND DISCUSSION

During the fabrication of hard disk drives, UV curable adhesives are used in sundry bonding operations ranging from wire tacking to voice coil assembly. As such , the cured adhesives typically reside in direct line-of-sight of the thin film disk. During storage conditions (32 C/85% RH), volatile components outgas from the adhesives, condense on the disk surface, and induce corrosion of the underlying metallurgy. Depicted in Figure 1 is an example of corrosion, evident as nodules following the disk texture lines, induced by outgassing from a commercially available, UV curable adhesive. The nodules degrade file performance by altering the flying height of the magnetoresistive head over the thin film disk. To the naked eye, the corrosion manifests itself as haze on an otherwise highly reflective disk surface. AES analysis of the nodules revealed the presence of Ni and Cl (Table I), two elements absent in non-hazed regions of the disk. Nickel is present in the disk as a protective coating over the Al substrate. However, since a magnetic layer, a carbon overcoat, and a perfluoropolyether lubricant are deposited over the Ni-plated Al, the presence of Ni at the disk surface is invariably associated with disk corrosion. The Cl signal is attributed to an outgassed component

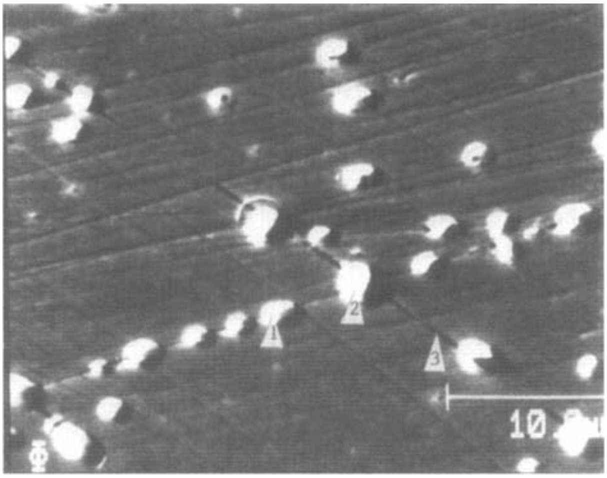


FIGURE 1 Adhesive-induced disk corrosion. The corrosion products are evident as nodules protruding above the surface of the disk.

TABLE I
AES Analysis of Disk Haze

	Atomic Percent						
	C	N	O	F	Co	Cl	Ni
As Received							
Point 1	87.3	0.0	6.3	0.8	0.0	0.5	8.6
Point 2	78.8	1.0	8.0	1.7	0.0	0.9	9.7
Point 3	97.2	0.0	2.1	0.6	0.0	0.0	0.0
Sputtered 1 min							
Point 1	68.7	1.1	5.6	16.7	0.0	0.5	7.3
Point 2	72.8	0.9	7.5	0.9	6.3	0.6	11.3
Point 3	95.6	0.8	3.6	0.0	0.0	0.0	0.0
Sputtered 2 min							
Point 1	82.0	0.0	3.1	0.0	0.0	0.0	15.0
Point 2	79.4	1.3	3.2	0.0	0.0	0.2	15.8
Point 3	98.0	0.4	0.6	0.0	0.0	0.0	0.9

See Figure 1 for location of the points.

of the UV curable adhesive. Sputtering into the nodule decreased the atomic percentage of Cl, indicating that the Cl is a surface contaminant. These results are consistent with a porous corrosion and surface creep mechanism observed for metal coatings overplated with gold.[3,4] Chlorine induces Ni corrosion at the texture lines with Ni eventually migrating through the porous overcoats or along the grain boundaries.

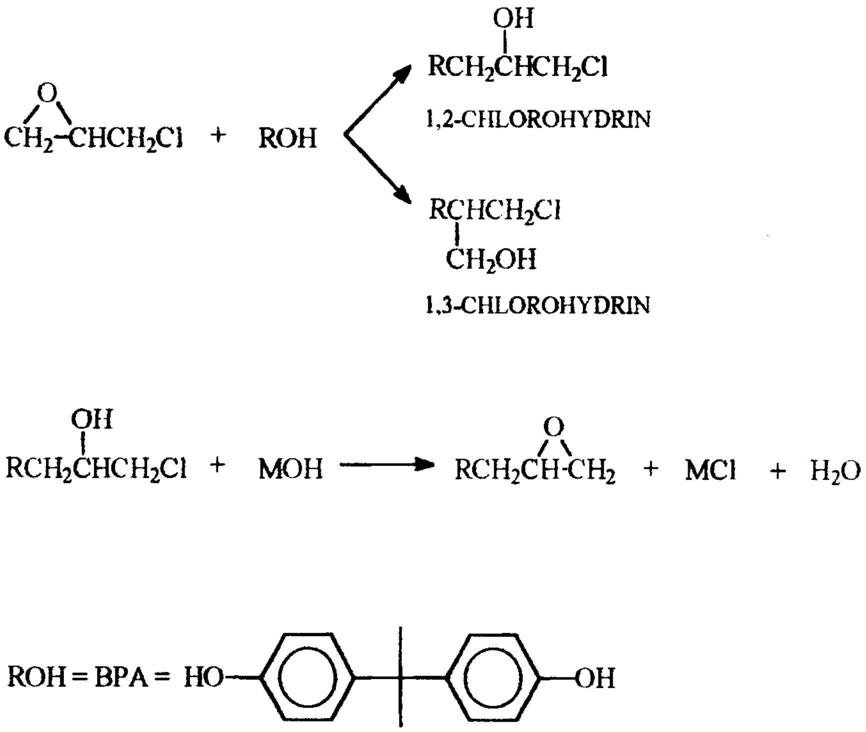
According to the manufacturer, the UV curable adhesive generating the disk haze is a bisphenol A/cycloaliphatic epoxy-based material filled with amorphous silica for rheology control. The two most probable sources of chlorine in the adhesive are the bisphenol A (BPA) epoxy resin and the filler.

BPA resins are commercially prepared *via* reaction of epichlorohydrin with BPA to yield the 1,2-chlorohydrin, as well as measurable amounts (~1200 ppm) of the 1,3-chlorohydrin product (Scheme 1).[5]

The 1,3-chlorohydrin product is not subject to ring closure. Consequently, the BPA epoxide contains bound chlorine in the form of chloromethyl groups. Another source of active chlorine in the epoxide is residual 1,2-chlorohydrin from incomplete dehydrohalogenation.

Amorphous silica is prepared by the hydrolysis of silicon tetrachloride vapor in a H_2/O_2 flame as shown in Scheme 2.

Residual, adsorbed hydrogen chloride is reduced to less than 200 ppm *via* calcination. Both the adsorbed hydrogen chloride and the chlorohydrin products can be quantitatively determined as hydrolyzable chloride *via* standard test methodology.[6] In an effort to determine whether or not disk haze is correlated with hydrolyzable chloride content, several model adhesives were prepared from various epoxy resins. The qualitative haze results from these experiments are illustrated in Table II.



SCHEME 1

$$SiCl_4 \xrightarrow[1800\ C]{2\ H_2/O_2} SiO_2\downarrow + 4\ HCl\uparrow$$

SCHEME 2

TABLE II
Hydrolyzable Chloride Content of Adhesive Formulations

Epoxy Resin	Hydrolyzable Chloride	Haze Rating
Union Carbide ERL 4221	< 10 ppm	0
Shell RSL 1457	54 ppm	0
Dow Quatrex 1010	50 ppm	0
Dow DER 361	54 ppm	0
Epi-Rez SU 2.5	1790 ppm	1
Commercial adhesive	33 ppm	3

The adhesive formulations consisted of 2 wt% of UVI 6974H, 3 wt% Cab-O-Sil M-5, plus the indicated epoxy resin. The formulations were cured as previously described. The haze rating followed the figure of merit scale detailed in the Experimental section.

Cycloaliphatic epoxides are synthesized *via* peroxidation of diolefins whereby active chlorine is absent from the reactants and, therefore, the epoxy resin. The formulation comprised of the Union Carbide cycloaliphatic resin (ERL 4221) is chloride free (< 10 ppm, the limit of detection) and benign to the disk metallurgy. Shell RSL 1457, Dow Quatrex 1010, and Dow DER 361 are all BPA-based resins of similar hydrolyzable chloride content. Formulations prepared from these resins were also benign to the disk metallurgy even though the hydrolyzable chloride level was substantially greater than that of the commercial adhesive that resulted in severe disk corrosion. Also of interest was the observation that Epi-Rez® SU-2.5, a polyfunctional BPA-novolac epoxide with a chloride content in excess of 50X that of the commercial adhesive, produced very little haze. These data indicated that the magnitude of the hydrolyzable chloride concentration was not solely responsible for the corrosion phenomenon. If such were the case, the SU-2.5 formulation would have excessively hazed the disk, whereas the commercial UV curable adhesive would have exhibited the least corrosion potenial. These results suggest that effusion of chlorine out of the adhesives is responsible for the observed corrosion behavior.

In addition to the epoxy resins, the commercially available adhesive also contains a polyether polyol at concentrations approaching 40 wt% of the formulation. The polyol is present to impart flexibility and reduce brittleness of the cured adhesive. The effect of a polyether triol, Voranol 2070, on the corrosion potential of model adhesive formulations is depicted in Table III. Inspection of the data reveals that a clear demarcation

TABLE III
Effect of Flexibilizer on Model Adhesive Corrosion

Wt% DER 331	Wt% ERL 4221	Wt% Voranol 2070	Haze Rating[†]
0	80	15	0
5	75	15	0
10	70	15	0
20	60	15	0
0	75	20	0
5	70	20	0
10	65	20	0
20	55	20	0
0	70	25	0
5	65	25	1
10	60	25	3
20	55	25	0
0	65	30	3
5	60	30	1
10	55	30	3
20	45	30	1
0	60	35	3
5	55	35	3
10	50	35	2
20	40	35	1

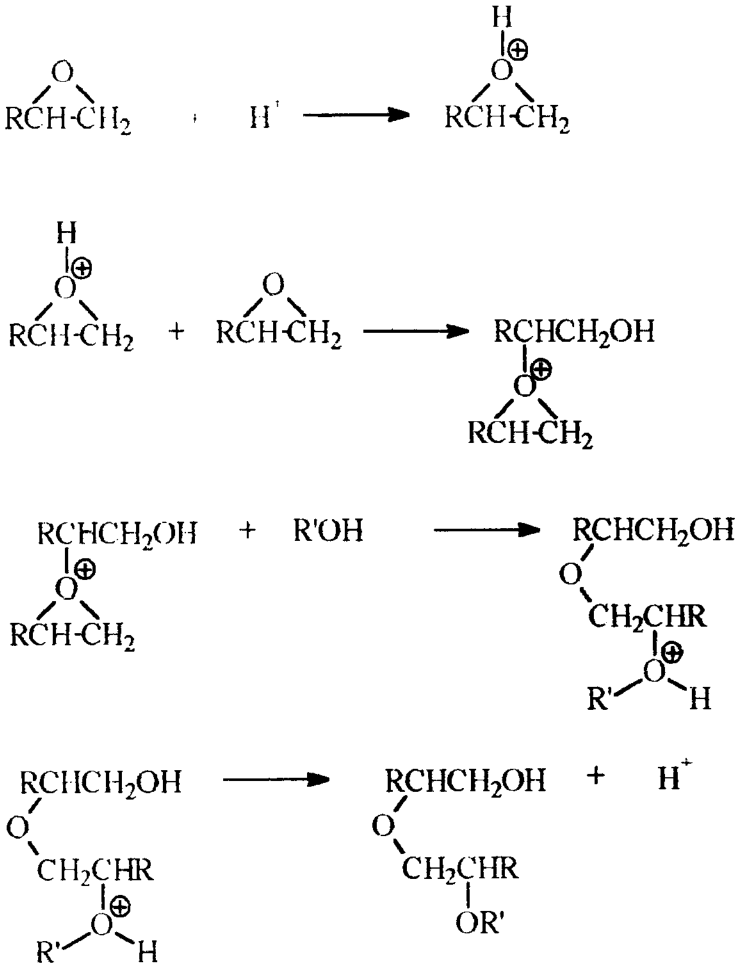
[†] Following 21 days exposure to 60/80 T&H conditions.

The adhesive formulations consisted of 2 wt% of UVI 6974H, 3 wt% Cab-O-Sil M-5, plus the indicated resins. The formulations were cured as previously described. The haze rating followed the figure of merit scale detailed in the Experimental section.

exists with respect to corrosion and polyether triol content. At Voranol concentrations exceeding 20 wt%, the formulations exhibited varying degrees of corrosion of the disk metallurgy; at Voranol concentrations less than or equal to 20 wt%, no corrosion was observed.

Polyether polyols function as chain transfer agents during epoxy polymerization (Scheme 3).[7]

The polyol competes with the epoxy monomer for the cationic center. The growing chain is terminated by reaction with the polyol hydroxyl group, forming an ether linkage with concomitant release of a proton. The proton can initiate polymerization by reaction with the monomer. During chain transfer, the growing polymer chain is terminated and smaller chain propagating species are formed. For multifunctional epoxies, the molecular weight is decreased, the cross link density is reduced, and the T_g is suppressed. This effect is illustrated by the data in Figure 2, where the flexibilizer



SCHEME 3

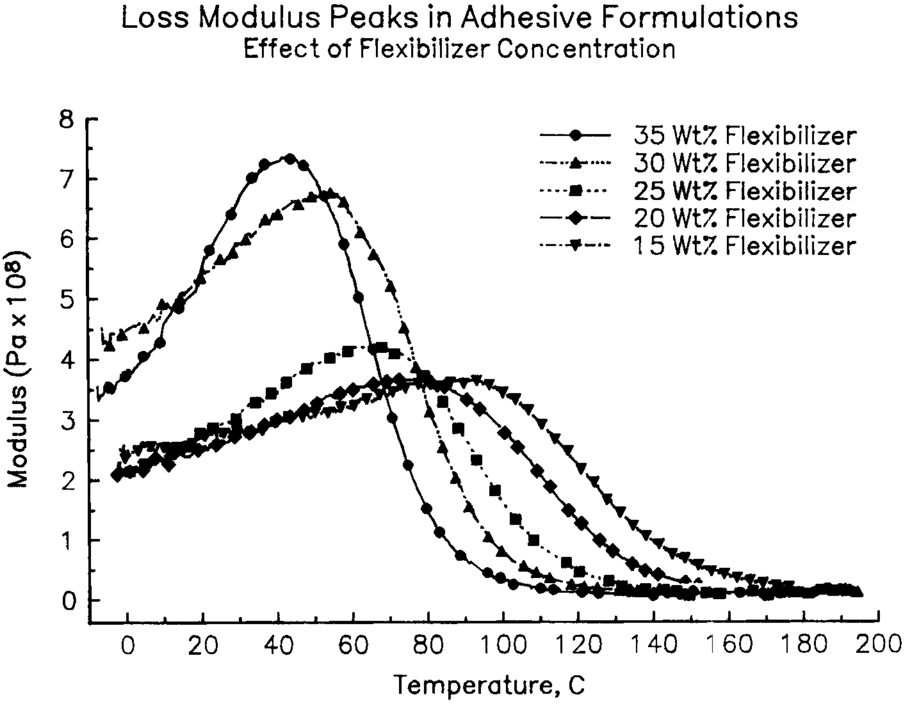


FIGURE 2 The effect of Voranol 2070 flexibilizer on the T_g of model UV curable adhesive formulations. The T_g is taken as the peak in the loss modulus curve.

concentration is varied in 5 wt% increments from 15–35 wt% of the formulation. For these samples, the BPA epoxy concentration was held constant at 10 wt% and the cycloaliphatic epoxy concentration was varied accordingly. At the lowest Voranol concentration, the T_g is approximately 90 C; as the Voranol concentration increases, the T_g stepwise shifts to lower temperatures and the magnitude of the loss modulus increases. Identical results were obtained at different BPA epoxy concentrations (Fig. 3). In all cases, as the flexibilizer concentration increases, the T_g decreases and the magnitude of the loss modulus increases, indicating that the samples are becoming softer.

The T_g of the flexibilized epoxy adhesives was shown to vary proportionately with the weight percentage of the flexibilizer in the formulation. The effect of the flexibilizer on the corrosion potential of model adhesives is depicted graphically in Figure 4. There are two noteworthy features of the graph. At Voranol concentrations less than or equal to 20 wt%, the formulations are benign to the disk metallurgy; Voranol concentrations greater than or equal to 25 wt% haze the disk to variable extent, the trend being an increase in the severity of corrosion with increasing Voranol content. Furthermore, there appears to be a critical T_g value of 60–65 C, below which the formulations all haze the disk. It is interesting to note that the corrosion evaluation is conducted at 60 C/80 RH, implying that effusion of volatiles out of the adhesive is enhanced above T_g.

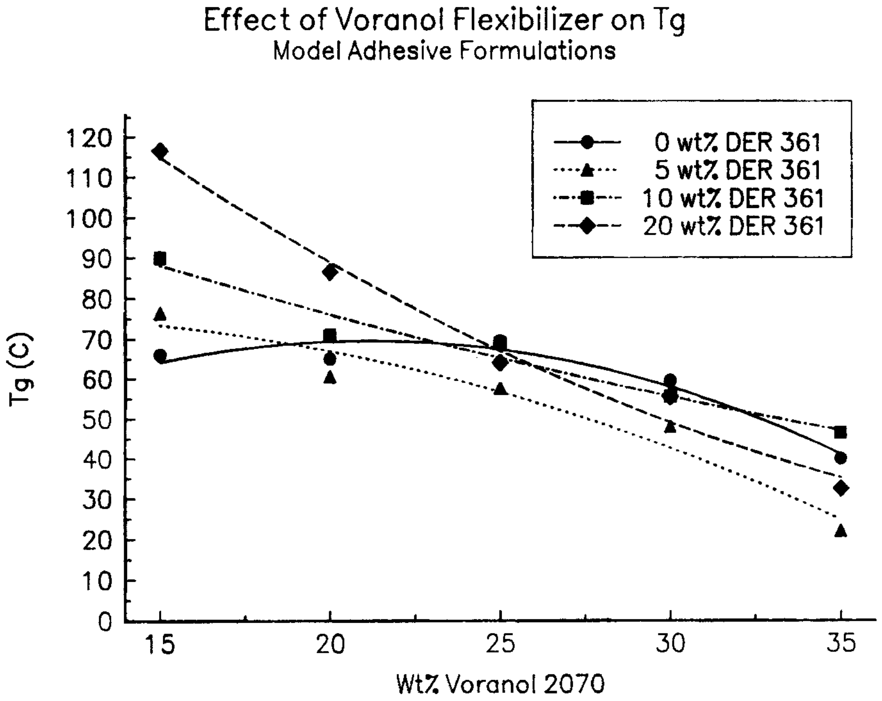


FIGURE 3 The effect of Voranol 2070 flexibilizer on the T_g of various model UV curable adhesive formulations.

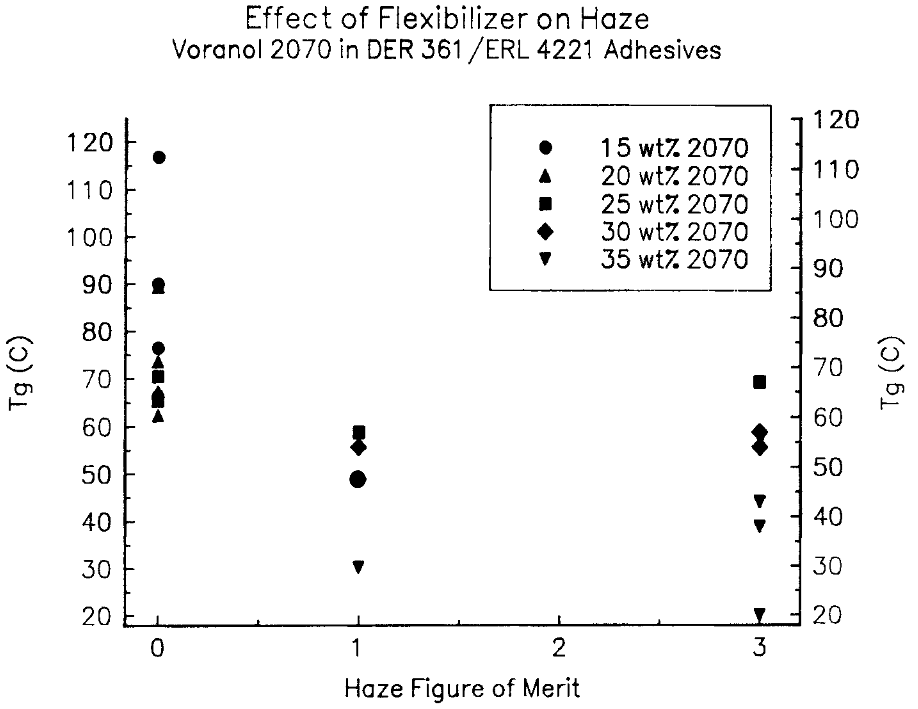


FIGURE 4 The effect of Voranol 2070 flexibilizer on disk haze.

Applying the foregoing results to the commercially available adhesive, the vendor was requested to decrease the flexibilizer[8] concentrations and submit samples for evaluation. The results are illustrated in Figure 5, where the loss modulus is plotted against the temperature. Once again, the T_g is observed to decrease, and the magnitude of the loss modulus increases, as the flexibilizer concentration increases. In fact, a linear relationship exists between the T_g and the weight percent flexibilizer (Fig. 6). From the data in Figure 6, coupled with the preceding results, one can predict that the modified, commercially available adhesives with flexibilizer concentration greater than 20 wt% would be corrosive to the disk metallurgy. The data of Table IV indicate that this is precisely the case. Conversely, from the results of Table IV, one would predict that only the 19 wt% flexibilizer sample would possess a T_g in excess of 60–65 C, which is indeed observed.

To return to the original problem of how to minimize outgassing of volatile species into the disk environment, it is now intuitive to investigate the weight loss behavior of the modified, commercially available adhesives. Identification of trapped, volatile compounds from the virgin and modified adhesives is shown in Table V. The only formulation difference between the virgin adhesive and the modified adhesive (Mod-3) is the weight percentage of the polycaprolactone triol flexibilizer. In the Mod-3 adhesive, the flexibilizer concentration was reduced from 37 wt% to 19 wt%. The ratio

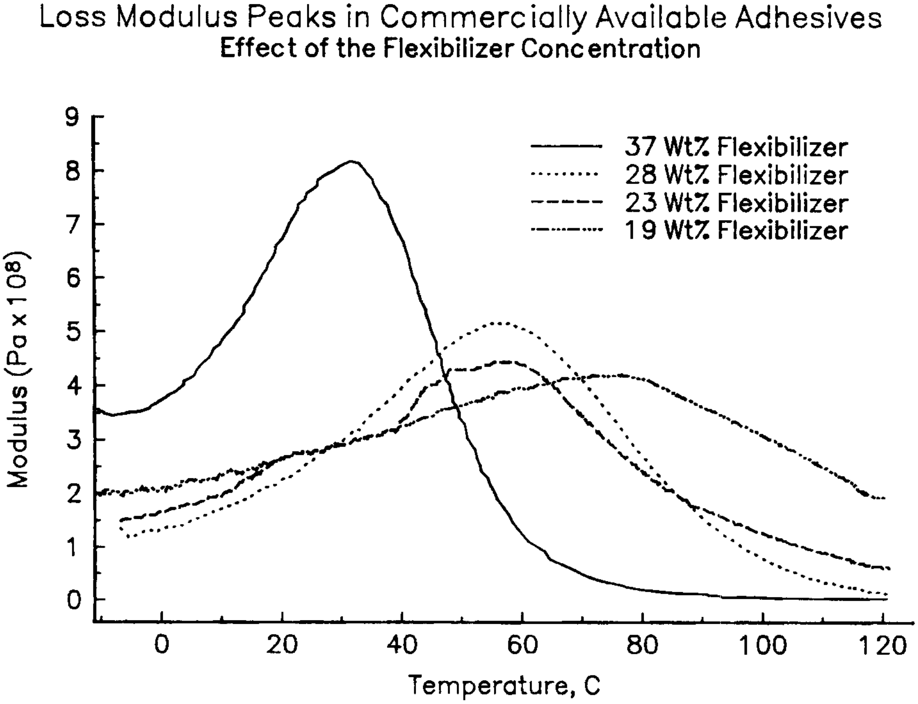


FIGURE 5 The effect of reduced flexibilizer concentration on the T_g of commercially available UV curable adhesives.

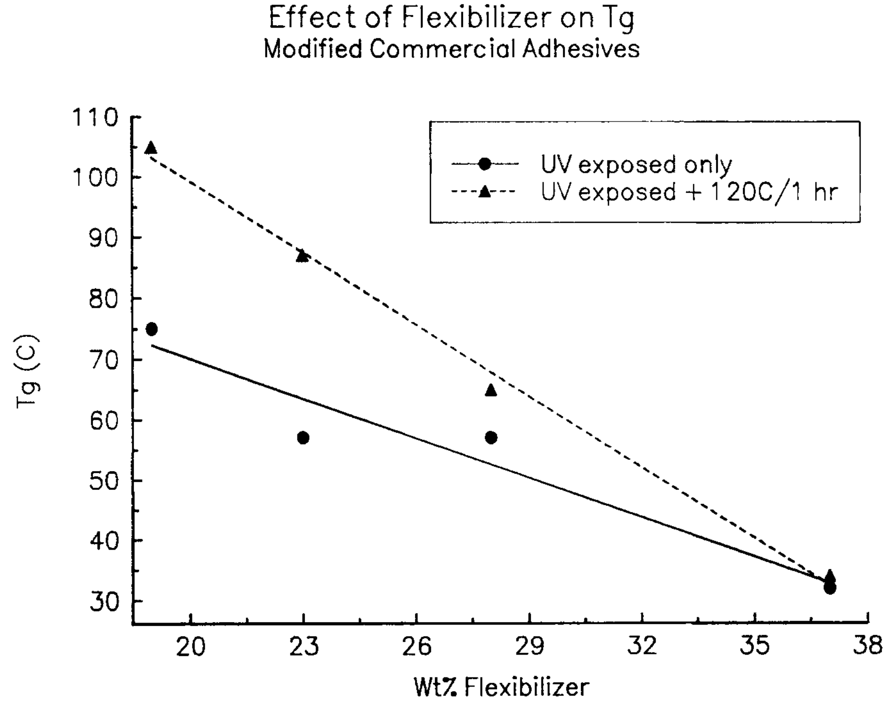


FIGURE 6 The relationship between T_g and flexibilizer content in modified, commercially available UV curable adhesives.

TABLE IV
Corrosion Potential of Modified Adhesives

Sample ID	% Flexibilizer	T_g (unbaked)	T_g (baked)†	Haze Rating
Virgin	37	32C	34C	3
Modification-1	28	57C	65C	3
Modification-2	23	57C	87C	1
Modification-3	19	75C	105C	0

† Baked at 120 C for 60 min.
The haze rating was determined on the unbaked samples.

of the BPA epoxy to the cycloaliphatic epoxy was kept constant the concentrations of the filler and triarylsulfonium salt were also maintained at constant levels between the virgin and modified adhesives. From the data in Table V, it is immediately obvious that the Mod-3 adhesive outgasses virtually an order of magnitude less than the virgin material. Propylene carbonate, which is present in equal quantities in both adhesives, is the major outgassing component. Effusion of propylene carbonate out of the adhesive, is severely retarded in the 19 wt% flexibilizer material. Isothermal weight loss data clearly depict the remarkable difference between the volatility of the virgin and modified adhesives (Fig. 7). Total weight loss tracks nicely with the poly(caprolactone)

TABLE V
Outgassing of UV Curable Adhesives

			Trapped Organics (μg/g adhesive)			
Sample	% Flex	Amount Trapped	PC	Ph_2S	CHC	Flex
Virgin	37	6.55 g	2363	323	68	396
Mod-3	19	6.92 g	413	45	7	23

PC = Propylene carbonate, the solvent from the photoinitiator package
Ph_2S = Phenyl sulfide, a photolysis product of the triarylsulfonium salt[7]
CHC = Unsaturated precursor to 3,4-epoxycyclohexylmethyl-3',4'-epoxy cyclohexane carboxylate
Flex = Low molecular weight (200–400) species from the poly(caprolactone) triol flexibilizer
Exposure dose of 2.5 J/cm^2. Isothermal weight loss at 100 C. Volatile compounds trapped on a Kynol filter and identified *via* NMR. Volatiles were trapped over a course of 24 hrs and 72 hrs, for the virgin and Mod-3 adhesives, respectively.

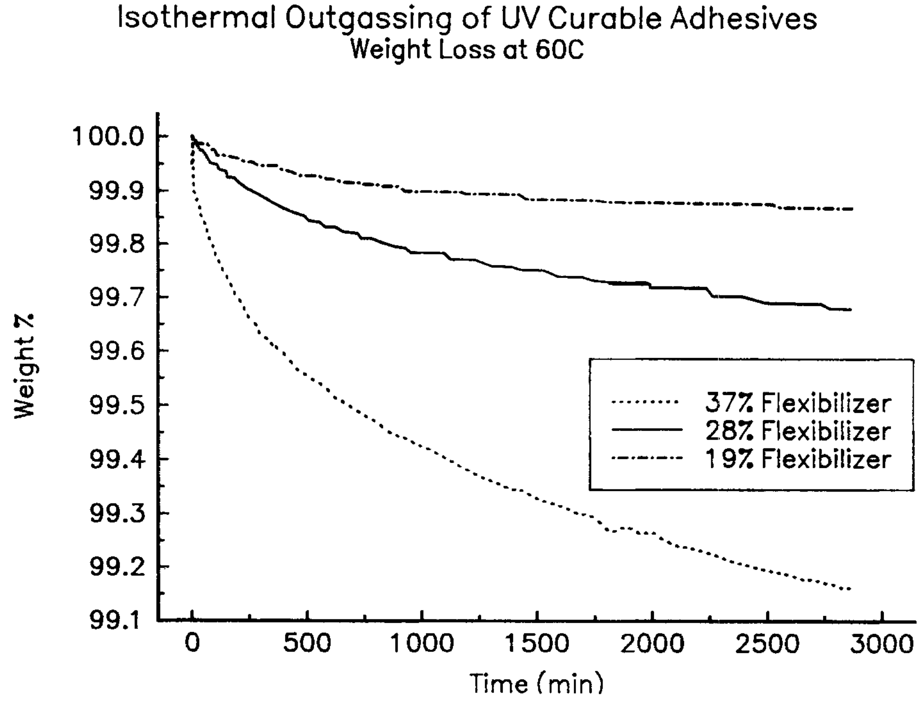


FIGURE 7 Isothermal weight loss at 60 C for the virgin and modified adhesives.

triol concentration as well as with the adhesive's glass transition temperature. From the isothermal outgassing data it becomes obvious why the Mod-3 adhesive does not initiate disk corrosion: total outgassing is reduced an order of magnitude compared with the virgin adhesive.

CONCLUSIONS

Effusion of Cl-containing species from UV curable adhesives has been demonstrated to induce Ni corrosion in the disk metallurgy of hard disk drives. Outgassing of volatile components from UV curable adhesives can be systematically controlled by altering the flexibilizer concentration in the resin package. UV curable adhesives modified such that the glass transition temperature exceeds the file operating temperature have been demonstrated to be benign to the disk metallurgy. The T_gs of the modified adhesives decrease linearly with increasing polyol content, whereas total outgassing increases with increasing flexibilizer concentration.

Acknowledgements

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References

1. R. Koka, *Microcontamination*, Sept/Oct, **41**, (1993).
2. P. H. Kasai and P. Wheeler, *Appl. Surf. Sci.* **52**, 91 (1991).
3. W. H. Abbott, *Thirteenth Int. Conf. on Electric Contacts*, Lausanne (1986), p. 343.
4. W. H. Abbott, *Twelfth Int. Conf. on Electric Contact Phenom.*, Chicago (1984), p. 47.
5. Y. Tanaka, in *Epoxy Resins*, C. May, Ed. (Marcel Dekker, NY, 1988), Chap. 1.
6. Dow Chemical Analytical Procedure RPM 105-D-85, May 1985.
7. J. V. Crivello, D. A. Conlon, D. R. Olson, and K. K. Webb, *Polym. Paint Colour J.* **178**, 696 (1988); *Spec. Chem.* **8**(5), 401 (1988); *J. Rad. Curing* **13**(4), 3 (1986).
8. The flexibilizer in the commercially available adhesive was determined to be a poly(caprolactone) triol, in contrast to the polyether triol of the model formulations.
9. J. V. Crivello, *Adv. Polym. Sci.* **62**, 1 (1984).