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Determination of the feasibility of using attenuated total reflectance Fourier transform–infrared spectroscopy to evaluate thermal ageing of enamel-coated magnet wire

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A study was initiated to determine the feasibility of employing attenuated total reflectance Fourier transform–infrared spectroscopy (ATR/FT–IR) to detect changes resulting from thermal ageing in the enamel of copper magnet wire. Polyamideimide (SX-81002) was cured on a zinc selenide (ZnSe) internal reflection element (IRE) coated with a thin film of metallic copper. The coated IRE was inserted in a Circle cell housed in a heating jacket and maintained at 250 °C on the optical bench of an infrared spectrometer to simulate thermal ageing of enamel-coated magnet wire. Evaluation of the infrared spectra in the fingerprint region suggested that the polymer experienced chemical degradation within a 23 day period of thermal ageing. Through comparisons with controls containing no copper coatings, and ageing studies carried out at 28 °C, it was determined that ageing at elevated temperature caused more pronounced chemical changes in the polymer than did exposure to the copper. These results indicate that ATR/FT–IR may be a useful tool to detect enamel fatigue after a short period of thermal ageing.

1. Introduction

The failure of copper wire at elevated temperatures, has been reported to result from the formation of copper oxides which react with the polymer coating surrounding the wire to cause dielectric failure [1]. Current procedures used to determine the stability of new polymer coatings involve ageing of the copper wire for periods of up to 2 years before testing its suitability for release to the customer. The development of a rapid technique to verify the stability of the polymer coating will enable quality assurance programmes to determine the suitability of a polymer coating in a shorter time frame. Furthermore, a knowledge of copper oxidation rates and polymer stability will facilitate the evaluation of corrosion/oxidation inhibitors incorporated in the coating process.

Fourier transform–infrared (FT–IR) reflection–absorption spectroscopy (RAS) has been used effectively to investigate both the effect of thermal ageing on polymers deposited on to copper surfaces [2, 3] and the behaviour of surface oxide layers of copper upon heating [4]. RAS is generally used to study films which are less than 100 nm thick [5], therefore the technique is not able to provide information on changes within a polymer film deposited on to a copper substrate and on changes occurring simultaneously in the valence state of the copper surface.

Attenuated total reflectance (ATR) infrared spectroscopy has been used extensively to obtain information on substances at solid/solid interfaces [6]. A modification of this technique is the deposition of a thin metal film on to the surface of the internal reflection element (IRE) [7–9]. If the metallic film is thin enough, the energy transmission of the IRE remains sufficiently high to allow the detection of substances, such as polymers, at the metal interface [10–13]. A further advantage of this technique is that the penetration depth of the infrared into the sample is less than 1 μm, so only changes in the polymer that occur at the copper/polymer interface are recorded.

The aim of this research was to investigate the feasibility of using attenuated total reflectance Fourier transform–infrared spectroscopy (ATR/FT–IR) to (1) study the oxidation of metallic copper in contact with polymer coatings at elevated temperatures; (2) determine chemical changes that occur in the polymer during thermal ageing; (3) relate the observed chemical changes in the polymer coating to the copper oxidation reaction.

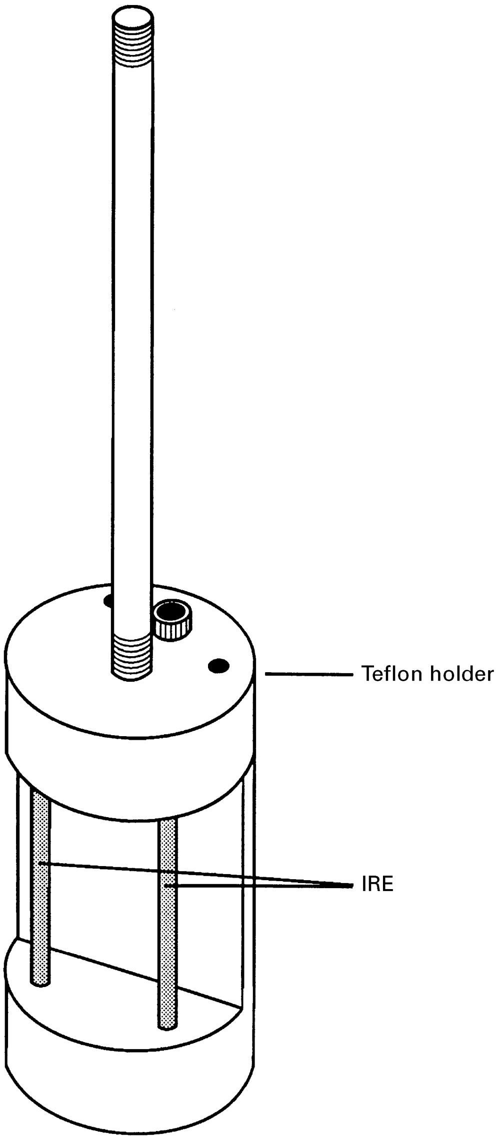

Figure 1 Schematic diagram of the Teflon holder used in the polymer coating of internal reflection elements.

2. Experimental procedure

2.1. Curing of a polyamideimide polymer on a ZnSe IREs

An enamel polymer (SX-81002), commonly used in the production of enamel-coated magnet wire, was obtained from Dr Francois Lavalle (Essex Group, Inc, Fort Wayne, IN). A coating and curing regime was developed so that the polymer coatings on ZnSe IREs were similar to coatings of SX-81002 on copper magnet wire. Two factors were critical during the polymer coating; the temperature regime during curing of the polymer on to the IRE, and the thickness and uniformity of the polymer.

Coating and subsequent curing of the polymer on the IRE was complicated by two factors. Firstly, the end cones of the IRE through which the infrared radiation entered and exited had to be free of coating, and secondly, the ZnSe IRE could not withstand temperatures above 250 °C, which was 50 °C lower than the normal minimum curing temperature of SX-81002.

To facilitate polymer coating of the IRE, a Teflon holder was constructed which held two IREs and prevented coating of the end cones (Fig. 1). For logistical reasons, the development of a low-temperature polymer-curing regime was carried out using glass rods instead of ZnSe IREs. The glass rods were dipped in various concentrations of polymer diluted with a 1 : 1 mix of *N*-methyl-2-pyrrolidone and xylene and subjected to a variety of curing regimes. The following coating and curing procedure produced a coating similar to the polymer on copper wire; ZnSe IREs were positioned in the Teflon holder and dipped into a container of undiluted SX-81002. The holder and IREs were then immediately placed in a muffle furnace at 200 °C for 24 h. The temperature was subsequently increased over a 10 min interval to 225 °C and maintained at 225 °C for 20 min, then further increased over a 10 min interval to 250 °C. After 20 min at 250 °C, the muffle furnace was turned off and left to cool overnight (16 h). Polymer coatings produced in this manner had a glass transition temperature of 552 °C and a thickness of between 0.01 and 0.0039 in (0.0254 and 0.0099 cm), both parameters were within the normal range for this polymer on copper wire [14].

2.2. Performance of ZnSe IREs at elevated temperatures

Two Circle cells (Spectra Tech, Stamford, CT), each containing a ZnSe IRE, were aligned in separate paths of a dual-beam Perkin–Elmer model 1800 FT–IR spectrometer (Fig. 2). One of the Circle cells was contained within a heating jacket (Spectra Tech). The FT–IR was equipped with a 2 mm diameter *L*-alanine-doped deuterated triglycine sulphate (DTGS) detector. Operating parameters were adjusted to achieve a maximum signal/noise ratio over the spectral range of 4000–500 cm^{-1}. The parameters depended on the energy throughput and were as follows: the interferometer OPD velocity was set at either 0.1 or 0.05 cm s^{-1} and the Jacquinot stop used was either 3 or 6, depending on whether or not the IRE had been copper-coated.

All interferograms were double-sided and apodized with a medium Beer-Norton function prior before the fast Fourier transformation using the Model 1800 computer software. Scans were taken over the range of 4000–450 cm^{-1} with an interval of 2 cm^{-1} and a nominal resolution of 4.0 cm^{-1}. A single-beam spectrum was calculated from 100 averaged scans.

To determine the effect of heating on the energy throughput of a ZnSe IRE, the temperature of the Circle cell contained within the heating jacket was increased in 25 °C increments to a maximum of 250 °C. After each change in temperature, a spectrum was obtained from the heated Circle cell, as well as from an unheated Circle cell, which served as a control. The energy throughput and the signal/noise ratio at each temperature were also monitored. After the IRE had been heated to 250 °C for 20 min, it was cooled to 25 °C and an additional spectrum was obtained.

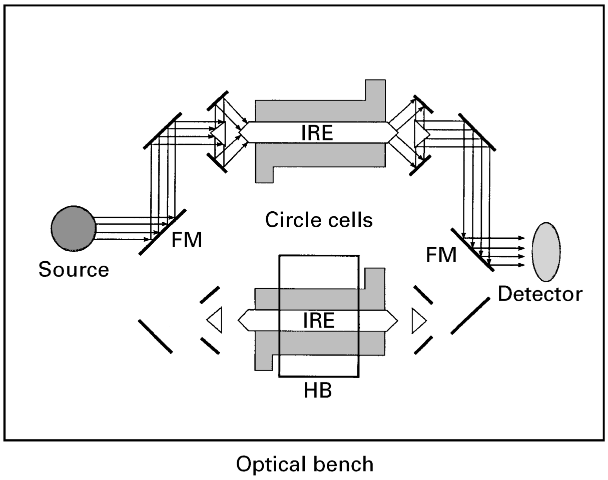

Figure 2 Schematic diagram showing the position of the Circle cells on the optical bench of the FT–IR spectrometer and the path of the infrared radiation to the IRE. IRE = internal reflection element, FM = flip mirror, HB = heating block.

2.3. Evaluation of the stability of polymer coating during thermal ageing

Two polymer-coated, ZnSe IREs were positioned within Circle cells on the optical bench of a model 1800 FT–IR spectrometer. One Circle cell was housed in a heating jacket maintained at 250 °C to stimulate thermal ageing, while the other was maintained at 28 °C as a control. Spectra were obtained from both Circle cells at intervals over a period of 23 days. A spectrum of the cured polymer on a ZnSe IRE was obtained by ratioing the spectrum obtained from the coated ZnSe IRE against a spectrum obtained from the bare IRE before coating. Changes in the absorbance spectrum of the polymer coating during ageing were determined by ratioing the spectra obtained at various times after initiation of an experiment against the spectrum obtained at the start of the experiment. Throughput energy of the IREs was also monitored over time.

In another experiment, a thin film (4.7 nm, nominal thickness) of metallic copper was evaporated on to two ZnSe IREs using a technique described by Bremer *et al.* [15]. The copper-coated IREs were subsequently polymer-coated, placed in Circle cells and spectra obtained as described above.

3. Results and discussion

3.1. Performance of ZnSe IREs at elevated temperatures

The effect of heating on the infrared transmitting capacity of a ZnSe IRE was determined by monitoring the change in energy throughput (interferogram peak to peak) (Table I). Heating the IRE to 250 °C resulted in a 28% decrease in the energy throughput, which was reversible on cooling. It is not possible to determine from this experiment whether the decrease in throughput energy at elevated temperatures resulted from absorption by increasing numbers of thermally generated holes as has previously been reported in such crystal materials as germanium, or simply because the heat induced distortions in the mirrors used to focus the IR radiation on to the IRE and subsequently on to the detector. However, it was concluded that the ZnSe IREs transmitted sufficient energy at 250 °C to obtain a good signal-to-noise ratio in the resulting spectra and were therefore suitable for use in this experiment.

TABLE I Effect of heating on IRE energy throughput

Heated IRE		Unheated IRE	
Temperature (°C)	Energy throughput (%)	Temperature (°C)	Energy throughput (%)
25	37.77	25	30.68
50	35.77	28	30.73
75	34.56	28	30.71
100	34.17	28	30.70
125	33.07	28	30.73
150	32.60	28	30.74
175	31.04	28	30.70
200	29.88	28	30.72
225	28.72	28	30.69
250	27.41	28	30.68
25	37.54	25	30.64

Heating the one IRE to 250 °C had little effect on the temperature of the IRE in the adjacent Circle cell (maximum of 3 °C increase above ambient temperature), with no significant change in throughput energy. It was therefore possible to run a "room temperature" control in conjunction with the high-temperature ageing experiment.

3.2. Evaluation of the stability of a polymer coating during thermal ageing

ZnSe IREs were coated with SX-81002 polymer in a Teflon holder (Fig. 1). The polymer coating was heat-cured to achieve a composition similar to that obtained for enamel coatings on copper magnet wire. ATR spectra of SX-81002 cured on a bare ZnSe IRE and on a copper-coated ZnSe IRE were compared to each other (Fig. 3a and b) and to a reflectance spectrum of polymer-coated copper wire, obtained from Dr Francois Lavalle (Fig. 4). The ATR and reflectance spectra exhibited very similar absorption bands.

Spectra of polymer coatings subjected to ageing on bare ZnSe IREs at 250 °C, when compared to spectra of coatings maintained at ambient temperature (28 °C) revealed differences in the "finger print region" (2000–700 cm^{-1}) that suggest that changes were thermally induced in the polymer over a period of 23 days (Fig. 5a and b). The differences in the spectra below 700 cm^{-1} are more difficult to interpret, because the low signal/noise ratio in this region makes it difficult to distinguish contribution of noise from true vibrational features of the polymer and other chemical species at the IRE surface.

When the polymer was cured and aged on copper-coated IREs, the spectra obtained after 23 days displayed some differences from the spectra obtained when the polymer was cured and aged on bare IREs

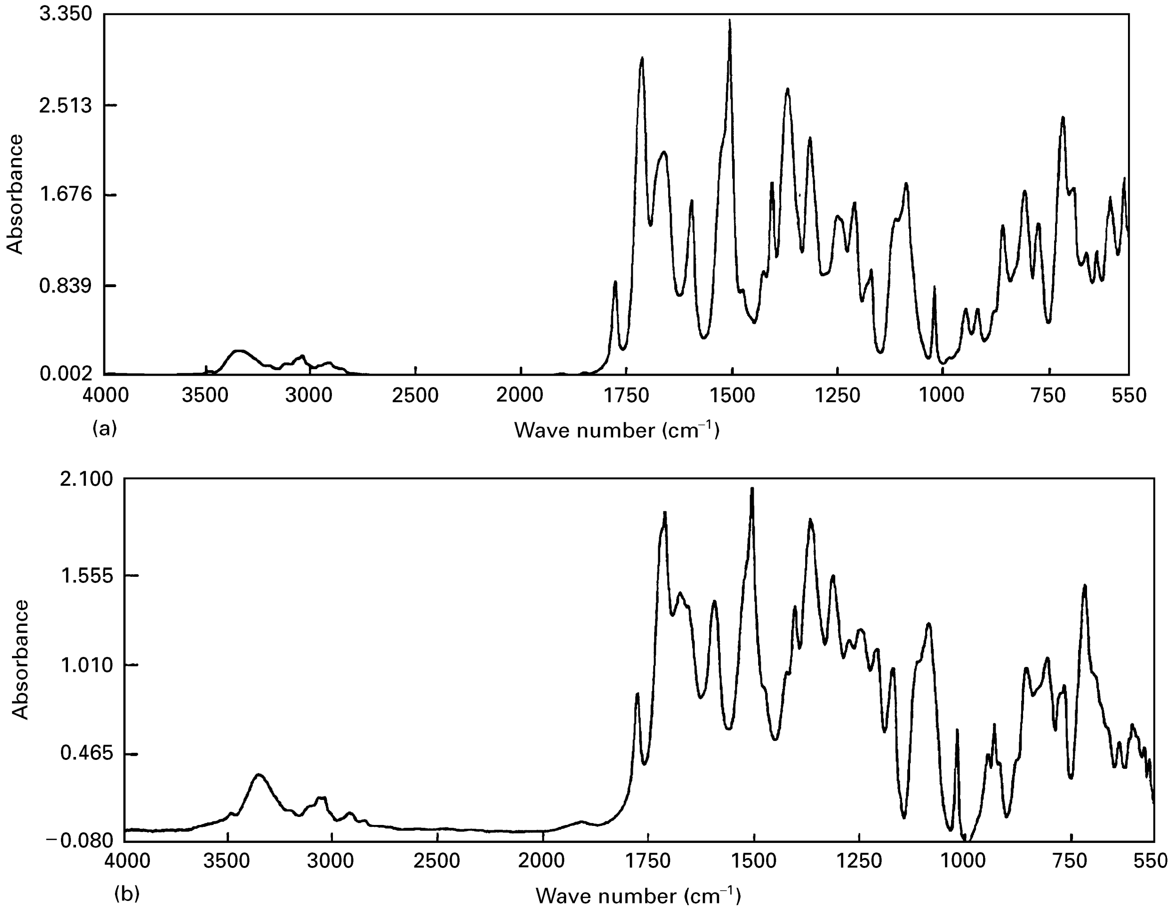

Figure 3 ATR spectra of polymer (SX-81002) after curing on (a) a bare ZnSe IRE, (b) a copper-coated ZnSe IRE.

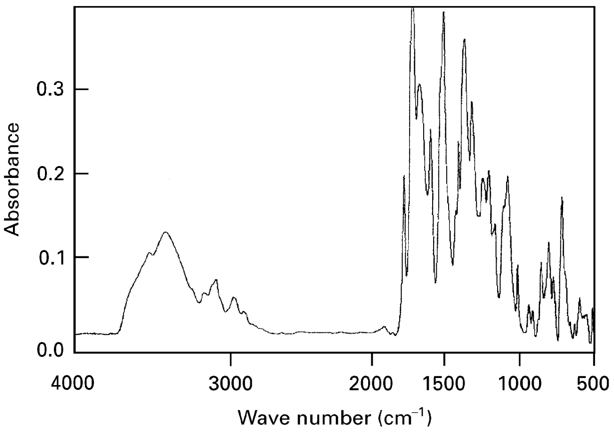

Figure 4 Transmission spectrum of cured polymer (SX-81002), obtained from Dr Francois Lavalle.

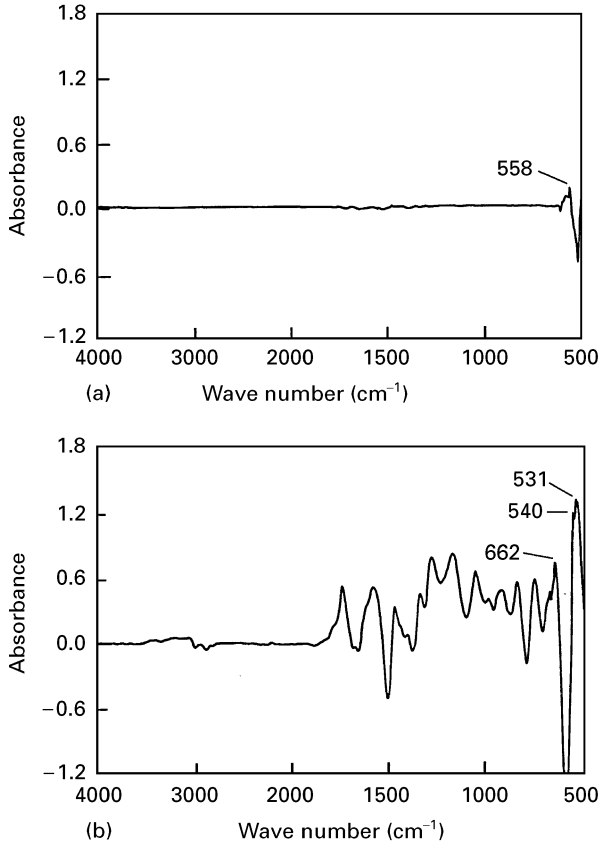

Figure 5 Difference spectra generated from polymer-coated ZnSe IRE after 23 days at (a) 28 °C and (b) 250 °C.

(Fig. 6a and b). The appearance of absorption bands in the fingerprint region of a spectrum taken from the polymer-coated, copper-coated IRE aged at 28 °C, suggests that exposure to copper in the absence of heating, induced changes in the chemistry of the polymer. However, the changes in polymer chemistry attributed to copper were not as pronounced as those induced by heating alone. This conclusion was further supported by comparison of spectra collected from polymer-coated, copper-coated IREs aged at 28 and 250 °C with those collected from polymer-coated IREs

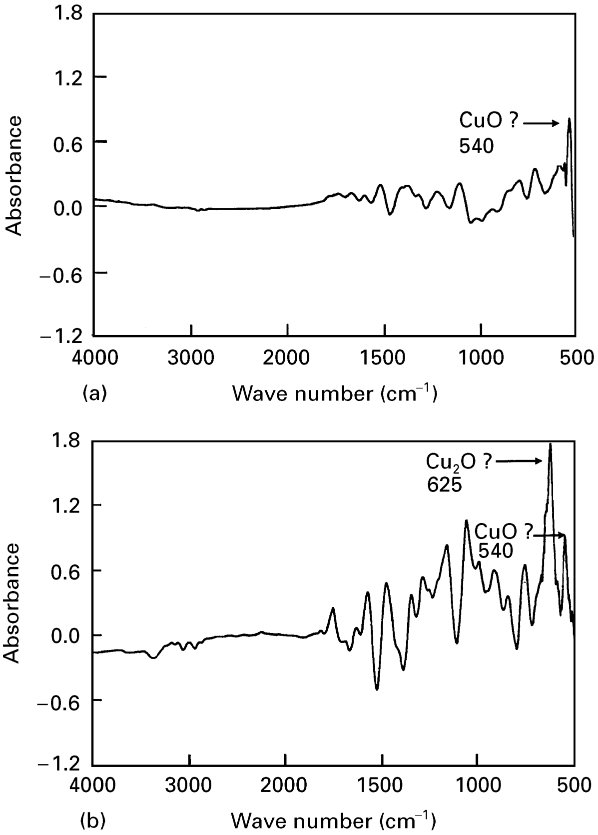

Figure 6 Difference spectra generated from polymer-coated, copper-coated ZnSe IRE after 23 days at (a) 28 °C or (b) 250 °C.

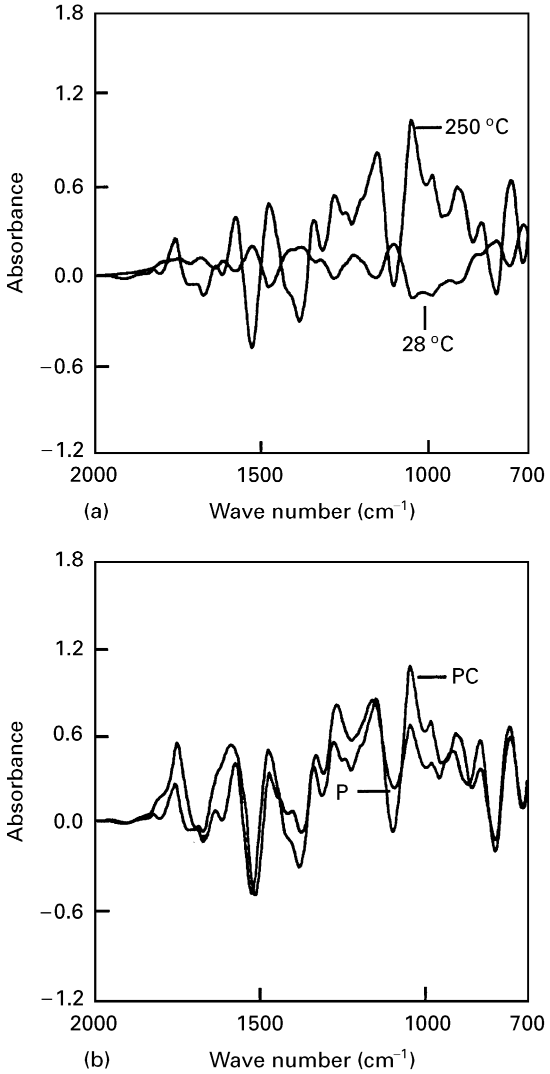

Figure 7 Difference spectra of (a) polymer-coated, copper-coated IREs aged at 28 and 250 °C, (b) polymer-coated IREs with (PC) and without (P) copper thin films after ageing for 23 days at 250 °C.

with and without a copper coating after ageing at 250 °C (Fig. 7a and b). The spectrum of the polymer on the copper-coated IRE was similar to that of the polymer on the IRE without copper. It appears that heating rather than contact with the copper was responsible for most of the chemical changes in the polymer during ageing.

A band appeared in a region of the spectrum obtained from the polymer-coated, copper-coated IRE aged at 28 °C (Fig. 6a) where cupric oxide (540 cm^{-1}) absorbs [16, 17]. The low signal/noise ratio in this region, though, makes this band assignment questionable until it is studied further. An absorbance band at 625 cm^{-1} was observed after thermal ageing of the polymer in the presence of copper that was not detectable in the absence of copper (Fig. 6a and b). This band corresponds closely with that contributed by cuprous oxide, but because of the low signal/noise ratio in this region of the spectrum, further study is needed to verify that the copper has been oxidized during thermal ageing. Strehblow [18] reported that the formation of copper oxides on a copper surface involves a duplex structure; the inner layer consisting of cuprous oxide and the outer layer of cupric oxide and hydroxide. If the band at 625 cm^{-1} is real, then the data suggest that growth of the inner Cu_2O layer is promoted by thermal ageing.

Polymer-coated, copper-coated, ZnSe IREs were visually compared immediately after curing and then after ageing for 23 days at 28 and 250 °C. The polymer maintained at 28 °C did not show any visible signs of change, while the polymer aged at 250 °C darkened considerably. The colour change further indicated that chemical changes had occurred in the polymer coat during thermal ageing.

The energy throughput of a polymer-coated, copper-coated, ZnSe IREs and a polymer-coated IRE without copper, were compared over a 23 day period (Fig. 8). The energy throughput of the IRE coated only with polymer remained stable during ageing at both 28 and 250 °C. Slight fluctuations in energy throughput in both IRE are likely related to changes in instrument response, rather than changes in the coating. Likewise, the energy throughput of the polymer-coated, copper-coated, IRE maintained at 28 °C was stable over a 23 day period. The dramatic increase at 156 h resulted from a change in instrument alignment after a power failure caused the spectrometer to shut down. The energy throughput in the polymer-coated, copper-coated, IRE maintained at 250 °C increased during thermal ageing. Over 23 days (552 h) the energy throughput increased by an estimated 35%, after adjusting for the 7% increase in energy throughput of the control IRE (at 28 °C) which occurred after the power failure. Energy throughput has

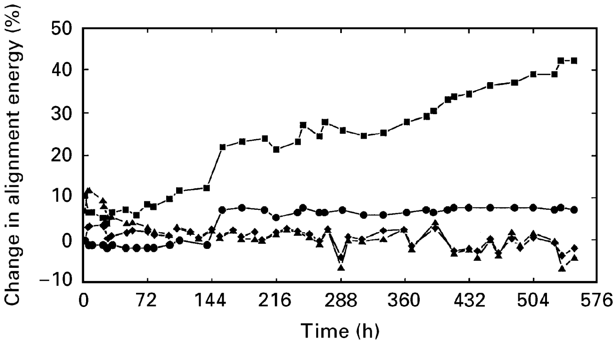

Figure 8 Change in alignment energy (throughput) of IREs exposed to different conditions during ageing: polymer-coated, copper-coated and aged at (■) 250 °C or (●) 28 °C (concurrent experiments); polymer-coated without copper and aged at (▲) 250 °C or (◆) 28 °C (concurrent experiments).

been previously shown to be related to the thickness of a copper thin film on the surface of an IRE [8, 11, 15]. The increase in energy throughput may reflect destabilization of the copper thin film at 250 °C in the presence of the polymer.

4. Conclusion

ATR/FT–IR appears to be a means of detecting chemical changes in polymers used as enamel coatings on copper magnet wire that occur during contact with metallic copper over a period of thermal ageing. Changes could be detected within a 23 day ageing period at 250 °C. Future studies should investigate the application of this surface analytical technique to evaluate the stability and activity of inhibitors of copper oxidation at elevated temperatures and their effect on polymer stability. Studies should also be initiated to determine whether chemical changes in the polymer that were noted within this 23 day ageing study correlate with failure data obtained by conventional analytical methods.

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References

1. F. P. ENG and H. ISHIDA, *J. Appl. Polym. Sci.* **32** (1986) 5035.
2. S. YOSHIDA and H. ISHIDA, *J. Mater. Sci.* **19** (1984) 2323.
3. F. P. ENG and H. ISHIDA, *J. Electochem. Soc.* **135** (1988) 603.
4. S. YOSHIDA and H. ISHIDA, *J. Adhesion* **16** (1984) 217.
5. H. ISHIDA, *Rubber Chem. Technol.* **60** (1987) 497.
6. P. R. GRIFFITHS and J. A. DE HASETH, "Fourier Transform Infrared Spectroscopy" (Wiley, New York, 1986).
7. R. J. JAKOBSEN, in "Fourier Transform Infrared Spectroscopy," Vol. 2 "Applications to Chemical Systems", edited by J. R. Ferraro and L. J. Basile (Academic Press, New York, 1979) p. 165.
8. T. IWAOKA, P. R. GRIFFITHS, J. T. KITASAKO and G. G. GEESEY, *Appl. Spectrosc.* **40** (1986) 1062.
9. A. J. PEDRAZA, M. J. GODBOLE, P. J. BREMER, R. AVCI, B. DRAKE and G. G. GEESEY, *ibid.* **47** (2) (1993) 161.
10. G. G. GEESEY, T. IWAOKA and P. R. GRIFFITHS, *J. Coll. Interface Sci.* **120** (1987) 370.
11. J. G. JOLLEY, G. G. GEESEY, M. R. HANKINS, R. B. WRIGHT and P. L. WICHLACZ, *Appl. Spectrosc.* **43** (1989) 1062.
12. G. G. GEESEY and P. J. BREMER, *Mar. Sci. Technol. J.* **24** (1990) 36.
13. P. J. BREMER and G. G. GEESEY, *Appl. Environ. Microbiol.* **57** (1991) 1957.
14. F. LAVALLE, personal communication, 1991.
15. P. J. BREMER, G. G. GEESEY, B. DRAKE, J. G. JOLLEY and M. R. HANKINS, *Surf. Interface Anal.* **17** (1991) 767.
16. P. DEZERGVILLE, M. LENGLET, E. BEUCHER, S. WEBER and S. SCHERRER, "Corrosion inhibition of copper by polyvinylimidazole by X-Ray diffraction SIMs, UV-Vis-NIR and FTIR reflectance spectroscopy", in "Proceedings of the 7th European Symposium on Corrosion Inhibitors", Italy, 17–21 September 1990. Ferrara, Universita degli Studi di Ferrara, 1990. Vol. 2, pp. 861–872.
17. G. W. POLLING, *J. Electrochem. Soc.* **116** (1961) 958.
18. H. S. STREHBLOW, in "Corrosion '91", paper 76 (1991).

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