

Studies on the ageing behavior of various synthetic and natural insulation oils

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Abstract- Dodecylbenzene (DDB) is now widely used in UK underground high voltage cables due to its biodegradability and improved gas absorbing properties. However, the potential of vegetable oils as high voltage insulation liquids has yet to be fully realized. These liquids could be used as direct replacements where traditional synthetic oils are currently used. In this paper we report on the ageing behavior of dodecylbenzene, mineral oil and a range of different vegetable oils. These were thermally aged under an oxidizing atmosphere and their ageing behavior was then characterized by ultra-violet/visible, infrared and dielectric spectroscopy techniques. Measurements of viscosity were also undertaken to supplement the spectroscopic data.

I. INTRODUCTION

Increasing awareness of the environment and the need to limit the impact of human activity gives a clear impetus to replace conventional insulating oils in high voltage plant with environmentally friendly alternatives. In addition, oil leakage from equipment is a serious concern, both in terms of the clear up operation and equipment replacement costs.

Dodecylbenzene is now widely used in UK paper/oil cable systems due to its biodegradability and improved gas absorbing properties [1]. In addition, vegetable oils have been used successfully in a number of small transformer installations in the USA [2]. In such systems, the oil provides a convenient medium for sampling to indicate the overall condition of the plant. Whilst the general indicators of oil ageing, for example, coloration [3], oxidation [4], increased acid number, water content [5] and increased dielectric loss [6] are well understood and appreciated, there still lacks a general consensus as to which is the best indicator of the overall condition of the oil. In practice a number of different ageing indicators have to be considered to gauge accurately the overall condition of the oil [7].

In this paper we have compared the ageing behavior of a number of different insulation oils under a fixed ageing regime. This, along with a broad range of diagnostic indicators, allows a systematic comparison of the effects of ageing and allows the disadvantages and advantages of the various oil systems to be highlighted.

II. EXPERIMENTAL

Mixed isomer dodecylbenzene (BICC cable oil type C148 batch 5808), mineral oil (Nynas Naphthenics ISHL HDS/137), sunflower oil (Co-op brand), olive oil (Philippo Berio) and Envirotemp FR3 oil (Cooper Industries) were all used as

supplied. Ageing was undertaken in air at 135 °C and during ageing samples were covered to minimize evaporation but were not sealed. Copper at a fixed concentration of 3.2 cm² in 5 ml of oil was added to a subset of the samples.

Ultra violet/visible (UV/vis) spectroscopy was carried out in quartz cells of path length 10 mm using a Perkin Elmer Lambda 35 spectrometer. Infra-red spectroscopy was carried out using a Nicolet 710 FTIR using KBr windows and a path length of 0.1mm. Dielectric loss measurements were carried out at room temperature using a parallel plate testing cell (diameter 33 mm, thickness 0.1 mm) using a Solartron 1296 dielectric interface linked to a Schlumberger SI 1260 impedance-gain-phase analyzer. Measurements of oil viscosity were performed at room temperature using a Physica Rheolab MC1 testing system with a cylindrical geometry (diameter 25 mm, gap 0.2 mm).

III. RESULTS

A. Dodecylbenzene and mineral oil

Both oils darken on ageing as expected [3], this is manifested in the UV/vis spectra by a shift in the absorption edge to longer wavelengths (arrowed in Fig. 1). The extent of oil ageing can be conveniently summarized by determining the wavelength associated with 50% transmission (Fig. 2).

Compared with DDB (Fig. 2), mineral oil is darkened much

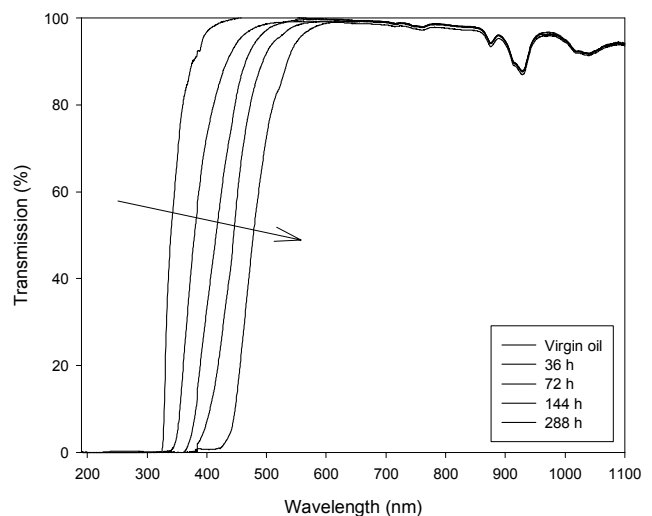


Fig. 1. Raw UV/Vis data for DDB aged without copper

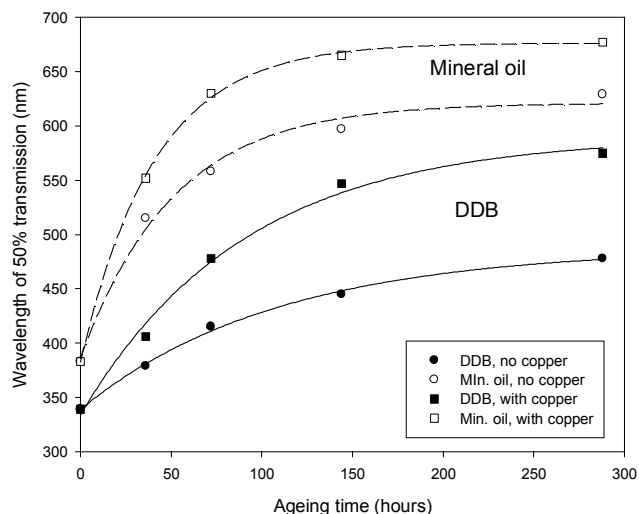


Fig. 2. UV/Vis summary plot for DDB and mineral oil aged with and without copper

more after any given period of ageing and also produces a solid precipitate which is removed here by centrifuging. In both oils, the effect of copper is to cause more darkening of the oil to occur on ageing and hence, the curves shift upwards towards longer wavelengths. The variation with ageing time follows an exponential form as the fitted lines indicate.

Dodecylbenzene oxidizes on ageing in air as expected [4] and hydroxyl (O-H), carbonyl (C=O) and a broad absorbance associated with C-O groups occur as shown in Fig. 3. Mineral oil by contrast shows a remarkable resistance to oxidation and the infrared spectrum of this oil after the longest period of ageing shows only a residual carbonyl absorbance. The oxidation is slightly increased on ageing with copper.

Fig. 4 shows that the dielectric loss of both oils increases with ageing time as expected [6]. The dielectric loss of both

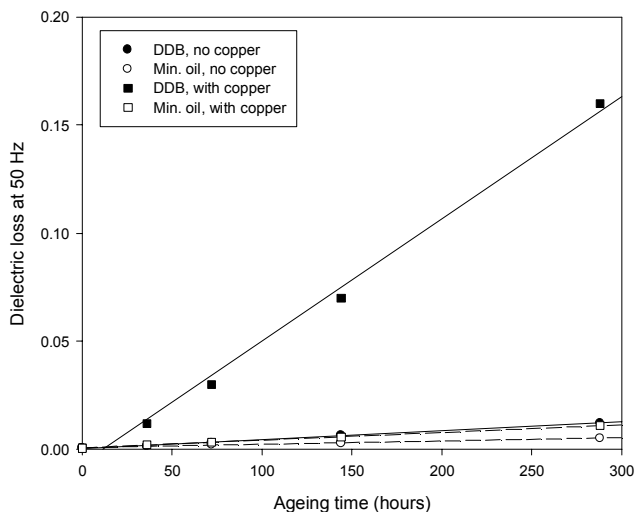


Fig. 4. Dielectric loss of DDB and mineral oil aged with and without copper

oils for any given ageing time is significantly increased after ageing with copper. DDB shows a much higher dielectric loss than mineral oil in line with the increased oxidation seen by infrared spectroscopy. It is clear that DDB aged in the presence of copper results in very high values of dielectric loss which could cause potential problems in equipment under certain conditions. However, blends of mineral oil and DDB provide a convenient way of overcoming this problem and combining the desirable properties of both oils [8].

B. Vegetable oils

All three vegetable oils darken on ageing in a manner akin to DDB and mineral oil. Representative UV/vis spectra from sunflower oil are shown in Fig. 5. Adding copper accelerates the ageing process and causes the absorption edge for any given ageing time, to appear further to the right (arrowed). In

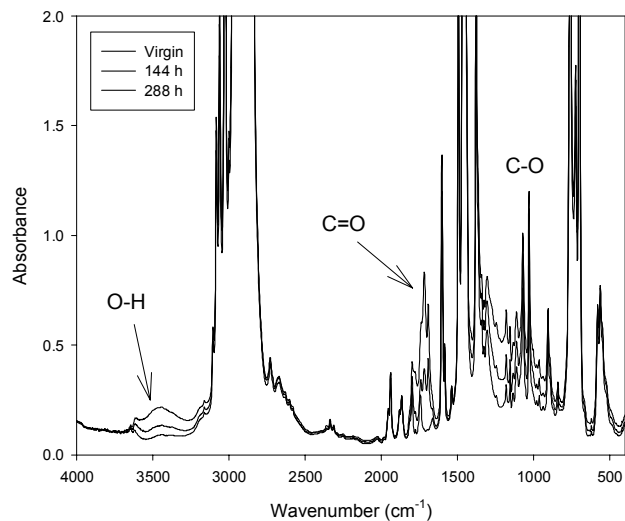


Fig. 3. Infrared spectra of DDB aged with no copper present

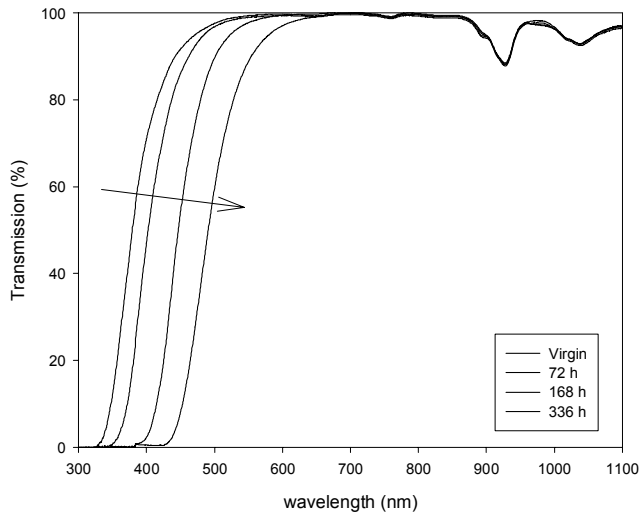


Fig. 5. UV/Vis spectra of sunflower oil aged without copper

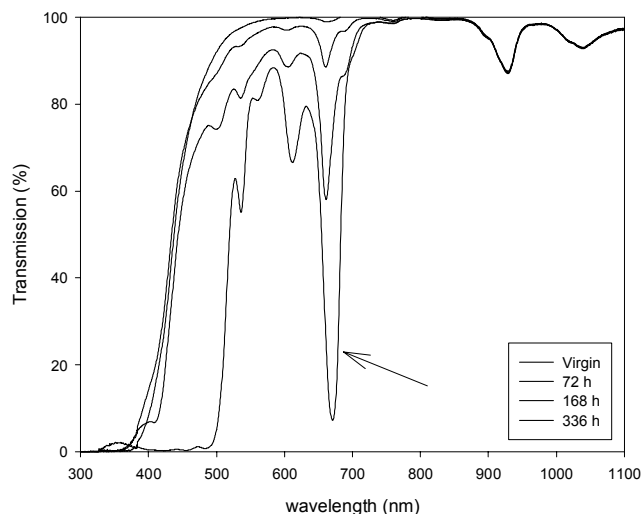


Fig. 6. UV/Vis spectra of olive oil aged with no copper

addition, olive oil shows two chlorophyll peaks (Fig. 6); a sharp absorbance at ~ 680 nm (arrowed) and a broader absorbance from 400 - 500 nm. These features gradually reduce in intensity as the oil is aged indicating that destruction of the chlorophyll is occurring on heating. The presence of the latter chlorophyll peak does not allow any meaningful values to be obtained for the wavelength of 50% transmission in the case of olive oil. Consequentially, the summary plot of Fig. 7 includes only results for sunflower and envirotemp oil. Both oils show the same effect of ageing and comparison with Fig. 2 reveals that the optical properties are similar to DDB. The accelerating effects of copper are clear from the figure.

The infrared spectra of the virgin oil shows that a significant intrinsic absorbance occurs in the carbonyl (~ 1600 cm^{-1}) region, which obscures any effects due to ageing in this region. However all three oils develop a significant hydroxyl absorbance on ageing (arrowed in Fig. 8), the largest

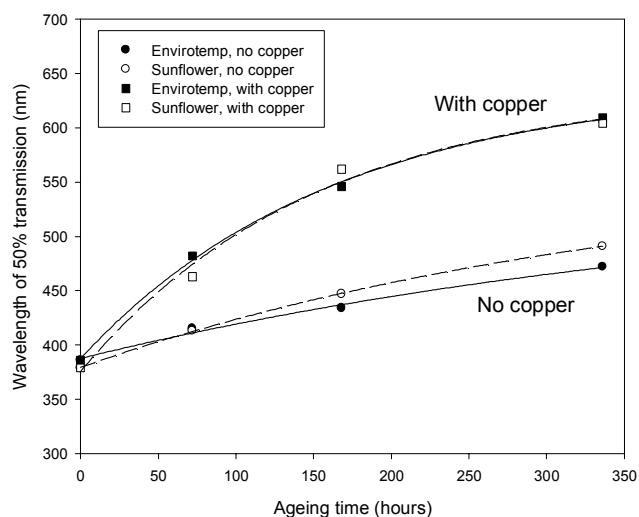


Fig. 7. UV/Vis summary plot for Envirotemp and sunflower oils

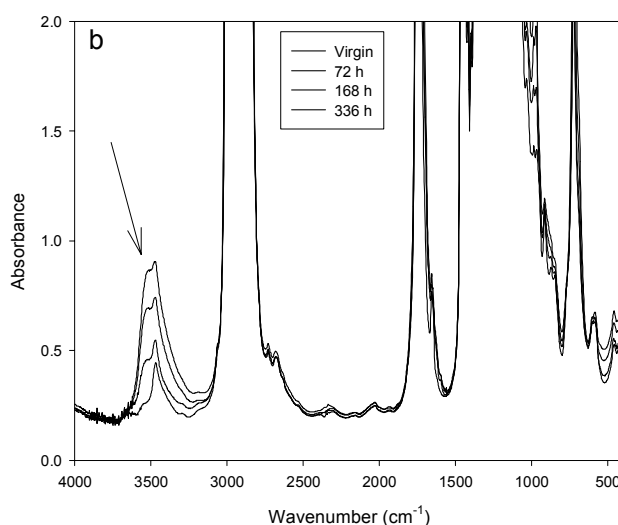
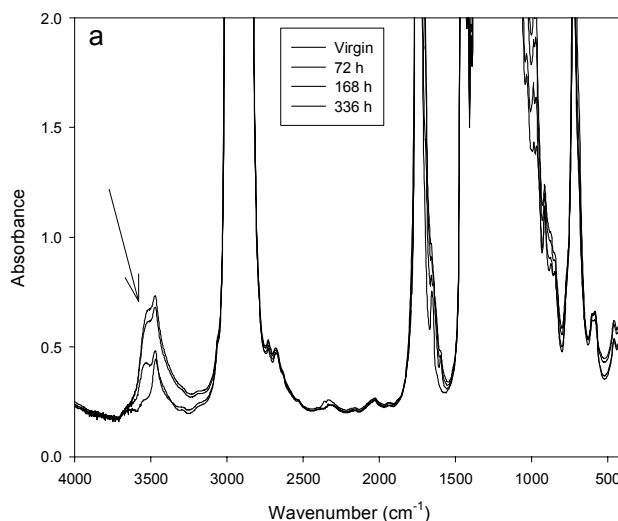


Fig. 8. Infrared spectra of sunflower oil aged (a) without copper (b) with copper

absorbance occurs in sunflower oil aged with copper. Envirotemp oil appears to show the least oxidation on ageing, which is not surprising since this oil is known to contain antioxidants, and olive oil shows intermediate levels of oxidation. Nevertheless, in each oil, the absorbance is increased somewhat on ageing with copper, reflecting its catalytic effect.

Dielectric spectroscopy results for all the vegetable oils are shown in Fig. 9; as with DDB and mineral oil the dielectric loss increases linearly with ageing time. Compared with DDB, the dielectric loss of all three vegetable oils is much lower even after the maximum period of ageing with copper, and are hence most similar to mineral oil. Olive oil shows the highest dielectric loss after ageing, with the envirotemp oil giving the least increase in dielectric loss in line with its reduced oxidation.

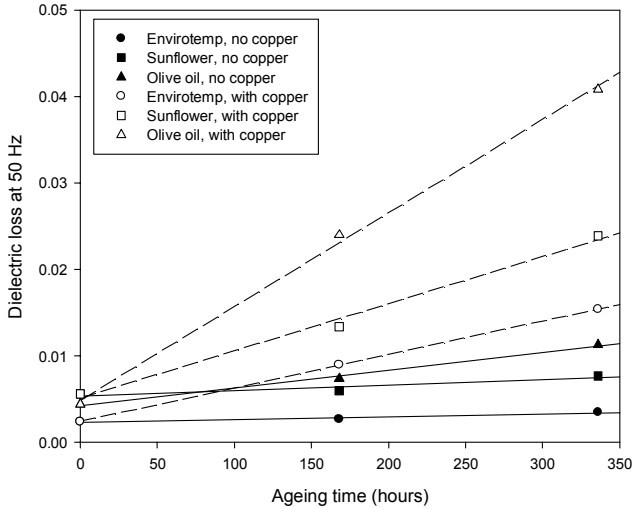


Fig. 9. Dielectric loss of all oils at room temperature

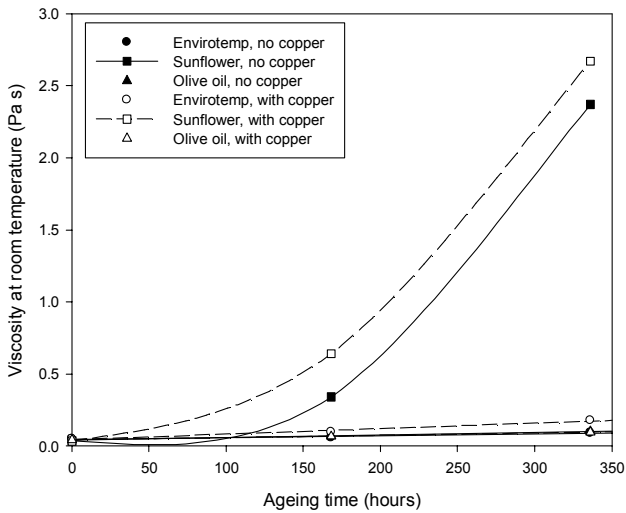


Fig. 10. Viscosity of all oils at room temperature

Fig. 10 shows measurements of viscosity for all 3 vegetable oils after ageing. The viscosity of olive and envirotemp oil increases linearly on ageing from ~ 0.05 Pa s to ~ 0.1 Pa s and the values are slightly higher for the oils aged in the presence of copper. By contrast, sunflower oil shows a non-linear increase in viscosity to very high values at long ageing times. The viscosity of DDB and mineral oil is ~ 0.006 Pa s and is not significantly affected by ageing.

IV. CONCLUSIONS

The ageing of a number of insulating oils were followed by various analytical techniques. Dodecylbenzene darkens on ageing and the darkening can be quantified by UV/vis spectroscopy by measuring the shift in the electronic absorption edge. Infrared spectroscopy shows that it oxidizes significantly in air and, after ageing in the presence of copper,

can exhibit very high dielectric loss. Mineral oil blackens more on ageing but shows superior resistance to oxidation and shows much lower dielectric loss after ageing. Copper accelerates the ageing process causing the oils to become darker, more oxidized and to have a higher dielectric loss after any given period of ageing.

Vegetable oils darken on ageing in a similar manner to DDB and mineral oil. Sunflower oil shows the most oxidation and envirotemp oil shows the least oxidation after any given period of ageing. The dielectric loss was highest in olive oil and lowest in envirotemp oil, but all of the vegetable oils showed reduced dielectric loss compared with DDB aged for the same time. DDB and mineral oil show no detectable increase in viscosity after ageing whilst the viscosity of envirotemp and olive oil roughly double. By contrast, sunflower oil shows a dramatic increase in viscosity which may form the basis of a “smart” self sealing system for cable applications. From these investigations it was found that overall mineral oil performs much better than DDB showing less oxidation and less dielectric loss after any given period of ageing, however all three vegetable oils performed no worse than mineral oil and hence they could form the basis of a suitable replacement for mineral oils in high voltage equipment. Other tests such as flashover and voltage breakdown will, however, need to be performed to fully characterize these systems.

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