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TRANSPORT PROPERTIES OF NANOLUBRICANTS BASED IN POLYOLESTER REFRIGERATION OIL AND DIAMOND NANOPARTICLES

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Abstract. *The focus of this work is the synthesis and the measurement of the thermophysical properties of nanolubricants with a dispersion of nanodiamonds in polyolester refrigeration oil as base fluid at three different mass concentrations 0.01, 0.05 and 0.1%. The density and the viscosity were measured at different temperatures from 10 to 100 ^oC, and the thermal conductivity was measured from 5 to 65 ^oC. It was observed that the viscosity of the nanolubricants increases slightly at low concentration but achieves significant values up to 7% for 1.0% mass concentration, otherwise the viscosity is reduced exponentially with the increment of the temperature. The thermal conductivity of pure POE oil and the nanolubricants showed a trend to decrease with the increment of the temperature and to increase up to 12% as the mass concentration of nanoparticles increases.*

Keywords: *nanolubricants, polyolester, diamond, thermal conductivity*

1. INTRODUCTION

The nanolubricants are another type of nanofluids, defined by Choi and Eastman (1995) as a dispersion of particles with size between $1 - 100$ nm in a usual base fluid to enhance this thermal properties. The dispersion of nanoparticles in a based fluid can improve not only the thermal properties but also the tribological behavior of the two surfaces in contact. Nanolubricants can work as friction modifiers by the following mechanisms: surface coatings, mending effect and polishing effect, (Dai *et al.*, 2016) . Currently, nanolubicant research is pointing to the application of this type of lubricants in refrigeration compressors. Krishna Sabareesh *et al.* (2012) found an enhancement up to 17% of the coefficient of performance (COP) using a nanolubricant with a 0.01% volume concentration of TiO_2 nanoparticles dispersed in mineral oil, as a lubricant compressor in an air conditioning system operating with R12 as refrigerant. Abbas *et al.* (2013) reached a 4% increment in the COP using CNT (Carbon Nanotubes) and POE (Polyolester) oil operating with R134a. Shan Bi *et al.* (2008) studied the influence of the nanolubricant based in mineral oil (MO) with TiO_2 and Al_2O_3 nanoparticles on the cooling capacity and the energy consumption of a domestic refrigeration system operating with R134a. A reduction on the energy consumption of 26.1% and 23.44% were found for the highest concentration. Another advantage was the reduction of the operating time of the refrigeration system when TiO_2 and Al_2O_3 nanoparticles are used as lubricant additives in polyolester lubricantion oil. Wang *et al.* (2010) used $NiFe_2O_3$ to enhance the miscibility of HFC refrigerants with mineral oils. They found that the refrigeration system operates correctly with enhancements for $4 - 6\%$ in the coeficient of performance when compared with the system operating with R410a. Kumar and Elansezhian (2012, 2014) found a reduction of 13.32% and 21% in energy consumption of the compressor energy consumption of a refrigeration system using Al_2O_3 and ZnO nanoparticles, respectively, as lubricant additive in a PAG (Polyalkylene Glycol) oil.

The viscosity of lubricants usually increases with the addition of nanoparticles. In a tribological system an increase in viscosity improves the load carry capacity of the lubricant, but at same time increases the energy consumption in an hydrodynamic lubrication regime, as reported by Krishna Sabareesh *et al.* (2012). This property of nanolubricants is strongly influenced by the volume or mass concentration of nanoparticles as reported by the following authors: Ghazvini *et al.* (2012) evaluated the influence of the concentration of diamond nanoparticles on the viscosity in 20W50 automotive oil for mass concentration from 0.2 to 1%, an increment of 16% was found in the viscosity for the highest concentration when compared with the pure lubricant. Krishna Sabareesh *et al.* (2012) added TiO_2 nanoparticles to refrigeration mineral oil for a volume concentration of 0.005%, 0.01% and the increment of the viscosity at 40^o was 19%, 24.6% and 28%, respectively. Conversely, (Almeida, 2015) reported with experimental measurements that the dynamic viscosity of nanolubricant based on mineral oil and Al_2O_3 nanoparticles at low concentrations can be sightly reduced.

Different authors have studied extensively the thermal conductivity of nanofluids, principally water, ethylene-glycol and insulating transformer oil based nanofluids. In general this property of nanofluids depends on: the nature, the size and morphology of the dispersed particle, the volume or mass concentration, the ratio of the base fluid and the dispersed nano-material thermal conductivity and the use of surfactants to improve the stability etc. Hwang *et al.* (2006) found an increment of 8.4% in the thermal conductivity of refrigeration mineral oil with the addition of carbon nanotubes at 0.5% volume concentration. Jwo *et al.* (2008) increased the thermal conductivity of POE refrigeration oil in 4.5% with the addition of 1.5% mass concentration of Al_2O_3 nanoparticles. Ghazvini *et al.* (2012) reached 36% higher thermal conductivity than the automotive lubricant thermal conductivity dispersing diamond nanoparticles at the highest concentration evaluated. They also found that the thermal conductivity increases with the increment of the mass concentration and the temperature. Sousa (2017) studied the thermal conductivity of nanolubricants with different refrigeration oils as base fluids and indium nanoparticles with the concentration of 0.3 g/l. The results showed enhancements of 38.8%, 27,7% and 38% for mineral oil ISO$-$68, ISO$-$32 and POE ISO$-$32, respectively. Kedzierski *et al.* (2016) measured the thermal conductivity in a wide range of mass concentrations of Al_2O_3 and ZnO nanoparticles up to 38% in POE refrigeration oil. Both nanoparticles presented almost the same enhancement in this property, also the measured data showed that the thermal conductivity increases as the mass concentration increases. Sharif *et al.* (2016) tested the influence of Al_2O_3 nanoparticles in polyalkylene glycol (PAG) thermal conductivity and they found a maximum increment of 4% compared with the base fluid at the maximum concentration. Finally, the focus of this work was the synthesis and the measurement of the density, viscosity and thermal conductivity of the nanolubricants with a dispersion of nanodiamonds in polyolester refrigeration oil as base fluid at three different mass concentrations 0.01, 0.05 and 0.1 %, and its relation with the temperature.

2. EXPERIMENTAL PROCEDURE

2.1 Synthesis of nanolubricants

The two-step method was used to synthesise the four nanolubricants prepared in this work, since it is widely used and recommended by different authors as: (Kedzierski *et al.*, 2016), (Sharif *et al.*, 2016), (Almeida, 2015) etc. The diamond nanoparticles with a purity of 97.7% and 3-6 nm in size were acquired separately from Nanostructured & Amorphous Materials, Inc and then dispersed in the base fluid. Also, Commercial lubricant polyolester refrigeration oil 160PZ (ISO$-$32) was used as base fluid. The properties used for all the calculations in this work of the base fluid and the diamond nanoparticles are presented in Tab. 1.

Table 1. Properties of lubricating oil and nanoparticles.

Properties	POE-160$^{(1)}$	Diamond$^{(2)}$
$k(W/m \cdot K)$	0.139	2200
$\mu(mPa \cdot s)$	80.961	$\cdots$
$\rho(kg/m^3)$	0.978	3530

$^{(1)}$ measured at 25^{o}C
$^{(2)}$ Reported by the manufacturer

First, the mass of nanoparticles was estimated for each mass concentration according to the Eq. (1) for 0.01, 0.05 and 0.1% mass concentrations, and weighted in a precision balance with an accuracy of 0.001 g from the GEHAKA BK500, after that, the nanoparticles at each concentration were dispersed in oleic acid as surfactant using an ultrasonic vibrator to improve the stability of the colloidal suspension. Then, the oleic acid and nanodiamonds suspensions were separated using a centrifuge at 8000 rpm for 10 minutes, then the excess of oleic acid was drained and finally the nanoparticles decanted at the bottom of the falcon tube were dispersed in the base using an ultrasonic vibrator for 30 minutes at 650 W to reach an homogeneous dispersion and clusters separation. Just for comparison purposes the mass concentrations and the volume concentration are related by the Eq. (3), the respectively volume concentration of the nanolubricants prepared are 0.02%, 0.14% and 0.29%. In the Fig. 1 are presented the nanolubricants prepared, parting from the pure oil at the left side and increasing with the volume concentration to right.

$$\phi_m = \frac{m_{np}}{(m_{np} + m_{fb})} \cdot 100 \tag{1}$$

$$\phi_v = \frac{m_{np}/\rho_{np}}{(m_{np}/\rho_{np} + m_{bf}/\rho_{bf})} \cdot 100 \quad (2)$$

$$\phi_v = \frac{\phi_m}{\rho_{np}(\frac{\phi_m}{\rho_{np}} + \frac{(1-\phi_m)}{\rho_b f})} \quad (3)$$

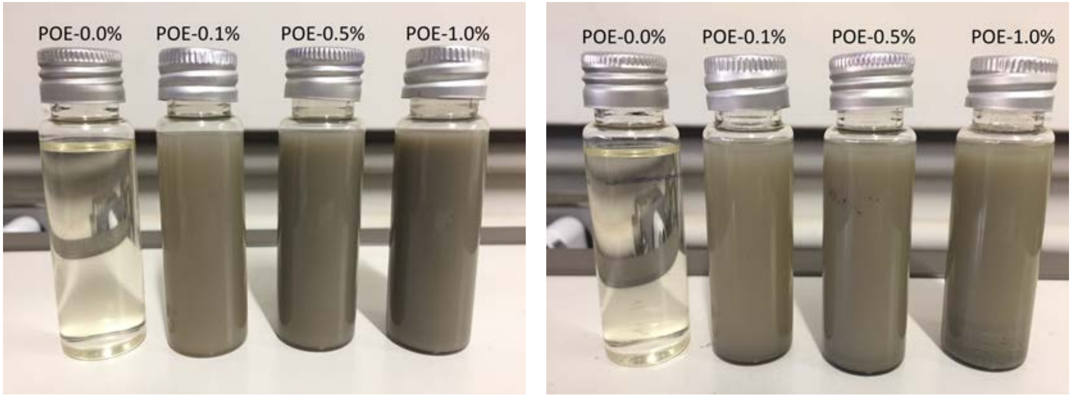

Figure 1. a) Nanolubricants right after it had been prepared and b) after one week.

2.2 Viscosity and density

The density, the dynamic and the kinematic viscosity of the samples were measured using an Anton Paar SVM 3000/G2 Stabinger viscometer with an accuracy of the 0.1%, 0.0002 g/cm3 and 0.02 ^{o}C, respectively. The measure range of the equipment covers from 0.2 to 20.000 mPa·s. The viscosity and the density were measured varying the temperature from 10 to 100 ^{o}C with the increment of 10 C. The measurements of the properties were repeated four times for each temperature and concentration starting from the lower concentration to the highest.

The classical viscosity models of Brinkman (1952), Batchelor (1977) and Wang *et al.* (2003) experimental correlation are presented in the in the Eq. (4), Eq. (5) and Eq. (6), respectively in order to compared the measured data.

$$\frac{\mu_{nf}}{\mu_{bf}} = \frac{1}{(1-\phi_{vol})^{2.5}} \quad (4)$$

$$\frac{\mu_{nf}}{\mu_{bf}} = (1 + 2.5\phi_{vol} + 6.5\phi_{vol}^2) \quad (5)$$

$$\frac{\mu_{nf}}{\mu_{bf}} = (1 + 7.3\phi_{vol} + 123\phi_{vol}^2) \quad (6)$$

2.3 Thermal conductivity

The measurement of the thermal conductivity of the nanolubricants at different concentrations were measured with the transient hot bridge method using a LINSEIS model THB-1 thermal conductivity meter, able to measure until 1 $W/m{\cdot}K$ with an uncertainty better than 2% of the measured value. A MQBMP-01 water bath was used to control the temperature of the sample for each measurement. The thermal conductivity was measured in a range of temperature from 5 to 65 ^{o}C by steps of 10 ^{o}C, every measurement was repeated 30 times for each temperature and the average value will be assumed as the thermal conductivity of the fluid at the specified temperature.

The measured thermal conductivity of the nanolubricants were used to compare with some theoretical models presented in the literature. The model presented by Maxwell (1904) presented in the Eq. (7). This model involves only the volume concentration of nanoparticles ϕ_{vol}, the thermal conductivity of the nanoparticles k_{np} and of the base fluid k_{np}. (Timofeeva *et al.*, 2007) presented another theoretical model for predicting the thermal conductivity of the nanofluids expressed as shown in the Eq. (8).

$$\frac{k_{nf}}{k_{nf}} = \frac{k_{np} + 2k_{bf} + 2(k_{np} - k_{bf})\phi_{vol}}{k_{np} + 2k_{bf} - (k_{np} - k_{bf})\phi_{vol}} \quad (7)$$

$$\frac{k_{nf}}{k_{bf}} = 1 + 3\phi_{vol} \quad (8)$$

3. RESULTS AND DISCUSSION

3.1 Density measurement

Figure 2 (a) depicts the measured values of the density of raze polyolester oil and the nanolubricants as a function of the temperature. It can be seen that the density of the lubricant oil and of the nanolubricants decreases linearly with the temperature. The maximum density reduction caused by the temperature increment, was presented at the highest temperature evaluated (100 ^oC) for the all of the tested lubricants and the maximum average was 6.75%. Otherwise, the density of the nanolubricants tends to increase with the nanoparticles concentration as can be seen in the Fig. 2 (b). In order to predict the density values of the nanolubricants was used the correlation proposed by Pak and Cho (1998) showed in the Eq. (9).

$$\rho_{nf} = (1 - \phi_{vol})\rho_{bf} + \phi_{vol}\rho_{np} \tag{9}$$

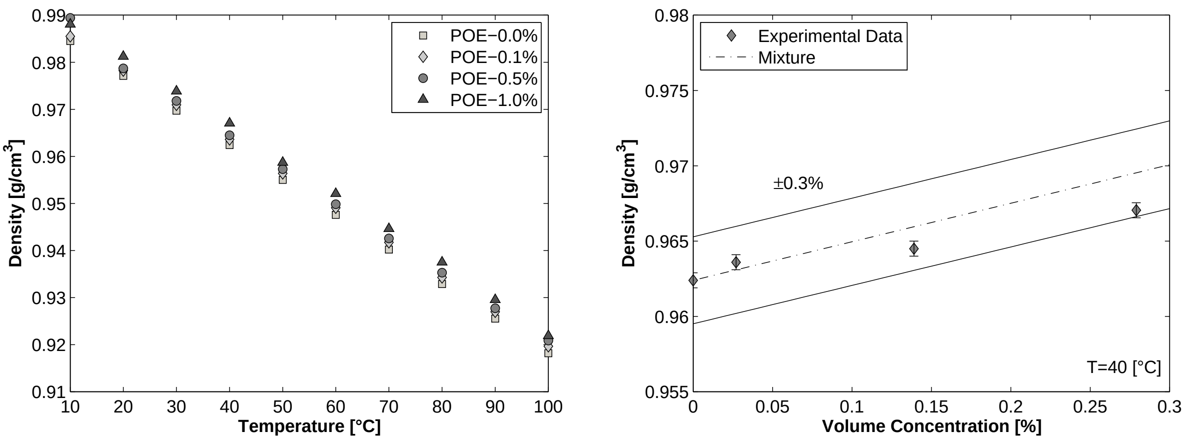

Figure 2. Density of POE/Diamond nanolubricants: a) the density as a function of the temperature and b) the density as a function of the volume concentration at 40 ^oC.

Figure 2 (b) compares the experimental data with the theoretical values of the density computed from the Eq. (9) at 40 ^oC. A maximum deviation of approximately 0.3% was found at the highest concentration. Also, the deviation increases with the volume concentration.

3.2 Viscosity measurement

Figure 3 (a) shows the values measured of the dynamic viscosity of the pure oil and the nanolubricants at diferent volumetric concentration as function of the temperature. At low temperatures (up to 20 ^oC) were found a reduction in the viscosity of the nanolubricant with 0.1% of diamond mass concentration. The same behaviour was reported by Almeida (2015) with refrigeration mineral oil and low concentrations of Al_2O_3 nanoparticles. For temperatures above 20 ^oC the viscosity of for all concentrations were found higher than the base fluid viscosity. The viscosity of all the tested samples decreased exponentially with the temperature. The average reduction on the viscosity was almost the 96% between the lowest and highest temperature. caused by the concentration were found at 100 ^oC. Nevertheless the temperature has reduced the viscosity of the nanolubricants, the volume concentration has increased it, even at high temperatures.

Figure 2 (b) presents the effect of volume concentrations in the nanolubricants dynamic viscosity and the predicted viscosity computed from the models presented above at 40 ^oC. The increments of the viscosity were 0.6%, 2.5% and 7% for the 0.1%, 0.5% and 1.0%, respectively. The Fig 2 (b) also shows that the theoretical models of Brinkman (1952),Batchelor (1977), and Wang *et al.* (2003) under predict this property. Sharif *et al.* (2016) tested the model of Wang *et al.* (2003) and it also under estimate the viscosity of the nanolubricants based on PAG refrigeration lubricant oil and alumina nanoparticles for all the concentrations evaluated. Oliveira (2012) in all of the correlations studied for the viscosity of the nanofluids, he did not found any one with the enough accuracy to predict this property. Principally, because these models do not involve the influence of the temperature and the nature of the nanoparticles.

According to the ASTM standard D2422−97 the upper and lower limits for the kinematic viscosity of ISO 32 viscosity grade lubricant oil at 40 ^oC are 28.8 and 35.2 mm^2/s, respectively and the mid-point viscosity is the same grade of classification. The kinematic viscosity of the pure oil at 40 ^oC was 33.35 mm^2/s and the as expected the this property also was increased with the volume concentration. The kinematic viscosty of the 0.1%, 0.5% mass concentration stayed inside the boundaries defined by the standard with the values of 33.51 and 34.1 mm^2/s but the highest concentration reaches the upper limit with the value of 35.5 mm^2/s.

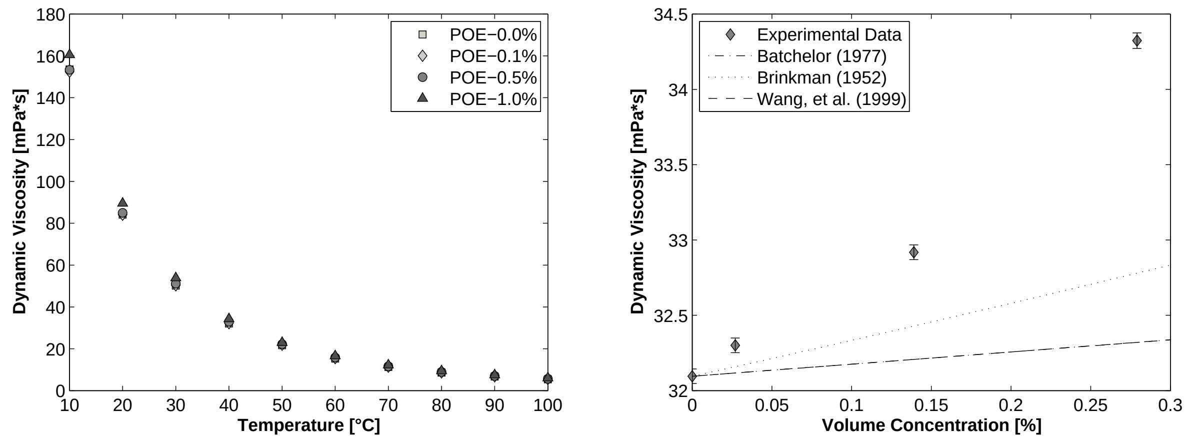

Figure 3. Dynamic viscosity of POE/Diamond nanolubricants: a) the Dynamic viscosity as a function of the temperature and b) the Dynamic viscosity as a function of the volume concentration at 40 ^{o}C.

3.3 Thermal conductivity measurement

The mean values of the thermal conductivity of the pure oil and the nanolubricants as a function of the temperature at different volume concentrations are given in the Fig. 4 (a). The figure shows that the thermal conductivity of the pure POE oil and of the nanolubricants decreases with the temperature but increases with the volume concentration. This reduction is in accordance with the data reported by (Kedzierski *et al.*, 2016), (Sousa, 2017) for POE oil and by (Sharif *et al.*, 2016) for PAG refrigeration oil. They explained this behavior as a separation of the fluid molecules induced by an increase in temperature of the fluid. So, that reduces the probability of collision of the molecules and consequently the thermal conductivity of the fluid.

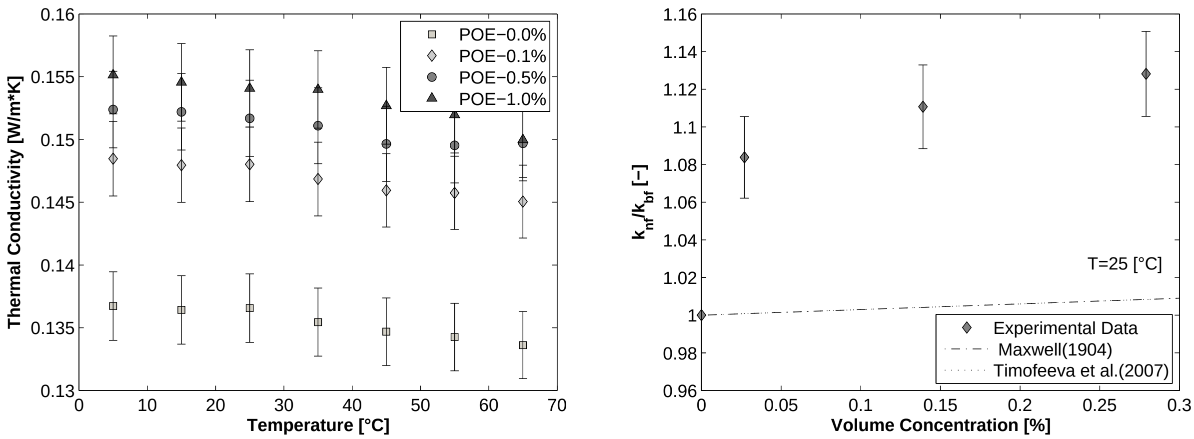

Figure 4. Thermal conductivity of POE/Diamond nanolubricants: a) the thermal conductivity as a function of the temperature and b) the thermal conductivity as a function of the volume concentration at 25 ^{o}C.

Figure 4 (b) presents the ratio between the thermal conductivity of the nanolubricant over the base fluid as a function of the volume concentration at 25 ^{o}C. As can be seen in this figure, it is possible to reinforce the idea that the thermal conductivity of the lubricant increases with the volume concentration. Enhances of 8%, 11% and 12% in the thermal conductivity of the lubricant were found for the 0.1%, 0.5% and 1.0% mass concentrations, respectively. In addition it is possible observe from the Fig 4 (b) that the thermal conductivity ratio curve is highly steep at very low volume concentrations, but also shows a trends to flatten from the 0.5% mass concentration. In other words, from the measured data it is possible to conclude that the enhance in the thermal conductivity with the volume concentration is not as pronounced at high concentrations of nanoparticles for POE/Diamond nanofluids. Also, when elevated volume or mass concentrations of nanoparticles are used, directly increases the cost of production by the elevated mass of nanoparticles needed, harder to reach a good stability of the dispersion by the reduction of the probability of flocculation of the particles and higher viscosity that can increase the power consumption.

4. CONCLUSIONS

The development and the measurement of the density, the viscosity and the thermal conductivity of a nanolubricant based in polyolester refrigeration oil with a dispersion of diamond nanoparticles at different concentrations have been studied. The two-step method where with the addition of oleic acid as a surfactant, which brings a better stability of the colloidal suspension. The density measurement showed a trend to increase with the addition of nanoparticles and also to decrease almost linear with the temperature. The mixture model predicts the density of the nanolubricants as a function of the volume concentration with a maximum deviation of 0.3%.

For the lowest evaluated diamond concentration and in temperatures below 20 ^{o}C were found a slightly decrease in the dynamic viscosity. However for higher concentrations the viscosity was incremented up to 7%. For the 1.0% mass concentration the kinematic viscosity reaches the upper limit of the ASTM standard D2422−97. The theoretically models evaluated in this work in order to predict the dynamic viscosity of the nanolubricants failure with a large deviation of the experimental measured data.

The thermal conductivity of the nanolubricant increases with increment of the mass concentration up to 12% at 25 ^{o}C. And also the experimental data showed a trend to decrease with the increment of the temperature. As well as the viscosity the models available in the literature for predicting the thermal conductivity of the nanolubricants does not predicts this property correctly, underestimating for all the evaluated conditions.

Further investigation on the thermophysical properties is important focusing on the rheological behaviour of the nanolubricants, and the thermal conductivity, viscosity of the refrigerant-nanolubricant mixtures.

5. ACKNOWLEDGEMENTS

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