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Effect of Refrigerant Oil Additive on R134a and R123 Boiling Heat Transfer Performance and Related Issues for GSA[1]

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ABSTRACT[2]

This paper investigates the effect that an additive had on the boiling performance of an R134a/polyolester lubricant (POE) mixture and an R123/naphthenic mineral oil mixture on a roughened, horizontal flat surface. Both pool boiling heat transfer data and lubricant excess surface density data are given for the R134a /POE (98 % mass fraction/2 % mass fraction) mixture for before and after use of the additive. A spectrofluorometer was used to measure the lubricant excess density that was established by the boiling of the R134a/POE lubricant mixture before and after use of the additive. The measurements obtained from the spectrofluorometer suggest that the additive increases the total mass of lubricant on the boiling surface. The heat transfer data show that the additive caused an average and a maximum enhancement of the R134a/POE heat flux between 5 kW/m^2 and 22 kW/m^2 of approximately 73 % and 95 %, respectively. Conversely, for nearly the same heat flux range, the additive caused essentially no change in the pool boiling heat flux of an R123/mineral oil mixture. The lubricant excess surface density and interfacial surface tension measurements of this study were used to form the basis of a hypothesis for predicting when large liquid-vapor surface-tension additives will enhance or degrade refrigerant/lubricant pool boiling. The results of a compatibility study of the additive with typical commercial refrigerants and lubricants are included along with a survey of chiller manufacturers on the use of additives.

Keywords: additive, alternative refrigerants, boiling, enhanced heat transfer, fluorescence, non-adiabatic lubricant excess surface density, refrigerant/lubricant mixtures, polyolester lubricant, naphthenic mineral oil

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[1] GSA (U.S. General Services Administration)

[2] Only pool-boiling heat transfer laboratory tests are presented in this report. Full-scale chiller tests would be required to observe the change in performance for a particular chiller. In addition, heat transfer improvements do not necessarily guarantee improvements and/or changes in chiller performance because of other factors that influence HVAC equipment performance.

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INTRODUCTION

The importance of improving the efficiency of existing air-conditioning equipment has been significantly emphasized with the 2003 blackout of the U.S. Northeast. A refrigerant oil additive that improves water chiller efficiency could be a cost-effective and immediate means of reducing operating costs and improving the reliability of (reduced demand on) our nation's electricity grid. Some manufacturers of oil additives claim as much as a 30 % reduction in chiller energy usage. If it were possible to achieve an energy reduction of this magnitude in air conditioning chillers, millions of dollars a year could be saved in operating costs. This would also offer a significant contribution toward satisfying Section 202 of Executive Order 13123, which requires agency energy use reductions of 35 % by the year 2010. In addition, the current version of the "Energy Bill of 2003"[3] encourages all federal agencies to take actions to maximize the efficiency of air conditioning and refrigeration equipment which may include the use of any additive. Unfortunately, only field data have been used to support oil additive manufacturer claims of system improvement. The lack of controlled experimental data has been one of the greatest obstacles to large-scale applications of refrigerant oil additives.

Several refrigerant oil additives similar to that which was awarded an U.S. Patent in 1990 (Wilkins et al., 1990) are available today. The premise of the patent claim is that if the additive is sufficiently polar, it will attach to the "highly electron charged" metal surface via Van de Waals forces and displace the oil at the surface. The additive proposed by the patent is a chlorinated α-olefin or paraffin. In response to the "ozone crisis" a chlorine-free oil additive, PROATEQ[4] is available. Although the PROATEQ is not covered by the Wilkins et al. (1990) patent due to the absence of chlorine, the mechanistic heat transfer claims are similar if not identical to those of the patent.[5]

Recent studies have shown that refrigerant boiling heat transfer is a strong function of lubricant properties (Kedzierski and Kaul 1993, Kedzierski 2001c, and Kedzierski 2002b). When a lubricant is added to a refrigerant, either an enhancement or a degradation in heat transfer performance is achieved relative to that of the pure refrigerant depending on the lubricant viscosity, miscibility, and concentration. In addition, Kedzierski (2001b) has shown that if heat transfer degradation exists due to the use of a lubricant, reducing the lubricant layer will lessen lost performance. Consequently, if the additive behaves as outlined in the patent, it is possible that performance improvements could occur as long as both the additive and the displaced lubricant do not detrimentally affect performance in other ways.

The primary goal of this study was to determine if the pool boiling performance of two refrigerant/lubricant mixtures could be improved with the addition of a liquid additive. PROATEQ was chosen as the test additive because it has low sulfur content and it does

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[3] H.R. 6, Energy Policy Act of 2003, Section 553, pgs. 22-23. http://www.house.gov/rules/text_6cr.pdf

[4] Certain trade names and company products are mentioned in the text or identified in an illustration in order to adequately specify the experimental procedure and equipment used. In no case does such an identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products are necessarily the best available for the purpose.

[5] http://www.molecular-solutions.com

not contain chlorine. The lubricants chosen were a polyolester (DE589[6]) for use with R134a and a naphthenic mineral oil (York-C) for use with R123. The viscosities of DE589 and York-C at 313.15 K were 21.76 $\mu m^2/s$ and approximately 60 $\mu m^2/s$, respectively. The viscosity of the additive at 313.15 K taken from its Material Safety Data Sheet (MSDS) was approximately 32 $\mu m^2/s$. The MSDS also indicated that the additive has a naphthenic petroleum hydrocarbon base.

The secondary goals of the study were to test the additive enhancement mechanism of lubricant displacement. The recently developed measurement technique (Kedzierski, 2001b) for measuring the lubricant mass on a boiling surface was used to determine if the additive had displaced lubricant from the surface. Appendix A provides the test results of the additive's compatibility with commercial lubricants. It is essential to understand the compatibility of additives with lubricants and refrigerants given that chiller reliability may depend on it. In addition, the survey that was given to the major chiller manufacturers to solicit their comments on the use of the additive in their equipment is given in Appendix B.

APPARATUS

Figure 1 shows a schematic of the apparatus that was used to measure the pool boiling data of this study. More specifically, the apparatus was used to measure the liquid saturation temperature (T_s), the average pool-boiling heat flux (q''), the wall temperature (T_w) of the test surface, and the fluorescence intensity from the boiling surface (F). The three principal components of the apparatus were the test chamber, the condenser, and the purger. The internal dimensions of the test chamber were 25.4 mm × 257 mm × 1.54 m. The test chamber was charged with approximately 7 kg of refrigerant, giving a liquid height of approximately 80 mm above the test surface. As shown in Fig. 1, the test section was visible through two opposing, flat 150 mm × 200 mm quartz windows. The bottom of the test surface was heated with high velocity (2.5 m/s) water flow. The vapor produced by liquid boiling on the test surface was condensed by the brine-cooled, shell-and-tube condenser and returned as liquid to the pool by gravity.

Figure 1 also shows the spectrofluorometer that was used to make the fluorescence measurements and the fluorescence probe perpendicular to the heat transfer surface. The fluorescence probe was a bifurcated optical bundle with 168 fibers spanning from the spectrofluorometer to the test surface. The 168 fibers of the probe were split evenly between the fibers to transmit the incident intensity (I_o) to the test surface and those to receive the fluorescence intensity (F) from the lubricant on the test surface. Further details of the test apparatus can be found in Kedzierski (2002a) and Kedzierski (2001a).

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[6] ICI's EMKARATE RL DE 589 (A model polyolester made for NIST. Not a commercial product.)

TEST SURFACE

Figure 2 shows the oxygen-free high-conductivity (OFHC) copper flat test plate used in this study. The test plate was machined out of a single piece of OFHC copper by electric discharge machining (EDM). A tub grinder was used to finish the heat transfer surface of the test plate with a crosshatch pattern. Average roughness measurements were used to estimate the range of average cavity radii for the surface to be between 12 µm and 35 µm. The relative standard uncertainty of the cavity measurements were approximately ± 12 %. Further information on the surface characterization can be found in Kedzierski (2001a).

MEASUREMENTS AND UNCERTAINTIES

The standard uncertainty (u_i) is the positive square root of the estimated variance u_i^2. The individual standard uncertainties are combined to obtain the expanded uncertainty (U), which is calculated from the law of propagation of uncertainty with a coverage factor. All measurement uncertainties are reported at the 95 % confidence level except where specified otherwise. For the sake of brevity, only an outline of the basic measurements and uncertainties is given below. Complete detail on the heat transfer measurement techniques and uncertainties can be found in Kedzierski (2000, 2001a and 2001b).

Heat Transfer

All of the copper-constantan thermocouples and the data acquisition system were calibrated against a glass-rod standard platinum resistance thermometer (SPRT) and a reference voltage to a residual standard deviation of 0.005 K. Considering the fluctuations in the saturation temperature during the test and the standard uncertainties in the calibration, the expanded uncertainty of the average saturation temperature was no greater than 0.04 K. Consequently, it is believed that the expanded uncertainty of the temperature measurements was less than 0.1 K.

Twenty 0.5 mm diameter thermocouples were force fitted into the wells of the side of the test plate shown in Fig. 2. The heat flux and the wall temperature were obtained by regressing the measured temperature distribution of the block to the governing two-dimensional conduction equation (Laplace equation). In other words, rather than using the boundary conditions to solve for the interior temperatures, the interior temperatures were used to solve for the boundary conditions following a backward stepwise procedure given in Kedzierski (1995). Fourier's law and the fitted constants from the Laplace equation were used to calculate the average heat flux (q'') normal to and evaluated at the heat transfer surface based on its projected area. The average wall temperature (T_w) was calculated by integrating the local wall temperature (T). The wall superheat was calculated from T_w and the measured temperature of the saturated liquid (T_s). Considering this, the relative expanded uncertainty in the heat flux ($U_{q''}$) was greatest at the lowest heat fluxes, approaching 10 % of the measurement near 10 kW/m^2. In general, the $U_{q''}$ remained approximately within 3 % and 5 % for heat fluxes greater than 30 kW/m^2. The average random error in the wall superheat (U_{Tw}) was between 0.02 K and 0.1 K. Plots of $U_{q''}$ and U_{Tw} versus heat flux can be found in Appendix C.

Fluorescence

Kedzierski (2002a) describes the method for measuring the excess mass of lubricant on the boiling surface per surface area, i.e., the surface excess density (Γ). Because the molar mass of the lubricant is unknown, Γ is defined in this work on a mass basis as:

$$\Gamma = \rho_e x_e l_e - \rho_b x_b l_e \tag{1}$$

where the l_e is the thickness of the lubricant excess layer. Precedence for reporting the surface excess density in mass units is given by citing the work of McBain and Humphreys (1932) in which they experimentally verified the Gibbs adsorption equation by measuring Γ at a liquid-vapor interface.

The equation for calculating the lubricant excess surface density from the measured fluorescence emission intensity (F_m) is (Kedzierski, 2002b, 2003):

$$\Gamma = \rho_e x_e l_e - \rho_b x_b l_e = \frac{\rho_b x_b \left(\frac{\rho_{L,T_e}}{\rho_{L,T_b}} - \frac{\rho_b x_b}{\rho_{L,T_b}} \right) \left(\frac{F_m}{F_c} - 1 \right)}{\frac{I_{oe}}{I_{ob}} \left(1 + 1.165 \frac{\varepsilon}{M_L} x_b \rho_b l_b \right) \frac{e^{\beta (T_e - T_b)}}{l_b} - 1.165 \frac{\varepsilon}{M_L} x_b \rho_b \left(\frac{F_m}{F_c} - 1 \right)} \tag{2}$$

where the value of $\frac{\varepsilon}{M_L}$ was obtained from the fluorescence calibration as 0.0646 m^2/kg, and the fluorescence temperature dependence coefficient (β) of DE589 was experimentally determined to be 0.01 K^{-1} (Kedzierski, 2003). The β accounts for the difference in temperature between the excess layer and the bulk fluid. The density of the pure lubricant is ρ_L. All of the fluid properties are evaluated at the bulk fluid temperature (T_b) with the exception of the $\rho_{L,Te}$, which is the pure lubricant density evaluated at the average temperature of the excess layer (T_e).

Input for eq. (2) is as follows. The fluorescent intensity from the calibration (F_c) is obtained from eq. (1) of Kedzierski (2003) evaluated at the charged bulk lubricant concentration of test fluid in the boiling apparatus. The l_b is the distance between the probe and the heat transfer surface and $l_b >> l_e$. The ratio of the absorption of the incident excitation in the bulk to that in the excess layer (I_{oe}/I_{ob}) was 0.985 for the R134a/DE589 (98/2) mixture.

EXPERIMENTAL RESULTS

Heat Transfer

The heat flux was varied roughly between 100 kW/m^2 and 5 kW/m^2 to simulate more than most possible operating conditions for R134a and R123 chillers. All pool-boiling tests were taken at 277.6 K saturated conditions. The data were recorded consecutively starting at the largest heat flux and descending in intervals of approximately 4 kW/m^2. The descending heat flux procedure minimized the possibility of any hysteresis effects on the data, which would have made the data sensitive to the initial operating conditions. Table 2 presents the measured heat flux and wall superheat for all the data of this study. Table 3 gives the number of test days and data points for each fluid.

The mixtures were prepared by charging the test chamber (see Fig. 1) with pure refrigerant (either R134a or R123) to a known mass. Next, a measured mass of lubricant (DE589 with R134a and York-C for R123) was injected with a syringe through a port in the test chamber. The refrigerant/lubricant solution was mixed by flushing pure refrigerant through the same port where the lubricant was injected. After the tests with the refrigerant/lubricant mixture were completed, the PROATEQ additive was added to the existing test chamber charge in the same manner as for the lubricant. PROATEQ was added to the refrigerant/lubricant (98/2) mixture as roughly 10 % of the existing mass of lubricant in the system giving an R134a/DE589/ PROATEQ (97.8/2/0.2) mixture and an R123/York-C/ PROATEQ (97.8/2/0.2) mixture. All compositions were determined from the masses of the charged components and are given on a mass fraction percent basis. The maximum uncertainty of the composition measurement is approximately 0.02 %, e.g. the range of a 2.0 % composition is between 1.98 % and 2.02 %.

Figure 3 is a plot of the measured heat flux (q'') versus the measured wall superheat (T_w - T_s) for the R134a/DE589 (98/2) mixture at a saturation temperature of 277.6 K. The opened circles represent 16 days of boiling measurements made over a period of approximately four weeks. The solid lines shown in Fig. 3 are cubic best-fit regressions or estimated means of the data. Three of the 144 measurements were removed before fitting because they were identified as "outliers" based on having both high influence and high-leverage (Belsley et al., 1980). Table 4 gives the constants for the cubic regression of the superheat versus the heat flux for all of the fluids tested here. The residual standard deviation of the regressions - representing the proximity of the data to the mean - are given in Table 5. The dashed lines to either side of the mean represent the lower and upper 95 % simultaneous (multiple-use) confidence intervals for the mean. From the confidence intervals, the expanded uncertainty of the estimated mean wall superheat was 0.15 K and 0.26 K for superheats less than and greater than 7 K, respectively. Table 6 provides the average magnitude of 95 % multi-use confidence interval for the fitted wall superheat for all of the test data.

Figure 4 plots the measured heat flux (q'') versus the measured wall superheat (T_w - T_s) at a saturation temperature of 277.6 K for the R134a/DE589/ PROATEQ (97.8/2/0.2) mixture. The mean of the R134a/DE589 (98/2) mixture is plotted as a coarsely dashed line. Comparison of the two boiling curves shows that they intersect at a superheat of approximately 8 K. For mean superheats less than 8 K, the R134a/DE589/ PROATEQ (97.8/2/0.2) mixture exhibits an enhancement in the heat flux as compared to the R134a/DE589 (98/2) mixture. In contrast, the R134a/DE589 (98/2) mixture heat flux is greater than that of the R134a/DE589/ PROATEQ (97.8/2/0.2) mixture for superheats greater than 8 K. Apparently, the additive enhances the site density and, in turn, the heat transfer at superheats less than 8 K. For superheats greater than 8 K, the degradation exhibit by the R134a/DE589/ PROATEQ (97.8/2/0.2) mixture is likely to have resulted from the decreased in bubble size as compared to the two-component mixture (see Kedzierski, 2001c).

Figure 5 is a plot of the measured heat flux (q'') versus the measured wall superheat ($T_w - T_s$) for the R123/York-C (98/2) mixture at a saturation temperature of 277.6 K. The closed circles represent nine days of boiling measurements made over a period of approximately six months. The average expanded uncertainty of the estimated mean wall superheat averaged over all heat fluxes was 0.14 K.

Figure 6 is a plot of the measured heat flux (q'') versus the measured wall superheat ($T_w - T_s$) for the R123/York-C/ PROATEQ (97.8/2/0.2) mixture at a saturation temperature of 277.6 K. The closed squares represent 17 days of boiling measurements made over a period of approximately four weeks. The expanded uncertainty of the estimated mean wall superheat for the entire range of measured superheats was 0.13 K. The mean of the R123/York-C (98/2) mixture heat transfer measurements is provided as a coarsely dashed line for comparison.

A more detailed comparison of the refrigerant/lubricant and the refrigerant/lubricant/additive heat transfer performances for the R134a and the R123 mixtures is given in Fig. 7. Figure 7 plots the ratio of the R134a/DE589/ PROATEQ (97.8/2/0.2) heat flux to the R134a/DE589 (98/2) heat flux ($q''_m/q''_{2\%}$) versus the R134a/DE589 (98/2) mixture heat flux ($q''_{2\%}$) at the same wall superheat. Likewise, the R123/York-C/ PROATEQ (97.8/2/0.2) heat flux to the R123/York-C (98/2) heat flux ($q''_m/q''_{2\%}$) versus the R123/York-C (98/2) mixture heat flux ($q''_{2\%}$) at the same wall superheat is also plotted. A heat transfer enhancement exists where the heat flux ratio is greater than one and the 95 % simultaneous confidence intervals (depicted by the shaded regions) do not include the value one. Figure 7 shows that R134a/DE589/ PROATEQ (97.8/2/0.2) mixture exhibits an enhancement over the R134a/DE589 (98/2) mixture for heat fluxes between 5 kW/m^2 and 30 kW/m^2. The maximum heat flux ratio was 1.95 ± 0.02 at 13 kW/m^2. The heat transfer data shows that the additive caused an average and a maximum enhancement of the R134a/DE589 (98/2) mixture heat flux between 5 kW/m^2 and 22 kW/m^2 of approximately 73 % and 95 %, respectively. Figure 7 also shows that the R123/York-C/ PROATEQ (97.8/2/0.2) mixture exhibits a heat transfer degradation for all heat fluxes between approximately 22 kW/m^2 and 78 kW/m^2. The additive caused essentially no change in the heat transfer performance in the R123/York-C (98/2) mixture from approximately 8 kW/m^2 to 22 kW/m^2 given that the average heat flux ratio in that region approximately 1.0. The minimum heat flux ratio for this mixture was 0.73 ± 0.05 at approximately 73 kW/m^2. The average heat flux ratio for the R123/York-C/ PROATEQ (97.8/2/0.2) mixture from approximately 10 kW/m^2 to 80 kW/m^2 was 0.88.

Excess Surface Density

The primary purpose of the excess surface density measurements presented here was to test the enhancing mechanism proposed in a 1990 U.S. Patent (Wilkins et al., 1990), which claims that certain refrigerant oil additives displace chiller lubricants from the heat transfer surface[7]. One way to accomplish this would be to develop a new fluorescence calibration, F_c, for the R134a/DE589/PROATEQ mixture composition that exists at the wall. As Fig. 8 shows, determination of the wall composition is problematic because it depends on the physical chemistry of the surfaces. Do the lubricant and the additive form a well-mixed[8] excess layer on the wall as shown in system 1? Or does an additive monolayer form between the wall and the lubricant/additive excess layer as claimed in the patent and shown in system 2? With these questions in mind, a method is required to measure the excess surface density that relies neither on the knowledge of its composition at the wall nor its surface chemistry.

It would not be necessary to know the surface chemistry and/or the composition if the additive and the lubricant had the same fluorescence and adsorption characteristics. In fact, measurements of DE589 and PROATEQ in two separate cuvettes showed that the fluorescence intensity of PROATEQ for the same excitation and emission wavelengths was approximately half that of DE589. Given that the additive is approximately 2 % of the mass of the lubricant, and that the thickness of a monolayer is approximately four orders of magnitude thinner than the thickness of the entire excess layer, it is expected that both system 1 and system 2 will exhibit nearly 98 % of the mass in the excess layer as lubricant. Consequently, any difference in the fluorescence characteristics of the additive should have a relatively small effect on the fluorescence intensity of the excess layer given its relative fluorescence with the lubricant. Following this reasoning, the original R134a/DE589 calibration was used for the R134a/DE589/ PROATEQ mixture. The resulting excess surface density measurement underestimates the true mass of lubricant and additive on the wall because the fluorescence intensity of the PROATEQ is overestimated by using the R134a/DE589 calibration.

Lubricant excess surface density measurements were made for the R134a/DE589/ PROATEQ (97.8/2/0.2) and the R134a/DE589 (98/2) mixtures according to the measurement technique outlined in Kedzierski (2003) and above. Fluorescence measurements were made between 50 kW/m^2 and 15 kW/m^2 to limit the time required to quench the boiling below the fluorescence probe. The reported excess surface density measurements were obtained by extrapolating the measured Γ to just before quenching.

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[7] PROATEQ^{TM} makes the same mechanistic claims even thought it is not covered by this patent because it does not contain chlorine.

[8] The additive was observed to be soluble in the lubricant at the test temperature.

Figure 9 shows the lubricant excess surface density measurements, as calculated with eq. (2), for the two R134a/DE589 mixtures versus the following excess property group that was developed in Kedzierski (2003):

$$\frac{(\rho_L - \rho_b x_b)\, x_b^{1.8} T_s \sigma P_r}{(1-x_b)\, \rho_L h_{fg} (T_w - T_s)} \tag{3}$$

where the properties of the refrigerant are the reduced pressure (P_r), the latent heat of vaporization (h_{fg}) and the liquid-vapor surface tension (σ).

The measured Γ for the R134a/DE589 (98/2) mixture are shown as open circles and were taken from Kedzierski (2003). The measured Γ for the R134a/DE589/ PROATEQ (97.8/2/0.2) mixture (closed squares) are on average significantly greater than the measured Γ for the R134a/DE589 (98/2) mixture. This suggests that the additive contributes to the mass of lubricant that is on the wall rather than reducing the lubricant mass as the patent claims. The average lubricant excess surface density for the R134a/DE589/PROATEQ (97.8/2/0.2) mixture was 0.96 kg/m^2 ± 0.23 kg/m^2 at the 95 % confidence level. This is approximately 81 % greater than the average Γ for the mixture without the additive, which was 0.53 kg/m^2 ± 0.06 kg/m^2. Considering that the confidence intervals do not coincide, the two means differ at the 95 % confidence level. Even though the present excess measurement have shown that the additive has caused an increased excess layer, it has validated neither system 1 nor system 2 shown in Fig. 8.

Given that the excess surface density measurement is valid for either system 1 or system 2, this measurement has not disproved either system. A different means must be used to validate one of the systems. If we assume that system 2 evolves from system 1, the evolution can occur spontaneously only if the change from system 1 to system 2 results in a reduction of system surface energy (Rosen, 1978). The requirement for system 2 to exist can be expressed in terms of surface energies by applying the analysis of spreading coefficients given by Rosen (1978):

$$a\gamma_{\mathrm{m_2b}} + a\gamma_{\mathrm{Am_2}} + a\gamma_{\mathrm{wA}} < a\gamma_{\mathrm{wm_1}} + a\gamma_{\mathrm{m_1b}} \tag{4}$$

Here a is the surface area, γ_{m2b} is the interfacial free (surface) energy per unit area at the lubricant/additive mixture 2 - bulk refrigerant/lubricant/additive mixture interface. Similarly, γ_{Am2}, γ_{wA}, γ_{wm1}, and γ_{m1b} are the surface energies of the additive – lubricant/additive mixture 2, the wall - additive, the wall – lubricant/additive mixture 1, and the lubricant/additive mixture 1 - bulk refrigerant/lubricant/additive interfaces, respectively. Subscripts 1 and 2 on the lubricant-additive mixture allow the compositions of the two excess layers to slightly differ owing to the loss of some additive to the monolayer in system 2.

By assuming that the additive monolayer does not significantly deplete the lubricant/additive excess layer of additive, γ_{m1b} and γ_{m2b} are approximately equal for the two systems. Many of the additive and the lubricant/additive mixture fluid properties are similar because they are essentially both lubricants. Consequently, the surface energy between the additive and the lubricant/additive mixture is expected to be small and can be neglected. Using the two above approximations eq. (4) reduces to:

$$\gamma_{\mathrm{wA}} < \gamma_{\mathrm{wm_1}} \cong \gamma_{\mathrm{wL}} \tag{5}$$

Equation 5 is a necessary condition for the additive monolayer to exist at the surface. Note that γ_{wL} and γ_{wm1} are nearly equivalent because the lubricant/additive mixture 1 is well-mixed (by definition of the system) and at least 98 % lubricant by mass. An estimate of the relative magnitudes of the surface energies in eq. (5) can be obtained from surface-tension measurements and an analysis of drops on copper plates exposed to air. For lubricant drops exposed to air, Young's equation (Adamson and Gast, 1997) represents the equilibrium surface force balance on a droplet as:

$$\gamma_{\mathrm{wv}} = \gamma_{\mathrm{Lv}}\cos\theta + \gamma_{\mathrm{wL}} \tag{6a}$$

Likewise, Young's equation for additive drops exposed to air is:

$$\gamma_{\mathrm{wv}} = \gamma_{\mathrm{Av}}\cos\theta + \gamma_{\mathrm{wA}} \tag{6b}$$

where the contact angle, θ, is the angle between the droplet liquid-vapor interface and the substrate measured at the wall. For equilibrium, $\cos\theta$ is approximately one.

Capillary rise measurements show that $\gamma_{\mathrm{Lv}} \cong 0.026$ N/m and $\gamma_{\mathrm{Av}} \cong 0.03$ N/m (Appendix D). Eliminating γ_{wv} between eqs. (6a) and (6b) and substituting the values for the measured liquid-vapor surface-tensions yields:

$$\gamma_{\mathrm{wL}} - \gamma_{\mathrm{wA}} = \gamma_{\mathrm{Av}} - \gamma_{\mathrm{Lv}} = 0.004\mathrm{N/m} \tag{7}$$

Equation 7 suggests that requirement for a pure additive monolayer to exist at the surface as given by eq. (5) is satisfied. In other words, the preceding analysis, which is based on physical chemistry and indirect measurements, suggests that the forces are sufficient for the additive to spontaneously form a monolayer[9] and act as a barrier between the wall and the lubricant/additive similar to what was outlined in the patent (Wilkins et al., 1990).

Heat Transfer Enhancement

As shown by Kedzierski (2001c), the viscosity, miscibility and concentration of the lubricant strongly influence refrigerant/lubricant pool boiling. The lubricant closest to the wall essentially controls the boiling. Consequently, if an additive (or added lubricant) is to have an impact on a given refrigerant/lubricant system, there would be a greater likelihood for influence if the additive can exist as a monolayer on the surface (system 2 in Fig. 8). If the additive is well-mixed in the excess layer as in system 1 in Fig. 8, it will have minimal influence on the heat transfer if it is only 2 % by mass of the lubricant

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[9] For the lubricants and additives examined in this study

(recommended charge) that is next to the wall in the excess layer. For this reason, it is believed that the additive enhances R134a/DE589 pool boiling because it exists as a monolayer on the surface and its viscosity is greater than the lubricant. Kedzierski (2001c) has shown that lubricants with larger viscosities tend to have larger boiling heat transfer coefficients because the thermal boundary layer (δ) is thicker:

$$\frac{\delta_1}{\delta_2} = \sqrt{\frac{\mu_1 c_{p_2}}{\mu_2 c_{p_1}}} \qquad (8)^{10}$$

In general, the specific heat (c_p) does not differ much from lubricant to lubricant despite a large variation in viscosity. Consequently, eq. (8) shows that the thermal boundary layer is a strong function of viscosity providing for a larger active site density for thicker boundary layers (Hsu, 1962), which improves the boiling heat transfer.

The viscosity of the additive is approximately 45 % greater than that of the DE589 lubricant. As a result, an enhancement of the pool boiling may be expected if the additive exists as a monolayer on the surface. On the other hand, the additive viscosity is approximately half that of the York-C lubricant. This would suggest that a significant degradation should have occurred as a result. However, the York-C lubricant and the additive are both naphthenic base. For this reason it is likely that that additive remains well mixed in the excess layer with the York-C and has a minimal influence on the pooling properties because it is only 2 % by mass of the lubricant. As a result, essentially no change in the heat transfer performance was observed for the R123/lubricant/additive mixture.

The thickness of the thermal boundary layer may extend past the monolayer. However, the largest temperature gradients exist at the wall. Consequently, the fluid properties of the monolayer are expect to significantly affect the thickness of the thermal boundary layer given that the potential for the thermal boundary layer is established at the wall.

FUTURE RESEARCH

Lubricants for air-conditioning and refrigeration applications tend to have viscosities between 32 $\mu m^2/s$ and 220 $\mu m^2/s$ at 313.15 K (Randles, 2004). In addition, POEs are typically very polar which would suggest that both a polar additive and a POE would have the propensity to form a monolayer at the surface (Randles, 2004). These considerations suggest that several variables should be investigated to test the hypothesis that has been proposed in preceding section. First, the proposed effect of the relative viscosity of the lubricant and the additive needs to be further investigated with boiling heat transfer measurements with additives that have viscosities that are greater and less than lubricant viscosities that typically exist for real applications. Second, the effect of additive liquid-vapor surface tension should also be investigated. Will further increases in additive surface-tension improve heat transfer or is large surface-tension relative to the lubricant only important in establishing the monolayer? Third, the effect of lubricant miscibility and

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[10] Corrected equation but same trend as given in Kedzierski (2001c)

additive miscibility with the refrigerant should be investigated. Fourth, it should be determined how the thermal boundary layer interacts with the excess layer and its properties. Fifth, the effect of the lubricant type and its polarity should be investigated. These are just a few of the possible future research directions that may be pursued to improve the usefulness of this type of research for the refrigeration and air-conditioning industry.

CONCLUSIONS

The effect of an additive on the boiling performance of an R134a/ polyolester lubricant (POE) mixture and an R123/naphthenic mineral oil lubricant mixture on a roughened, horizontal flat surface was investigated. The pool boiling heat transfer data shows that the additive caused an average and a maximum enhancement of the R134a/POE heat flux between 5 kW/m^2 and 22 kW/m^2 of approximately 73 % and 95 %, respectively. For nearly the same heat flux range, the additive caused essentially no change in the pool boiling heat flux of an R123/naphthenic mineral oil mixture. In addition, a maximum degradation of the heat flux for the R123/naphthenic mineral oil mixture caused by the addition of the additive was observed to be approximately 27 % at a heat flux of 73 kW/m^2.

Excess surface density measurements were used to test the enhancing mechanism proposed in a 1990 U.S. Patent, which claims that certain refrigerant oil additives displace chiller lubricants from the heat transfer surface. The measurements showed that the accumulated mass on the heat transfer surface for the R134a/POE mixture with the additive was greater than that without the additive, which contradicts the patent claims. However, surface-tension measurements and other surface chemistry analysis were done to support the opinion that the additive can form a monolayer between the wall and the lubricant/additive excess layer if the lubricant and additive are sufficiently dissimilar chemically. An enhancement mechanism was proposed based on previous studies with heat transfer enhancing lubricants. It may be the case that the additive replaces less viscous lubricant at the immediate wall (monolayer), which in turn is responsible for the heat transfer enhancement. It was also hypothesized that a monolayer will not form if the additive and the refrigerant oil are too chemically similar, e.g., as for the additive/R123/ naphthenic mineral oil mixture. For this case, the additive will have little influence on the refrigerant/lubricant pool boiling given that it is typically only 2 % by mass fraction of the lubricant charge.

Only pool-boiling heat transfer laboratory tests are presented in this report. Full-scale chiller tests would be required to observe the change in performance for a particular chiller. In addition, heat transfer improvements do not necessarily guarantee improvements and/or changes in chiller performance because of other factors that influence HVAC equipment performance.

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NOMENCLATURE

English Symbols

A_n	regression constant in Table 4 n=0,1,2,3
a	surface area, m^2
c	concentration, mol/m^3
c_p	specific heat of liquid, kJ/K·kg
F	fluorescence intensity
F_c	fluorescence intensity from calibration (eq. 1)
F_m	fluorescence intensity measured from boiling surface
g	gravitational acceleration, m/s^2
h	capillary rise height, m
h_{fg}	latent heat of vaporization of refrigerant, kJ/kg
I_o	incident intensity, V
l	path length, m
l_e	thickness of excess layer, m
L_y	length of test surface (Fig. 2), m
M_L	molar mass of lubricant, kg/kmol
m	mass, kg
P	vapor pressure, kPa
P_c	critical pressure, kPa
P_r	reduced pressure (P/P_c), kPa
q''	average wall heat flux, W/m^2
r	radius of capillary tube, m
T	temperature, K
T_w	temperature at roughened surface, K
U	expanded uncertainty
u_i	standard uncertainty
x	mass fraction of lubricant
X	model terms given in Table 1
y	test surface coordinate in Fig. 2, m
z	test surface coordinate in Fig. 2, m

Greek symbols

β	temperature dependence of fluorescence coefficient, K^{-1}
δ	thermal boundary layer thickness, m
Γ	lubricant excess surface excess, kg/m^2
γ	surface free energy, kg/s^2
ΔT_s	wall superheat: $T_w - T_s$, K
ε	extinction coefficient, m^2/mol
ρ	mass density of liquid, kg/m^3
$\Delta\rho$	difference between liquid and vapor density, kg/m^3
μ	dynamic viscosity, kg/m·s
σ	surface tension of refrigerant, kg/s^2

English Subscripts

A	additive
b	bulk
e	excess layer
L	lubricant
m	measured, mixture
q"	heat flux
s	saturated state
Tw	wall temperature
v	vapor
w	wall or surface

Superscripts

-	average

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Table 1 Conduction model choice

<table>
<tr><td colspan="2">X_0= constant (all models) X_1= x X_2= y X_3= xy
X_4=x^2-y^2
X_5= y(3x^2-y^2) X_6= x(3y^2-x^2) X_7= x^4+y^4-6(x^2)y^2
X_8= yx^3-xy^3</td></tr>
<tr><td>Fluid</td><td>Most frequent models</td></tr>
<tr><td>R134a/DE589 (98/2)
(File: 589pln2.dat)</td><td>X_1,X_3,X_4 (66 of 141) 47 %
X_1,$X_3$$X_4$,$X_6$(31 of 141) 22 %
X_1,X_2,X_4 (24 of 141) 17 %</td></tr>
<tr><td>R134a/DE589/PROATEQ
(97.8/2/0.2)
(File: 134apro.dat)</td><td>X_1,X_3,X_4,X_6 (74 of 109)68 %
X_1,X_3,X_4 (16 of 109) 15%
X_1,X_3,X_4,X_5,X_6 (7 of 109) 6 %</td></tr>
<tr><td>R123/York-C (98/2)
(File: Ycpln2.dat)</td><td>X_1,X_3,X_4 (40 of 98) 41 %
X_1,X_3 (32 of 98) 33 %
X_1,$X_3$$X_4$,$X_6$ (13 of 98) 13 %</td></tr>
<tr><td>R123/York-C/PROATEQ
(97.8/2/0.2)
(File: YcPro.dat)</td><td>X_1,X_3,X_4 (51 of 139) 37 %
X_1,X_3 (28 of 139) 20 %
X_1,$X_3$$X_4$,$X_6$ (26 of 139) 19 %
X_1,X_3,X_6 (22 of 139) 16 %</td></tr>
</table>

Table 2 Pool boiling data

R134a/DE589 (98/2)
File: 589pln2.dat

ΔT_s (K)	q'' (W/m^2)
7.186	18086.7
7.201	17863.7
7.240	17886.1
7.645	25700.9
7.687	25787.1
7.711	25612.1
6.397	11990.1
6.390	11967.4
6.372	11864.0
4.766	6431.0
4.757	6431.1
7.537	28984.5
7.556	28726.1
7.744	32903.0
7.519	27362.7
7.531	27235.3
7.186	21490.8
7.223	21860.5
7.207	22130.9
6.689	15668.1
6.685	15761.2
6.699	15848.0
5.284	8595.6
5.320	8569.3
7.827	45607.0
7.827	44786.2
7.824	44691.8
6.198	12273.6
6.232	12852.7
5.769	9990.1
5.729	9982.1
5.713	9842.0
5.195	7817.7
5.200	7834.6
4.815	6557.4
4.772	6542.7
3.555	4572.7
7.029	17636.4
7.054	17443.4
6.950	16418.2
6.932	16506.9
6.640	13984.9
6.659	14134.5
6.449	12715.8
6.459	12794.9
6.136	11281.3
6.081	11114.9
5.534	8879.4
5.539	8881.8
5.251	7893.8
5.248	7826.4
4.769	6669.0
7.361	22959.0
7.374	23056.1
6.581	14962.7
6.555	14612.0
4.051	5556.0
3.781	5356.2
3.734	5174.6
2.986	4097.4
2.979	4764.3
2.859	3878.7
2.845	3916.6
2.878	3888.7
7.462	36190.9
7.964	27087.5
7.953	27390.7
8.094	36326.3
8.072	35943.7
7.262	26252.0
7.451	27790.0
7.499	28420.9
6.582	17475.5
6.598	17754.5
6.465	15268.5
7.198	28948.5
10.633	141842.9
8.546	65681.4
8.382	58204.1
8.332	57389.2
8.057	50040.1
7.870	43679.6
7.689	35013.6
7.429	27463.8
8.900	74073.3
9.008	81913.5
8.936	85781.4
9.509	95938.3
9.642	95398.6
9.616	89179.1
9.625	88812.8
9.142	81875.2
9.077	82321.5
8.703	77453.5
8.690	78284.6
8.505	73557.1
8.483	73636.1
8.290	64416.9
7.999	55533.2
11.170	123502.0
11.261	122922.0
11.250	113726.7
11.065	110160.6
11.066	110923.8
10.215	78752.6
10.215	78752.6
10.193	77702.3
9.705	64873.0
9.599	65184.6
8.736	77911.8
8.651	79115.7
7.945	72996.3
7.993	70318.4
7.751	58493.4
7.822	58444.0
7.661	44684.8
11.080	128082.3
11.025	129260.0
10.583	114869.1
10.556	119695.9
9.614	94875.4
9.596	96202.7
9.094	75539.6
9.109	74972.0
8.723	56773.2
10.709	128565.2
10.696	128282.8
10.200	109381.7
10.191	109414.6
9.702	90982.4
9.515	90650.8
9.152	75616.6
9.117	74819.3
8.779	65973.7
8.778	65882.6
8.478	54770.4
10.309	112886.2
10.083	111072.4
9.056	70277.2
9.026	70993.5
8.629	56290.8
10.279	113188.5
10.223	114290.3
9.878	103487.9
9.780	103377.9

R134a/ DE589/PROATEQ (97.8/2/0.2)
File: 134aPRO.dat

ΔT_s (K)	q'' (W/m^2)
9.924	72806.6
11.913	112997.2
12.002	113406.8
9.495	66903.1
9.539	67360.9
9.170	61904.5
9.189	61956.1
8.712	51006.6
8.702	50837.2
8.175	40948.4
8.168	41244.0
7.663	33709.5
7.652	33943.2
6.701	22021.7
10.938	94495.0
10.826	96330.4
8.243	52004.6
8.256	52342.5
7.065	33084.6
7.113	34246.4
6.653	28360.8
6.637	27439.2
6.189	21776.5
6.230	21855.7
5.740	16210.1
5.732	15934.5
4.526	7788.7
10.331	92391.2
10.244	93136.6
8.403	56243.2
8.447	56363.1
8.040	47546.5
8.071	47938.1
7.820	43024.5
8.002	43210.8
6.327	20140.3
10.266	89438.1
10.234	92295.3
9.185	78573.1
9.147	77679.1
8.421	57435.6
8.431	58100.6
7.994	49947.5
7.991	49148.4
7.455	40469.5
7.503	40721.4
7.122	33780.3
9.982	79347.6
9.928	79695.8
9.241	61509.9
9.331	63346.6
7.560	40659.4
7.555	41061.9
6.745	30213.2
6.762	30084.0
6.420	25299.1
6.400	25295.3
5.833	17534.8
11.341	100285.1
11.424	100507.4
10.470	92036.9
10.400	91687.8
9.099	65002.9
9.148	65748.6
8.585	54529.7
8.570	53906.0
7.261	35321.4
11.391	97763.6
11.246	99372.9
10.024	80752.5
10.022	80731.4
9.430	67419.0
9.491	67610.6
8.693	55770.7
8.536	60593.1
7.643	46045.8
10.942	92839.0
10.856	93713.0
8.756	55888.6
8.768	55948.9
5.977	22178.7
5.988	22139.7
6.431	27634.4
6.474	28230.9
5.430	15778.7
5.459	15752.2
4.292	6922.6
4.249	6923.7
1.687	832.1
8.751	57822.7
5.742	16950.4
5.820	16654.2
4.953	9795.3
4.919	9430.0
3.354	3772.4
10.529	97577.4
6.665	24073.2
5.969	18945.1
5.680	15830.5
5.393	13808.1
5.084	11507.7
5.075	11526.7
4.819	9945.4
3.979	6089.2
3.965	5862.3
3.486	4957.6
5.375	11635.9
5.409	11720.2
4.066	6271.7
4.363	7056.8
3.400	4696.8
3.395	4673.9
1.318	779.2
1.154	717.1

R123/York-C (98/2)
File: YCPLN2.dat

ΔT_s (K)	q'' (W/m^2)
21.150	61586.8
20.589	52822.3
19.838	43539.5
18.068	33358.5
16.442	28060.2
14.067	21646.4
12.205	17533.9
10.546	14596.4
10.527	14484.2
8.936	12853.7
8.979	12956.7
20.830	56066.4
20.902	56567.3
19.511	40795.3
14.543	22510.9
12.187	16849.0
10.719	14407.9
9.154	11998.8
5.371	6962.0
5.135	6469.2
5.066	6332.9
3.504	3933.3
17.359	30960.6
14.647	23503.3
10.113	13690.9
20.645	50772.3
21.199	63837.3
17.989	33546.3
18.117	34159.8
14.543	22723.4
13.988	21479.1
14.016	21901.5
10.520	14356.0

21.978	85532.1
21.961	85422.1
21.567	75482.7
21.584	76394.0
21.194	65885.8
21.203	66005.7
20.791	57898.8
20.707	58080.7
20.210	49809.9
20.229	49950.4
19.508	41822.7
19.395	41159.5
18.629	34744.6
21.313	67251.3
21.256	66248.7
20.007	46090.6
20.137	47014.3
14.567	22195.8
14.711	22712.2
12.967	18222.0
13.075	18396.6
11.114	15106.8
22.397	89589.0
22.463	91422.9
22.299	87272.4
22.138	82337.5
22.124	82407.2
22.075	81057.2
21.894	76905.6
21.766	73179.8
21.681	71212.1
21.670	71254.6
21.539	67478.0
21.248	62923.0
20.968	59703.1
20.821	55726.2
20.402	48394.5
19.916	43932.5
18.495	36018.4
17.906	33242.7
18.053	33777.1
20.502	49426.9
19.846	42768.4
19.066	37850.5
18.822	34695.3
17.617	31024.2
16.682	27205.7
14.863	22789.3
15.616	24606.2
14.945	23069.4
13.773	20654.3
13.116	19300.6

12.124	17168.1
11.024	15327.9
9.098	12164.1
7.913	10368.7
22.405	85407.9
21.798	69486.8
21.487	62910.3
20.732	51766.5
20.262	45640.0
19.426	39695.7
18.896	35632.3
16.415	27095.5
15.649	25146.4
14.738	22992.4
13.212	18581.0
13.046	18608.0
11.630	16185.4
10.200	13779.9

R123/York-C/PROATEQ
(97.8/2/0.2)
File: YCPRO.dat

22.768	89364.6
22.398	80792.1
22.137	73690.0
21.741	65045.7
20.858	46754.4
20.218	41356.8
19.172	34324.7
18.307	32060.3
15.953	24971.7
14.518	21711.0
21.949	63779.7
21.294	49711.5
20.765	43731.4
20.170	37975.8
17.585	30036.2
17.070	28349.5
15.794	25416.6
14.965	23073.3
15.019	23303.9
12.724	17786.2
11.125	15094.7
21.764	57888.5
20.400	42243.2
19.612	35824.3
16.899	28156.5
14.696	21872.4
15.388	23412.6
14.824	21721.2

12.082	16500.0
11.217	15127.3
9.010	11799.4
6.797	8119.6
21.894	64281.4
21.792	64674.1
21.434	57311.6
21.285	51865.0
20.966	48118.9
20.127	40276.5
18.367	31677.7
18.037	30478.0
15.446	23899.9
22.236	77705.1
21.971	71568.8
21.848	68329.3
21.646	61481.4
21.324	54442.7
20.852	45901.5
19.443	34886.1
18.025	30783.5
16.773	26927.9
14.656	21706.5
12.606	17349.0
22.617	87736.3
22.486	83888.5
22.170	76336.1
21.498	57135.4
21.064	48714.4
18.970	34039.9
17.955	30732.8
17.239	28589.6
16.054	24830.1
22.519	83959.4
20.118	39391.7
15.994	25299.6
15.605	24189.9
14.773	22067.0
14.648	21926.9
13.696	19522.6
13.160	18492.4
12.219	16808.9
11.534	15979.2
10.890	14785.6
22.411	89641.7
20.898	49558.8
16.029	25771.3
14.143	20743.4
10.970	15292.5
8.473	11206.1
8.386	10824.8
7.802	9988.6

22.449	85378.3
22.445	86801.5
21.075	49700.9
21.023	50697.0
21.035	50597.3
18.735	33099.1
18.771	33293.5
22.641	91336.9
22.649	91592.6
22.664	92005.2
18.526	33051.4
18.594	33176.7
18.605	33254.5
15.725	24336.0
15.568	24083.3
15.664	24786.3
13.725	20293.8
13.571	20048.9
12.903	19739.5
12.942	19986.5
13.003	20256.8
12.350	18105.8

12.231	17120.5
12.223	17215.1
10.644	15546.8
10.321	14941.2
9.590	13568.0
9.652	13674.2
9.678	13229.6
7.876	10443.2
7.870	10435.8
7.944	10479.6
7.005	9108.0
7.143	9238.5
22.047	79063.1
21.945	76907.5
21.980	77613.7
22.015	77948.8
21.849	70870.5
21.794	70337.5
21.746	70120.2
20.751	48144.7
20.711	48224.6
20.753	48838.3

20.170	42924.1
20.201	43234.2
20.195	43233.5
18.750	32241.4
18.633	31781.0
22.606	91197.5
22.583	90835.9
22.555	90639.2
22.287	79980.6
22.260	80504.0
22.614	96385.3
22.537	94998.9
22.580	96703.9
22.185	84234.1
22.530	89576.8
22.536	89682.7
22.537	89871.5
21.544	64318.3
21.582	66307.0
21.575	66231.7

Table 3 Number of test days and data points

Fluid (% mass fraction)	Number of days	Number of data points
R134a/DE589 (98/2) $3\ \mathrm{K} \le \Delta T_s \le 11\ \mathrm{K}$	15	144
R134a/DE589/PROATEQ (97.8/2/0.2) $3\ \mathrm{K} \le \Delta T_s \le 12\ \mathrm{K}$	11	109
R123/York-C (98/2) $3.5\ \mathrm{K} \le \Delta T_s \le 22.5\ \mathrm{K}$	9	98
R123/York-C/PROATEQ (97.8/2/0.2) $6.5\ \mathrm{K} \le \Delta T_s \le 22.5\ \mathrm{K}$	17	139

Table 4 Estimated parameters for cubic boiling curve fits for plain copper surface

$$\Delta T_s = A_0 + A_1\, q'' + A_2\, q''^2 + A_3\, q''^3$$

ΔT_s in Kelvin and q'' in W/m^2

Fluid	A_o	A_1	A_2	A_3
R134a/DE589 (98/2)				
$3\ \mathrm{K} \le \Delta T_s \le 7\ \mathrm{K}$	-1.76162	$1.53377\text{x}10^{-3}$	$-1.01205\text{x}10^{-7}$	$2.41953\text{x}10^{-12}$
$7\ \mathrm{K} \le \Delta T_s \le 11\ \mathrm{K}$	6.91642	$1.57640\text{x}10^{-5}$	$1.97728\text{x}10^{-10}$	$-5.36523\text{x}10^{-16}$
R134aa/DE589/PROATEQ (97.8/2/0.2)				
$3\ \mathrm{K} \le \Delta T_s \le 7\ \mathrm{K}$	1.45977	$5.25209\text{x}10^{-4}$	$-2.10525\text{x}10^{-8}$	$3.15524\text{x}10^{-13}$
$7\ \mathrm{K} \le \Delta T_s \le 12\ \mathrm{K}$	3.16112	$1.60861\text{x}10^{-4}$	$-1.52139\text{x}10^{-9}$	$7.03271\text{x}10^{-15}$
R123/York-C (98/2) $3.5\ \mathrm{K} \le \Delta T_s \le 22.5\ \mathrm{K}$	-0.26241	$9.35500\text{x}10^{-4}$	$-1.39311\text{x}10^{-8}$	$7.11354\text{x}10^{-14}$
R123/York-C/PROATEQ (97.8/2/0.2) $6.5\ \mathrm{K} \le \Delta T_s \le 22.5\ \mathrm{K}$	-0.84726	$9.83088\text{x}10^{-4}$	$-1.43136\text{x}10^{-8}$	$6.99224\text{x}10^{-14}$

Table 5 Residual standard deviation of ΔT_s

Fluid	u (K)
R134a/DE589 (98/2)	
$3\ \mathrm{K} \leq \Delta T_s \leq 7\ \mathrm{K}$	0.14
$7\ \mathrm{K} \leq \Delta T_s \leq 11\ \mathrm{K}$	0.39
R134a/DE589/PROATEQ (97.8/2/0.2)	
$3\ \mathrm{K} \leq \Delta T_s \leq 7\ \mathrm{K}$	0.16
$7\ \mathrm{K} \leq \Delta T_s \leq 12\ \mathrm{K}$	0.26
R123/York-C (98/2)	
$3.5\ \mathrm{K} \leq \Delta T_s \leq 22.5\ \mathrm{K}$	0.22
R123/York-C/PROATEQ (97.8/2/0.2)	
$6.5\ \mathrm{K} \leq \Delta T_s \leq 22.5\ \mathrm{K}$	0.24

Table 6 Average magnitude of 95 % multi-use confidence interval for mean T_w-T_s(K)

Fluid	u (K)
R134aa/DE589 (98/2)	
$3\ \text{K} \le \Delta T_s \le 7\ \text{K}$	0.15
$7\ \text{K} \le \Delta T_s \le 11\ \text{K}$	0.26
R134a/DE589/PROATEQ (97.8/2/0.2)	
$3\ \text{K} \le \Delta T_s \le 7\ \text{K}$	0.17
$7\ \text{K} \le \Delta T_s \le 12\ \text{K}$	0.21
R123/York-C (98/2)	
$3.5\ \text{K} \le \Delta T_s \le 22.5\ \text{K}$	0.14
R123/York-C/PROATEQ (97.8/2/0.2)	
$6.5\ \text{K} \le \Delta T_s \le 22.5\ \text{K}$	0.13

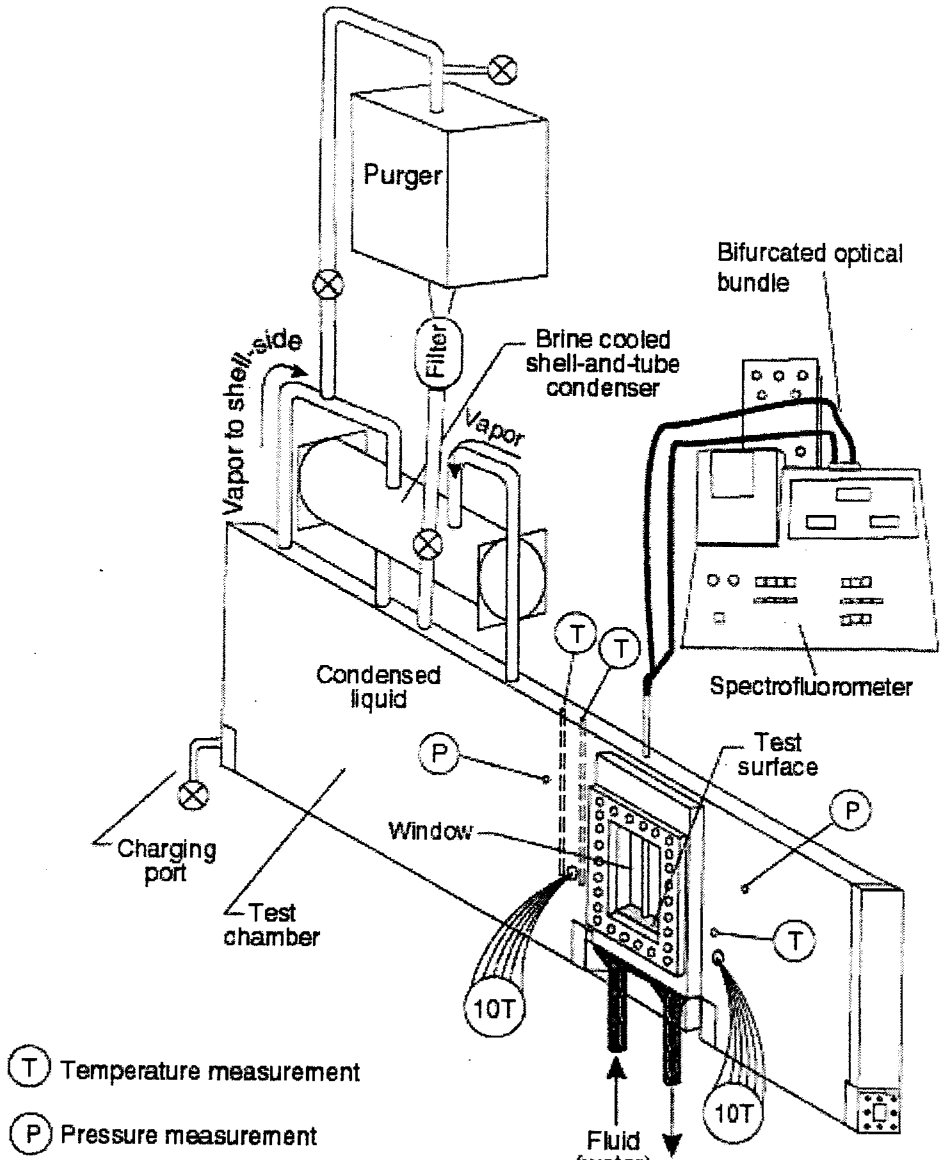


Fig. 1 Schematic of test apparatus

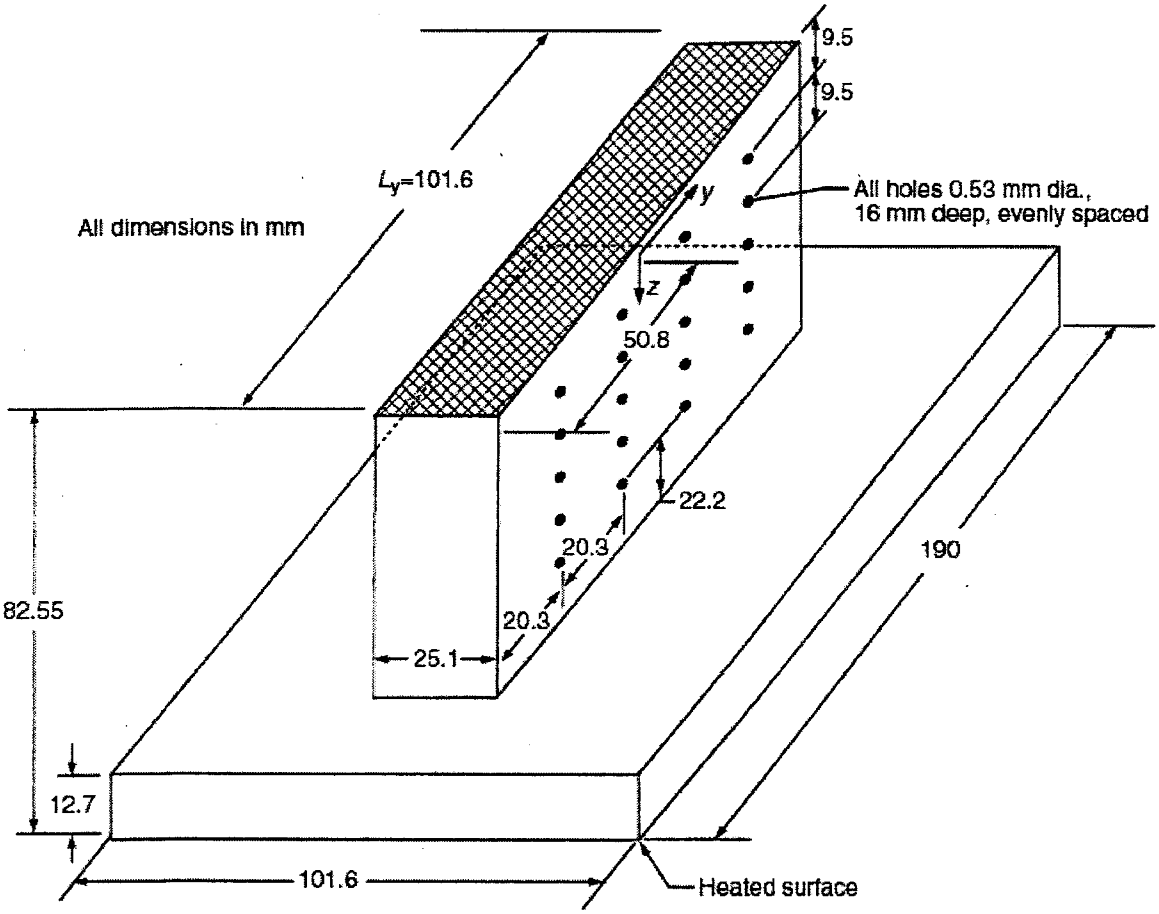


Fig. 2 OFHC copper flat test plate with cross-hatched surface and thermocouple coordinate system

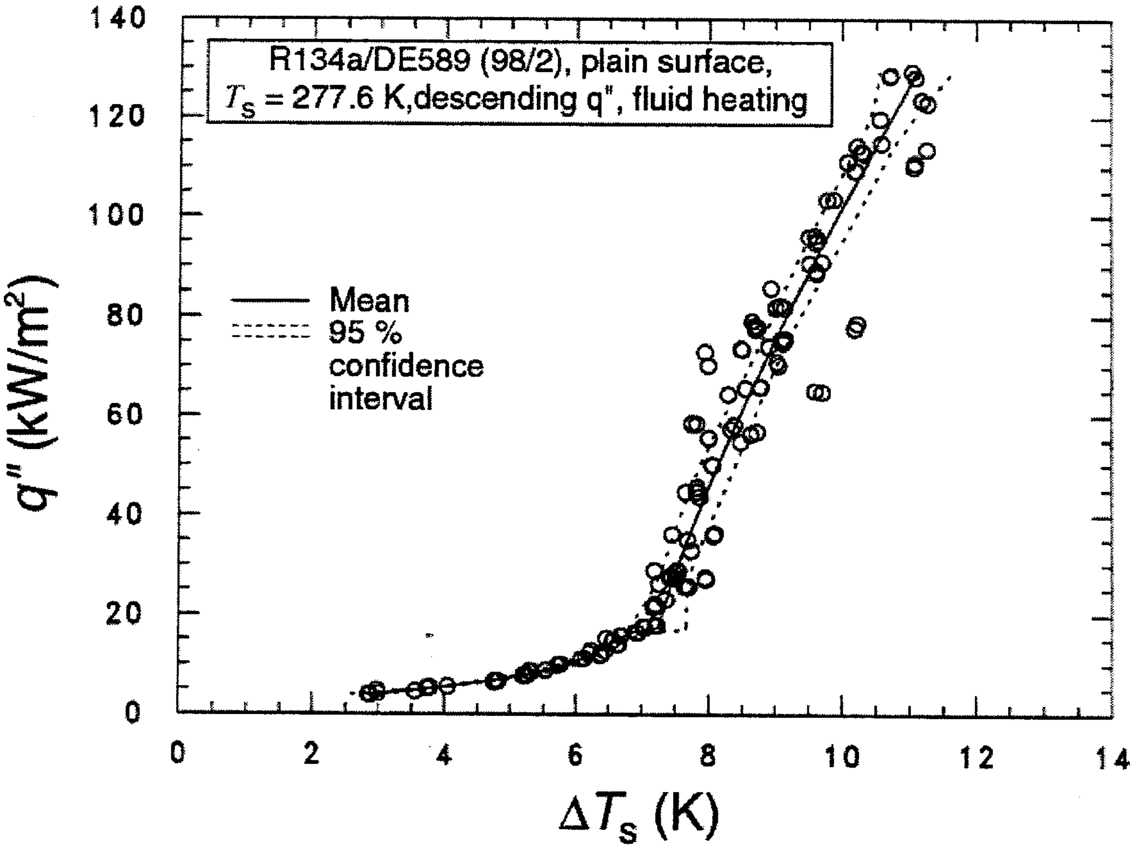


Fig. 3 R134a/DE589 (98/2) boiling curve for plain surface

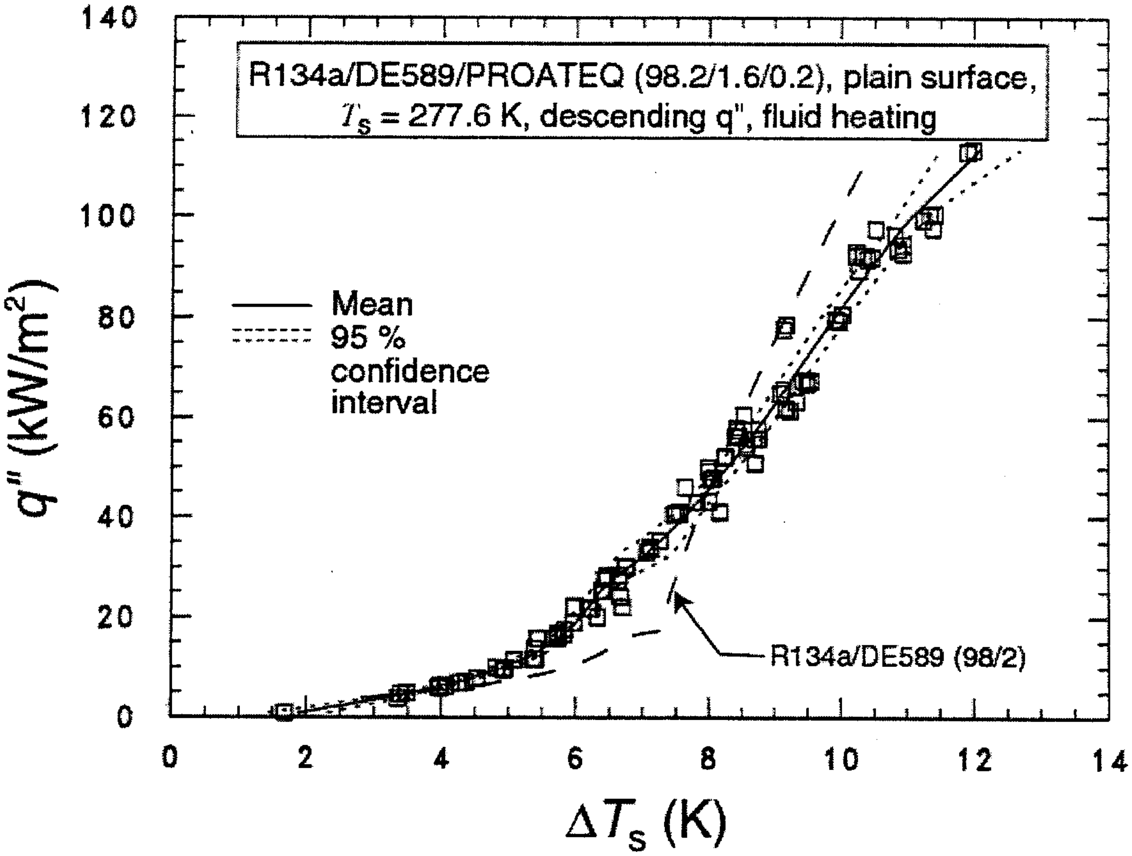


Fig. 4 R134a/DE589/ PROATEQ (97.8/2/0.2) boiling curve for plain surface

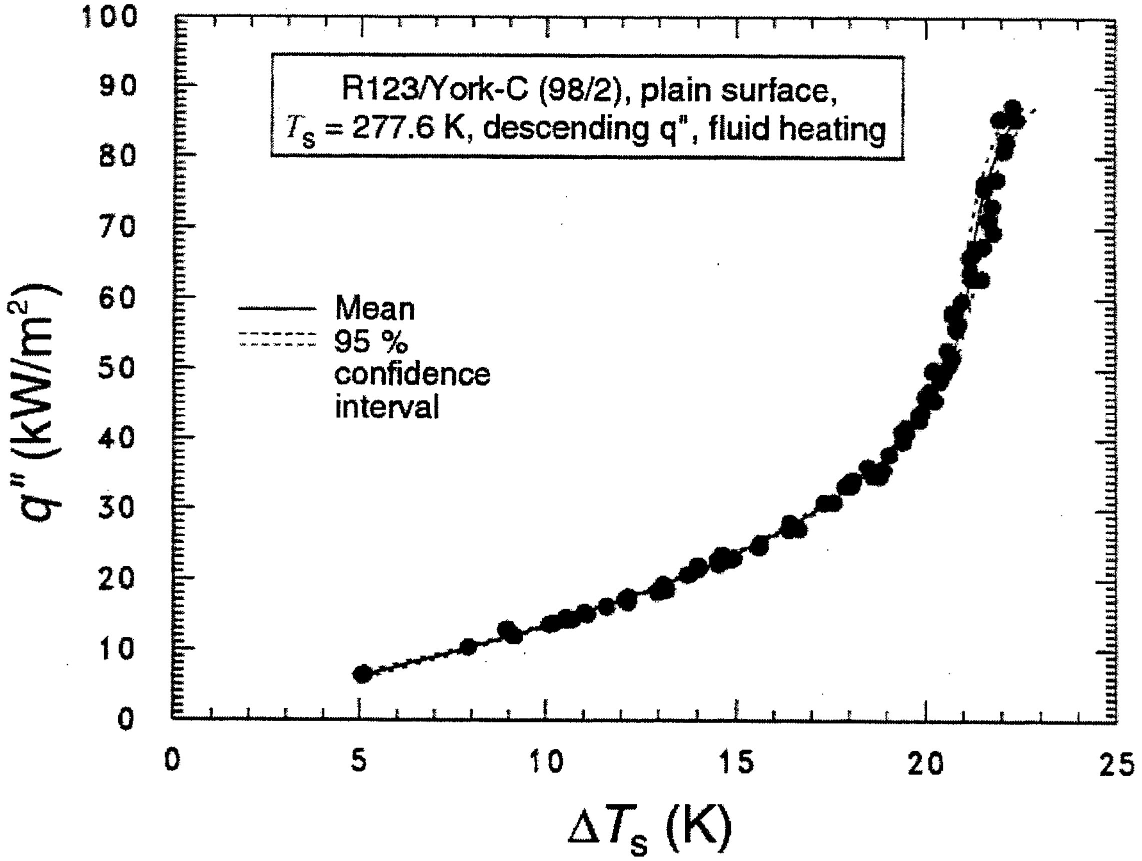


Fig. 5 R123/York-C (98/2) boiling curve for plain surface

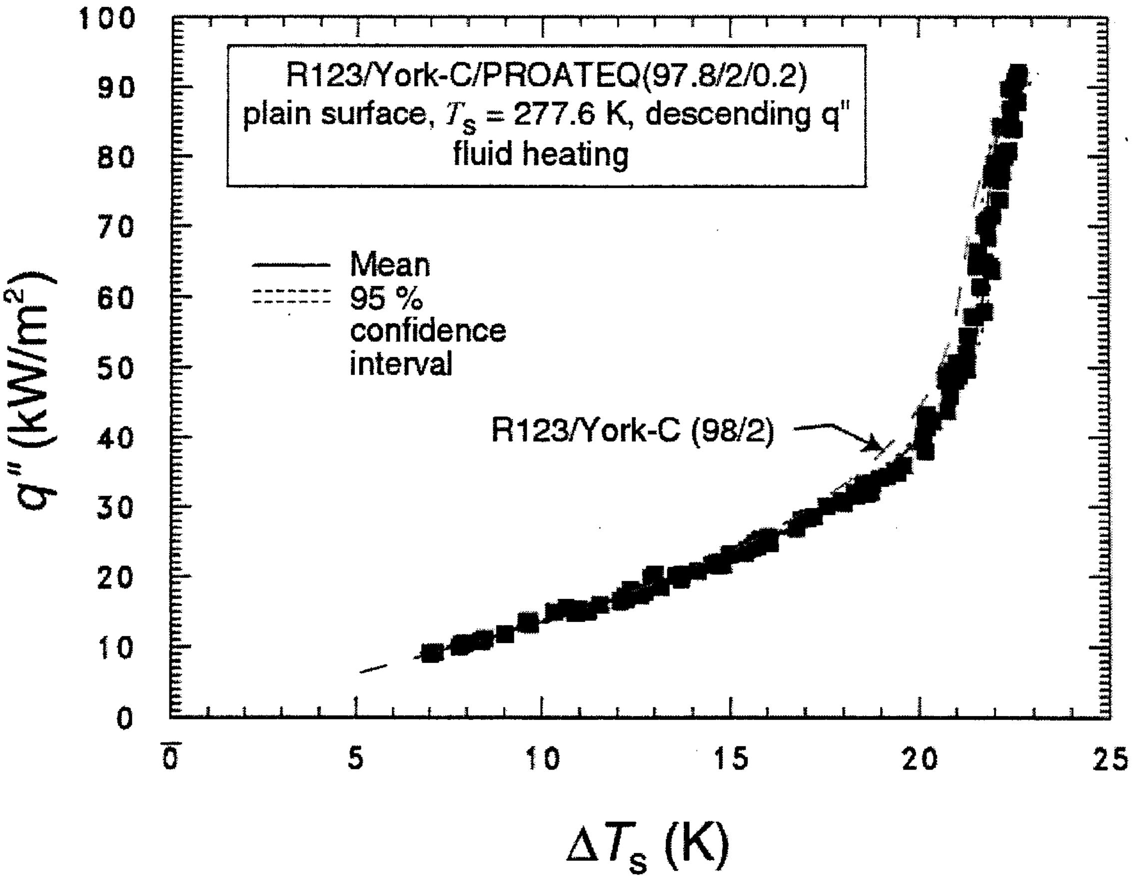


Fig. 6 R123/York-C/ PROATEQ (97.8/2/0.2) boiling curve for plain surface

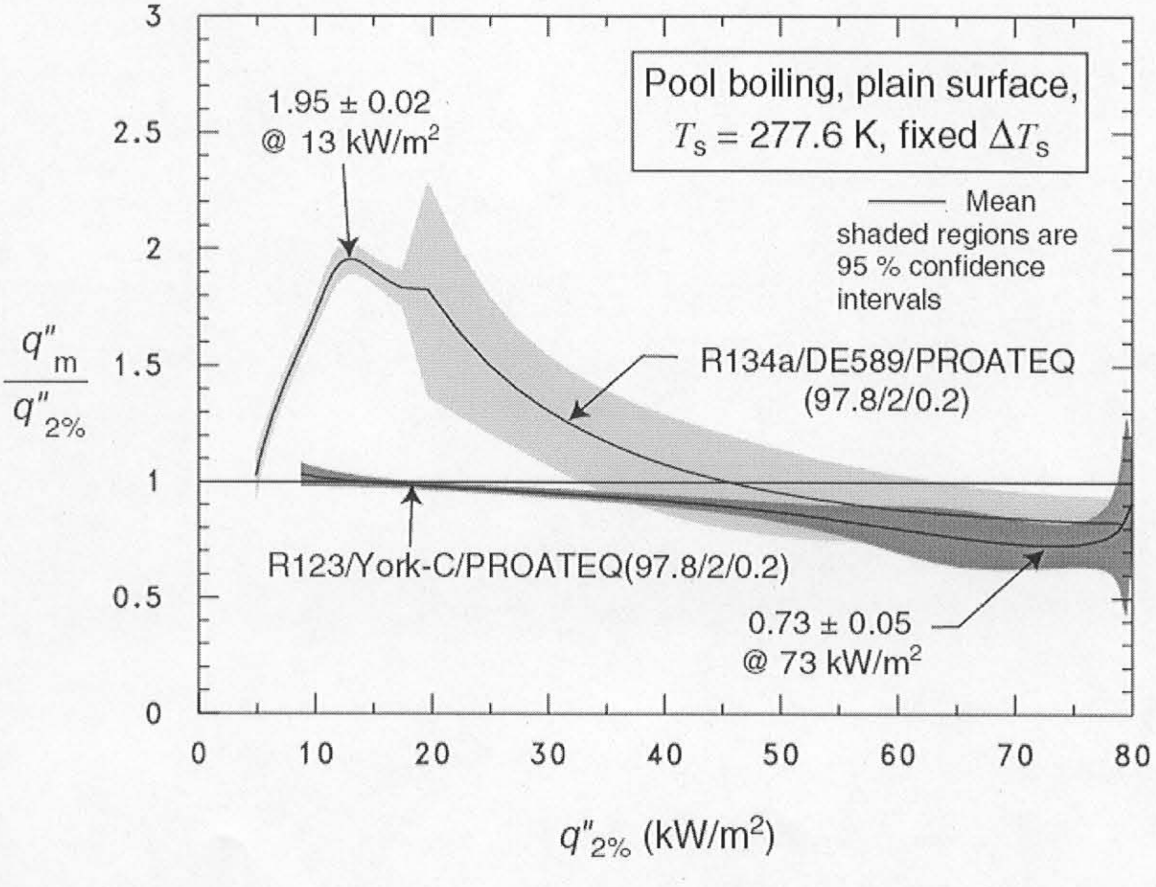
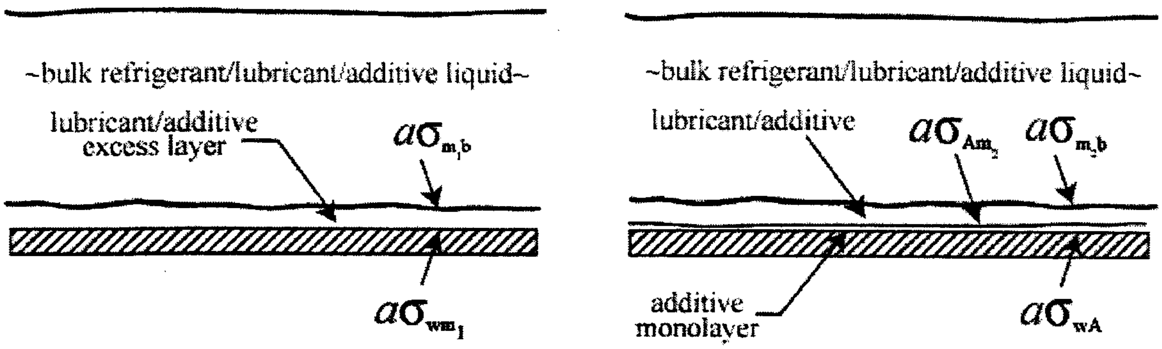


Fig. 7 R134a/DE589/ PROATEQ (97.8/2/0.2) and R123/York-C/PROATEQ (97.8/2/0.2) mixture heat fluxes relative to that of the refrigerant/lubricant (98/2) mixture for a plain surface



System 1: Additive and lubricant mixed in excess layer

System 2: Additive and lubricant mixed in excess layer with additional additive monolayer at surface

Fig. 8 Two possible surface energy systems for the R134a/DE589/PROATEQ mixture

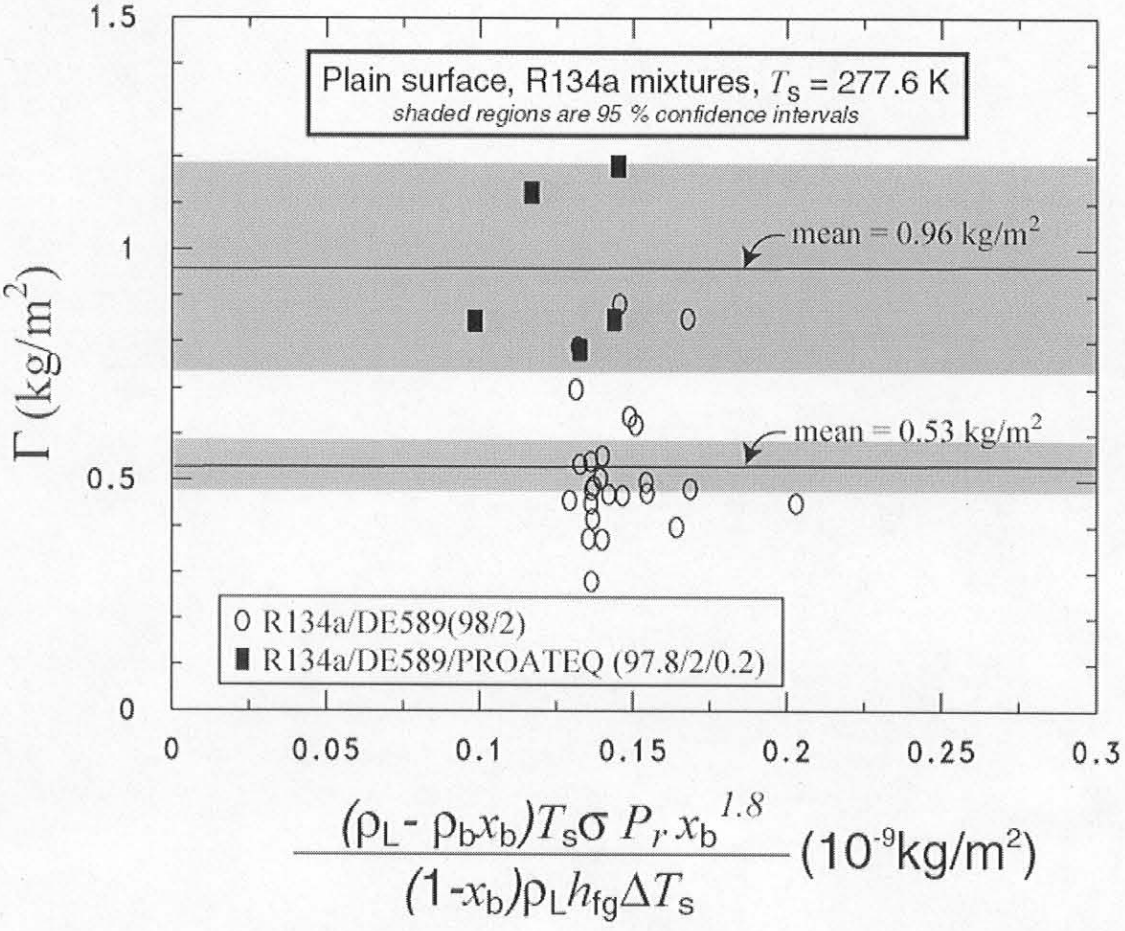


Fig. 9 Lubricant excess surface density for R134a mixtures

APPENDIX A: COMPATIBILITY STUDIES

This appendix contains four compatibility studies that were perform by Spauschus Associates, Inc. of Winder Georgia. The refrigerants investigated were R134a, R123, and R22. The lubricants investigated were Carrier SW-220, Trane oil 22, and York-C. The first report (January 8, 2004) covers accelerated aging tests of the oil additive PROATEQ with three different refrigerant/lubricant mixtures. The aging tests with R123 were done at a temperature that decomposed the refrigerant. Consequently, aging tests with R123/lubricant/additive at a lower temperature are presented in the last (fourth, May 24, 2004) report of Appendix A. The second report (December 23, 2003) from Spauschus Associates analyzed used lubricant samples from chillers that had been operating with refrigerant/lubricant and PROATEQ. The used samples were analyzed for Total Acid Number (TAN) and by Ion Chromatography (IC). The samples from the Lincoln Property Company were taken from a chiller that had a documented (Smith, 2004) "burn out" several years before the additive was injected in the system. It is likely that the compressor failure contributed significantly to the refrigerant decomposition in these samples. The third report (January 12, 2004) provides lubricity tests with two refrigerant saturated lubricant/additive samples. The lubricity tests were 5 h Falex wear tests with steel pin and aluminum V-blocks. No control was used for these tests. Consequently, it is not known if the additive has increased or reduced the wear.

The policy of the National Institute of Standards and Technology is to use the International System of Units (metric units) in its publications. This Appendix reproduces a report written under contract by a commercial laboratory. In some instances, the use of the measurement units in this contractor's report is not in full accordance with NIST policy on SI units. The copy in this Appendix is reprinted in its original format to preserve the integrity of the contractor's report.

The uncertainty of the TAN measurement was approximately ± 100 µg/g (± 0.1 mg KOH/g) (Rohatgi, 2004). The uncertainty of the metal and ion concentration measurements were approximately ± 10 µg/g (Rohatgi, 2004).

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REACTION TESTS OF OIL ADDITIVE PROATEQ: ANALYSES OF USED LUBRICANT SAMPLES

INTRODUCTION

Used lubricant samples from chillers that had been operating with refrigerant/lubricant and Proateq were analyzed for Total Acid Number (TAN) and by Ion Chromatography (IC) to determine their acid concentrations and by Atomic Emission Spectroscopy to determine their elemental metal concentrations. Of the nine samples were received for analysis (one from LSU and eight from Lincoln Property Company in Dallas as shown in Figure1), only three representative samples were analyzed. These included the sample from LSU, and samples 2B and 3C from Lincoln Property Company.

EXPERIMENTAL METHODS

Total Acid Number. The method for measuring TAN is based on ASTM D664 with the following modifications to accommodate small sample sizes.

- Calibration in solvent solution with oil, rather than water solution
- KOH normality of 0.01, rather than 0.10
- Use of 8 ml of solvent, rather than 125 ml.
- Titration of the lubricant samples was to a pH of 11.

Ion Chromatography. In the determination of anion concentrations by ion chromatography (IC), about one gram of the lubricant sample was added to a pre-weighed cup containing 30 milliliters of deionized water. The water/lubricant mixture was stirred continuously for 24 hours to allow for extraction of halide ions and acid anions from the lubricant. The water extract was then analyzed by ion chromatography. The concentrations of fluoride ions, chloride ions, organic anions (such as formate, acetate, butyrate, pentanoate, hexanoate) and inorganic anions (such as nitrate, sulfate) were obtained by calibrating the ion chromatograph with standard solutions so that the peak area was proportional to the anion concentration.

Metal Concentration. Elemental analysis by atomic emission spectroscopy was performed according to ASTM D6595 to determine the metal concentrations (in parts per million) in the lubricant.

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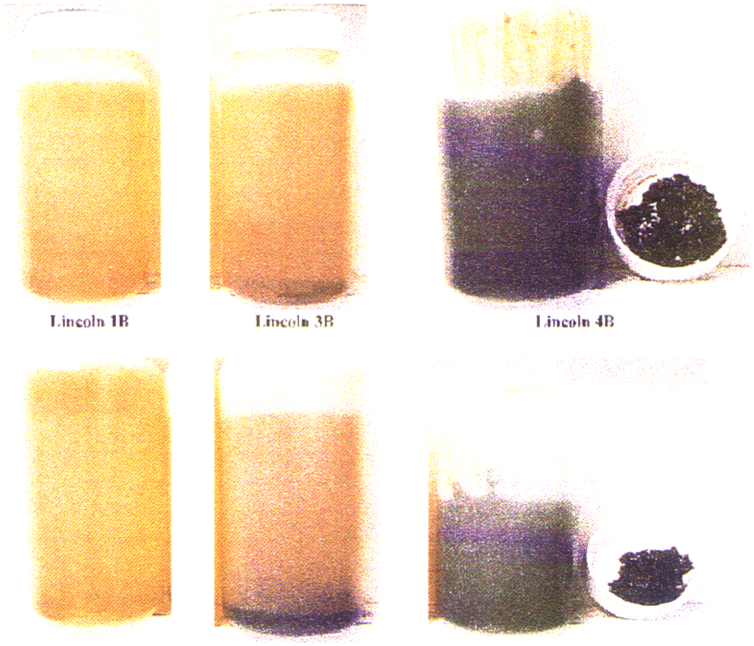
Date: January 8, 2004

LSU sample Lincoln 2B Lincoln 3C

The three samples used for analysis



Lincoln 1B Lincoln 3B Lincoln 4B

Lincoln 1C Lincoln 2C Lincoln 4C

Figure 1. Used Lubricant Samples from Chillers

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RESULTS AND DISCUSSIONS

The results of the analyses are shown in Tables 1-2. The sample from LSU was fairly clean, pale yellow with light cloudiness, low TAN and a very small concentration of acetate. The Lincoln 2B sample showed a slightly cloudy yellow liquid phase above a thick layer of black deposit, while the 3C sample was yellow-orange in color with light cloudiness and a ring of brown deposit. Sample 2B had a very high TAN and high concentrations of fluoride and chloride, indicative of significant refrigerant decomposition, while sample 3C had moderate TAN and moderate concentrations of fluoride and chloride. In addition, there was a small amount of formate present in sample 2B, probably due to of a small amount of lubricant decomposition. The presence of significant amounts of metallic iron, copper, tin, and zinc in both lubricant samples showed that there were reactions between the refrigerant, lubricant and metal parts of the chillers at the Lincoln Property Company.

Table 1: Total Acid Number and Ion Chromatography Results

Lubricant Sample	TAN mg KOH/g	Ion Chromatography Results ppm						
		Fluoride	Acetate	Butyrate	Formate	Pentanoate	Chloride	Sulfate
LSU	0.01	0	36	0	0	0	3	14
Lincoln 2B	10.13	176	0	0	124	0	3016	42
Lincoln 3C	1.58	72	0	0	0	0	626	53

Table 3: Metal Analysis Results of Sealed Tubes After Aging at 175° C for 14 Days

Lubricant Sample	Dissolved Metal Concentrations ppm									
	Fe	Cr	Al	Pb	Cu	Sn	Si	B	P	Zn
LSU	<1	<1	<1	<1	<1	<1	2	<1	<10	<1
Lincoln 2B	116	<1	<1	<1	62	34	2	3	127	14
Lincoln 3C	138	<1	<1	2	84	47	3	3	156	19

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COMPATIBILITY TESTING OF OIL ADDITIVE PROATEQ WITH REFRIGERANT/LUBRICANT MIXTURES

INTRODUCTION

The chemical compatibility of oil additive Proateq with refrigerant/lubricant mixtures was tested through accelerated aging in pressure bombs due to the high refrigerant concentrations. The three refrigerant/lubricant mixtures tested included:

1. R-134a/Carrier SW-220
2. R-123/Trane oil 22
3. R-22/York C.

EXPERIMENTAL METHODS

The compatibility of oil additive Proateq with refrigerant/lubricant mixtures was determined in pressure bombs due to the high refrigerant concentrations. A mixture of 10 ± 1% Proateq in lubricant was first prepared by adding together 8.0-8.1 g of lubricant and 0.81-0.82 g of Proateq. Next, 4.41 to 4.43 g of the mixture were placed in a beaker along with two standard Cu/Al/Steel coupons. The beaker was then placed in a pressure vessel, which was sealed, evacuated and charged with 195.5 to 195.6 g of refrigerant from a calibrated manifold, yielding a lubricant concentration of 2.0 ± 0.3 %. The pressure vessel was placed in a temperature-controlled oven at 175° C for 14 days.

Control samples containing refrigerant/lubricant mixtures without Proateq (R-134a/Carrier SW-220 and R-22/York C) were also tested and their compatibility results were compared to those of samples containing Proateq.

After aging the gas phase in the vessel was analyzed by gas chromatography to determine refrigerant decomposition. The liquid phase was visually examined for change in lubricant color, cloudiness in the lubricant, floc or particulate formation, film formation on the walls of the beaker. The metal coupons were observed for corrosion and/or copper plating. The liquid phase was analyzed for Total Acid Number (TAN) and by ion chromatography to determine chloride, fluoride and organic acid ion concentrations. Three bombs were be prepared for the three refrigerant lubricant mixtures, including R-134a/Carrier SW-220, R-123/Trane oil 22, and R-22/York C.

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Date: December 23, 2003

Analysis by GC was conducted by expanding the gas content of the pressure vessel into a calibrated manifold, from which a sample was injected into the gas chromatograph. Gas chromatography was run isothermally in a ten foot-long by 1/8 inch ID Supelco (5 % fluorcol 143 HMW 60/80 Carbo Pack B) column. The injection temperature was 25° C. The oven and column temperatures were at 38° C, and the thermal conductivity detector was at 98° C. Helium at 40 psi was used as the carrier gas, and the gas sample size was about 500 microliters.

The total acid number (TAN) was determined according to a modified ASTM D664. The method was modified to accommodate the small sample size by reducing the alcoholic KOH titrant concentration from 0.1 Normal to 0.01 Normal. Titration of the lubricant samples was to a pH of 11. This yielded sufficient sensitivity to determine acid numbers down to 0.1 mg KOH/g with a standard deviation of ± 0.05.

In the determination of anion concentrations by ion chromatography (IC), about one gram of the lubricant sample was added to a pre-weighed cup containing 30 milliliters of deionized water. The water/lubricant mixture was stirred continuously for 24 hours to allow for extraction of halide ions and acid anions from the lubricant. The water extract was then analyzed by ion chromatography. The concentrations of fluoride ions, chloride ions, organic anions (such as formate, acetate, butyrate, pentanoate, hexanoate) and inorganic anions (such as nitrate, sulfate) were obtained by calibrating the ion chromatograph with standard solutions so that the peak area was proportional to the anion concentration.

RESULTS AND DISCUSSIONS

The results of the compatibility tests are shown in Tables 1-2 and Figures 1-4. With R-134a/Carrier SW-220, both the control and the sample with Proateq had a small amount of lubricant decomposition as indicated by the increase in total acid number along with the presence of pentanoate ions in the aged lubricant. In addition, the aged sample containing Proateq showed significant blackening of the copper surface when compared to the control sample.

The aged sample containing R-22/York C with Proateq showed a significant amount of reaction when compared to the control sample, as indicated by the blackening of copper and steel coupons and the increase in total acid number. The refrigerant decomposition was also greater in the presence of Proateq, as indicated by the higher chloride ion concentration. The concentration of chloride ion present in the aged lubricant with Proateq corresponded to 0.001% R-22 decomposition (calculated based on the assumption that one mole of R-22 decomposed would yield one mole of chloride ion).

Because R-123 has been reported as being very reactive at temperatures greater than 105°C [1], the results of the sealed tube tests of R-123/Trane oil 22 with Proateq, which were conducted at 175°C for 14 days, could not be used to correctly assess the compatibility of Proateq with R-123/Trane oil.

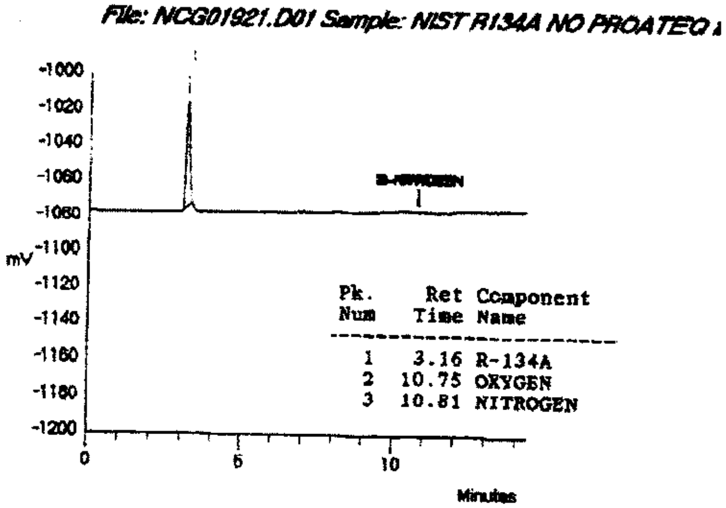
Table 1: Visual Observations After Aging at 175° C for 14 Days

Refrigerant/ Lubricant	Proateq	Visual Observations	
		Liquid	Metal Coupons
Control: R-134a/ Carrier SW-220	No	Liquid lighter color (color = 3.0 versus 4.0 for unaged); no particulate; no deposit	Copper slightly tarnished; steel and aluminum unchanged
R-134a/ Carrier SW-220	Yes	Liquid slightly lighter color (color = 3.5 versus 4.0 for unaged); white coating on walls of beaker	Copper dark black; steel and aluminum unchanged
Control: R-22/ York C	No	Liquid color unchanged (color = 3.5); very light black particulate in bottom of beaker; no coating on walls	All metals unchanged
R-22/York C	Yes	Liquid color unchanged (color = 3.5); light particulate coating on walls of beaker; black particulate in bottom of beaker	Copper and steel dark black; aluminum unchanged

Table 2: Ion Chromatography Results

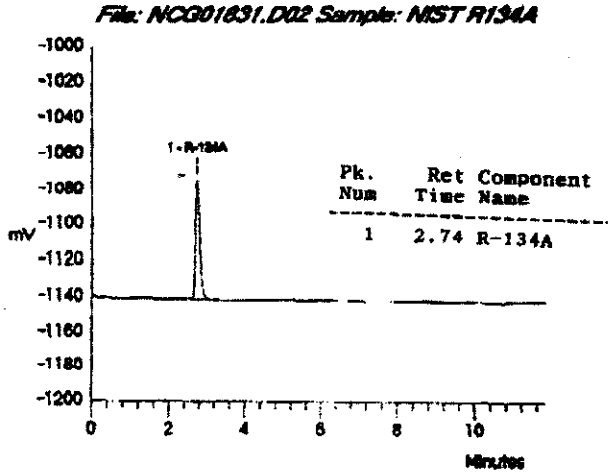
Refrigerant/ Lubricant	Proateq	TAN mg KOH/g	Ion Chromatography Results ppm							
			Fluoride	Acetate	Butyrate	Formate	Pentanoate	Chloride	Heptanoate	Sulfate
Unaged SW-220	No	0.12	0	0	0	2	0	2	0	8
Unaged York C	No	0.01	0	0	0	2	0	2	0	9
R-134a/ SW-220	No	0.70	0	51	0	0	825	3	94	6
R-134a/SW220	Yes	0.61	0	0	0	0	112	0	0	10
R-22/York C	No	0.15	0	144	0	0	0	29	0	13
R-22/York C	Yes	1.89	0	0	143	0	0	261	293	0

[1] D.F. Huttenlocher. 1992. Chemical and Thermal Stability of Refrigerant-Lubricant Mixtures with Metals. Report DOE/CE/23810-5 Air-Conditioning and Refrigeration Technology Institute, Arlington, VA.



Pk. Num	Ret Time	Component Name
1	3.16	R-134A
2	10.75	OXYGEN
3	10.81	NITROGEN

Figure 1: Gas Chromatogram of Aged Control Sample Containing R-134a/Carrier SW 220 Without Proateq



Pk. Num	Ret Time	Component Name
1	2.74	R-134A

Figure 2: Gas Chromatogram of Aged Sample Containing R-134a/Carrier-SW220 With Proateq

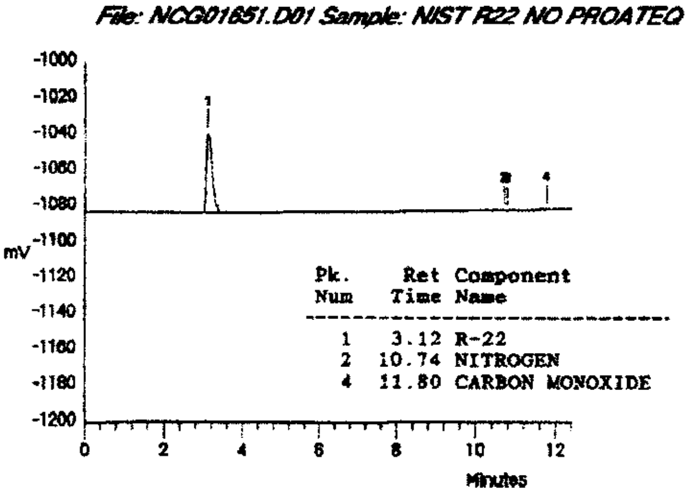


Figure 3: Gas Chromatogram of Aged Control Sample Containing R-22/York C Without Proateq

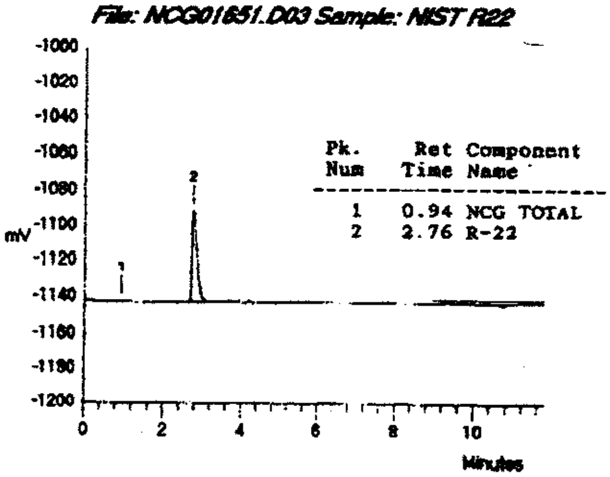


Figure 4: Gas Chromatogram of Aged Sample Containing R-22/York C With Proateq

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LUBRICITY OF YORK C WITH PROATEQ AND SW220 WITH PROATEQ

INTRODUCTION

Two lubricant samples (York C and Carrier SW220) containing oil additive Proateq were tested for lubricity in five-hour Falex wear tests with steel pin and aluminum V-blocks.

EXPERIMENTAL PROCEDURES

A mixture of 10 ± 1% Proateq in lubricant mixture was first prepared by adding together 200 g of lubricant and 20 g of Proateq. A sample of the lubricant mixture was saturated with refrigerant (R-22 for York C and R-134a for SW220) at one atmosphere pressure before and during the test. A run-in period of two minutes at 150 pounds direct load was used. The load was then increased to 250 pounds and held at that level throughout the five-hour period.

RESULTS

The results of the five-hour Falex wear tests, shown in Table 1 and Figures 1-4, indicated relatively good lubricity for York C with Proateq in R-22 and for SW220 with Proateq in R-134a. However, it was noted after the tests that the Aluminum V-blocks in both cases were coated with a gray, black, slightly sticky residue, which was primarily on the surfaces of the V and was very hard to remove. Figure 5 showed photographs under the microscope of the V-blocks after the Falex tests as compared to a new V-block and a scarred but clean V-block. The presence of the residue indicated that there might be decomposition of the Proateq and/or the lubricant under the test conditions.

Table 1: Results of Five-hour Falex Wear Tests of York C with Proateq and SW22 with Proateq

Lubricant/ refrigerant	Load supported Psi	Wear scar mm	Total wear mm	Weight change Block #1 Grams	Weight change Block #2 Grams	Weight loss Pin grams	Maximum Temperature °C
York C with Proateq/R-22	16,600	0.548	0.011	+0.0011	+0.0013	0.0002	78
York C with Proateq/ R-22 (duplicate run)	16,100	0.564	0.009	---	---	0.0083	78
SW22 with Proateq/ R-134a	17,600	0.516	0.005	+0.0025	+0.0024	0.0057	71
SW22 with Proateq/ R-134a (duplicate run)	11,100	0.818	0.044	---	---	0.0176	73

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Midland, MI 48642

Date: January 12, 2004

York C with Proateq and R22

Wear Scar	Load	Total Wear	Weight Change, g			Max. Temp.
mm	psi	mm	Block #1	Block #2	Pin	Deg. C
0.548	16,600	0.011	+.0011	+.0013	0.0002	78

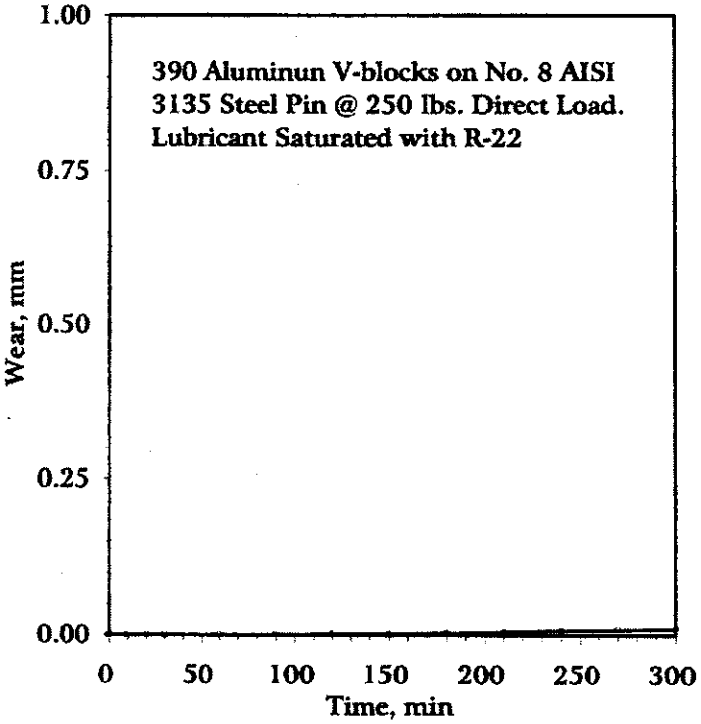


Figure1: Falex Test Result of York C with Proateq and R-22

York C with Proateq and R22						
Wear Scar mm	Load psi	Total Wear mm	Weight Change, g			Max. Temp. Deg. C
			Block #1	Block #2	Pin	
0.564	16,100	0.009			0.0083	78

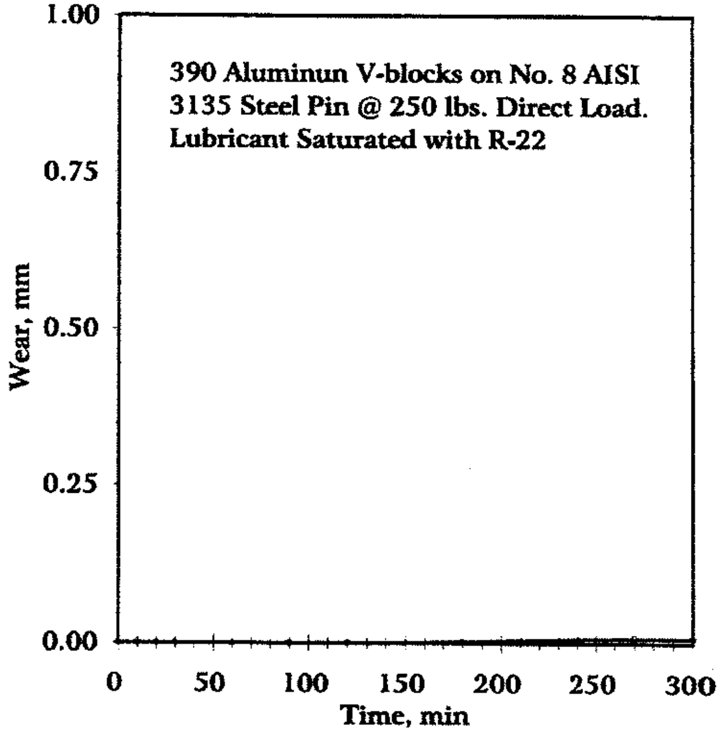


Figure2: Falex Test Result of York C with Proateq and R-22 (Duplicate Run)

SW220 with Proateq and R134a

Wear Scar mm	Load psi	Total Wear mm	Weight Change, g			Max. Temp. Deg. C
			Block #1	Block #2	Pin	
0.516	17,600	0.005	+.0025	+.0034	0.0057	71

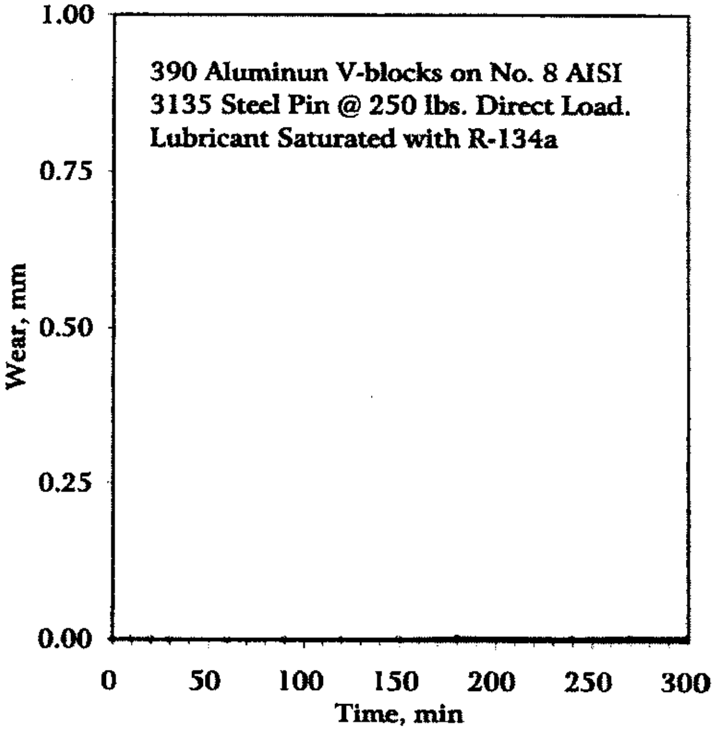


Figure3: Falex Test Result of SW220 with Proateq and R-134a

SW220 with Proateq and R134a						
Wear Scar	Load	Total Wear	Weight Change, g			Max. Temp.
mm	psi	mm	Block #1	Block #2	Pin	Deg. C
0.818	11,100	0.044			0.0176	73

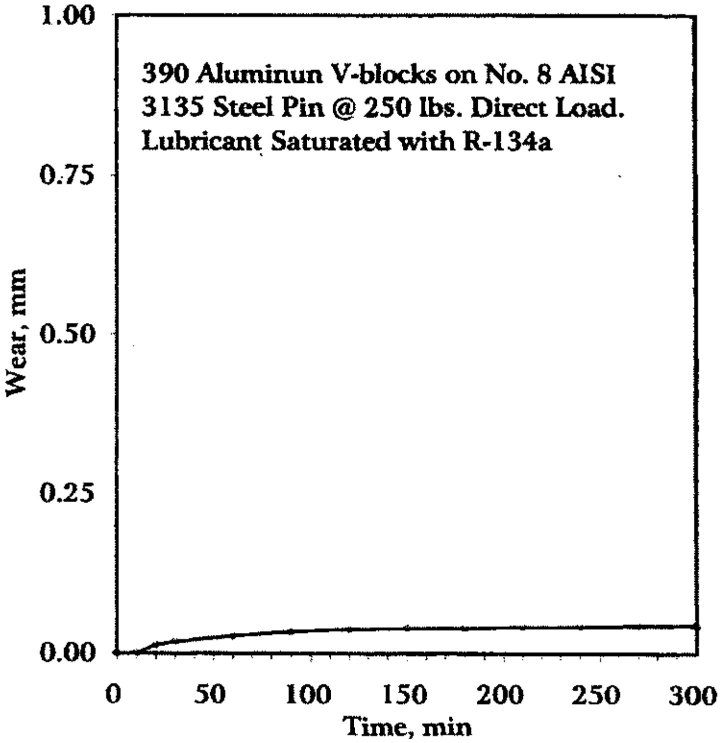
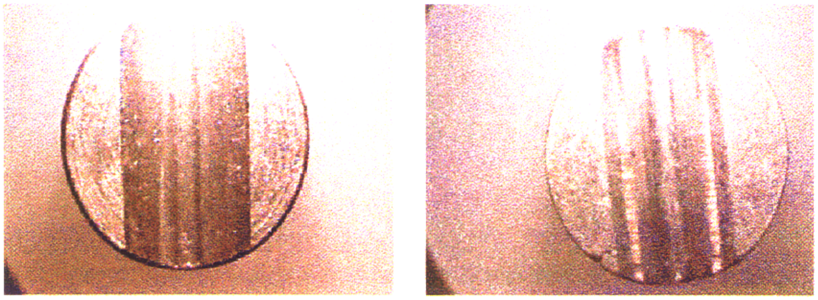
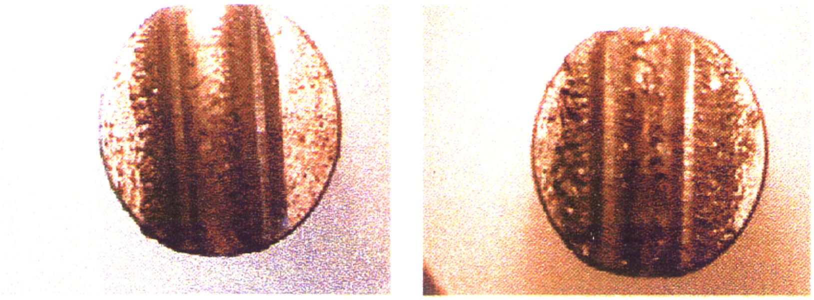


Figure 4: Falex Test Result of SW220 with Proateq and R-134a (Duplicate Run)



New Aluminum V-Block **Aluminum V-Block with normal clean wear**



Aluminum V-block After Falex test with York C-Proateq and R-22 **Aluminum V-block After Falex test with SW220-Proateq and R-134a**

Figure 5: Photographs of Aluminum V-Blocks After the Falex Tests Showing Residue with York C-Proateq and SW220-Proateq as Compared to Clean Vee-Blocks

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COMPATIBILITY TESTING OF OIL ADDITIVE PROATEQ WITH R-123/TRANE OIL 22

INTRODUCTION

The chemical compatibility of oil additive Proateq with R-123/Trane Oil 22 was tested through accelerated aging at 105°C for 30 days in pressure bombs due to the high refrigerant concentrations.

EXPERIMENTAL METHODS

A mixture of 10 ± 1% Proateq in lubricant was first prepared by adding together 8.0-8.1 g of lubricant and 0.81-0.82 g of Proateq. Next, 4.43 g of the mixture were placed in a beaker along with two standard Cu/Al/Steel coupons. The beaker was then placed in a pressure vessel, which was sealed, evacuated and charged with 196 g of refrigerant from a calibrated manifold, yielding a lubricant concentration of 2.0 ± 0.3 %. The pressure vessel was placed in a temperature-controlled oven at 105° C for 30 days. A control sample containing metal coupons and R-123/Trane Oil 22 without Proateq was also tested and its compatibility results were compared to those of the sample containing Proateq.

After aging, because we were unable to obtain a refrigerant R-123 peak from our gas chromatograph, a sample of the gas phase from the bomb was bubbled through a graduated cylinder containing 100 milliliters of deionized water to remove HCl and HF gases for analysis by ion chromatography. 6.9 g of refrigerant was bubbled through for the control and 16.7 g was bubbled through for the test sample with Proateq. The bomb was then opened and liquid phase in the beaker was visually examined for change in lubricant color, cloudiness in the lubricant, floc or particulate formation, film formation on the walls of the beaker. The metal coupons were observed for corrosion and/or copper plating. The liquid phase was analyzed for Total Acid Number (TAN) and by ion chromatography to determine chloride, fluoride and organic acid ion concentrations.

> The total acid number (TAN) was determined according to a modified ASTM D664. The method was modified to accommodate the small sample size by reducing the alcoholic KOH titrant concentration from 0.1 Normal to 0.01 Normal. Titration of the lubricant samples was to a pH of 11. This yielded sufficient sensitivity to determine acid numbers down to 0.1 mg KOH/g with a standard deviation of ± 0.05.

Prepared for: NIST
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Date: December 23, 2003

In the determination of anion concentrations by ion chromatography (IC), about one gram of the lubricant sample was added to a pre-weighed cup containing 30 milliliters of deionized water. The water/lubricant mixture was stirred continuously for 24 hours to allow for extraction of halide ions and acid anions from the lubricant. The water extract was then analyzed by ion chromatography. The concentrations of fluoride ions, chloride ions, organic anions (such as formate, acetate, butyrate, pentanoate, hexanoate) and inorganic anions (such as nitrate, sulfate) were obtained by calibrating the ion chromatograph with standard solutions so that the peak area was proportional to the anion concentration.

RESULTS AND DISCUSSIONS

The results of the compatibility tests are shown in Tables 1-2. When compared to the control, the sample with Proateq showed a small increase in lubricant decomposition as indicated by the increase in total acid number and the higher concentrations of organic acid anions in the aged lubricant. However, the steel coupons did not show sign of copper plating in the presence of Proateq as compared to the extensive copper plating observed with the control. The refrigerant decomposition for the test sample with Proateq was comparable to that of the control (around 0.004%). The percent refrigerant decomposition was calculated based on the chloride ion concentrations measured by ion chromatography in both the refrigerant and lubricant phases and on the assumption that one mole of R-123 decomposed would yield one mole of chloride ion.

Table 1: Visual Observations After Aging at 105° C for 30 Days

Refrigerant/ Lubricant	Proateq	Visual Observations	
		Liquid	Metal Coupons
Control: R-123/ Trane oil 22	No	Liquid darker (color=5.0 versus 2.0 for unaged); light brown stain on sides of beaker with brown ring at the top. Small tan particulate in bottom	Extensive copper plating on steel; copper heavily tarnished; aluminum unchanged
R-123/ Trane oil 22	Yes	Liquid darker (color=4.5 versus 2.0 for unaged); light brown stain on sides of beaker with brown ring at the top; black, soot-like deposit in bottom	Steel darker, but no copper plating; copper with black coating; aluminum unchanged

Table 2: Ion Chromatography Results

Refrigerant/ Lubricant	Proateq	TAN mg KOH/g	Ion Chromatography Results ppm							
			Fluoride	**Acetate**	**Butyrate**	**Formate**	**Pentanoate**	**Chloride**	**Heptanoate**	**Sulfate**
Unaged Trane oil 22	No	0.01	0	0	24	0	0	0	0	5
Control Oil sample	No	0.55	0	0	0	0	73	12	0	6
Test with Proateq Oil sample	Yes	2.36	0	0	0	0	0	257	293	72
Control Gas sample	No	---	0	0	0	0.2	0	0.8	0	0.1
Test with Proateq Gas sample	Yes		0	0	0	0.1	0	0.2	0	0.2

Prepared for: NIST
Date: May 24, 2004

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APPENDIX B: CHILLER MANUFACTURER SURVEY

The below survey was administered by the Air-Conditioning and Refrigeration Institute (ARI). Nine individuals from various companies that manufacture vapor-compression chillers were asked to complete the survey. Only two companies responded. The summarized results of the completed surveys are given parenthetically next to each answer as the percentage of the surveys that had that answer checked.

A Questionare for Chiller Manufacturers on Use of Chiller Oil Additive

In the following questionnaire, you as a representative of a chiller manufacturer will be asked about your opinion of the impact of refrigerant additives on water chillers. Please choose the best answer to each of the questions below. Your answers will be treated confidentially by ARI and not associated with your company (please see last question (Q21)).

First a few questions about your general background

Q1. Do you have influence on company direction?
- ○ Yes *(100 %)*
- ○ No

Q2. To which group do you belong?
- ○ Engineering (preferred responder) *(100 %)*
- ○ Sales
- ○ Law office
- ○ Marketing
- ○ Other

Q3. I am mostly concerned with
- ○ the production of new equipment *(50 %)*
- ○ chillers in the field
- ○ both *(50 %)*

The following questions are related to your company's mission

Q4. Please score (not necessarily rank) the importance of the following goals, using a scale of 1 to 5 where 1 is "not important at all" and 5 is "of greatest importance"?

Increasing chiller efficiency
- ○ 1
- ○ 2
- ○ 3
- ○ 4 *(100 %)*
- ○ 5

Reducing chiller manufacturing cost

- ○ 1
- ○ 2
- ○ 3
- ○ 4 *(100 %)*
- ○ 5

Maintaining chiller reliability

- ○ 1
- ○ 2
- ○ 3
- ○ 4 *(50 %)*
- ○ 5 *(50 %)*

Providing innovative chillers

- ○ 1
- ○ 2
- ○ 3 *(100 %)*
- ○ 4
- ○ 5

The following questions are related to a hypothetical heat transfer enhancement and hypothetical additive compatibility test results

Q5. A 75 % enhancement of boiling heat transfer would be worth obtaining if there were absolutely no reliability nor compatibility concerns.

- ○ True *(100 %)*
- ○ False
- ○ it depends

Q6. Please score the truth of the following statement using a scale of 1 to 5 where 1 is "definitely not true" and 5 is "completely true" : *We would consider using additives that were shown to significantly improve system efficiency and shown to have minor compatibility issues with chiller materials/components.*

- ○ 1 *(50 %)*
- ○ 2
- ○ 3 *(50 %)*
- ○ 4
- ○ 5

Q7. Please score the truth of the following statement using a scale of 1 to 5 where 1 is "definitely not true" and 5 is "completely true" : *We would consider using additives that were shown to significantly improve system efficiency and shown to have major compatibility issues with chiller materials/components.*

- ○ 1 *(100 %)*
- ○ 2
- ○ 3
- ○ 4
- ○ 5

Q8. Assuming that a 75 % increase in heat transfer can be obtained, I believe that my company would consider using additives (or sanction the use of additives) in chillers (check all that apply)

- ○ in the production line *(50 %)*
- ○ that are still under warranty *(50 %)*
- ○ in the field that are no longer under warranty *(50 %)*
- ○ that are manufactured by their competitors

Q9. In general, I believe that my company would:

- ○ recommend against the use of the additive *(50 %)*
- ○ recommend the use of the additive
- ○ recommend for certain situations/applications
- ○ make no recommendation at all concerning the additive *(50 %)*

The following questions are related to your company's past experience with additives

Q10. Has your company independently investigated the effect of oil additives that claim to enhance system performance?

- ○ Yes *(50 %)*
- ○ No (skip Q11 - Q15 and go to Q16)
- ○ No comment *(50 %)*

Q11. My company has tested the following additives in our equipment:

- ○ PROATEQ
- ○ Polarshield
- ○ FRIGAID
- ○ Compress Shield
  Other(s) Sundial ROC *(50 %)*
- ○ No comment

Q12. The greatest enhancement in system COP we found due to oil additives was:

- ○ 0 % to 1 % *(50 %)*
- ○ 1 % to 5 %
- ○ 5 % to 10 %
- ○ 10 % to 15 %
- ○ 15 % to 20 %
- ○ greater than 20 %
- ○ no increase in COP was ever observed
- ○ a COP penalty was observed

Q13. My company would be willing to share their research findings on oil additives concerning system performance with GSA.

- ○ True
- ○ False
- ○ Not known at this time *(50 %)*

Q14. The additives that my company have tested have caused operations and maintenance requirements to

- ○ be reduced
- ○ experience no change *(50 %)*
- ○ marginally increase
- ○ significantly increase
- ○ We have no data concerning operations and maintenance requirements

Q15. My company would be willing to share their research findings on oil additives concerning operations and maintenance requirements with GSA.

- ○ True
- ○ False
- ○ Not known at this time *(50 %)*

Q16. Our company

- ○ currently uses additives in our new equipment
- ○ may possibly use additives in our equipment in the future
- ○ currently is <u>not</u> using additives in our new equipment *(100 %)*
- ○ has made no decision concerning the use additives in our equipment

Q17. The decision made on Q16 was based on (check all that apply)

- ○ our previous research findings *(50 %)*
- ○ research available in the literature *(50 %)*
- ○ research made available by other companies
- ○ Other ______ *no comment* ______ *(50%)*

Q18. Use of an oil additive in our equipment would void the warranty of that equipment

- ○ True *(50 %)*
- ○ False *(50 %)*
- ○ Not known at this time *(50 %) [based on failure mode]*

Q19. Use of an oil additive in our equipment would affect service agreements

- ○ True *(50 %)*
- ○ False
- ○ Not known at this time *(50 %)*

Q20. Our company has demonstrated that oil additive(s) cause harm to our equipment.

- ○ True: which additive(s) (check all that apply)
  - ○ PROATEQ
  - ○ Polarshield
  - ○ FRIGAID
  - ○ Compress Shield
  - ○ Other(s) ______________________________
- ○ False *(50 %)*
- ○ No comment *(50 %)*

Q21. Contact

- ○ I choose not to provide contact information
- ○ I provide contact information for ARI only *(100 %)*
- ○ My company may be identified as a survey participant in the publically available survey summary but my company name will not be associated with the particular answers given in this survey

Please supply us with your contact information (optional):

Name ______________________________
Title ______________________________
Organization ______________________________
Address ______________________________
City, State Zip ______________________________
Email ______________________________
Phone ______________________________
Fax ______________________________

Please fax the completed questionnaire to Zubin Dastoor at ARI (703) 524-9011. For questions, Zubin may be reached by phone (703-524-8800) or email (zdastoor@ari.org)

APPENDIX C: UNCERTAINTIES

Figure C.1 shows the relative (percent) uncertainty of the heat flux ($U_{q''}$) as a function of the heat flux. Figure C.2 shows the uncertainty of the wall temperature as a function of heat flux. The uncertainties shown in Figs. C.1 and C.2 are "within-run uncertainties." These do not include the uncertainties due to "between-run effects" or differences observed between tests taken on different days. The "within-run uncertainties" include only the random effects and uncertainties associated with one particular test. All other uncertainties reported in this study are "between-run uncertainties" which include all random effects such as surface past history or seeding.

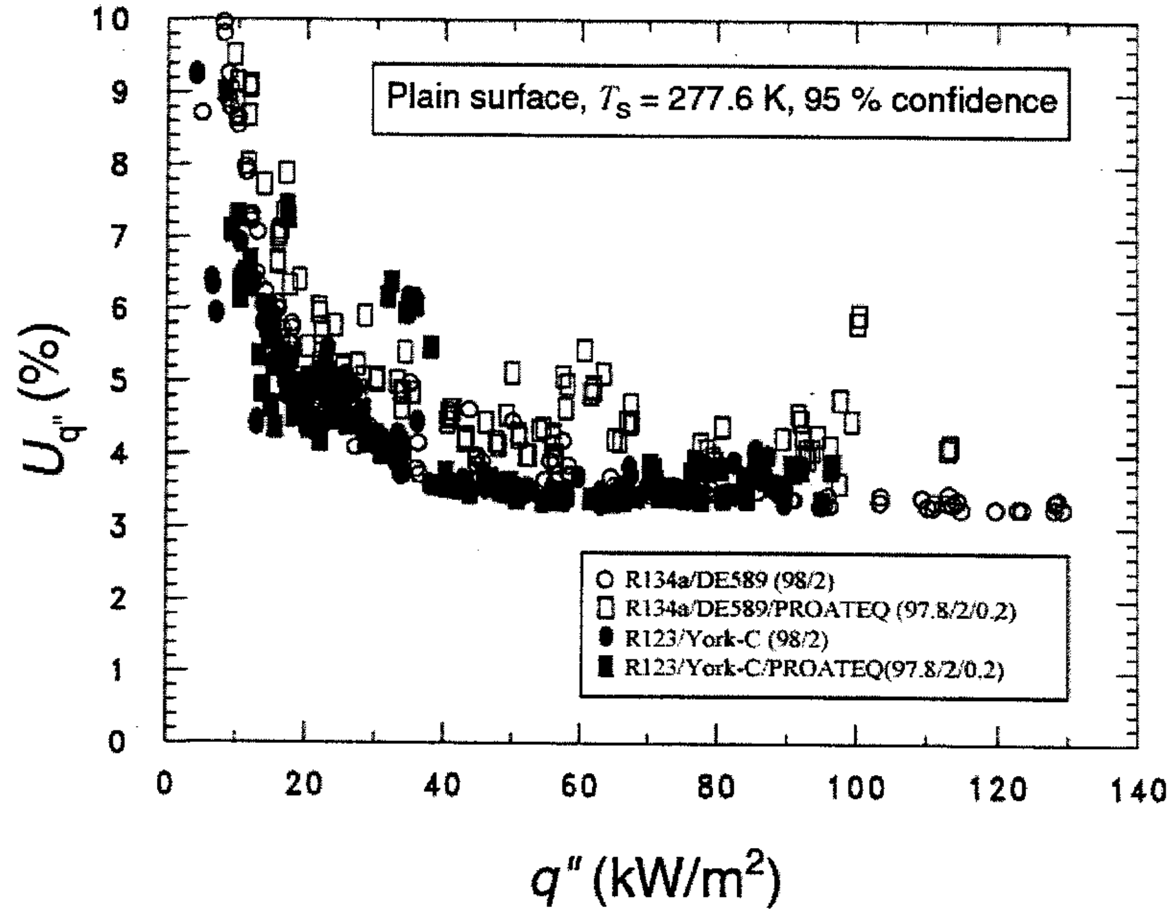

Fig. C.1 Expanded relative uncertainty in the heat flux of the surface at the 95 % confidence level

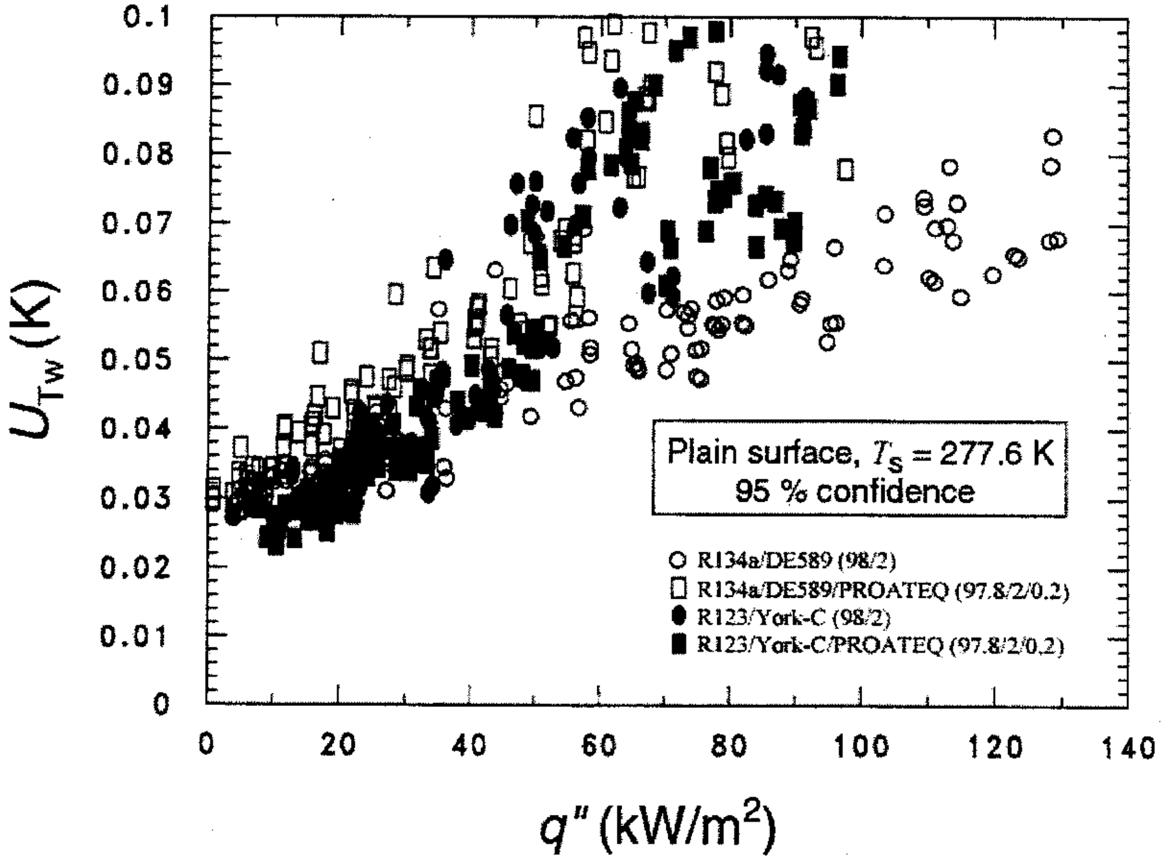

Fig. C.2 Expanded uncertainty in the temperature of the surface at the 95 % confidence level

APPENDIX D: CAPILLARY RISE MEASUREMENTS

This appendix presents capillary rise measurements for DE589, York-C and PROATEQ at approximately 24 °C. Table E.2 provides the capillary rise height measurements (*h*) that were used to calculate the surface tension for the lubricant and the additive. The first column for each fluid gives the height of the liquid in the tube after it had been removed from the liquid pool while placing a finger over the tube opening. The second column for each liquid gives the rise height by subtracting off the height of the pool (*d*) from the first column measurements. The standard deviation of the mean measurement for this method was approximately 0.5 % of the measurement. The pool height was kept small so that if a 100 % error had occurred in the measurement of the pool depth it would contribute only approximately 10 % to the measurement of the capillary rise-height.

A force balance on the column of liquid in the capillary tube was used to calculate the surface tension (Adamson and Gast, 1997):

$$\sigma = \frac{r\Delta\rho g h}{2} \approx \frac{r\rho_l g h}{2} \tag{D.1}$$

where the measured radius of the capillary tube (*r*) was 0.97 mm with a B-type estimated uncertainty of ± 0.03 mm. The liquid densities (ρ_l) for DE589 and York-C at approximately 24 °C were measured in previous studies (Kedzierski 2003, 2001b) as 974 kg/m^3 and 907 kg/m^3, respectively. A single measurement of the PROATEQ liquid density was made using the same procedure and was found to be 906 kg/m^3 at approximately 24 °C. The uncertainty of the density measurements is approximately ± 1 kg/m^3.

The liquid-vapor (air) surface tensions as calculated from eq (D.1) for the DE589, York-C and PROATEQ were 0.027 N/m ± 0.001 N/m, 0.026 N/m ± 0.001 N/m and, 0.030 N/m ± 0.001 N/m, respectively.

Table D.1 Capillary rise measurements at 24 °C

PROATEQ		DE589		York-C	
h + d (mm)	h (mm)	*h* + *d* (mm)	*h* (mm)	*h* + *d* (mm)	*h* (mm)
14.28	12.56	12.81	10.68	9.5	6.01
15.23	13.51	14.12	11.99	10.84	7.35
15.4	13.68	14.36	12.23	12.36	8.87
15.84	14.12	13.92	11.79	13.29	9.8
15.7	13.98	13.61	11.48	14.28	10.79
15.84	14.12	13.37	11.24	14.39	10.9
16.7	14.98	13.74	11.61	14.9	11.41
16.78	15.06	13.55	11.42	15.01	11.52
16.23	14.51	13.43	11.3	15.04	11.55
15.91	14.19	13.94	11.81	15.1	11.61
15.78	14.06	13.64	11.51	15.64	12.15
14.96	13.24	13.03	10.9	15.63	12.14
15.28	13.56	13.27	11.14	15.89	12.4
15.5	13.78	13.07	10.94	16.2	12.71
15.73	14.01	13.11	10.98	16.38	12.89
15.43	13.71	13.56	11.43	16.73	13.24
15.34	13.62	13.65	11.52	16.7	13.21
15.67	13.95	13.72	11.59	17.24	13.75
15.77	14.05	13.51	11.38	17.35	13.86
15.91	14.19	13.79	11.66	17.22	13.73
15.29	13.57	13.87	11.74	17.09	13.6
15.1	13.38	13.88	11.75	17.11	13.62
15.52	13.8	13.47	11.34	16.89	13.4
15.72	14	13.48	11.35	16.93	13.44
15.69	13.97	13.75	11.62	17.11	13.62