

## REFRIGERANT/LUBRICANT MIXTURE BOILING HEAT TRANSFER RESEARCH AT NIST

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### ABSTRACT

*This paper overviews the boiling heat transfer research of the recent few years at NIST (National Institute of Standards and Technology) on refrigerant/lubricant mixtures. The aim of the research was to fundamentally understand the effects of lubricant properties and bubble parameters on heat transfer performance. The magnitude of the effect of lubricant viscosity, miscibility, and concentration on the heat transfer has been quantified. The mechanistic cause of each effect was given based on a new theoretical interpretation and/or one from the literature. The NIST research illustrates that large improvements over pure R134a heat transfer can be obtained for R134a/lubricant mixtures with small lubricant mass fraction, high lubricant viscosity, and a large critical solution temperature (CST). A mechanistic explanation for the observed R134a/lubricant boiling is provided. A fluorescence measurement technique is currently under development with the purpose of unlocking the mechanisms of the lubricant excess layer.*

### INTRODUCTION

The ability to predict the effect of lubricant on the pool boiling heat transfer of refrigerants based on the properties of the lubricant has been elusive for some time. Heat exchanger designers are interested in knowing how lubricant/refrigerant phase separation, lubricant viscosity, and lubricant mass fraction affect the performance of the evaporator. Modeling of refrigerant/lubricant mixture pool boiling has two main obstacles. First, it must be determined what lubricant properties are important and how they influence heat transfer. Second, a mechanistic model that physically represents the way a lubricant interacts with a refrigerant in the determination of heat transfer must be developed. Most of the work in refrigerant/lubricant mixture pool boiling has been done with these goals in mind.

For example, Sauer et al. (1978) believed that lubricant viscosity and surface tension effects were important in determining the magnitude of the nucleate boiling of refrigerants, but they could not correlate these effects. Hahne and Noworyta (1984) also presumed that the lubricant viscosity should have an effect on pool boiling of refrigerant/lubricant mixtures, but they were unable to include it in their heat transfer correlation.

Another important parameter for pool boiling is the lubricant mass fraction. For instance, the effect of lubricant on the pool boiling performance of a Turbo-BII<sup>TM1</sup> tube for R114, and R124 has been investigated by Memory et al. (1993), and Memory et al. (1995), respectively. Although improvements in heat transfer with the addition of lubricant were measured by Memory et al. (1993 and 1995) for finned tubes, only degradations in heat transfer were measured for the refrigerant/lubricant mixtures and the Turbo-BII<sup>TM</sup> tube. In both of the Memory et al. (1993 and 1995) studies, they also found that for lubricant mass fractions greater than 6 %, increases in lubricant concentration led to decreases in heat transfer.

Although no studies investigating the effect of lubricant miscibility on heat transfer were found, several works correlate the lubricant effect to the properties of the refrigerant/lubricant mixture. For example, Jabardo and da Silva (1991) developed a model for the pool boiling of R11, R113 and R114

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<sup>1</sup> Certain trade names and company products are mentioned in the text or identified in an illustration 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.

lubricant mixtures by correlating the Rohsenow (1951) surface/liquid parameter to the bubble Stanton number and to the Jakob number for each refrigerant/lubricant mixture. Another study by Chongrungreong and Sauer (1980) developed a correlation for the pool boiling heat transfer of refrigerant/lubricant mixtures based on the refrigerant volume fraction and the mixture liquid Prandtl number.

Many researchers hypothesize that foaming is the main governing heat transfer mechanism for refrigerant/lubricant mixtures. Stephan (1963) was one of the first researchers to connect foaming and refrigerant/lubricant evaporation and to note that an oil-rich layer exists near the tube wall. Memory et al. (1993 and 1995) also attributed the enhancement of refrigerant pool boiling heat transfer with lubricants to lubricant foaming. Other models, such as those by Jensen and Jackman (1984) and Mitrovic (1998), focus on the lubricant-rich layer that exists around the liquid-vapor interface of the bubble. Yet, Burkhardt and Hahne (1979) believed that the influence of lubricant on pool boiling cannot be completely explained by liquid-vapor surface tension effects or by foaming.

The mechanistic model that is endorsed in this manuscript was developed in a series of studies: Kedzierski (1993) and Kedzierski and Kaul (1993), Kedzierski (1999), and Kedzierski, (2000a). In these studies, it was speculated that the pool boiling enhancement/degradation mechanism associated with the addition of a lubricant to refrigerant is due to an accumulation of lubricant at the boiling surface. The enhancement mechanism of lubricants is analogous to the action of surfactants in that both enhancements arise from the creation of an excess layer. Kedzierski (1999) measured a significant enhancement of R123 pool boiling with the addition of 1 % and 2 % hexane by mass to R123. He used the Gibbs adsorption equation (Rosen, 1978) and the Young and Dupre equation (Adamson, 1967) to speculate that the boiling heat transfer enhancement of R123 by the addition of hexane was caused by an accumulation of hydrocarbon at the boiling surface. In essence, the greater concentration of hydrocarbon or "excess layer" at the heat transfer surface caused a reduction of the surface energy between the solid surface and the liquid. The existence of an excess layer at the liquid-solid interface is analogous to the existence of a surfactant-induced excess layer at a liquid-vapor interface. Consequently, hydrocarbons and lubricants are not typical surfactants because

they accumulate at the solid-liquid interface rather than at the liquid-vapor interface. However, the reduction in the liquid-solid surface energy results in a similar reduction in bubble departure diameter that occurs with a conventional surfactant. As a consequence of the bubble size reduction, the active site density increases. A heat transfer enhancement exists when a favorable balance between an increase in site density and a reduction in bubble size occurs.

## R134a/LUBRICANT BOILING MECHANISMS

With recent research at NIST, Kedzierski (2000b) has shown that the viscosity, the critical solution temperature (CST), and the lubricant mass fraction are important factors for R134a pool boiling. The analysis also showed that the viscosity and the CST are coupled. The role that the lubricant mass fraction, the viscosity, and the miscibility have on R134a pool boiling can be understood by analyzing how these parameters interact with the lubricant excess layer. The lubricant excess layer exists as a region of liquid near a heated wall with a lubricant concentration that is greater than that of the bulk fluid. In the following, mechanistic interpretations are offered to explain how each of the influential factors affect R134a pool boiling.

Larger lubricant mass fractions promote smaller bubble departure diameters, which, in turn, can lead to poorer heat transfer (Kedzierski, 1992 and Kedzierski and Kaul, 1993). As outlined by Kedzierski (2000a), the excess layer causes a reduction in the liquid-solid surface energy ( $\sigma_{ls}$ ) that results in a simultaneous reduction in the bubble departure diameter and an increase in the site density. This was illustrated with the Gibbs adsorption equation for a dilute solution (Rosen, 1978), which shows that a greater surface energy reduction results for increases in the surface excess concentration ( $\Gamma$ ) and/or increases in the bulk lubricant concentration ( $c$ ):

$$d\sigma_{ls} = -RT_0\Gamma dc \quad 1$$

where  $R$  is the universal gas constant, and  $T_0$  is the temperature of the interface. A heat transfer enhancement existed when the increase in site density more than compensated for the reduction in bubble size. However, as the lubricant mass fraction increases, the bubble size decreases while the site density increases. The Mikic and Rohsenow (1969) pool boiling model shows that

the heat flux is directly proportional to the product of the site density and the square of the bubble departure diameter. Consequently, the influence of the bubble size on the heat transfer is greater than that of the site density. As a result, the pool boiling heat transfer eventually degrades with increased lubricant mass fraction.

Even for small bulk lubricant mass fractions, a large lubricant viscosity benefits pool boiling by promoting a thick thermal boundary layer. The existence of the excess layer accentuates the influence of the lubricant properties on the heat transfer because pool boiling is controlled in large part by the fluid properties at the heated wall. Because of the excess layer, the viscosity of the liquid near the wall can be significantly greater than what it would have been for the bulk mixture. An estimate of the relative pool boiling thermal boundary layer thickness for two lubricants (subscripts 1 and 2) was derived from the model of Bosnjakovic (1930) while assuming that the bubble frequency was not influenced by lubricant properties:

$$\frac{\delta_1}{\delta_2} = \sqrt{\frac{v_1 Pr_2}{v_2 Pr_1}} \quad 2$$

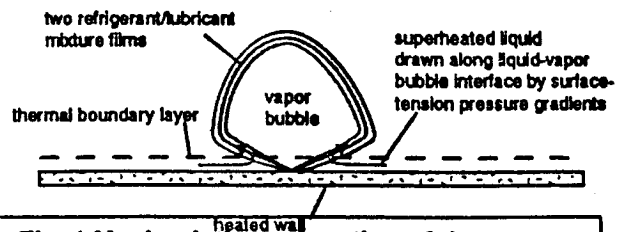
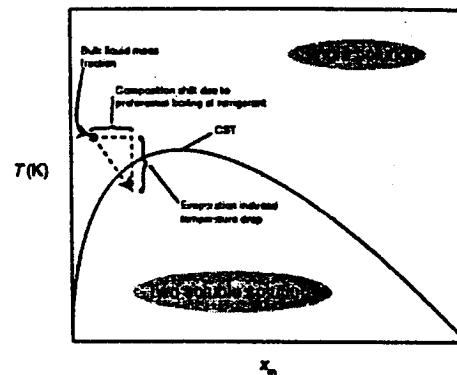
In general, the Prandtl number ( $Pr$ ) does not differ much from lubricant to lubricant despite a large variation in viscosity. Consequently, Eq. 2 shows that the thermal boundary layer is a strong function of viscosity providing a thicker thermal boundary layer for larger viscosities. A thicker thermal boundary, in turn, provides for a larger active site density (Hsu, 1962), which improves the pool boiling heat transfer.

The fact that viscosity and CST are coupled is analogous with the prediction of viscosity relative to the proximity of the CST. Laesecke (1999) has observed that the deviation of the measured viscosity from an ideal mixing rule for R32/propane increases as the CST is approached. Laesecke (1999) believes that the interaction between the polar R32 and the nonpolar propane is responsible for the nonideal behavior of the viscosity near the CST. Because the R134a/lubricant mixture is a polar/nonpolar mixture, a similar nonideal behavior of the viscosity near the CST should be expected. Although this does not explain the interdependence of the lubricant viscosity and the CST, it does establish precedence for the interaction.

The proximity of the bulk fluid temperature to

the CST of the mixture benefits pool boiling heat transfer by the formation of additional excess liquid films that draw superheated liquid onto the bubble sides. Mitrovic (1998) describes how a lubricant-rich film exists around the liquid-vapor interface of the refrigerant bubble. According to Jensen and Jackman (1984), the lubricant-rich layer is formed by preferential evaporation of the refrigerant at the bubble's liquid-vapor interface. However, it is possible that the bubble may also lift a portion of the lubricant excess layer from the heated wall. In any case, given that an excess lubricant layer surrounds the bubble, Fig. 1 shows how a small difference between the bulk fluid temperature and the CST can dramatically affect the pool boiling heat transfer.

Figure 1 shows a theoretical critical solution diagram for a refrigerant/lubricant mixture and a bubble on a heated wall. The critical solution diagram gives the temperature and the compositions for which the lubricant and refrigerant are miscible. Above the dome, the lubricant and refrigerant are completely miscible for all compositions. Within the dome, two soluble solutions of refrigerant and lubricant exist at different compositions. The closed circle on the critical solution diagram represents the



**Fig. 1 Mechanistic explanation of the influence of lubricant miscibility on boiling**

state of the bulk liquid mixture that is close to, but greater than, the CST. The arrow shows how the state of the liquid in the immediate vicinity of the bubble transitions to a two-phase state by a combination of composition shifting and evaporation

at the liquid vapor interface. Once this happens, two thin layers of different refrigerant/lubricant soluble solutions rest on the liquid-vapor interface of the bubble. Of course, only a partial separation is likely because of the short time available before the bubble temperature equilibrates with the bulk liquid. It is also likely that these films are actually liquid droplets that cover regions of the bubble but act like films due to the relative size of the bubble and the droplet. Droplets could also lie adjacent to rather than on top of one another. In any case, the interfaces of the two liquid films are drawn in Fig. 1 to have large curvature gradients. The curvature gradients induce film pressure gradients that transport superheated liquid to the sides of the bubble. The additional bubble superheat is the cause of the pool boiling heat transfer enhancement.

Another plausible mechanistic reason for the boiling enhancement obtained with lubricants that are partially miscible in the refrigerant is that liquid-liquid phase separation causes additional active sites. Oxtoby (1998) shows that increased nucleation is possible for a mixture of water and hydrogen via liquid-like rather than vapor seed bubbles. Laesecke (1999) suggests that because the volatility of the components of both the water/hydrogen mixture and the refrigerant/lubricant mixture differ greatly, the mixtures may exhibit similar phase separation behavior at the critical nucleus. Further understanding of this mechanism can be achieved through investigation of the concentration of the lubricant excess layer at the boiling surface.

## FLUORESCENCE MEASUREMENT TECHNIQUE

Several different measurement techniques exist to measure the lubricant concentration in a refrigerant (Navarro de Andrade et al. (1999)). These techniques rely on various properties of the lubricant: mass, density, ultra light absorption, viscosity, and acoustic velocity. All of these methods are more suited for the measurement of the bulk lubricant concentration of a non-boiling fluid rather than that of the localized excess layer. Kedzierski et al. (1998) proposed an insitu technique for measuring the concentration of a lubricant on a boiling heat transfer surface. The method was proposed to confirm the existence of the excess layer and to quantify its concentration. The technique used the fluorescent properties and/or the harmonic focusing properties of several lubricants to measure the concentration of lubricant on an aluminum vignetting target. The lubricant concentration on the adiabatic target was shown to be linear with respect to the fluorescence intensity and the reflected harmonic from the surface.

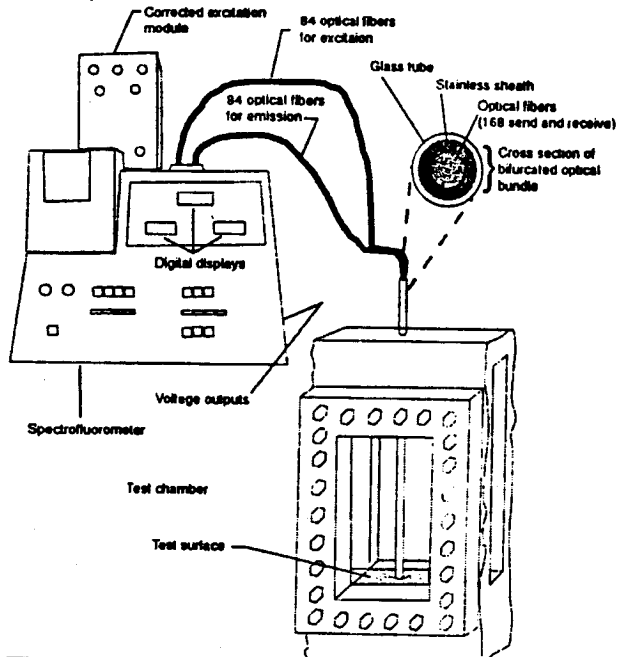
The measurement technique is an adaptation of the insitu technique to an actual pool-boiling surface. In the present study, pure R123 and an R123/lubricant mixture were tested in various concentrations with R123 in an effort to investigate the enhancement mechanism of the excess layer and to measure its concentration. The lubricant was chosen for its favorable fluorescence characteristics. Certain criteria must be met for fluorescence to be useful in measuring lubricant concentration. First, the lubricant must be fluorescent while the refrigerant should be non-fluorescent. Given that the present refrigerant/lubricant mixture satisfies this criteria, the amount of lubricant in the mixture can be calculated from the intensity of the fluorescence emission ( $F$ ) using the Beer-Lambert-Bouguer law (Amadeo et al. (1971)):

$$F = I_0(\lambda) [1 - 10^{-\epsilon c d}] \Phi \quad 3$$

where  $c$  is the concentration of the fluorescent substance and  $\Phi$  is the quantum efficiency of the fluorescence. The extinction coefficient and the path length are  $\epsilon$  and  $d$ , respectively. And,  $I_0$  is the intensity of the incident radiation. The  $I_0$  and  $\epsilon$  were found from calibration to be 116 and -0.0016, respectively.

Figure 2 shows a view of the spectrofluorometer that was used to make the fluorescence measurements and the test section in the test chamber with the fluorescence probe perpendicular to the heat transfer surface. The fluorescence probe shown in Fig. 2 was a bifurcated optical bundle with 168 fibers spanning from the spectrofluorometer to the test surface. Two optical bundles consisting of 84 fibers each originated from the spectrofluorometer. One of the bundles transmitted the excitation light to the test surface. The other bundle carried the emission from the test surface to the spectrofluorometer. The optical bundles originating from the spectrofluorometer merged into a single probe before entering the test section chamber. The sensor end of the fluorescence probe was sheathed with a quartz tube to protect it from reacting with the R123 test fluid. The 168 fibers of the probe were split evenly between the fibers to transmit the incident intensity ( $I_0$ ) to the test surface and those to receive the fluorescence from the test surface. The transmitting and sending fibers were arranged randomly with respect to one another. Fluorescence data from this technique is presently being realized. The results of this study will

be published in the near future.



**Fig. 2 Schematic of test chamber and spectrofluorometer**

## CONCLUSIONS

The mechanistic cause of the effect of lubricant mass fraction, viscosity, and miscibility on heat transfer performance was given based on new theoretical interpretation and/or that from the literature. For example, the literature shows that the larger lubricant mass fractions promote smaller bubble departure diameters, which, in turn, leads to poorer heat transfer. New speculation suggests that the proximity of the bulk fluid temperature to the CST of the mixture benefits pool boiling heat transfer by the formation of additional excess liquid films that draw superheated liquid onto the bubble sides. In addition, even for small bulk lubricant mass fractions, a large lubricant viscosity benefits pool boiling by promoting a thick thermal boundary layer. To summarize, the model illustrates that larger heat transfer enhancements can be obtained for small lubricant mass fraction, high lubricant viscosity, and a small difference between the refrigerant saturation temperature and the critical solution temperature of the lubricant.

A new technique for using the fluorescent properties of lubricants to measure the concentration of lubricant on a heat transfer surface was outlined. The measurement method is being developed to determine the concentration of lubricant insitu on a boiling heat transfer surface.

The ability to measure the lubricant concentration on the heat transfer surface would lead to a fundamental understanding of the mechanism by which lubricants can degrade or improve boiling performance.

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## NOMENCLATURE

### English Symbols

$c$	molar concentration of the solute
$F$	fluorescence emission
$Pr$	liquid Prandtl number
$R$	universal gas constant (8.314 J/K•mol)
$T$	temperature (K)
$x_m$	lubricant mass fraction

### Greek Symbols

$\Gamma$	surface excess concentration of solute
$\delta$	thermal boundary layer thickness (m)
$\epsilon$	extinction coefficient (m <sup>2</sup> /mol)
$\lambda$	wavelength (m <sup>-1</sup> )
$\sigma$	surface tension (kg/m s <sup>2</sup> )
$\nu$	viscosity (m <sup>2</sup> /s)

### Subscripts

$c$	lubricant critical solution temperature
$e$	excess layer interface
$L$	lubricant
$ls$	liquid-solid interface

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