

Cold-Plus™ Air Conditioning Treatment

I. Introduction

An air conditioning system provides a cooling effect according to a closed thermal refrigeration cycle. As illustrated in Figure 1, an air conditioning system comprises three primary components: a compressor, a condenser, and an evaporator interconnected by pipes carrying a refrigerant. The refrigerant alternates between a liquid state and a gas state as it circulates through a high-pressure section and a low-pressure section of the system.

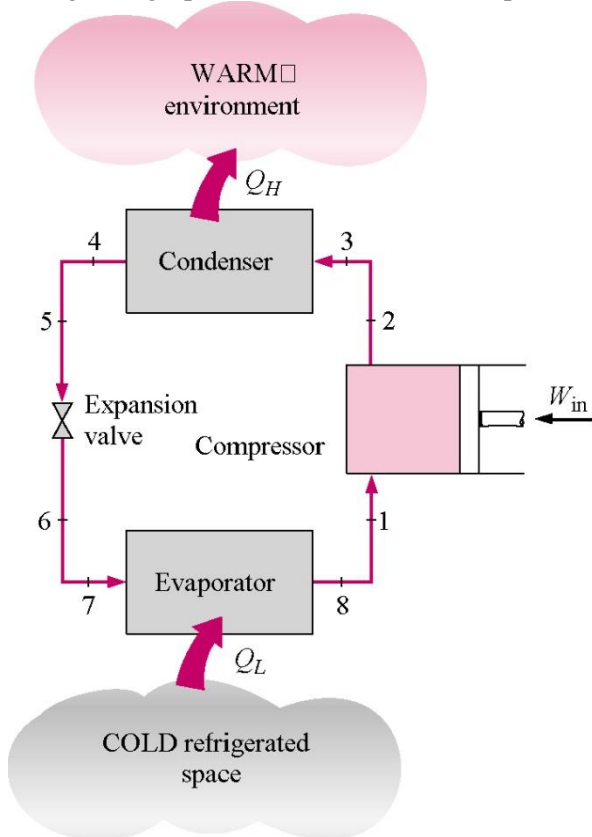


Figure 1

A pressurized liquid refrigerant, such as Freon, enters the evaporator via an expansion valve that lowers the liquid pressure, allowing the refrigerant to vaporize (boil) at a lower temperature, thus ensuring that the refrigerant absorbs a maximum quantity of heat as it passes through the evaporator coil. As the reduced-pressure, liquid absorbs heat from the air (the cold refrigerated space) surrounding the evaporator the refrigerant reaches its boiling point and evaporates to a gas.

From the evaporator, the low-pressure gas flows to the compressor for compressing the gas to a high-pressure state. The higher pressure permits the gas to give up more heat (than a lower pressure gas), ensuring that the gas condenses to a liquid state during the next stage of the refrigeration cycle. From the compressor, the pressurized gas enters the condenser where the gas condenses to a high-pressure liquid, giving up heat to the warm environment surrounding the condenser. The refrigerant then returns to the evaporator via the expansion valve as a low pressure liquid.

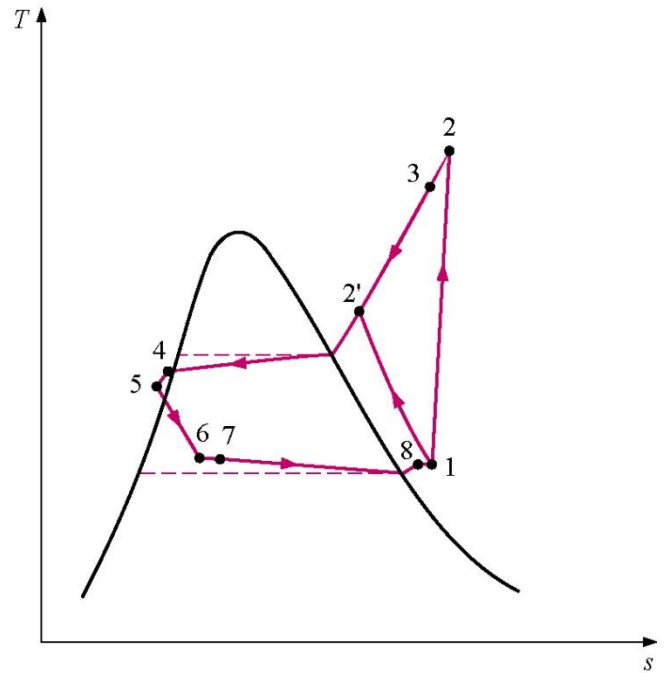


Figure 2

An electric motor or an internal combustion engine supplies the mechanical rotational energy required to operate the compressor to compress the vapor and circulate the refrigerant. Power consumed by the air conditioning system is directly related to the energy required to operate the compressor and in turn related to compressor frictional forces that must be overcome by the electric motor or the internal combustion engine. Higher frictional forces raise the power consumption of the compressor. Generally, a lubricating oil is added to the system to circulate with the refrigerant to reduce these frictional forces.

Figure 2 illustrates a temperature-entropy curve for the refrigeration cycle of the air conditioning system. The numerals on the curve correspond to like numerals adjacent the elements of the air conditioning system. Points 1 and 2 indicate the temperature and entropy for the slightly superheated refrigerant after having been heated and vaporized in the evaporator. Points 2 and 3 are the superheated vapor points after the vapor has been compressed to a higher pressure in the compressor. Points 4 and 5 represent the compressed liquid state of the refrigerant after it has passed through the condenser. Finally, points 6 and 7 represent the saturated and reduced pressure mixture of the refrigerant after passing through the expansion valve.

To minimize power consumption, it is desired to maintain the air conditioning system compressor in a lubricated condition. However, the refrigerant circulating through the system exhibits substantial degreasing properties. As the refrigerant passes through the compressor it tends to remove lubricant from compressor surfaces. The lubricant remains dispersed in the refrigerant and its viscosity decreases when the lubricant reaches the relatively low-temperature evaporator. The lubricant tends to accumulate in the evaporator, starving the compressor of needed lubrication. As the compressor frictional forces increase the compressor operating life is shortened and the motor or internal combustion engine must supply additional energy to drive the compressor.

II. Boiling Heat Transfer

A boiling process dissipates thermal energy within the evaporator when the refrigerant is heated (boils) as it traverses through the evaporator coil and withdraws heat from the cooled space. The heat energy in the surrounding cooled space is dissipated into the liquid by the transfer of heat from the cooled space through the walls of the evaporator coil to the refrigerant within the evaporator coil.

As energy (heat) flow increases from a solid surface, such as the inside wall surface of the evaporator coils, to a liquid, such as the refrigerant liquid flowing in the evaporator coils, the fluid temperature increases and a point is reached (referred to as the nucleate boiling point) where vapor bubbles form (i.e., the fluid begins to boil) on the inside wall surface of the coils. These bubbles form at preferred sites. If the liquid temperature is below a saturation temperature, the vapor bubbles collapse soon after formation. However, as the liquid temperature increases responsive to the transfer of more heat energy into the liquid (from the surrounding space to be cooled) the bubbles become more numerous and are released from the formation sites and carried into the fluid as shown in the Figure 3 below. This process is referred to as nucleate boiling.

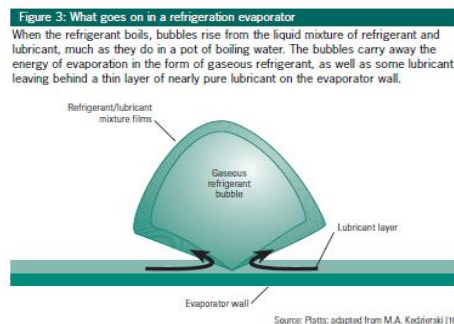


Figure 3

Figure 4 illustrates a typical boiling curve, including a heat flux plot (total heat flow divided by area (q/A) and a heat transfer coefficient (h) curve. The heat flux and heat transfer coefficient are plotted on the ordinate against a temperature difference between the heated surface and the saturation temperature of the liquid on the abscissa. Five curve regions are identified: natural convection (free-surface evaporation), nucleate boiling, transition boiling, and film boiling. The first two regions are commonly referred to as pool boiling regions.

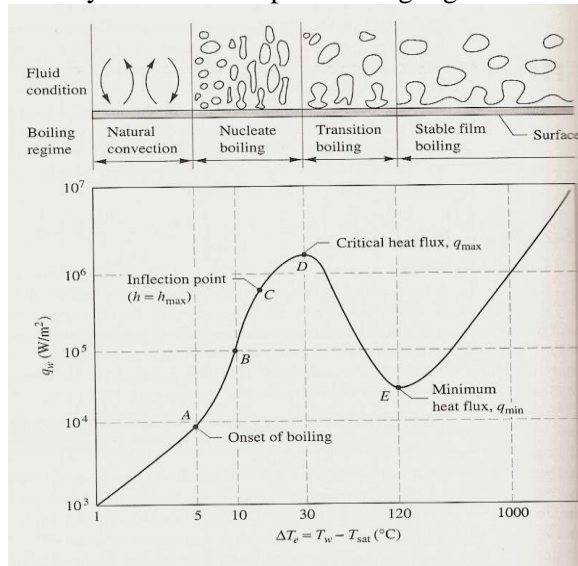


Figure 4

For low values of heat flux the heat flux plot is a straight line, only a portion of which is shown in Figure 4. In this regime, as applied to a refrigeration cycle, heat transfer to the refrigerant fluid is primarily via conduction from the ambient air of the cooled space through the interface with the fluid (e.g., through the walls of the evaporator coil). The heat is then transferred by forced convection throughout the fluid. The fluid evaporates at an open or free surface when the fluid temperature reaches its boiling point. The heat flux in this regime is relatively low compared to the other regions of the curve and as expected the associated heat transfer coefficient (h) as depicted by the curve is also relatively low. As the refrigerant in the evaporator tubes absorbs heat, it moves toward the superheat region. In this regime a convective heat transfer coefficient can be determined and used to calculate the heat transfer rate and the increase in heat flux as the refrigerant moves through the evaporator tubing.

In a region of the curve between curve points A and B the temperature of the evaporator coil/ambient air interface continues to increase by conduction from the space to be cooled, causing individual bubbles to form on the heated surface, i.e., the inside wall surface of the evaporator coil. The appearance of the bubbles increases the heat flux from the heated surface to the fluid, as indicated by a steady increase in the heat flux curve in the Figure 3. The heat transfer coefficient also increases in this region of the curve.

From curve points B to C (a relatively linear segment of the plot) bubble columns form in the column as a result of the increased heat transferred to the fluid refrigerant as indicated by the increase in the heat flux and the heat transfer coefficient. At the point C the heated surface is crowded with vapor bubbles and the rate of increasing heat transfer begins to decline. The point C denotes a departure from nucleate boiling (DNB).

If the heat flux is raised further to a maximum heat flux point, q_{max} , an insulating film comprising a blanket of vapor bubbles begins to form on the heated surface. As the excess temperature increases along the abscissa the insulating film lowers the heat flux. This film boiling is unstable in the region between points D and E, a stable film region beyond point E and

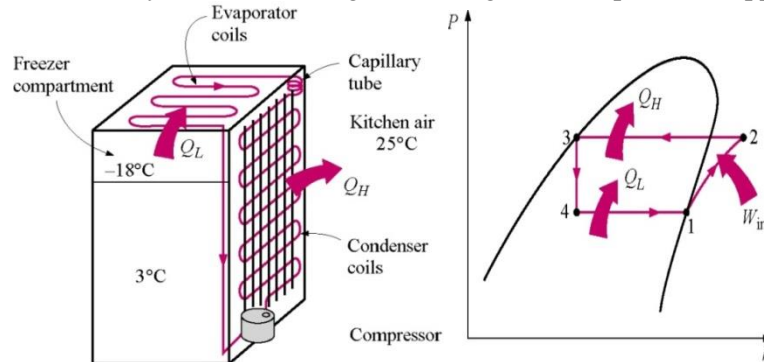
a region where radiation from the surface affects the insulating film. As illustrated, the temperature difference changes rapidly in this region to a curve endpoint. For any practical cooling system it is desired to maintain the operating point at or below the point C thereby avoiding a departure from nucleate boiling region.

III. Cooling Load Analysis

The ordinary household refrigerator is a good example of the application of this cycle.

Refrigeration Example:

The ordinary household refrigerator is a good example of the application of this cycle.



Results of First and Second Law Analysis for Steady-Flow

Component	Process	First Law Result
Compressor	$s = \text{const.}$	$\dot{W}_{in} = \dot{m}(h_2 - h_1)$
Condenser	$P = \text{const.}$	$\dot{Q}_H = \dot{m}(h_2 - h_3)$
Throttle Valve	$\Delta s > 0$	$h_4 = h_3$
	$\dot{W}_{net} = 0$	
	$\dot{Q}_{net} = 0$	
Evaporator	$P = \text{const.}$	$\dot{Q}_L = \dot{m}(h_1 - h_4)$

$$COP_R = \frac{\dot{Q}_L}{\dot{W}_{net,in}} = \frac{h_1 - h_4}{h_2 - h_1}$$

$$COP_{HP} = \frac{\dot{Q}_H}{\dot{W}_{net,in}} = \frac{h_2 - h_3}{h_2 - h_1}$$

Refrigerant-134a is the working fluid in an ideal compression refrigeration cycle. The refrigerant leaves the evaporator at -20°C and has a condenser pressure of 0.9 MPa. The mass flow rate is 3 kg/min. Using the Refrigerant-134a Tables, we have:

$$T \left. \begin{array}{l} \text{State 1} \\ \text{Compressor inlet} \\ T_1 = -20^\circ\text{C} \\ x_1 = 1.0 \end{array} \right\} \left\{ \begin{array}{l} h_1 = 238.41 \frac{\text{kJ}}{\text{kg}} \\ s_1 = 0.9456 \frac{\text{kJ}}{\text{kg} \cdot \text{K}} \end{array} \right. \quad \left. \begin{array}{l} \text{State 2} \\ \text{Compressor exit} \\ P_{2s} = P_2 = 900 \text{ kPa} \\ s_{2s} = s_1 = 0.9456 \frac{\text{kJ}}{\text{kg} \cdot \text{K}} \end{array} \right\} \left\{ \begin{array}{l} h_{2s} = 278.23 \frac{\text{kJ}}{\text{kg}} \\ T_{2s} = 43.79^\circ\text{C} \end{array} \right.$$

$$\left. \begin{array}{l} \text{State 3} \\ \text{Condenser exit} \\ P_3 = 900 \text{ kPa} \\ x_3 = 0.0 \end{array} \right\} \left\{ \begin{array}{l} h_3 = 101.61 \frac{\text{kJ}}{\text{kg}} \\ s_3 = 0.3738 \frac{\text{kJ}}{\text{kg} \cdot \text{K}} \end{array} \right. \quad \left. \begin{array}{l} \text{State 4} \\ \text{Throttle exit} \\ T_4 = T_1 = -20^\circ\text{C} \\ h_4 = h_3 \end{array} \right\} \left\{ \begin{array}{l} x_4 = 0.358 \\ s_4 = 0.4053 \frac{\text{kJ}}{\text{kg} \cdot \text{K}} \end{array} \right.$$

The Coefficient of Performance for the refrigerator is

$$\begin{aligned} COP_R &= \frac{\dot{Q}_L}{\dot{W}_{net,in}} = \frac{\dot{m}(h_1 - h_4)}{\dot{m}(h_2 - h_1)} = \frac{h_1 - h_4}{h_2 - h_1} \\ &= \frac{(238.41 - 101.61) \frac{kJ}{kg}}{(278.23 - 238.41) \frac{kJ}{kg}} \\ &= 3.44 \end{aligned}$$

The tons of refrigeration, often called the cooling load or refrigeration effect, are:

$$\begin{aligned} \dot{Q}_L &= \dot{m}(h_1 - h_4) \\ &= 3 \frac{kg}{min} (238.41 - 101.61) \frac{kJ}{kg} \frac{1Ton}{211 \frac{kJ}{min}} \\ &= 1.94Ton \end{aligned}$$

Another measure of the effectiveness of the refrigeration cycle is how much input power to the compressor, in horsepower, is required for each ton of cooling.

$$\begin{aligned} \frac{\dot{W}_{net,in}}{\dot{Q}_L} &= \frac{4.715}{COP_R} \\ &= \frac{4.715 \text{ hp}}{3.44 \text{ Ton}} \\ &= 1.37 \frac{hp}{Ton} \end{aligned}$$

As can be seen from the equations above, the cooling load and hp/ton cooling is enhanced if the enthalpy difference, $h_1 - h_2$, is increased. By increasing the onset of boiling in Fig. 4, the ΔT_e , and Δh is increased, resulting in an increased cooling load, Q_L .

IV. Nucleate Boiling

A process referred to as superheated boiling occurs in the nucleate boiling region as the temperature of the fluid within cavities on the surface of the heat transfer interface exceeds the boiling point. The liquid in the immediate vicinity of these cavities is super-heated. These surface conditions affect the shape of the boiling curve for a given interface material and liquid.

Superheated boiling involves a phase transition (liquid to gas) in a small but stable region of the liquid. The liquid (fluid) boils as the gas bubbles are formed (see Fig.3) in the microcavities of the surface on the surface of the refrigerant tubing. The bubbles grow until they reach a critical size; then they separate from the surface and enter the liquid stream, transferring heat energy from the cooled space to the refrigerant fluid. This process denotes the beginning of the boiling process as depicted at point A on the boiling curve of Figure 4.

Three parameters affect the superheated boiling heat transfer performance of a wall or plate and a surface that is exposed to a fluid (such as the inside surface of an evaporator coil that

is exposed to the refrigerant). The first parameter is the liquid superheat required to initiate boiling. To initiate the nucleation process, the wall, the surface and then the liquid (e.g., the refrigerant) must reach an incipient superheat condition. The incipient superheat condition is inversely proportional to a volume of any vapor or gas trapped within voids of the wall or irregularities in the surface, because the trapped gas lowers the thermal conductivity of the wall/surface.

The second performance parameter is the surface-to-liquid heat transfer coefficient (see the curve of Figure 4) when the liquid is in the nucleate boiling regime since this is the desired condition for boiling. The heat transfer coefficient is affected by the properties of the surface (including irregularities and particles on the surface) and is directly proportional to the density of the nucleation sites on the surface. Increasing the heat transfer coefficient leads to higher heat flux as more heat is transferred from the surface to the boiling fluid. In the evaporator, increasing the heat transfer coefficient increases the heat flux and therefore causes more heat to be removed from the cooled space to the circulating refrigerant.

The third boiling performance parameter is the critical heat flux (CHF), defined as the highest heat flux that can be removed without exposing the surface to film boiling. Generally this value is represented by the point q_{\max} in Figure 4.

An air conditioning fluid (refrigerant and lubricating oil) or a treatment added to the fluid of an existing air conditioning system, comprising particles that modify the surface characteristics of the system's heat exchangers, that is, the inside surface of the evaporator tubes and the condenser tubes. The particles are deposited on the inside surface of these tubes as the fluid circulates through the system. The enhanced heat transfer, and thus increased system efficiency, is due to one or more of the following effects caused by the deposited particle layer: increasing the number and/or density of superheated boiling sites, increasing the heat transfer coefficient of the coil inside surface (increasing heat transfer to the fluid), increasing the critical heat flux (i.e., increasing the heat flux, q_w , for the same excess temperature, ΔT , and lowering the temperature at which the liquid incipient superheat condition occurs (i.e., the particulate layer produces the same heat flux at a lower temperature or a higher heat flux for the same temperature). Alone or in combination these conditions increase the heat transfer efficiency from the space to be cooled to the system fluid.

The particles in the fluid or fluid treatment adhere to or deposit on inside surfaces of the evaporator coil, forming a particle layer that comprises superheated boiling-site cavities. The particles can be referred to as cavity-generating particles. As used here, "cavity-generating particles" means any particles capable of forming depressions in a particle layer having a width from about 0.5 μm to about 10 μm . Such depressions are suitable for promoting superheated boiling. Preferred particles include crystals, flakes and randomly shaped particles, but could also include spheres or any other shaped particle that provide suitable cavities. The particles can comprise up to about 25% by weight of the fluid circulating in the AC system (the fluid typically comprising the refrigerant and the lubricant).

The superheated boiling sites may present pointed features, such as the cavity edges or areas of roughness in the particle layer, that promote the formation of bubbles. The formation of bubbles from more boiling sites increases heat transfer from the heat transfer surface into the fluid. Within the fluid the heat is transferred by forced and natural convection.

V. Polymer Application

The cavity generating particles comprise polymer particles that tend to impregnate or embed in surfaces they contact. These particles impregnate the inside surface of the evaporator coils (and condenser coils) to form a new heat transfer surface with the fluid refrigerant circulating within the coils. In addition to forming the advantageous superheated boiling sites that improve the boiling performance of the refrigeration system, the particle layer also affects the conduction and

convection heat transfer characteristics between the space to be cooled and the refrigerant circulating within the evaporator coil. The irregular surface characteristics (e.g., the nucleating site cavities) formed as the particles deposit on the surface increase the surface area along the fluid/surface interface, increasing the fluid-surface contact and thereby increasing the conductive heat transfer from the cooled space to the fluid. With increased heat transfer to the surface, the superheated boiling sites reach a higher temperature. This temperature is a defining driver for boiling (forming bubbles) the fluid at the nucleating sites.

For any given application and a specific particle material, particle size and shape, there is an optimum particle layer thickness that maximizes heat flux from the surface to the refrigerant fluid.

$$\delta_{opt} = 7.1429 [(\beta g \Delta T_w D^3 Pr_f) / \nu_f^2]^{-1/3} \quad \text{Eqn. (1)}$$

where:

- β =boundary thickness
- g =gravity
- ΔT_w =temperature difference at the wall
- D = particle size
- ν_f =kinematic viscosity of fluid
- Pr_f = Prandtl No.

Further, since the particles have a higher heat transfer coefficient than the fluid, they increase the thermal conductivity (and thus the heat flux) from the space to be cooled into the refrigerant fluid. This effect also raises the temperature of the superheated boiling sites, improving the boiling characteristics of the fluid. Since any voids formed in the particle layer during deposition tend to fill with fluid and thereby decrease the thermal conductivity of the particle layer (since the fluid has a lower thermal conductivity than the particle material), particles that are shaped and sized to fit the voids tend to reduce the formation of fluid-filled voids and are therefore desired. Also, as illustrated by the film boiling region of the boiling curve in Figure 4, to the extent the fluid-filled voids form a fluid film, the heat transfer characteristics are drastically reduced. Generally, relatively smaller particles in the particle layer increase the heat transfer rate more than larger particles, as the smaller particles tend to pack more closely, reducing the number of fluid-filled voids.

The increased heat transfer rate observed appears to be at least partially caused by the relatively high thermal conductivity of the particles and their single-phase heat transfer coefficient proximate the heat transfer sites of the interior walls of the evaporator coil. Thus the heat is transferred from the space to be cooled to the refrigerant by conduction through the material of the evaporator coil walls and the particulate layer formed as described above and by convection as the heat enters the air conditioning fluid. As heat is transferred into the fluid the fluid temperature increases and boiling occurs, i.e. bubbles form at the boiling sites. It is therefore desired to utilize particles that can both form the superheated boiling sites and present a relatively high thermal conductivity. Further, the particles increase the heat transfer process in the refrigerant by improving the mixing and turbulence of the fluid as it traverses through the system.

Using polymer particles (in the micron or nano size range), the particles are combined with other fluids (e.g., a suspension agent) to create a liquid formulation that is added to the circulating fluid of an operating AC system. Due to its lubricating properties, thermal conduction properties and propensity to create boiling sites on the inside surface of the evaporator coil, the particles increase the efficiency, including heat transfer efficiency, of the air conditioning system, thereby reducing its power consumption (the energy required to operate the compressor). Tests have indicated a 14% to 17% energy reduction. The beneficial operating features are realized

within minutes of adding the particles to the fluid. The particles may also extend the life of system components and reduce the requirements for regular maintenance. A higher ratio of particles to refrigerant/lubricant may produce higher efficiency increases than set forth above.

The polymer also tends to adhere to the compressor surfaces, lowering the friction between the surfaces. The lower friction allows the compressor to operate more efficiently and reduces the power consumption of the air conditioning system.

The density of the particles and the viscosity of the material in which the particles are suspended within the circulating fluid also affect the heat transfer properties of the system. A higher particle density may permit deposition of a sufficient number of particles on the heat transfer surfaces to reduce formation of voids in the particle layer.

The particles are added to a lubricant that is added to the refrigerant. A lubricant or other additive (that is, an additive carrying the particles in suspension) having a viscosity greater than the viscosity of the refrigerant promotes formation of a particulate monolayer on the heat transfer surface should be used, allowing the particles to offer the beneficial heat transfer characteristics described above. The additive may replace less viscous lubricant on the heat transfer surfaces, causing formation of the particle layer on those surfaces. If the refrigerant and the additive are substantially chemically similar, the layer of particles may not form as desired. The miscibility of the additive also affects the deposition of particles on the heat transfer surfaces and thus the heat transfer characteristics of those surfaces.

The surface tension of the particles also affects the heat transfer characteristics. As the surface tension of the particles increases the heat transfer rate is reduced, reducing the boiling initiation point.

The paper by Dr. Mark Kedzierski of NIST, Effect of Refrigerant Oil Additive on R134a and R123 Boiling Heat Transfer Performance and Related Issues for GSA, points out two advantages that can be obtained by using the proper additive with a refrigerant. He points out that 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. Also, he points out that the lubricant that can form a monolayer on the surface of the evaporator and will result in a positive effect on the performance of the cooling system. Since the polymer in the Cold Plus additive fuses with the surface, this should enhance the formation of this monolayer and increase the rate of heat transfer.

Dr. Kedzierski shows through experimentation and analysis that the lubricants with viscosities greater than the refrigerants will enhance the pool boiling heat transfer rate and will form a monolayer on the evaporator surface. He tested a lubricant with a viscosity of 32cSt in refrigerant 134 (with a viscosity of 21.76cSt). The heat transfer data from his tests showed that using the additive, with a viscosity ratio of $32/21.76 = 1.47$, resulted in an average increase in heat transfer of 73%, and a maximum heat transfer rate of 95%. Since the Cold Plus treatment has a viscosity of 65.6cSt at 40C, the ratio of the Cold Plus additive viscosity to the refrigerant is 3.01, or twice the ratio of the additive tested. Based on the NIST tests, the Cold Plus additive should enhance the heat transfer rate by an average of 146%, with a maximum expected in the 190% range. The formation of the monolayer on the evaporator surface and the enhanced heat transfer characteristics resulting from the higher viscosities of the Cold Plus treatment indicates that the Cold Plus treatment would have a very positive effect on the chiller performance. In addition, when the particles are suspended in a refrigerant fluid and caused to deposit on heat transfer surfaces, a microporous coating of desired particles (where the particles are generally in the micron size range) can be applied to the heat transfer surfaces to increase heat transfer performance. Such a coating or boundary layer improves the heat transfer characteristics (conduction, convection and boiling) over the entire nucleate boiling regime.

Also, it should be pointed out that since the particles are imbedded in the surface of the tubing, they will remain there for the life of the tubing. One of the main advantages of the Cold Plus

technology is its ability to provide a longer lasting protection than any other product on the market.

VI. Cold-Plus™ Applications

The treatment of the present invention can be added to the fluid (refrigerant and lubricant) of an operating HVAC (heating ventilating air conditioning) system and to the fluid of an operating packaged AC system. Alternatively, the treatment material is included with the fluid at the point of manufacture and injected into the air conditioning system when it is charged with refrigerant.

Although the beneficial effects associated with increased heat transfer due to the characteristics of the particle surface layer have been described in conjunction with an air conditioning system evaporator, the process is also applicable to the AC system condenser. The heat transfer improvements described above for the evaporator side of the refrigerant cycle also present for the condenser side. It is known however, that the properties of the fluid differ as the fluid state moves from the superheat to the saturated mixture to the compressed liquid region (i.e., from point 2 to point 5 of Figure 2).

This process can also be applied to cooling elements or components that are to be maintained below a predetermined temperature for proper operation. Packaged electronic components are cooled by immersion in a cooling fluid or by passing cooling fluid proximate the external surfaces thereof. By treating the surfaces according to the present process the heat transfer characteristics are improved and the cooling efficiency increased.

Although described in the context of an air conditioning (cooling) system, these processes are applicable to any refrigeration or cooling system. The lubricant can be used with other types of cooling systems, including automotive, residential and building air conditioning systems, further including refrigerators, heat pumps, air conditioning systems and chillers. The material is also suitable for use with systems for cooling semiconductor devices and electronic components.

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