GENERIC SYNTHETIC REFRIGERANT ADDITIVES

Abstract

This essay documents the discovery that Polarized Refrigerant Oil Additives (PROAs) would improve the energy efficiency of air conditioning and refrigeration equipment and systems. It traces some of the scientific work that preceded the discovery, and then it describes, in some detail, the initial discovery as documented in the first-ever US Patent for the concept.

It is important to note that the first Patent didn't patent a particular PROA, or PROA formula. Indeed, the inventor used a commercially available product, a polar compound which was a chlorinated α-olefin named Chlorowax 500AO, sold commercially at the time of the Patent, by Diamond Shamrock Corporation[1], with disclosed formula $C_{12}H_{20}Cl_6$. In the Patent, Wilkins wrote, "Essentially any polar compound meeting the foregoing criteria (suitable polarity, phase stability over the unit's operating conditions, compatibility with the air conditioning components, and compatibility with the compressor lubricating oil) can be utilized in the practice of the present invention."[2]

Rather, the Patent covered the concept that such a product, a chlorinated α-olefin, which was heretofore used for lubrication, also had the effect of improving heat transfer, overcoming oil fouling, and was shown to be stable in the liquid phase over the range of operating conditions encountered. The discovery that these products were effective in reducing the energy use per unit of cooling load by up to 45% from baseline conditions was demonstrated.

The kinds of Polarized additives used in the patent, while effective in saving energy, were quickly shown, in the 1990-1997 period, to be unsafe for equipment. The presence of Chlorine in the product used in the original Patent proved to create Hydrochloric Acid when moisture was encountered in systems. This led to unacceptable corrosion on system components. The development of ProaTEQ, by EnSaTEQ, was an answer to this. It is a product that offers the energy efficiency benefits discovered in this Patent but has none of the harmful effects.

The PROA that Georgetown Utilities provides and installs is based on the work in this Patent. ProaTEQ, our product, was developed by EnSaTEQ as an outgrowth of this seminal research. ProaTEQ is not patented. It is a Trade Secret of EnSaTEQ. ProaTEQ contains no Chlorine and has never harmed equipment. None the less, the discovery and patent of the Concept that PROAs improve energy efficiency, started it all. That story is told below.

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[1] Diamond Shamrock was an oil refiner and retail gasoline distributor headquartered in San Antonio Texas. Diamond Shamrock later merged with Ultramar Corporation, becoming Ultramar Diamond Shamrock. That entity has since been acquired by Valero Oil Co.

[2] US Patent 4,963,280, Oct. 16, 1990: "Method and Composition for Improving the Energy Efficiency of Heat Pump Systems." Charles H.T. Wilkins, Jack Hammack, and Charles B. Thompson, inventors.

Background Research

Research in the 1970s and 1980s on lubricants produced some threads that led in the late 1980s to the work of Dr. Charles Wilkins, Dr. Charles Thompson, and John Hammack, which resulted in a watershed 1990 Patent on the applicability of polarized molecules to enhance refrigeration system performance and in particular to overcome the adverse effects of oil fouling on heat transfer and system capacity.

Polarized molecules had been under development as lubricants in traction applications. Also, with the growth of the heat pump, in the 70s and 80s, there was interest in refrigeration system compressor lubricants that would perform well and remain stable, not change phase, under a broad range of operating conditions. The research led to two Patents cited by Wilkins, et al, one for polarized molecules as machinery lubricants[3]; and another for lubricants and lubricant additives that would remain in liquid phase over a broad range of high and low temperatures characterized by the heat pump's new all year operating conditions[4].

Wilkins, Thompson, Hammack Patent

Based on research and testing conducted in 1987, Wilkins, et al., were awarded US Patent #4,963280, on October 16, 1990, for "A method of improving the efficiency of a heat pump system comprising introducing into the system a polar compound which is liquid under said systems operating conditions".

Quoting from the Patent,

> "The polar organic compound of the present invention contains sufficient polar groups so as to provide regions of the molecule which have high electron densities and other regions which have low electron densities…Essentially any polar compound meeting the foregoing criteria (polarity, ability to remain liquid under operating pressures and temperatures, compatibility with refrigeration system components, and compatibility with refrigerant lubricant installed by manufacturer) can be utilized in the practice of the present invention.
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> "The preferred polar compounds are the liquid halogenated α-olefins and liquid halogenated paraffins; preferably the halogen is chlorine. With the most preferred group of polar compounds being liquid chlorinated α-olefins"

NOTE it was later learned that chlorinated compounds, while successful at improving system heat transfer, formed Hydrochloric acid in the presence of moisture in the system and caused

[3] US Patent 3,972,243, Aug 3, 1976: "Traction Drive with a Traction Fluid Containing Gem-Structured Polar Organo-Compound." Gary L. Driscoll and Marcus W. Haseltine, inventors.
[4] US Patent 4,359,394, Nov. 16, 1982: "Thermally Stable Lubricants for Refrigeration Systems." Gordon C. Gainer, Russell M. Luck, Hendrie J. Grant, inventors.

excessive corrosion. ProaTEQ is not made with Chlorine. Chlorinated products do, however, remain on the market

A critical passage in the Patent presentation was,

> "The polarity of the molecule is believed to result in the polar compound physically attaching itself to the metal walls of the heat pump system. The metal surfaces of the heat pump system are believed to contain a high electron charge such that the present polar molecule will orient itself towards and form a Vander Waals bond with the metal surface. Without being bound by any particular theory it is believed that when the polar compound binds to the metal wall that this results in a reduction in the boundary layer phenomenon which is encountered in the transfer of heat from a fluid contained within a tube through the tube wall to the surrounding fluid. This boundary layer phenomenon reduces the heat transfer coefficient thereby decreasing efficiency. From test conducted to date, it appears that the utilization of the polar compound significantly reduces the effect of this boundary layer phenomenon. Tests thus far have demonstrated not only lower energy consumption but also substantially increased heat transfer across the heat transfer surfaces. This improved heat transfer is demonstrated by an increase in the heat transfer coefficient for the system, and by shorter system cycle times. As a result of the improved heat transfer, one achieves significantly reduced power consumption in the heat pump system. Further energy savings can be achieved by taking advantage of the increased heat transfer by reducing the overall size of the heat pump system for any given load thereby resulting in further energy efficiencies from the use of smaller compressors, and the like."[5]

In this writing, Wilkins, et al. revealed that they had "cracked the code" to overcome oil fouling by the introduction of polar molecules into the lubricating oil. This was the first use of polarized lubricants or lubricant additives for this purpose.

<u>The Experiment That Proved the Case</u>

The Patent presented experimental results based on a study characterized as follows:

1. The study was performed in a test room, a teaching laboratory at the University of Alabama, for 85 days between March 6 and May 28, 1987.
2. The room had ceiling and interior walls connected to other internal surfaces, and an external wall and windows exposed to the sun and ambient conditions.
3. The rooms was cooled by a 1962-vintage, 3.3 ton York water-cooled, self-contained air conditioning unit, using Freon R-22, with 0.875 gal of York "C" oil as a lubricant. The room was held at 71 deg. F by the thermostat continuously throughout the 85-day test.

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[5]Wilkins, et al., ibid column 3, lines 17-46

4. Measurement was set up to monitor power to the air conditioning unit, the temperature in the room, and from these, daily kWh and daily cooling degree hours, each on an aggregated 24-hour basis.
5. Over the 85 days of the test, a polarized compound, found in a commercially available chlorinated α-olefin, Chlorowax 500AO was gradually added to the lubricating oil of this unit.
    a. The Polarized Refrigerant Oil Additive (PROA) was added in 12 injections of 15 ml each.
    b. The 12 injections were spaced anywhere from 0 to 46 days apart. Eleven of the injections were 0 to 6 days apart; injection 7 followed injection 6 by 46 days[6].
    c. Due to the staging of injections, the concentration of the PROA in the lubricating oil varied over the period of the study. For example:
        i. On day 1, 3/6/87, injections #1 and #2 were made, 15 ml each, totaling 30 ml. At that point the system PROA concentration was 0.83% by volume
        ii. The system ran at 0.83% for three days. No energy measurements were recorded.
        iii. On day 4, injection #3 was inserted. Total volume increased to 45 ml. Volumetric percentage increased to 1.25%
        iv. On day 7, injection #4 was made, now 60 ml, 1.67%
        v. On day 11, injection #6 was made, now 90 ml and 2.5%
        vi. The system was held at 90 ml and 2.5% for 46 days, as noted above. On day 14, the first 24-hr kWh and 24-hr CDH recordings were made. Recordings were also made on days 16 through 24 and on days 35 and 36.
        vii. On day 58, injection #7 was made, now 105 ml, 3.0%. 24-hr kWh and CDH readings were recorded each day until Injection #8 on day 61.
        viii. The final injection was #12, on day 78, making 180 ml and 5.1%. That concentration was held until the end of the test on day 85. kWh and CDH readings were taken on days 80, 81, and 84.
        ix. In total there were 24-hr kWh and CDH readings recorded on 35 of the 85 days of the test.
        x. The investigators reported that the kW was monitored multiple times, and held at 2.79 kW whenever the system was operating.
        xi. From the constant kW, the daily kWh recordings could be converted to daily run time in hours or minutes.

<u>The Reported Results</u>

The investigators reported that the optimum concentration of PROA in the system tested was 4.7% by volume[7]. The additional substantive claims in the patent are:

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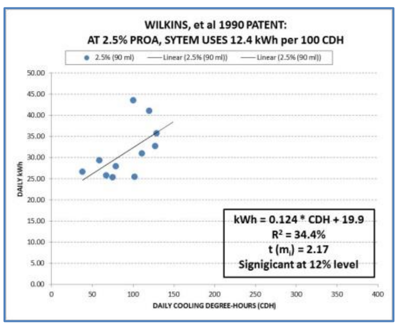
[6] Notes in the Patent Document say there were some equipment problems after injection #6 that had to be addressed, and there was some cooler weather that didn't cause the air conditioning system to operate.

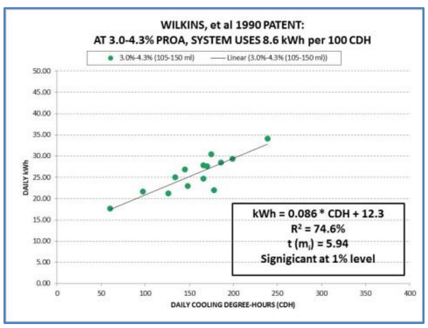
1. Introducing a polar compound comprising a chlorinated α-olefin or a chlorinated paraffin, into the system, is shown to improve energy efficiency; and
2. The particular chlorinated α-olefin used, Chlorowax 500AO, remained liquid under the entire set of operating conditions encountered in the test; and
3. Any of several chlorinated α-olefins could be used, as long as they had 6-24 carbon atoms and 1-12 halogen atoms; and
4. The additive should be in proportion of 0.1 to 10% by volume mix in the refrigeration lubricating oil; and
5. Carrier oils of white oil or naphthenic oil can be used, approximately equal volume mixtures are recommended; and
6. A Buffer should be added to prevent halogens from free halogens from forming and causing corrosion in the event of moisture in the system.

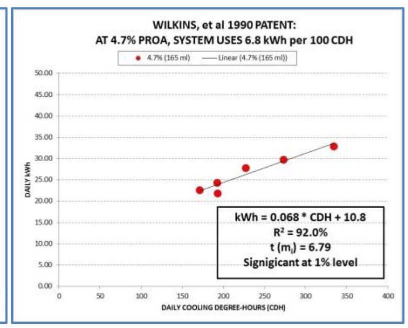
As can be seen, the focus of the Patent was more about the lubricant aspects of the test than of the energy efficiency achievements. Because our interest now, 25 years later, is in the energy efficiency achievements of the Patent research, GU had performed a re-analysis of the Wilkins, et al data which is provided below.

<u>Georgetown Utilities Re-Analysis of Wilkins, et al Data</u>

Additional analyses of the data published in the Patent were conducted by Georgetown Utilities. The following results are highly relevant, in our opinion.







The three plots represent the data on daily kWh and daily cooling load as expressed in cooling degree-hours per day (65 base). The left is data from days 16 through 57, a total of 11 observations, when the system held 90 ml and 2.5% concentration (low dosage). The data in the middle chart are from days 58 through 71, 14 observations, when the concentration was at 3.0% to 4.3%, increasing slightly every few days. The data in the right chart was from days 72 through 77, containing 6 observations, with concentration at 4.7%.

The fourth chart, provided below, combines data from days 72 through 85, which provides 9

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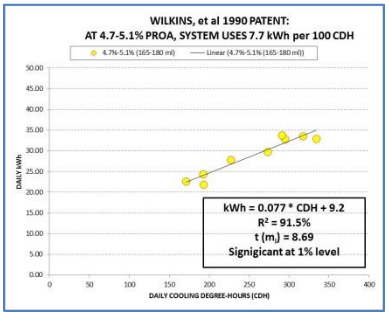
[7]Wilkins, et al, US Patent 4,963,280, column 8, line 4-6, "These tests reveal an optimum concentration of 4.7% for the Chlorowax"



observations, 6 at 4.7% concentration and thee at 5.1% concentration.

The data are taken directly from the patent document with two exceptions; one datum was found impossible and was replaced by a model-based imputed value[8]. Another datum was dropped because it was an extreme outlier and technical factors rendered it likely erroneous[9].

On each plot, the linear regression line for the following linear equation is provided:

kWh/day = m * CDH/day + b

Where m is the slope of the line shown, which is the sensitivity of daily kWh to cooling load. Note that since there are four charts, with four lines, the lines are parametric in increasing concentration of PROA in the lubricating oil. The slope of the line, m_i is estimated by regression and shown, and the lines are drawn on each chart. The steeper the line, the MORE energy is used per unit of cooling load. The flatter the line, the LESS energy is used per unit of cooling load. Note that in the top three, the line gets flatter and flatter as you move from left to right, indicating more PROA reduces energy use. The bottom chart, in which the PROA is a mix of 4.7% and 5.1%, actually has a line that has become less flat. In other words, and optimum was reached at 4.7% (as reported in the Wilkins patent)[10] , and increasing the concentration up to 5.1% actually increased the energy use per unit of cooling load.

The specific key results are:

1. The left chart shows that at 2.5% PROA concentration by volume, the system used 12.4 kWh per 100 Cooling Degree Hours (CDH).
2. The center chart shows that as the PROA volumetric concentration was increased from 2.5% through 3.0%, 3.4%, 3.9% and 4.3%, the kWh usage fell to 8.6 kWh per 100 CDH.

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[8] On day 66, which was 5/9/87, and the day of the 9th injection, the 24-hr kWh datum recorded in the patent document was 123.02 kWh. This datum was impossible. All other data on daily kWh ranged from 17.6 to 44.8. Thus this datum was from 3 to six times larger than any other in the dataset. In addition, the Patent document said that all the kWh data were recorded over a 24-hour period, and that kW demand was constant at 2.79 kW. Based on that, the system would have had to run 44.1 hours in a 24-hour period; which was physically impossible. GU used data from days 58 through 71, omitting day 66, and modeled that data using linear regression, then imputed the data value for day 66 from that model. The imputed value was 29.38 kWh.

[9]On day 14, the very first day of recorded kWh data, the kWh was 44.83 (the largest kWh datum of all except the obviously flawed one from day 66). On that same day, the cooling degree hours were 32, the smallest of any of the observed CDH values. That was extremely suspicious. Also, day 14 was the very first day with kWh and CDH data recorded. The next observation (day 16) had comparable energy use, 43.55, but the CDH was more than triple, at 100. The datum for day 14 was so far out of range it was dropped from the data set. We assume there were recording errors on the initial day of data recording. There were ample remaining observations at the 90 ml, 2.5% concentration.

[10] Wilkins, et al, US Patent 4,963,280, column 8, line 4-6, “These tests reveal an optimum concentration of 4.7% for the Chlorowax”.

This is a 30.6% reduction in energy use per unit of cooling load in the experimental unit relative to the prior state at 2.5%

3. The right chart shows that for the PROA concentration of 4.7%, regarded as optimal by Wilkins, the energy usage is 6.8 kWh per 100 CDH. That is a 20.9% reduction relative to the medium concentration; and a 45.2% reduction relative to the low concentration PROA.
4. Note that when the data points for the 5.1% volumetric proportion are added, in the lower chart, the energy use goes up to 7.7 kWh per 100 CDH. This shows that the increased additive concentration beyond 4.7 had an effect of increasing the energy per unit load, indicating that an optimum had been reached at the level below 5.1%, i.e. at the 4.7% level.

Conclusion and Historic Implications

The research in the patent demonstrated that PROAs can reduce energy use per unit of load up to 45%, and that concentrations are optimal at 4.5%-5.1% by volume.

The discovery that PROAs reduced energy use and likely overcame the oil fouling effect, first documented here in 1990, led to a number of products entering the market. Many had chlorinated compounds without successful buffers. That is discussed in the essay on Chlorinated Olefins.

Georgetown Utilities and EnSaTEQ are proud to be heirs to the discovery of Wilkins, Thompson, and Hammack. The ProaTEQ product that Georgetown Utilities offers and installs is an heir, a much improved heir, to this seminal work.