



DIBENZYL TOLUENE
AND
PARTIALLY HYDROGENATED TERPHENYLS

A review of the distinguishing molecular and physical properties of Dibenzyltoluene and Partially Hydrogenated Terphenyls in heat transfer applications.

By

Pete Frentzos and Doug McKinney



DIBENZYLTOLUENE AND PARTIALLY HYDROGENATED TERPHENYLS

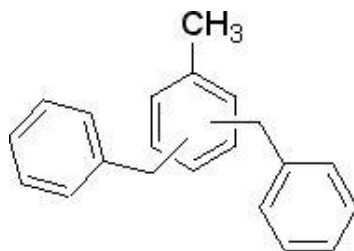
There are several physical properties that distinguish dibenzyltoluene-based heat transfer fluids (DBT) from partially hydrogenated terphenyls (PHT), however their characteristics, taken as a whole, make them both useful as heat transfer fluids in high temperature liquid phase thermal fluid heating systems. These differences illustrate that DBT is a more consistent molecular formulation than PHT. Furthermore, DBT is also an economic alternative to costly terphenyl-based fluids.

There is not a particular trait that defines a “good” heat transfer fluid. The most correct heat transfer fluid for a particular application is defined by several important physical characteristics. The sum total of these characteristics is measured in terms of efficiency (*heat transfer ability*) and thermal stability (*resistance to thermal degradation resulting in longer life*). Radco Industries, Inc. manufactures a proprietary DBT-based formulation, called **Xceltherm®HT**, which has been developed to be an ideal alternative in heat transfer applications that are designed to use PHT.

DBT is a mixture of predominately dibenzyltoluene molecules with benzyltoluene isomers. It is a stable, well-defined and pure molecular formulation. DBT’s pumpability limit (2000cP) is approximately -35°C (-37°F), and can cold start at this temperature without heat-tracing. It has an optimal operating range approximately between 182°C and 350°C (360°F and 662°F).

The beginning of a thermal fluid’s optimal operating range can be determined by its Reynolds number. The Reynolds number is the ratio of inertial forces on the fluid to the fluid’s viscosity when in motion. In other words, it is a calculation of the turbulence of thermal fluid flow. It is a dimensionless number that increases with increased turbulence. Sufficient turbulence is required for a liquid to take full advantage of its ability to absorb and release heat. The optimal operating range begins when the Reynolds number reaches 100,000. However, the fluid will have a much broader functional range that is defined by its pumpability point at the lowest temperature. The highest operating temperature is generally defined as the highest bulk temperature the fluid can withstand with a reasonable rate of degradation. When evaluating heat transfer fluids, it should be understood that this temperature limit is subjective and defined by each manufacturer.

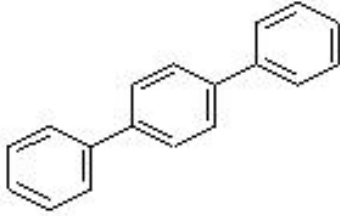
Dibenzyltoluene



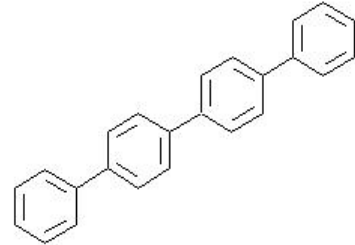
PHT is a less defined mixture of terphenyls and quaterphenyls. (Terphenyls are three hybridized benzene rings, and quaterphenyls are four hybridized benzene rings.) The optimal operating range of the PHT heat transfer fluid is similar to DBT, between 180°C and 345°C (356°F and 650°F). The pumpability limit (2000cP) of PHT is -3°C (27°F).



Partially Hydrogenated Terphenyls



***p*-terphenyl**



***p*-quaterphenyl**

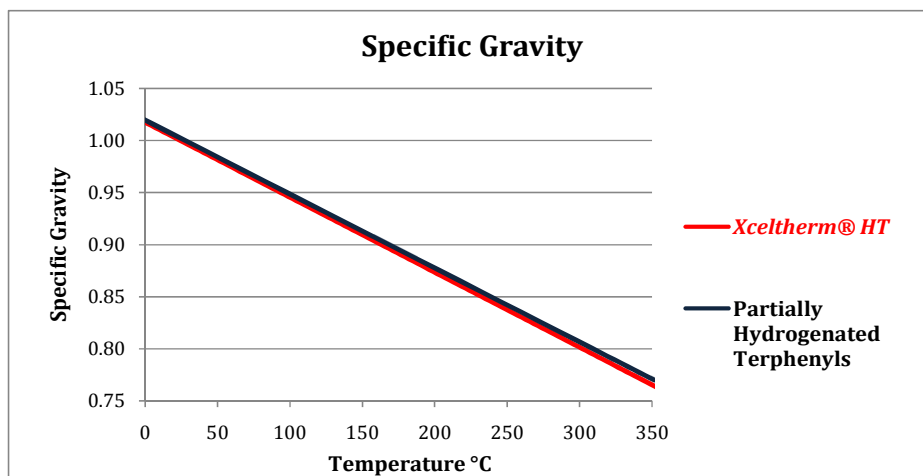
PHT's are generally manufactured from the preparation of biphenyl and benzene. However, there are a number of methods used to synthesize PHT. The ratio of terphenyls and quaterphenyls inconsistently varies depending on the manufacturing process.

DBT differs from PHT in that it is synthesized from extremely pure molecular components. The purity and quality control of DBT manufacture can yield very predictable physical characteristics between batches. The inconsistent ratio of terphenyls and quaterphenyls in PHT manufacture may exhibit inconsistencies and therefore may produce undesirable results.

For the next part of the discussion, individual physical characteristics are compared and analyzed for their effect on key indicators of heat transfer fluid functionality, heat transfer efficiency and thermal stability.

SPECIFIC GRAVITY

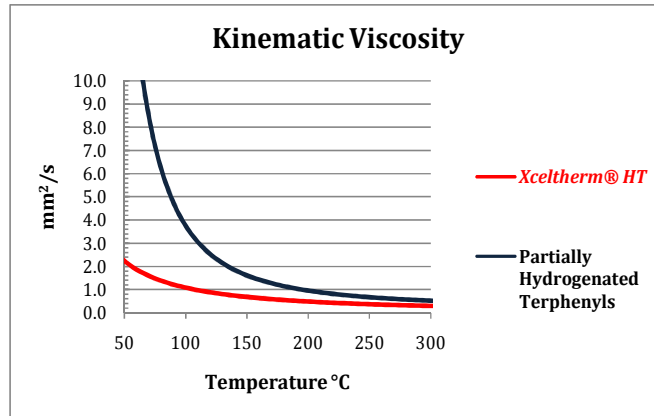
There is a linear relationship between the specific gravity of a heat transfer fluid and temperature. As the temperature increases, the specific gravity decreases in a predictably linear fashion. In general, ***Xceltherm®HT*** has a marginally lower specific gravity than PHT (approximately 1.5% difference).





VISCOSITY

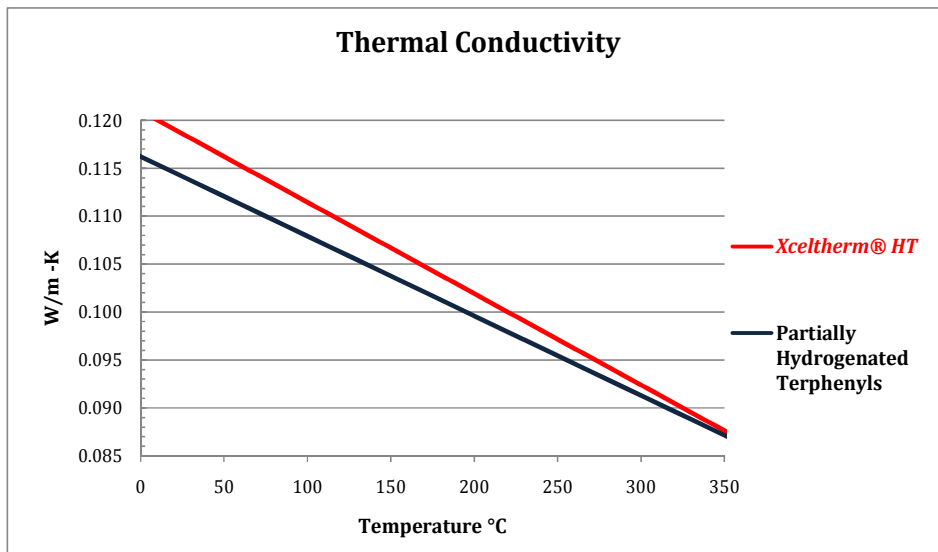
Viscosity is a significant factor in heat transfer calculations. There is an inverse, exponential relationship between viscosity and temperature. As the temperature increases, the viscosity rapidly decreases. Viscosity affects heat transfer: the lower the viscosity values, the greater the potential for turbulence as measured by the Reynolds number and the greater the heat transfer.



Xceltherm® HT heat transfer fluid has a lower viscosity than PHT. The viscosity values of DBT and PHT show some convergence at temperatures between 275°C (527°F) and 300°C (572°F), and at temperatures above 300°C (572°F) there is a negligible difference between kinematic viscosity values (Figure 1.1).

THERMAL CONDUCTIVITY

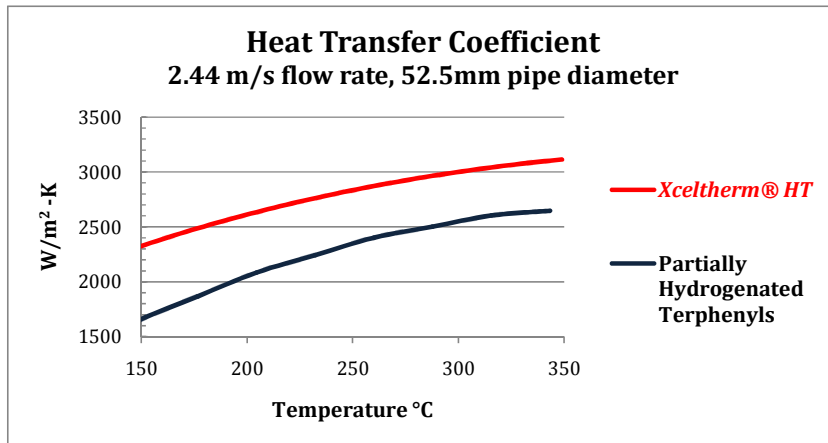
The *thermal conductivity* of a fluid is also an important factor in determining heat transfer efficiency of a fluid. Thermal conductivity describes the ability of a material to transfer or conduct heat. Thermal conductivity measures the *rate of heat flow* across a defined area. The rate of heat flow is the energy (Joules or Btu) that travels across a sectional area (1 meter or 1 foot) with respect to time. (The units are Watts/meters-Kelvin or Btu/hour-foot- $^{\circ}\text{Fahrenheit}$.) The larger the thermal conductivity value, the greater the heat transfer. **Xceltherm® HT** has 7% advantage in thermal conductivity over PHT as calculated from published data of a common PHT used as a heat transfer fluid.



HEAT TRANSFER COEFFICIENT

The *heat transfer coefficient* (or simply, *heat transfer*) is an important variable in system design. The heat transfer coefficient measures the thermal energy that is transferred between a fluid and solid by convection or phase change. The heat transfer calculation is dependent on the fluid's viscosity, thermal conductivity, and flow-rate of the fluid through a specific pipe diameter. The heat transfer coefficient is expressed in W/m^2K . For instance, in figure 1.2 the heat transfer values are modeled from a 52.5 mm diameter pipe with 2.44 m/s flow rate. In general, the greater the heat transfer value, the greater the capacity for thermal energy to pass from the pipe to the heat transfer fluid. However, the efficiency of the thermal energy transfer is limited by the design and function of the heat transfer system.

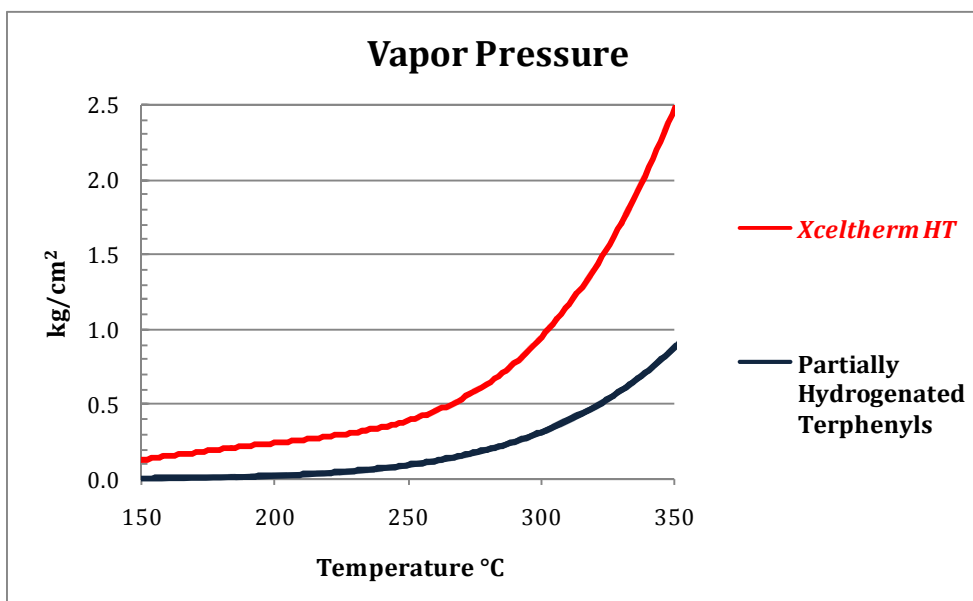
The calculated heat transfer of **Xceltherm®HT** is greater than PHT. However, the ranges of heat transfer values between both fluids are congruent between temperatures 200°C and 290°C (392°F and 554°F). Trending does illustrate a convergence of heat transfer values between DBT and PHT, albeit DBT's heat transfer remains slightly higher.



The proper design of heat transfer fluids takes into account several key properties and components that are limited by physical laws. For instance, the heat transfer coefficient is inversely related to viscosity, and directly related to thermal conductivity. Although it is desirable to design a fluid with the lowest viscosity and greatest thermal conductivity for maximum heat transfer, there are natural and physical limitations that prevent this formulation, including increased vapor pressure and/or decreased thermal stability.

VAPOR PRESSURE

Xceltherm[®]HT exhibits a higher vapor pressure than a typical PHT as a result of combining ideal characteristics to maximize the important combination of heat transfer efficiency and thermal stability. The above chart is derived from published information about virgin, unused material. Later in the discussion there is information about how PHT vapor pressure increases with use.





THERMAL DEGRADATION & HEAT TRANSFER FLUID ANALYSIS

Thermal oils, whether petroleum based or synthetic heat transfer fluids like the aromatics DBT and PHT, experience thermal degradation or oxidation when used at high temperatures. The use of a closed system padded by nitrogen can limit oxidation. Routine fluid analysis is the primary preventative method for monitoring the heat transfer fluid's condition.

Thermal degradation (or *thermal cracking*) of DBT and PHT is difficult to avoid and exponentially accelerates above 316°C (600°F). Thermal cracking is when the heat transfer fluid distills into lighter components. These *light distillates* have lower thermal stability than the virgin heat transfer fluid (light distillates are also called "*light ends*" or "*low boilers*"). Accelerated thermal degradation will result if there is localized overheating at the burner tubes, especially if recommended film temperatures are exceeded. Overheating of the thermal system's burner tubes can be caused by flame impingement in the burner, low flow rates through mechanical failure or poor heat transfer system design, laminating or *coking* of the tubes due to fluid degradation, or other causes. Coking is the formation of hard carbon particles that may clog filters and pipes. Coking may also foul burner heating tube bundles and clog heat exchangers. It can also reduce laminar flow from sludge formation.

The Acetone Insoluble test is used to measure the carbon content of a fluid in parts-per-million (ppm). If the ppm value exceeds specifications (more than 300ppm), corrective action is advised.

The ampule test measures thermal degradation of heat transfer fluids in a controlled environment in the absence of oxygen to give a relative comparison between fluids in a closed thermal oil system. The ampule test does not measure the fluids efficiency or life span in a specific system, but it is useful as a relative comparison between heat transfer fluids.

Oxidation of synthetic and petroleum-based thermal fluids also produces weak acid formation. Weak acid formation may occur from contamination from external sources, in open vent expansion tank operation due to hot fluid contact with air and/or from thermal degradation of the fluid. The molecular integrity of the fluid deteriorates when the acidity of the thermal fluid increases. Furthermore, weak acids produce insoluble materials that may cause mechanical failures in seals, valves, and/or pumps.

The Total Acid Number Test (Neutralization Number) is an acid-base titration that measures weak acids present in a heat transfer fluid. If the acid number is out of specification, it is strongly recommended that the heat transfer fluid be replaced. The average acid number for new material is between 0.00 and 0.10. If the acid number exceeds 0.50, corrective action may be necessary.

The Ampoule Test is generally accepted as an industry standard for the testing of relative thermal stability between heat transfer fluids. Although there is no standard ASTM-type Ampoule Test defined, the data generated by such testing has proven reliable over the course of many years.

Thermal stability can be defined as the time rate of change of the chemical composition of a fluid from its initial components to its degradation products at a given temperature. To compile this information over a range of temperatures, fluid samples are capped with nitrogen to remove oxygen and sealed. They are heated to specific temperatures over a specific period of time (two weeks in our current data) and compared. The amount of degradation is then plotted on a graph of degradation by percent of weight vs. temperature to indicate the relative ability of each fluid to withstand use at specific temperatures.



PHT and DBT degrade into different components, and require different system maintenance procedures. PHT tends to produce more light distillates than DBT. Light distillates increase the vapor pressure of PHT. Therefore, PHT heat transfer systems are periodically vented as the light distillates rise out of the expansion tank, and release through a pressure relief valve. These releases need to be monitored because upon disposal, PHT may be a hazardous waste as defined by the *Resource Conservation and Recovery Act (RCRA), 40 CFR 261.24*, due to its toxicity characteristic and should be tested for benzene.

An accumulation of light distillates can create air pockets that may lead to pressure drops within the system or pump cavitation. A decrease in liquid volume follows due to the loss of evaporated material, which will have to be made-up with a charge of heat transfer fluid.

Light distillates also decrease the flash point. The flash point is the minimum temperature the vapor released from a liquid will ignite in the presence of an external ignition source and oxygen. Virgin PHT has a comparatively higher flash point than virgin DBT, 184 °C (363 °F) and 160°C (320°) respectively. Since PHT primarily produces light distillates, thermal cracking can offset the higher flash point advantage of virgin material.

Light distillates that don't evaporate reform to create heavier compounds ("high boilers") that remain within the fluid. This is common with DBT and can still occur with PHT, though to a lesser degree. This physical property is demonstrated when there is an increase in specific gravity.

These compounds continue to be soluble if the concentration of DBT is greater than 60%. DBT needs to be periodically drained and topped off with fresh fluid when this occurs. If the DBT falls below 60% concentration, the heavier compounds begin to polymerize very rapidly due to high viscosity and low turbulent flow, preventing efficient heat transfer. Polymerized fluids decrease laminar flow, creating a laminate coating (or *coking*) on the interior of the pipe. The laminate coating drastically decreases heat transfer, and reduces the efficiency of the heater tubes to dissipate thermal energy. The resulting increase in film temperature then leads to further fluid degradation.

If either heat transfer fluid is neglected, it may lead to mechanical wear and other problems. Routine fluid analysis is necessary to diagnose thermal degradation. Radco Industries, Inc. provides its customers with a regular thermal fluid analysis at no additional cost.

It is important to recognize that both fluids require periodic replacement of fluid lost by venting or a required draining of the system. Off-spec fluid can be recovered by reprocessing it and a virgin heat transfer fluid "top off" of the system replenishes the fluid to acceptable use as an optimal thermal fluid.

Acetone Insolubles test measures the amount of inorganic (pipe slag, sand and other construction debris) and "hard" carbon (coke) carried by the fluid. High amounts of carbon indicate thermal degradation of the fluid and a probable coking/sludge problem on the heat exchanger/heater surfaces or fluid oxidation. Coke and sludge can adversely affect a system's heat transfer efficiency by heat transfer surface fouling. Level of 50mg solids /100ml fluids can sometimes indicate problems.

Total Acid Number (Neutralization Number) test is an acid/base titration that detects minute amounts of strong and weak acids in the fluid. Acids usually are formed in heat transfer fluid from contamination from material outside the system. Acids usually are formed in heat transfer fluid from contamination from material outside the system. Acid number increase usually is associated with open vent expansion tank operation, heat transfer fluid oxidation or heat transfer fluid degradation, producing weak acids. Process material containing oxidizing agents can contribute strong or weak acids.

Acids are harmful in two ways. First, acids tend to accelerate the molecular breakdown of the heat transfer fluid. Secondly, they tend to form insoluble solids that accelerate mechanical deterioration of seals, valves, pumps, etc. Most heat transfer fluids have an initial total acid number at 0.00 to 0.10. The maximum value in used fluid should not exceed 0.50.





COMPATIBILITY OF XCEL THERM® HT WITH PARTIALLY HYDRATED TERPHENYLS

Radco Industries, Inc. has completed two sets of tests to confirm the physical and chemical compatibility of Modified Terphenyl and Radco's *Xceltherm® HT* heat transfer fluids: the Chemical Compatibility Test and Acetone Insoluble Test. These tests confirm that *Xceltherm® HT* and Modified Terphenyl are completely compatible and can be co-mingled in high temperature liquid-phase heat transfer systems.

The two fluids were tested for physical compatibility, defined as the ability of two fluids to form a mixture at various dilutions with no physical fluid separation. Chemical compatibility was also tested. When mixed, no reaction (exothermic or endothermic) will occur to yield a precipitate.

CHEMICAL COMPATIBILITY TEST: FEDERAL TEST METHOD 791 B, PART 3403.2

Test Summary: Virgin *Xceltherm® HT* and virgin Modified Terphenyl sample mixtures of 100%, 90%/10%, 50%/50%, 10%/90%, and 100% were heated to 315°C for 72 hours, and then centrifuged. Sediment amounts (if any) were then measured. A second series of identical tests were performed with mixtures of virgin *Xceltherm HT* and "used" Modified Terphenyl. Sediment amounts (if any) were measured.

Chemical Compatibility Test Results

%Partially Hydrogenated terphenyl / % <i>Xceltherm® HT</i>	100% PHT	90% PHT / 10% <i>XHT</i>	50% PHT / 50% <i>XHT</i>	10% PHT / 90% <i>XHT</i>	100% <i>Xceltherm® HT</i>
Separation (after heating)	No	No	No	No	No
Sediment	Nil	Nil	Nil	Nil	Nil

Conclusion: No precipitate was created through chemical reaction in the various dilutions of *Xceltherm® HT* and Modified Terphenyl. No separation was noted after the heating period.

ACETONE INSOLUBLES TEST: ASTM D-893

Summary: To confirm if precipitates were formed when mixed, 100ml samples of virgin *Xceltherm® HT* and "used" Modified Terphenyl samples were heated to 315°C for 72 hours, then vacuumed through a 2.5 micron filter membrane. The membrane was then flushed with acetone, then oven dried for 24 hours. Sediment amounts were then measured.

Acetone Insolubles Test Results

%Partially Hydrogenated terphenyl / % <i>Xceltherm® HT</i>	100% PHT	90% PHT / 10% <i>XHT</i>	50% PHT / 50% <i>XHT</i>	10% PHT / 90% <i>XHT</i>	100% <i>Xceltherm® HT</i>
Separation (after heating)	No	No	No	No	No
Acetone Insolubles (mg/100 ml)	75mg	70mg	55mg	20mg	0mg

Conclusion: No separation of the combined fluids was noted after heating. No increase of insoluble material (large molecular weighted sediments) was noted in the dilution samples as compared to the 100% Modified Terphenyl. Predictable dilution factors and sediment amounts were observed, indicating that no new precipitates were formed through chemical reaction.



SUMMARY

The physical characteristics and formulations of DBT-based *Xceltherm® HT* and PHT are somewhat different, but the combinations of characteristics that define a heat transfer fluid allow them to be used in similar applications. *Xceltherm® HT* and PHT are also fully miscible and can be mixed in any combination. Depending on the heat transfer system design, *Xceltherm® HT* can provide improved heat transfer efficiency compared to PHT. The improved heat transfer efficiency of *Xceltherm® HT* is largely derived from the fact that it has greater thermal conductivity values than PHT. Furthermore, *Xceltherm® HT* and PHT have comparable thermal stability at temperatures below 290°C (554°F). Both are suitable for high temperature liquid phase operation in applications exceeding 315°C (600°F), the typical threshold for petroleum based thermal oils.