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PROGRESS REPORT

ORGANIC CHEMICALS DIVISION

ST. LOUIS RESEARCH DEPT.

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TITLE

Heat Transfer Fluids

PROBLEM

Provide to Development a heat transfer fluid capable of 800°F operation to sell in the $5-10/gallon range and provide heat transfer data to Marketing on Aroclor 1248.

SUMMARY

Loop Operations

Test loop operations during January and February consisted mainly of shakedown runs. Two extended runs at about 675°F were attempted, but were stopped because of a leaking pump gasket or instrument air failures. The instrument air failures caused high temperature build-up in the insulated heat transfer section which resulted in heavy coking of the heat transfer tube and damage to the thermocouples on the surface of the tube. Loop testing operations were stopped and a new heat transfer tube was prepared and installed. Modifications were made in the control and safety circuits, so that a heat build-up will be avoided in most instances resulting from an automatic shutdown. Additional protection from the radiant heat source and high temperature was also provided for the thermocouples on the surface of the tube.

The system was flushed with fresh Aroclor to remove the carbonaceous coking material from the system prior to calibrating the new heat transfer tube.

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800°F Heat Transfer Fluid Synthesis

The development of an aromatic ether-type product for use as an 800°F heat transfer fluid has been approached from two different raw material standpoints. Organic Research investigated the products produced from the Ullmann reaction of phenol and mixtures of ortho and para dichlorobenzenes and 1,2,4-trichlorobenzene. R&E Research delved into the Ullmann reaction products from phenol and dichlorobiphenyls (Aroclor 1132 and 1232). From these investigations the candidate fluid of choice is the product derived from Aroclor even though it is a semi-solid at room temperature.

The work with the di- and trichlorobenzenes did produce an eutectic melting at about 30°C composed of approximately 35% ortho-diphenoxybenzene, 35% para-diphenoxybenzene and 30% triphenoxybenzene. However, conversion of the ortho-dichloro- and trichlorobenzenes to the aromatic ether requires long, high temperature reaction periods and yields are poor. Coupled with the fact that they boil below 800°F (thus requiring less desirable pressurized systems in commercial application) this approach was abandoned in favor of the Aroclor derived product.

The solid which crystallizes from the Aroclor product has been identified as the 4,4'-diphenoxybiphenyl. Efforts to eliminate this material in the final product by removal of the 4,4'-dichlorobiphenyl in the starting material appreciably increased the processing costs and did not produce a crystal-free product. Consequently, the lowest cost product was chosen as the 800°F fluid candidate to be extensively tested in the experimental loop.

Future Plans

Loop Operation

The clean system will be checked for leakage and recalibrated prior to starting an extended data collecting run on Aroclor 1248.

Synthesis

Complete definition of the candidate fluid and method of preparation. Issue tentative process and assist Production in the preparation of 1200 pounds of the fluid.

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DETAILS - YES

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DETAILS:

Test Loop Operations (D. E. Rousn)

Several areas of difficutly were discovered during the recent shakedown runs on the heat transfer test loop.

A. High temperature leaks developed at several flanged joints throughout the system and at the pump housing gasket.

1. The leaks at the flanged joints resulted from use of spiral wound gaskets with wide faces (1/4 inch wide) which were difficult to compress and seal the joint. Use of spiral wound gasketing with a smaller face (3/16 inch wide) resulted in adequately sealed joints.

2. The pump housing leak resulted from the use of the wrong gasketing material. The pump was delivered with a teflon gasket instead of a spiral wound gasket. The teflon gasket softened at the higher temperatures and leaked. A spiral wound stainless-asbestos gasket was installed to seal the pump housing leak.

B. Instrument air failure due to a faulty compressor resulted in an automatic shutdown of the loop while operating at about 675°F. The control and safety circuit is such that power to the pump and heater is interrupted in case of shutdown, and the flow control valve fails closed on instrument air failure. Either case results in loss of fluid flow through the heavily insulated heat transfer section causing a heat build-up that exceeded 1200°F on the recent shut downs. The high temperature charred the contents of the heat transfer tube and burned thermocouple wires to the extent that they were easily broken.

A new heat transfer tube was prepared and installed in the loop. Additional protection was afforded the surface thermocouples by using 1/2 inch Rashig rings over the thermocouple wire insulators. The Rashig rings rest on the tube surface and protect the bare thermocouple wire near the tube surface from the radiant heat source as well as offer additional protection at the point where the wires pass through slots in the radiant heater.

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The control and safety circuit was also modified so that the pump will continue to circulate fluid for about 1 hour after heater shutdown except when trouble occurs in the pump electrical circuit, a thermal overload occurs in the cooled rotor area of the pump, a low system pressure exists which could result from a rupture or leak in the system, or when the emergency stop switch is activated. The flow control valve was modified to fail open on instrument air failure.

C. The system was very dirty after the coke-up and required several washes with fresh Aroclor 1248 to clean it prior to recalibrating the new heat transfer tube.

Synthesis of 800°F Heat Transfer Fluid

Studies were continued to find a low melting eutectic utilizing the 50:50 mixture of diphenoxybenzenes described in the previous report and synthesized half from Orthene and half from crude WGK dichlorobenzenes. A eutectic exists at a compositon of 25-33% 1,2,4-triphenoxybenzene and 67-75% 50:50 mixture, m.p. 31-33°C, c.p. ~25-26°C. Work with these materials was abandoned because of their borderline vapor pressure characteristics for high temperature heat transfer applications and because the o-di- and 1,2,4-tri-phenoxybenzenes would be too difficult to produce economically because of low conversion rates.

Attention was turned to the product which could be prepared from Aroclor 1232 (22% mono-, 65% di- and 13% tri-chlorobiphenyls) via the Ullmann reaction with potassium phenate. The mixture of phenoxybiphenyls which was obtained is a semi-solid, b.p. 150-255°C (0.4 mm.) solution pt. at 65-70°C. Although it is extremely viscous slush at room temperature, it can be stirred and worked.

Since the 4,4'-diphenoxybiphenyl has been established to be the solid which precipitates on cooling, efforts were made to reduce its content. Through a process of seeding and cooling (5°C for 3 hrs.) the amount of 4,4'-dichlorobiphenyl in starting Aroclor 1232 was reduced from 14.5% to approximately 5%. The Ullmann reaction with the resulting Aroclor (about 24% mono-, 65% di- and 11% tri-chlorobiphenyls) produced a viscous oil which becomes a semi-solid upon seeding. In spite of solids present, the material with b.p. 150-250°C (0.5 mm.) will flow at room temperatures. A high boiling fraction of this material with b.p. 180-250°C (0.5 mm.) provides a semi-solid very similar to that described in the previous paragraph.

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Cost Estimate

Since a number of possible solutions for the elimination of the 4,4'-dichlorobiphenyl (or the 4,4'-diphenoxybiphenyl) were being examined by R&E Research, an estimate of the level of manufacturing costs and capital requirements was in order.

The cost estimate, developed by J. O. Bright, indicates that only the simplest cases could be considered if the final product is to sell for $5-10 per gallon. The manufacturing costs for the Ullmann reaction with product distillation from either Aroclor 1132 or 1232 range from 69¢ to 39¢/lb. for the production volume of 100 M to 3 MM lbs./yr. The range of manufacturing costs for the process including an $AlCl_3$ isomerization of Aroclor 1132 is 84¢ to 45¢/lb.

The capital requirements for the products produced by the Ullmann reaction alone are $1.00-0.62/annual pound. The additional isomerization adds 9-14¢/annual pound to this figure for the volumes considered. It was thus concluded that, since the conversion cost for the Ullmann step and product distillation alone will run 26-15¢/lb. at the 1-3 MM lb. level, little additional processing can be added and still keep the product in the desired price range.

On the basis of these data, a decision was reached between Organic Research, Organic Development and R&E Research that the low cost 800°F heat transfer fluid would be the semi-solid material produced by direct reaction of phenoxide with either Aroclor 1132 or 1232 followed by distillation. R&E Research will continue a limited effort on the preparation of the lowest cost fluid product of this type.

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