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OXIDATION EXPERIMENTS ON ORGANIC REACTOR COOLANT

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TECHNICAL DATA RECORD		PAGE 1 OF 82	
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ABSTRACT <p>Commercial Santowax OM was oxidized with an oxygen-argon gas mixture. The Santowax OM was circulated around a loop countercurrent to the gas mixture bubbling up through the coolant in a reaction vessel which contained 90% of the liquid. The oxidation was studied at various temperatures (350° to 620°F), oxygen concentrations (1 to 4% O₂ in Ar), gas flow rates (0.15 to 0.66 moles/min), and pump rates (9 to 29 gph). The effluent gas stream was monitored continuously for oxygen and carbon dioxide content. The gas stream was also sampled periodically for off line analysis by mass spectrometry. Coolant samples taken during the experiments were analyzed for the oxygen containing compounds.</p> <p>The oxidation rate of freshly distilled Santowax OM at high temperatures ($\geq 580^\circ\text{F}$) initially increased rapidly to a maximum then slowly decreased by a factor of 3-5 to a steady-state oxygen consumption rate (about 20-25% of the oxygen being consumed). It was found that the nonterphenyl impurities present in the distilled Santowax OM caused the peaking in the oxidation rate and also resulted in a ten-fold higher steady-state oxygen uptake rate. The activation energy for the oxidation of Santowax OM was calculated at 13 ± 3 Kcal/mole. The production rate of oxygenated compounds including the gaseous products and bound oxygen compounds in the coolant, appeared to follow the oxygen consumption rate; thus at high temperatures the production rates rapidly increased then slowly decreased to a steady-state rate. At high temperatures a film containing about 4% oxygen was formed in the reaction vessel but not during the low temperature oxidations.</p> <p>The data also indicated that under the conditions studied the oxygen consumption rate (1) had a first order dependence on oxygen concentration, (2) decreased with increased gas flow and (3) decreased with decrease in pump rate.</p>			

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An irradiation dose of $\sim 3 \times 10^6$ rad/hr applied to the coolant circulating in a coiled section of the loop had no significant effect on the oxidation rate.

The amount of oxygenated compounds in unoxidized and oxidized Santowax OM was substantially reduced when circulated through Attapulugus clay by means of an absorption process and also by catalyzed decomposition of some of these compounds.

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I. INTRODUCTION

Most of the available information on oxidation of organic reactor coolants is discussed in Chapters 4 and 7 of the Organic Coolant Summary Report.⁽¹⁾ Oxidation caused serious corrosion and fouling in the Organic Moderated Reactor Experiment (OMRE). In spite of precautions to avoid it, some oxidation also occurred in the Piqua Nuclear Power Facility (PNPF), as shown by increases in the carbonyl oxygen content following opening of the reactor vessel, and by the substantial oxygen content of some deposits such as film, coke, and sludge.⁽²⁾ Concerning oxidation rates, it is known that unirradiated coolant (mostly terphenyls) is relatively inert toward oxidation, and that the rate of oxidation increases with increasing concentration of radiolysis products. Of the oxidation products, carbonyl compounds are among the most abundant. Carboxylic and phenolic compounds are also formed, and it was shown that carbonyl compounds are converted to carboxylic and phenolic compounds by pyrolysis.⁽¹⁾ In general, there has been little quantitative information on either the rate or the products of coolant oxidation.

A large amount of attention has been devoted to the study of the products and mechanism of the autoxidation (oxidation via molecular oxygen at moderate temperatures) of hydrocarbons. A number of good reviews are available on the subject.^(2,3) However, in contrast to the present work, most of the previous work was concerned with autoxidation of alkanes and alkenes at much lower temperatures ($< 120^{\circ}\text{C}$).

The original object of the present experiments was to study oxidation rates and products under conditions somewhat simulating those in a reactor. The radiation source initially available for this purpose was a cobalt-60 gamma irradiation facility.⁽⁵⁾ As will be seen, the dose rate obtainable with the actual experimental arrangement was not sufficient to produce a significant effect. The organic coolant program was terminated before any work could be done at higher dose rates, so that the results actually obtained are for pyrolytic oxidation. This proved, however, to be considerably more extensive than had been expected. It was shown that nonterphenyl impurities were responsible for initiating the oxidation. Although the experiments were far from complete when the

work was terminated, considerable information was obtained on kinetics and reaction products.

In addition to the oxidation studies, several experiments were carried out to measure the removal of oxygen compounds by Attapulugus clay. While clay adsorption has been tested extensively for coolant purification,^(1,6) its effect on oxygen compounds had not been measured directly.

These oxidation studies were originally a part of the Heavy Water Organic Cooled Reactor (HWOCR) program.⁽⁶⁾ Santowax OM (an ortho-rich mixture of ortho- and meta-terphenyls) was selected for study because it was the reference coolant for HWOCR.

The oxidation experiments were carried out in a small loop in which an argon-oxygen mixture was bubbled through the coolant in a heated reaction vessel. The coolant was stirred by circulating it through an irradiation coil (in which cobalt-60 rods could be inserted) through the clay column, or through a bypass. The absorption of oxygen was followed by monitoring the oxygen content of the effluent gas. Carbon dioxide was also monitored. Samples of gas and of coolant were taken periodically and analyzed for reaction products. Many changes were made in the equipment and procedures during the early runs; these are described in Section III. A and summarized in Appendix B.

II. EXPERIMENTAL

A. DESCRIPTION OF EQUIPMENT

1. Oxidation Loop

Piping and instrumentation drawings of the final configuration of the coolant oxidation loop are shown in Figures 1A and 1B. Photographs of the loop and several components are shown in Figures 2 through 6. Loop lines were 1/4 inch O.D. x 0.049 inch wall, 316 S.S. seamless tubing. Tubing connections were made with Swagelok* fittings.

*Trademark, Crawford Fitting Company

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FIGURE 1A. COOLANT OXIDATION LOOP PIPING AND INSTRUMENTATION

1/4" HYDRAULIC TUBING

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FIGURE 2. COOLANT OXIDATION LOOP

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The reaction vessel, Figure 3, was fabricated from standard pipe and fittings. A 2-1/2 inch, 600 pound, ring joint weld neck flange, 316 S.S. was welded to a section of 2-1/2 inch, schedule 40, 304 S.S. pipe which was welded at the other end to a 2-1/2 inch, schedule 40, 316 S.S. pipe cap. A 1/4 inch Swagelok fitting was welded to the pipe cap. Vessel closure was effected by a 2-1/2 inch, 600 pound, ring joint blind flange, 316 S.S., which was modified for attachment of gas inlet and outlet, coolant inlet, and over-pressure relief lines, and a thermocouple well. The coolant inlet line was 1/4 inch O.D. x 0.049 inch wall, 316 S.S. seamless tubing. Gas inlet and outlet lines and the over-pressure relief line were 1/2 inch O.D. x 0.065 inch wall, 316 S.S. seamless tubing. The thermocouple well was 1/4 inch O.D. x 0.035 inch wall, 316 S.S. seamless tubing. Gas was admitted to the organic coolant in the reaction vessel through a diffuser which consisted of a 1 inch, schedule 40, 304L pipe cap with a 40 micron nominal pore size, sintered 316 S.S., disc welded across the opening. Coolant and reaction gas flows were counter-current.

Outlet gas, with organic vapor, from the reaction vessel passed through a 45° inclined condenser where some of the organic vapor was condensed. The condenser was fabricated from 3/4 inch, schedule 40, 304 S.S. finned pipe, 9-3/4 inches long. The 1/2 inch high fins, at right angles to the pipe axis, were spirally wrapped, 5 per inch. An aluminum foil covering was placed over the fins. An air line, discharging over the fins, was provided. Two traps in series, downstream from the heat exchanger, were maintained at 0°C. The first trap was 1 inch, schedule 40 pipe, 11-1/2 inches long including weld caps on both ends. The inlet line extended to about 2 inches from the bottom. The second trap was a "U" tube of 1/2 inch O.D. x 0.065 inch wall, 316 S.S. seamless tubing. Both traps were immersed in an ice-water bath to a depth of 7-1/2 inches.

Reaction gas (3.7% O₂ in Ar) and blanket gas (Ar) were metered into the system with Nupro* needle valves, SS-4MA. Flow rates were measured with calibrated Brooks** rotameters, Model 1110, 150 mm scale.

* Trademark, Nupro Company

**Trademark, Brooks Instrument Division, Emerson Electric Company

FIGURE 3. REACTION VESSEL

FIGURE 4. IRRADIATION COIL

FIGURE 6. COOLANT SAMPLER

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An R-2-15-AAA tube with glass float was used for the oxygen flow. An R-2-15-C tube with glass float was used for the argon flow. The original installation used an R-6-15-B tube with glass float for argon for the first experiments. Three needle valves, Nupro SS-4M, were used to maintain system pressure and split the outlet gas into separate flows for the analysis instruments. Flow from the instruments was then combined and passed through a 3 liter "Precision" Wet Test Meter, Precision Scientific Company.

Coolant was circulated in the loop by a Milton Roy Model DMRI-55-142T/SM Simplex Milroyal Pump (Model A) with a remote diaphragm head assembly. A micrometer stroke adjuster provided variable pump capacity to a maximum of 29 GPH. This controlled volume pump is a reciprocating, positive displacement diaphragm type pump designed to meter liquids in measured volumes against a positive differential pressure between pump suction and pump discharge. This displacement of hydraulic fluid actuates the remote diaphragm (316 S.S.) to create pumping action. This diaphragm is hydraulically balanced by the hydraulic oil in the displacement chamber on one side and the organic coolant being pumped on the other side. Double ball, check valve cartridge assemblies on both suction and discharge ports of the diaphragm head ensure positive, repetitive accuracy.

The irradiation coil, Figure 4, was a 37-1/2 turn helix of 1/4-inch O.D. x 0.035 inch wall, 316 S.S. seamless tubing. The internal diameter of the helix was about 1-11/16 inches. The 1-9/16 inch O.D. basket, into which the Co⁶⁰ capsules were loaded, was lowered into the helix to irradiate the coolant.

A drawing of the clay column is shown in Figure 5. Inlet and outlet valves were Hoke bellows valves, Model TY 445. Coolant flow was downward through the clay bed (capped with 65 μ nominal pore size sintered metal discs) and upward in the annulus and through a fine (10 micron) screen backed-up with a perforated cylinder. The screen was meant to contain the clay particles if the sintered metal and disc should rupture.

FIGURE 5 CLAY COLUMN

Loop lines were traced with 1 ohm per foot heating cables, on two electrical circuits, with clamshell heaters used on the reaction vessel and the irradiation coil or clay column. The irradiation coil and clay column occupied the same site with jumper lines being used for attachment of the clay column. Thermocouples were clamped to outside surfaces at various locations on the loop. The thermocouple in the reaction vessel provided a signal for the temperature controller which regulated the clamshell heater. One inch thick, aluminum foil backed-fiberglass, insulation was used throughout. The loop was designed for 800°F, 500 psia operation and mounted on a small, movable cart with provision for enclosing the loop with sheet metal. An argon cover gas line was installed to blanket the loop in case of fire.

2. Sampling Equipment

a. Gas

The effluent gas stream could be sampled into one to three evacuated glass sampling bulbs for off line analysis. The 100 to 200 ml sampling bulbs with high vacuum stopcocks were fitted with a 19/38 standard taper inner joint which permitted the direct attachment of the sample bulb to the mass spectrometer used for gas analyses. The manifold, to which the gas sampling bulbs were attached, was a 12 mm diameter, 2 ft long glass tube with the inlet at one end and sealed at the other end, with three, equally spaced, 19/38 standard taper outer joints on the side. There were two Veeco vacuum valves on either side of the manifold inlet. One of the valves was used to admit the gas for sampling or isolate the manifold from effluent gas stream. The other valve was used to evacuate the sampling system by means of a diffusion pump protected by a liquid nitrogen trap which was connected to the manifold by 5 ft of 3/8 inch metal tubing. The vacuum obtainable with the sampling manifold in the system as measured between the diffusion pump and the liquid nitrogen trap was 5×10^{-6} Torr.

b. Coolant

Coolant could be sampled during the operation of the loop. The sampling system consisted of a sampling station for withdrawing the sample and a glass vessel for collecting one to three coolant samples

under an inert atmosphere. The components of the coolant sampling system are shown in Figure 6. The main sampling location was about 1 ft upstream from the vessel on the coolant inlet line. When the clay column was used a second sampling station was installed about 2 ft upstream from the clay column. The sampling station consisted of a 1/4 inch Nupro SS-4BG bellows valve (connected to the loop by means of 2 inch length of 1/4 inch stainless steel tubing and Swagelok fittings) to which was attached a 10 inch length of 18 gauge stainless steel hypodermic tubing, ground to a sharp point. The sampling vessel was fabricated from a 71/60 standard taper joint assembly. Three or four hollow legs, for holding polyethylene sample bottles were attached to the outer joint. The legs were of sufficient length (~ 3 inches) to prevent any coolant from splashing into one of the other samples while sampling. The inner joint was provided with 3 or 4 openings which are covered rubber serum bottle cap stoppers. The two joints were held together during purging of the vessel and coolant sampling with a wire loop. Hypodermic needles for purging and sampling were inserted through the serum caps.

3. Gas Monitoring Instrumentation

a. Oxygen Analyzers

Oxygen content of the loop effluent gas was monitored by a polarographic oxygen sensor and/or a residual gas analyzer.

(1) Polarographic Analyzer. The Beckman Instruments, Inc. Laboratory Oxygen Analyzer, Model 77700 is a direct reading instrument measuring the partial pressure of oxygen by the polarographic principle. Ranges used were 0-5% and 0-25% oxygen (referenced to one standard atmosphere). At constant temperature, this instrument was stated to have an accuracy of $\pm 1\%$ of full scale and a linearity of $\pm 0.5\%$ of full scale (with recorder output). System drift was stated as $\pm 2\%$ full scale per 24 hours and speed of response was 90% in 10 seconds. The sensor was recharged and the instrument calibrated in air (assuming 20% oxygen content) prior to each oxidation experiment.

(2) Residual Gas Analyzer. This instrument is an integrated system for analyzing and recording the composition of residual gases in evacuated chambers. Analysis is effected by a mass spectrometer. The

major disadvantage of the RGA is that only intermittent oxygen values are obtained while the polarographic analyzer gives continuous values. High vacuum (5×10^{-6} Torr) for operation of the mass spectrometer was maintained by admitting loop effluent gas through a Veeco Variable Leak, Model VL.

b. Carbon Dioxide Analyzer

The carbon dioxide content of the loop effluent gas was monitored with a Mine Safety Appliances Company, Lira Infrared Analyzer, Model 300. This instrument is based on the principle of infrared absorption and detects and measures the concentration of a single component in a mixture. A dual span accessory was added to provide 0-5% and 0-100% CO_2 ranges. Zero drift was stated to be $< 1\text{-}1/2\%$ in 24 hours, span drift $< 2\%$ in 24 hours, with 90% of final reading obtainable within 5 seconds. However, a noise factor was introduced when the output was expanded so that 50 mv was equivalent to about $1.2\% \text{CO}_2$. This noisiness may account for some of the fluctuations observed in the CO_2 data. The instrument was calibrated with 0% and $4.0\% \text{CO}_2$ in N_2 before each oxidation experiment. The recorder chart paper was then calibrated against the meter on the CO_2 instrument.

c. Water Analyzer

Water content of the loop effluent gas was determined by means of a Beckman Instruments, Inc. Electrolytic Hygrometer, Model 17901. This direct-reading instrument indicates the water content of a flowing gas stream by measuring the amount of electrical current produced by dissociation of the water. Ranges are 0-10, 0-30, 0-100, 0-300, and 0-1000 parts per million (ppm) of water by volume. Accuracy was stated to be $\pm 5\%$ of scale with a measurement sensitivity of less than 1 ppm water. Calibration of this instrument is not required.

d. Recorder

The polarographic oxygen, carbon dioxide, and water analyzers were connected to a multipoint recorder to provide a written record. This recorder was a Minneapolis-Honeywell, Brown Elektronik 0-50 mv input with a two speed chart drive. Oxygen, water and CO_2 values

were recorded 10 times per minute on low speed. High speed was 6 times as fast as low speed.

B. METHODS

1. Coolant Preparation

In oxidation experiments 16 through 89 commercial Santowax OM coolant was used. The coolant (about 3.5 liters) was vacuum distilled (210-220°C at 20 Torr) under a nitrogen atmosphere. A forerun of about 100 ml was initially collected and then the rest distilled until about 200-300 cc remained in the distillation flask. The distilled coolant was allowed to solidify and then the distillate receiver was removed. With a nitrogen purge, the coolant was remelted and the receiver was fitted with a filling device and a train of three, 1 liter, loading bulbs as shown in Figure 7. Nitrogen was bubbled through the melted coolant to further purge and stir the coolant. The coolant was then forced into the loading bulbs by opening stopcock C and closing stopcock B. A stream of nitrogen was allowed to bubble up through the train to further purge the coolant and then stopcock C was closed and the nitrogen pressure maintained until the coolant in the bulbs solidified. The bulbs were separated, capped and stored until used. Analysis of the distilled Santowax OM is presented in Section III. C.2.

In oxidation experiment 90 a "pure" OM mixture was prepared by mixing reagent grade (Eastman white label) o- and m-terphenyl in about 2 to 1 ratio. The solid mixture was put into a heated loading bulb. The OM mixture was reused in experiments 91 through 93. The mixture was stored overnight between runs in the original loading bulb in an argon atmosphere. For experiment 92, 0.1% fluorenone was added to this mixture and for 93, 0.1% each of 4-methyl - and 4-ethylbiphenyl was added.

2. Experimental Procedure

The procedure for an oxidation run was as follows. The loop, which had been thoroughly rinsed with hot benzene, was heated to 150°F under vacuum during the previous night. The loop was thoroughly purged with argon. The loading bulb containing distilled coolant was mounted as shown in Figure 2 and heated to about 150°F with a heating mantle

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FIGURE 7. SYSTEM FOR FILLING LOADING BULBS

(surrounding the bulb) and heating tape (around the glass inlet tube). With a small, continuous flow of argon in the reaction vessel (to avoid coolant backing up through the gas disperser), the melted coolant was gravity fed (using a pressure equalization line from the top of the loading system to the gas exit line of the loop) into the vessel. The coolant was then forced back into the loading bulb by closing the exit valve at the top of the condenser and letting the pressure in the vessel increase. This procedure was repeated twice to completely mix the coolant to assure that a uniform sample of unoxidized coolant is obtained. After the reaction vessel was again filled, the coolant inlet valve was closed and the coolant remaining in the loading system was collected through the drain valve. The valve to the pressure equalization line was closed and the loop brought to operating pressure. The pump was started and the loop heated to the desired temperature. During this time the instruments were checked and calibrated if necessary. The gas cylinder regulators were set at about 25 psig above the operating system pressure. The desired total gas flow rate was maintained by the angle needle valve just downstream from the argon tank and monitored by a rotameter, while the desired pressure and gas flow rate through the instruments were maintained by the three exit needle valves.

After operating conditions are established, the oxygen is turned on and the flow controlled and monitored as with the argon. Slight adjustment of the three exit needle valves was usually necessary to maintain the correct flow and pressure at this time and occasionally during the oxidation period.

During Runs 16 through 79 the coolant was circulated through the irradiation coil at a pump rate of 90-100%. When the coolant was to be irradiated (Runs 56, 61 and 79), the coolant was oxidized until a steady-state oxidation rate was reached, then the desired number of Co⁶⁰ rods were placed in the basket which was lowered into the coil for the desired period of time.

During Runs 81-93 the irradiation coil was replaced with a line for mounting a clay column and a bypass line with a valve. For experiments without a clay column, the clay column mounting lines were removed.

In the experiments in which the clay column was used, the pump rate was reduced to 30% (8.7 gph) before the clay was valved in, to prevent damage of the supporting sintered metal disc and increase coolant-clay contact time. This was the lowest pump rate at which the pump would operate with the clay column in the loop. The column was valved in by first slowly opening the column inlet valve, then the outlet valve and closing the bypass line valve. The clay was valved out by reversing this procedure.

Coolant samples and gas samples were taken periodically during the experiment, as described in the next section. When the residual gas analyzer (RGA) was used, the mass peaks were scanned from 28 to 44 and the ratio of peak height of mass 32 to mass 40 (oxygen to argon) was recorded. The pressure in the RGA analyzer tube was maintained at 5×10^{-6} Torr.

After completion of the experiment, the loop was cooled to about 200°F and the oxidized coolant drained and stored in a glass container (before Run 77, metal cans were used for storage). The next day the loop was heated to about 100°F and benzene (one liter) was circulated in the loop. This was repeated until GLC analysis of the benzene wash showed less than 0.1% terphenyls present (usually about 6-7 washes were necessary). The rinses were evaporated down and the amount of coolant remaining weighed (generally about 100 g). The cold traps and condenser were removed, weighed and also rinsed with benzene. The gas outlet line was periodically cleaned by flushing with benzene. These components were then reassembled and air dried at reduced pressure.

3. Sampling

a. Gas

With both the valve to the gas stream and the valve to the vacuum system closed, three empty gas sampling bulbs were secured to the manifold. The evacuation valve was opened and the bulbs and manifold were heated to 80-100°C by means of a heat gun. The vacuum was applied until a sample was desired; at least 5 minutes of evacuation were given before sampling. To sample, the valve to the vacuum system and the stopcocks on the sample bulbs not to be used were closed. Then

the sampling valve was opened very slowly; the wet test meter was watched while opening the valve to assure that the exit gas continued flowing through the meter. By the time the valve was completely open the gas bulb was filled with approximately one atmosphere of sampled gas. The stopcock to the sample bulb and the sampling valve were closed and the manifold re-evacuated after which the stopcocks to the unused bulbs were opened again. Upon filling the last of the bulbs and both valves closed, the sample filled bulbs were removed and the procedure repeated.

b. Coolant

Coolant samples were collected in screw-cap, high-density, polyethylene bottles utilized in the total oxygen determination by neutron activation. The preweighed sample bottles and a test tube were placed in the sample vessel which was then thoroughly purged with dry argon by piercing one of the serum caps with a hypodermic needle connected to an argon line. The argon flows out between the two standard taper joints thus supporting the top of the vessel on a cushion gas which allows easy rotation of the top. To sample, one of the other serum caps was pierced with the sampling needle and about six grams of coolant withdrawn into the test tube (to flush out the valve and short connecting line to the loop) and subsequently the desired number of sample bottles were filled with 3 to 4 grams of coolant. The argon purge was continued during the sampling period and until the coolant had reached room temperature or solidified. Then, immediately after opening the sampling vessel, the sample bottles were tightly capped and wiped with benzene soaked cloth to remove any coolant on the outside.

4. Analysis of Coolant Samples

a. Total Oxygen

The total oxygen content of the coolant was determined using fast neutron activation analysis. The equipment and procedure used are described in the literature.⁽⁷⁾ The activation analysis method involves exposing the sample to 14 mev neutrons produced by deuterons striking a Ti^3H surface. The neutron-induced nuclear reaction on oxygen produces radioactive nitrogen, ^{16}N (half-life 7.35 sec.), which

is determined by gamma scintillation counting using a NaI(Tl) crystal. The sample is transferred from the neutron generator to the counter in a pneumatically driven capsule.

The coolant was sampled directly into the polyethylene sample capsule (called a "rabbit") under a dry argon atmosphere. The sealed rabbit containing 3-4 g of coolant was wiped with a benzene soaked cloth to remove any dirt or coolant on the outside. The hot coolant sometimes caused the rabbits to swell slightly and then they had to be turned down on a lathe to fit the pneumatic transfer tube. The coolant samples and also a few air-filled rabbits from the same lot used for the samples were analyzed several times. The samples usually contained 2 to 14 mg oxygen while the empty rabbits, with the oxygen value due to air subtracted out, usually had 1.7 to 2.2 mg of oxygen. The error in the analysis was about ± 150 ppm oxygen. If each rabbit was analyzed before adding coolant (as was done for Runs 90-93) the error was about ± 100 ppm oxygen.

b. Water

Water is determined chemically by Karl Fischer electro-metric titration. The method is similar to that described by Rotheram⁽⁸⁾ with the following modifications. A one gram sample was added to 50 ml of predried pyridine-methanol solvent (60/40 V/V) followed by direct titration. The titrant was prepared by diluting the Karl Fischer reagent with methanol to an equivalence of about 0.4 to 0.5 mg of water/ml. This titrant was standardized against 1 mg of water each day. It was possible to titrate two samples before fresh pyridine-methanol solution was necessary. The precision was about ± 10 ppm.

c. Total Bound Oxygen (TBO)

This was calculated by subtracting $9/9$ of the amount of water in the sample (oxygen equivalence of the water) from the total oxygen of the sample.

d. Carbonyl Compounds

This method is applicable to certain carbonyl compounds (aldehydes and ketones) in which (1) the carbonyl group is adjacent to a highly conjugated system (i.e., aromatic ring), (2) a 2, 4-dinitro-

phenylhydrazone derivative (DNPH) will form under mild conditions ($< 90^{\circ}\text{C}$) and (3) the DNPH derivative is soluble in strong alcoholic potassium hydroxide solution. The procedure is described by Sullivan and Bowe⁽⁹⁾ and is based on the spectrophotometric determination of the DNPH derivative of the carbonyl compounds at $475\text{ m}\mu$. Detection limit is about 10 ppm with an accuracy of ± 30 ppm and a precision of ± 10 ppm.

e. Phenols and Carboxylic Acids

Phenols and carboxylic acids were determined by a near infrared spectrometric technique.⁽¹⁰⁾ The absorption of a dilute solution of the sample (to prevent shifting of the absorption due to hydrogen bonding) in a 10 cm cell is measured at $2.27 \pm .01\mu$ for acids. Molar absorptivities (liters/mole-cm) of 200 and 100 were used for phenols and carboxylic acids, respectively.⁽¹¹⁾ The most transparent solvents for this IR region are carbon disulfide (CS_2) and carbon tetrachloride (CCl_4). Historically, because of the greater solubility for p-terphenyl, CS_2 was chosen as the solvent. However, since Santowax OM has a low p-terphenyl content, CCl_4 was evaluated (on Runs 87 and 89) as a potentially better solvent (less handling hazards). It was observed that there were solvent effects in CS_2 which were less pronounced in CCl_4 . In CS_2 , the absorptions were not near as sharp and were shifted to a lower energy (longer wavelength) in comparison to CCl_4 . Also, there was less interference from the water absorption peak with CCl_4 as solvent. It was also noted that the molar absorptivity coefficients appeared to be 1.4-2.3 times greater in CCl_4 than in CS_2 . For these reasons CCl_4 is suggested as the preferred solvent when solubility permits.

f. Biphenyl and Terphenyl Isomers

The coolant was analyzed for biphenyl and terphenyl isomers by a gas chromatographic method described by Keen *et al.*⁽¹²⁾ About one gram of coolant sample and 0.5 g of triphenylmethane (internal standard) were dissolved in 10 ml of benzene and 10 μ l aliquot of the solution injected for analysis. Three determinations were averaged for each sample. A standard solution containing about 1 mg of biphenyl, 600 mg of o-terphenyl, 300 mg of m-terphenyl, 25 mg of p-terphenyl and 500 mg

of triphenylmethane was used to calculate the calibration height factor. A Loenco Model 70 gas chromatograph was used, with two 6 ft, 1/4 inch stainless steel columns packed with 20% DC-11 silicone oil on 60/80 mesh chromosorb P-AW. The operating conditions were:

Column temperature	250°C
Injector temperature	300°C
Detector temperature	300°C
Helium flow rate	67 ml/min (25 psig)
Detector filament voltage	80 ma
Attenuation	8x to 32x

g. High Boiler Content

The high boiler (HB) content of the coolant samples was determined by a microsublimation technique described by Stewart and Smee. (13) The conditions were modified in that the samples were heated at 175°C under a continuous vacuum of 0.8 Torr for four hours.

5. Analysis of Gas Samples

The contents of the gas sample bulbs were analyzed on a CEC103 mass spectrometer. The sample bulb was connected directly to the mass spectrometer and a small portion of the sample withdrawn and analyzed for all gases. The amount of nitrogen found in the sample was taken as an indication of the amount of air which had leaked into the sample bulbs. The instrument was calibrated with standard gas samples and the data reduced by a computer.

III. RESULTS AND DISCUSSION

A. DEVELOPMENT OF THE LOOP

In the original design of the loop, the reaction vessel contained loose mesh stainless steel baffle screens to increase stirring effect and help prevent frothing of the coolant. A flow of a mixture of argon and oxygen, each measured by a rotameter, was bubbled through the coolant by means of a 1/4 inch tube having 16, 1/16 inch diameter holes. The effluent stream was monitored by a Residual Gas Analyzer (RGA) mass spectrometer for oxygen loss and for volatile products. Argon was used as the inert gas to provide an internal standard.

Early oxidation runs were used to check out the apparatus at various gas flow rates. It was found that it was necessary to use needle valves for the exit valves to maintain satisfactory pressure and flow control. Running times were often very brief because massive transfer of coolant from the tank to the lines caused possible contamination of the RGA and plugging of the lines. This problem was considerably reduced by the use of the U-tube cold traps. The technique of applying a static sample taken from the gas stream to a permanent gold leak into the RGA analyzing tube was found to be slow and to give erratic results. Tapping the gas stream continuously by using a variable leak valve while the RGA analyzer tube was maintained at a constant dynamic pressure was found to give fast sampling (2 min.) and results regularly reproducible to 1%. It was also established that fresh coolant for each run was necessary in order to obtain reproducible results. The upgrading of the system and experimental methods described above occurred during Runs 1-41.

After several more runs, it became apparent that the RGA could not be used as first intended. The RGA was too insensitive to detect the small amounts of volatile products such as benzene, butane, etc. The carbon dioxide mass peak was masked by a much larger peak due to argon. The mass peak for carbon monoxide was also not reliable. The apparent carbon monoxide production was much higher than expected sometimes accounting for over 100% of the oxygen consumed. This arises in the mass spectrometer by the fact that carbon deposits can form near the filaments in the analyzer tube which, in the presence of molecular oxygen, can react to form carbon monoxide:

Other authors who have found this to occur have termed this peak a "ghost peak." The amount of oxygen in the analyzed gas and the quantity of carbon deposited determines the height of the ghost peak. A sample of pure oxygen gas can give a ghost peak as large as 2%. If new filaments are used or the old filaments are baked for long periods of time, there is no ghost peak observed. However, by the end of the run the ghost peak is again large and interfering with the analysis.

Another unexpected problem arose with the RGA. For no apparent reason the sensitivity of the instrument would start to drift or change erratically. An example of this behavior can be seen at the "steady-state" in Run 79 (see Figure 13). Furthermore, when the gas stream was diverted to bypass the tank and enter directly into the RGA so that a measurement of the oxygen concentration going into the reaction vessel could be made, the sensitivity would often change and sometimes drastically. An example of this can be seen in the results of Run 61. This run was carried out at 400°F in which very little oxidation of the coolant occurs. The curve was a typical low temperature curve (see next section). When an oxygen concentration measurement on the unreacted gas was made by diverting the gas stream, the results showed approximately 53% of the oxygen was being consumed at steady-state. However, the coolant that was drained from the reaction vessel was still yellow-brown (not black like highly oxidized coolant) and the total oxygen analysis showed only 240 ppm bound oxygen present. Thus it is inconceivable that the apparent 53% oxygen consumption rate is realistic.

To improve the data collection capability and accuracy, continuous analyzers for oxygen, carbon dioxide and water were added to the system. The carbon dioxide analyzer used was modified with a scale expander to cover a range 1-5% CO₂ and also the output voltage was increased so that 50 mv was equivalent to about 1.2% CO₂ (see Section II.A.3). The water analyzer was not very useful because the traps became saturated after a few minutes, so that the apparent rate of water production reflected only the vapor pressure of the water collected in the 0°C traps. These instruments were further backed up by adding a gas collecting system (see Section II.A.2) capable of taking three simultaneous samples for off line analysis with a CEC-103 mass spectrometer, for comparison purposes and also for detection of trace quantities of other volatile species.

The system was also modified to improve the loop's performance. In order to get better gas-liquid contact, the original gas bubbling tube, which was found to become plugged with film deposits, was replaced by a gas disperser made from a 40 μ sintered metal disc. Also, the baffle

screens were removed as they may have contributed to reducing gas-liquid contact by helping the bubbles to coalesce.

The system was still plagued by plugging of the lines with coolant at high temperatures and flow rates. The reflux condenser which had been vertical was tilted to a 45° angle and insulated so that it would self-heat to 140°F (in the middle) when the coolant was heated to 580°F . With this modification the loss of coolant from the reaction vessel was less than 10 g or 1% in a 24 hour period. As a further precaution more efficient traps were added to the system.

The technique of coolant handling before and after oxidation was also improved. A special glass system was developed so that the coolant could be melted and introduced into the reaction vessel under an inert atmosphere of argon to minimize air contact. The coolant, after oxidation, could either be forced back into the loading bulb or drained directly into a collecting flask under an argon cover.

A wet test meter was added at the end of the gas train in order to recalibrate and monitor the performance of the rotameter.

The loop was further modified to increase its capabilities so that the experiments with Attapulugus clay could be performed. A coolant sampling system (see Section II.A.2) was designed so that coolant samples could be taken while the loop was operating at high temperatures and pressure. The samples could be collected under an argon atmosphere directly in the rabbits used for oxygen analysis. A bypass line was added to the loop and the lines were modified to allow use of a clay column.

A summary of all modifications is given in Appendix B.

B. OXYGEN CONSUMPTION RATE

1. General Description

A typical high temperature ($\geq 580^\circ\text{F}$) oxidation rate curve (oxygen consumption rate vs time) observed with freshly distilled Santowax OM is illustrated in Figure 8. The period from A to B was the lag time for the oxygen to be first detected by the instruments after it was added. The observed BCD curve was the resultant of the two curves BF and ED.

FIGURE 8. TYPICAL HIGH TEMPERATURE
OXIDATION RATE CURVE

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Curve BF describes the concentration change in which the system was changing from pure argon to the oxygen concentration added as detected by the instruments. This curve was determined for the system empirically by monitoring the oxygen concentration change when oxygen was added under conditions in which very little oxidation was occurring; i.e., coolant at about 300°F. Curve ED was obtained by subtracting out the concentration effect (curve BF) from the observed BCD curve. Curve ED was more nearly representative of the real oxygen consumption rate during the initial oxidation period. The GH region of the curve was used to calculate the steady-state oxygen consumption rate.

If curve BC lies on the BF curve as depicted in Figure 8 (as it appeared to from comparison of the empirically derived curve for a run with no oxidation and several of the high temperature runs), then there was an initial short period of about 2 minutes in which no, or extremely little, oxygen was being consumed by the coolant. This delay is called an induction period which generally suggests that the reaction involves free radicals.

When the oxidation rate curve for a run is presented, the superfluous ABF curve is deleted to avoid unnecessary confusion concerning the initial oxidation rate.

As can be seen from the oxidation curve, at high temperature initially the oxygen consumption rate rapidly increased to a maximum rate. The rate then slowly decreased and eventually approached a fairly constant consumption rate (GH region) which was taken as the steady-state oxygen consumption rate. For a run at 580°F with a gas flow of about 0.158 moles/min (0.532 liters/min at 270 psig) the maximum of about 70-90% oxygen consumption was reached after about 30-60 min., and after about 150-200 min. the steady-state rate was reached. Generally, the steady-state rate was 3 to 5 times less than at the maximum or about 20-25% (average) oxygen consumption.

Figure 9 (Run 85) shows the oxidation rate curve measured by the residual gas analyzer (RGA) and by a polarographic electrode analyzer for a 580°F run. The electrode appeared quicker and more responsive than the RGA to a change in oxygen concentration. This was due to the

FIGURE 9. OXIDATION RATE CURVE FOR RUN 85

fact that the polarographic sampling point was about 6 min. upstream from the RGA sampling point, mainly because of a room temperature glass trap used to protect the RGA. Mixing of the gas entering the trap with that already present could cause the RGA to appear less sensitive to concentration changes. The polarographic electrode had less "mixing" space and, therefore, was more representative of the rapid concentration changes.

Both the peaking effect and the magnitude of the steady-state rate of high temperature oxidations were controlled by the nonterphenyl impurities (about 5%) in the commercial Santowax OM used in these experiments. This was quite clearly demonstrated by the results of Runs 90 to 93. For these experiments a "pure" OM mixture was prepared by mixing reagent grade (Eastman white label) o- and m-terphenyl in about 2 to 1 ratio. A gas chromatographic analysis of this mixture showed biphenyl (< 0.05 wt %) and p-terphenyl (about 2.5 wt %) as the only detectable impurities (see Table V). When 1000 g of this pure OM was oxidized under the usual conditions (580°F, 270 psig with 3.8% O₂ in Ar), the oxygen consumption rate did not exhibit the initial peaking. Furthermore, the steady-state rate was very low, about 1.5×10^{-4} moles/min or about 2.6% of the oxygen was being consumed. Coolant samples taken after the 8 hour oxidation period at 580°F did not have an increase in bound oxygen of more than 100 ppm.

The experiment was repeated (Run 91) with the same batch of pure OM which had been stored in the loading bulb overnight at room temperature with a blanket of argon. Again, during the two hours of oxidation at 580°F there was no peaking and a very low steady-state rate; about 1% of the oxygen was being consumed.

To demonstrate that only certain impurities could effect the oxidation rate, two further experiments were carried out with the pure OM. In the first experiment (Run 92), about 0.1% fluorenone was added to the pure OM mixture. Fluorenone was selected because it was an impurity in commercial Santowax OM and was expected to be fairly stable under the oxidation conditions used and hence contribute little to the oxidation rate. When this new mixture was exposed to oxygen under the

same conditions as in the previous two experiments the same results were obtained--no peaking observable and very low steady-state, about 2% of oxygen being consumed.

In contrast to the above results, when easily oxidizable compounds were added to the pure OM in just trace amounts a peaking in the oxidation rate was clearly detectable. In Run 93, about 0.1% each of 4-methyl- and 4-ethylbiphenyl was added to the pure OM used in the previous experiment. When this mixture was oxidized as before the oxidation curve exhibited a peak (6% of the oxygen being consumed) which slowly decreased to a rate of about 2.5% oxygen consumed at the end of the experiment. During the six hour oxidation period the coolant increased in bound oxygen by about 300 ppm and there was only a trace amount ($< 0.01\%$) of the alkylbiphenyls detectable by gas chromatograph analysis.

In Run 83 (see Figure 10), for no obvious reason, after the rate had peaked at 69% oxygen consumption, it slowly began to increase again to even a higher rate. When the oxygen was finally turned off, 8.4 hours later, the rate appeared to have steadied out at about 85% oxygen consumption. This was not a result of an instrument drift, as the gas sample data showed an equally high consumption rate, the total bound oxygen (TBO) in the coolant was over 8000 ppm (usually about 3000 ppm at these oxidation conditions) and the carbon dioxide was about 9×10^{-4} moles/min or 3-4 times greater than usual. The only factors that are apparently unique about this run in comparison to the other 580°F runs are (1) before the run the reaction vessel was cleaned as usual by sandblasting but then was washed with 2N nitric acid and then rinsed with water, and (2) a clay column used in Run 82 (a typical run) and containing the oxidized coolant from that run (~ 400 g) was valved in before the oxidation period (otherwise the coolant added was typical). The ash analysis of the oxidized coolant from the unusual Run 83 was very much higher than for the other 580°F runs with fresh clay (see Table I). It has been demonstrated by many authors that certain metallic ions or salts can catalyze the autoxidation of hydrocarbons. Whether the high ash results were because of the unusually high oxida-

TABLE I

ASH ANALYSIS FOR COOLANTS AFTER OXIDATION AT 580°F

Run No.	Ash (ppm)	Oxidation Rate	Clay Condition	Valve in Before Oxidation
82	< 0.1	Typical	Fresh	No
83	1.9	Very high (4X usual)	Dirty	Yes
85	0.4	Typical	None used	-
87	< 0.1	-	Fresh	Yes

tion rate or in fact caused the high oxidation rate is not known.

The oxidation rate curve observed for a low temperature run ($\leq 400^\circ\text{F}$) was basically like the ABF curve in Figure 8, which reached a steady-state rate of 0-2% oxygen consumption in 30-60 min. There was no observable peaking in the curve as observed with the high temperature runs. Other results, carbon dioxide production, TBO, etc. concurs with the extremely low oxygen consumption rate. The oxidation rate curve may then be only a result of the oxidation of the more reactive impurities and not the terphenyls at this temperature. Early low temperature runs in which the oxidation rate was only followed by the RGA gave very erratic results, varying from 0 to 53% oxygen consumption. However, these high oxidation rates were probably not correct and were probably due to instrument problems (see discussion on development of the loop, Section III.A).

Run 89 (see Figure 11) shows the results of varying the temperature during oxidation. This run was conducted at the usual conditions except that the temperature was varied. The oxidation was begun at 350°F . The temperature was increased stepwise to 400°F after 2.1 hours, to 480°F after an additional 1.7 hours, to 580°F after 1.5 hours, to 620°F after 5 hours and then decreased again to 350°F after 2.7 hours. At 350°F , 400°F and 480°F no peaking was observed and the steady-state oxidation rate increased with temperature (0.5-1.4% at 350° , 2.9-8.5 at 400° , 14.8-16% at 480°F). There was pronounced peaking when the temperature was increased to 580°F (~ 80%) and again when increased to 620°F (~ 30%). However, the steady-state oxidation rate at 580°F was unusually low (9.3-11.7%) and even lower than observed at 480°F , but the steady-state oxidation rate at 620°F again increased to about 17.7 or about what was observed at 480°F . On decreasing the temperature to 350°F the rate fell sharply to 0-1.4%. The results of this experiment demonstrate that temperature control during oxidation was a very important factor that can affect the oxidation rate. These unusual results were probably due to the affect of temperature on the impurities and their oxidized products rather than on the terphenyls.

2. Activation Energy

An activation energy (E_A) was calculated from the Arrhenius equation:

$$E_A = \frac{R \ln \left(\frac{K_2}{K_1} \right)}{\left(\frac{1}{T_1} - \frac{1}{T_2} \right)}$$

where $R = 1.99 \times 10^{-3}$ Kcal/mole-deg

K = observed rate (α % O_2 consumed)

T = temperature ($^{\circ}K$)

Only runs made at the same gas flow rate, pump rate and pressure can be used for comparison, since the rate was also dependent on these factors. The largest set of runs having all these factors the same (and also the most reliable data) include the series 78 to 88. Of this series Run 83 was omitted because of the abnormal behavior. The results are presented in Figure 12. There was only one run at a low temperature ($350^{\circ}F$) in this series and all the rest were at $580^{\circ}F$. Using the average of all the runs at $580^{\circ}F$, the $E_A = 12.8$ Kcal/mole; considering the extremes gives $E_A = 11.7$ to 14.2 Kcal/mole. Using the average for all the $580^{\circ}F$ runs (23.7%) but letting the lower temperature result (1.0%) vary from 0.5 to 1.5% gives $E_A = 11.2$ to 15.5 . Therefore the activation energy from these data was estimated at 13 ± 3 Kcal/mole. Autoxidation of hydrocarbons generally give activation energies of 15 to 20 Kcal/mole which are typical of catalyzed free radical reactions.

3. Flow Rate Effect

The oxidation rate was affected by changes in coolant flow rate and in gas flow rate. In each case a change in the flow rate resulted also in a change in other parameters and characteristics of the system which, in turn, could contribute to the observed effect on the oxidation rate. Many of these important variables (i.e., bubble size, coolant flow patterns) were not known for the system so that these factors cannot be evaluated for their contribution in the rate effect observed.

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FIGURE 12. ARRHENIUS PLOT OF OXIDATION EXPERIMENTS

The oxidation rate curve for Run 85 (Figure 9) illustrates the results when the coolant flow rate was varied. At steady-state the pump rate was reduced from 26.4 gph (90%) to 8.7 gph (30%) stepwise in three equal (20%) changes. Although the effect was not uniform with each pump rate change, the trend was quite apparent. With each decrease in coolant flow rate the steady-state oxidation rate likewise decreased. The overall decrease in the oxygen uptake rate was from 21% to 14%. The following factors probably contributed to this effect: at higher pump rates there was better stirring, more coolant per gas bubble, and more turbulence of the liquid-gas interfaces.

The results of Run 81 (see Table II) were typical of the effect when the flow of gas was changed. After steady-state oxygen uptake rate was reached, both the argon and oxygen flow rates were increased proportionally so that the gas flow was increased while the percent oxygen in the gas remained constant. An increase in gas flow caused a decrease in both the rate of oxidation and also the fraction of oxygen consumed. A simplified view of the system suggests that there should not be a change in the fraction of oxygen consumed. The residence time of the gas bubbles in the liquid coolant was theoretically independent of the amount of gas going into the system, depending only on gravity. An increase in the amount of gas would ideally only produce more bubbles of the same size. However, as obvious from the data, this is not true for this system. An increase in the flow of gas into the system could cause larger bubbles being initially formed, coalescing of bubbles in the liquid, less residence time for the gas above the liquid surface and greater competition between bubbles for the coolants. These were probably some of the factors which contributed to the decrease in oxygen consumption.

Similar results have been observed with laboratory experiments using irradiated PNPf coolant.⁽¹⁴⁾ The percent of oxygen consumed was found to decrease with an increase in gas flow rate (although the oxidation rate did increase) and increase with an increase in stirring.

The results show that the oxidation rate was dependent on the oxygen concentration in the liquid. In the next section, the order of this dependence is discussed and the importance of these results.

TABLE II

OXYGEN CONSUMPTION RATE AS A FUNCTION OF GAS FLOW RATE AND OXYGEN CONCENTRATION

Run	Flow Rates (mole/min)		% Increase in Flow Rate			Steady-State Oxygen Consumption		% Increase in O ₂ Consumption	
	O ₂	Ar	O ₂	Ar	Overall	%	(mole/min)	% ²	(mole/min)
78	.00583	.160				33.5	1.95		
	.00958	.160	64.3	0	2.4	33.5	3.21	0	64.6
79	.00583	.152				17.8	1.04		
	.00958	.152	64.3	0	2.5	17.7	1.70	-0.6	63.6
81	.00583	.152				33.3	1.94	143.1	81.3
						(26.6)*	(1.55)*	(81.0)	(34.8)
	.00783	.204	34.3	34.2	34.2	13.7	1.07		
						(14.7)*	(1.15)*		

*Data in parenthesis calculated from gas sample bulb results; all other data calculated from RGA results.

4. Oxygen Concentration Dependence

In two experiments (Runs 78 and 79) the oxygen concentration was varied at nearly constant flow rate to determine the dependence of oxidation rate on oxygen. Both experiments were carried out under essentially identical conditions, except that in one case a 3.5% oxygen in argon with a 0.166 moles/min total gas flow rate was used initially, and in the other case 3.7% oxygen in argon with 0.158 moles/min total gas flow rate. After a steady-state oxidation rate was reached, the oxygen flow was increased by 64% (the total flow rate increased by only about 2.5%). In each run there was a subsequent increase of about 64% in the steady-state oxidation rate so that the fraction of oxygen consumed remained constant (see Table II and Figure 13 [Run 79]).

The data indicated a first order rate dependence in this range on molecular oxygen. Therefore the fraction of oxygen consumed by coolant was independent of the initial concentration of oxygen going into the reaction vessel. This first order dependence on oxygen had also been observed when irradiated PNPF coolant was exposed to oxygen in a closed system.⁽¹²⁾

This indeed was a unique result if the oxidation proceeds by "normal" autoxidation mechanism. The oxygen partial pressure in the reaction vessel ranged from 550 to 850 Torr. There are numerous examples in the literature which have demonstrated that most chemical autoxidations are independent of oxygen concentration until an oxygen partial pressure well below 100 Torr is reached. This arises because in the propagation steps of the mechanism the reaction of the radical $R \cdot$ with oxygen (Eq. 1) is 10^4 to 10^5 times faster than hydrogen abstraction by peroxy radical (Eq. 2). This applies

to even highly resonance-stabilized radicals such as triphenylmethyl radicals. Therefore it is expected to hold true for organic coolants as well, especially at the high oxygen partial pressures used.

FIGURE 13. OXIDATION RATE CURVE FOR RUN 79

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One possibility is that the reaction is rate controlled by oxygen acting as the initiator. In certain cases, thermal initiation of the reaction between molecular oxygen and a hydrocarbon can occur at high temperatures. If hydrogen abstraction by molecular oxygen is slower than by peroxy radicals, and the termination steps fast then the rate determining step could be:

This mechanism could explain the peaking effect discussed earlier. Oxygen could react much more rapidly with the impurities possessing alkyl groups. As the impurities are used up or oxidized the rate would decrease and eventually reach a steady-state rate of abstracting aromatic hydrogens.

There is another important possible explanation of the data that should be considered. A diffusion controlled reaction would also yield a first order dependence. Ficks first law of diffusion (Eq. 4) states that the diffusion flux, ϕ , (moles area⁻¹ time⁻¹) is proportional to the gradient of concentration ($\partial c/\partial x$)

$$\phi = -D \frac{\partial c}{\partial x} \quad (4)$$

An increase in oxygen concentration in the gas would increase the diffusion gradient which would result in a higher flux across the gas-liquid boundary.

One could kinetically distinguish between chemical processes such as those discussed above and a diffusion process by appropriate experiments. Chemical processes would follow the equation

$$-\frac{d O_2}{d t} \propto [O_2]$$

while a diffusion process involves the square root of time (t) or:

$$-\frac{d O_2}{d \sqrt{t}} \propto [O_2]$$

C. REACTION PRODUCTS

1. Gas Products

During Runs 77-89, periodic samples of the effluent gas stream were collected and analyzed on a CEC-103 mass spectrometer. In addition, for Runs 82-93 the effluent gas stream was continuously monitored for carbon dioxide and water production.

The data from continuous monitoring of carbon dioxide indicate that the production rate follows the consumption rate of oxygen quite closely. Thus the carbon dioxide production rate curve was like the oxidation rate curve--an initial peaking period, which accounts for the major part of the carbon dioxide produced followed by a steady-state production rate (see curves for Runs 85 and 82, Figures 9 and 15, for comparison). During the steady-state oxidation period for a 580°F run, carbon dioxide formation accounted for 20-35% of the oxygen being consumed. Runs conducted at lower temperatures ($\leq 400^\circ\text{F}$) the carbon dioxide rate was very much lower, accounting for less than 2% of the oxygen consumed. This appears to apply to both the Santowax OM and the prepared pure OM mixture.

The gas sampling data indicate that the carbon monoxide production rate also follows the oxidation rate curve at high temperatures. The greatest amount of carbon monoxide produced was during the peaking period of the oxidation curve. At the steady-state oxidation rate the carbon monoxide accounted for 5-12% of the oxygen being consumed. However, in contrast to the carbon dioxide results, at low temperatures much more carbon monoxide appeared to be formed, accounting for over 50% of the oxygen being consumed. This apparent high result may have originated not from the oxidation of coolant but, instead, be a result of the "ghost" peak in the mass spectrometer previously discussed (see Section III.A). In fact, most of the carbon monoxide observed may be only a ghost peak.

The carbon dioxide and carbon monoxide production rate at steady-state conditions are given in Table III.

The amount of water detected in the effluent gas stream does not give the rate of production but rather only reflects the vapor

TABLE III

Carbon Dioxide and Carbon Monoxide Production Rates

Run No.	Temperature (°F)	Production Rate at Steady-state* (moles/min x 10 ⁴)		Percent of Reacted Oxygen** Found as		Comments
		CO ₂	CO	CO ₂	CO	
77	580	5.00	0.94	45.0	4.3	
78	580	5.73	2.72	29.4	7.0	at 3.5% O ₂
		7.11	4.00	22.1	6.2	at 5.6% O ₂
79	580	4.65	2.65	44.7	12.9	before irradiation
		3.24	2.59	27.5	11.0	during irradiation
81	580	5.63	2.16	29.0	5.5	low gas flow rate
		3.82	2.00	35.7	12.1	high gas flow rate (34% increase)
82	580	3.14	1.20	19.7	3.8	
		3.10**		19.5**		
83	580	10.1	8.20	20.3	8.3	
		9.2**		18.5		
85	580	5.99	2.84	48.3	11.5	pump 90%
		4.80**		38.7		
		2.68	2.05	33.5	12.8	pump 30%
		2.57**		32.1		
86	580	5.52	3.47	52.1	16.4	
		4.14 *		39.1		
88	350	< 0.01	1.26	< 2.0	~100	
89	350	< 0.01	1.07	< 2.0	67	
		< 0.01**				
	400	< 0.01	1.84	2.0	54	
		.25**		14.7		
	480	1.76	2.60	18.9	14	
		1.93**		20.8		
	580	< .01	7.88	< 2.0	73	
		2.72**		50.4		
	620	4.65**		45.1		
	350	.08	1.68	10	105	
		< 0.01**		< 2.0		

(continued)

TABLE III (Continued)

90	580	.23**	1.68	15.3
	350	.07**		<10
91	580	.30**		50.0
	350	< .01		< 2.0
92	580	.35		29.2
	350	< .01		2.0
93	580	.93		48.9
	350	< .01		< 2.0

* For runs 77-81 and 83 amount of oxygen consumed based on RGA data, all others based on Polarographic data.

** Data from Lira infrared CO₂ analyzer, all others based on gas sample bulb data.

pressure of the water which is collected in the traps at 0°C. There was a higher amount of water observed during the peaking period in the oxidation rate which suggested that the rate of water formation also followed the oxidation rate curve. If one assumes that the water and carbon dioxide are produced from complete oxidation of terphenyls (i.e., $C_{18}H_{14}$ (terphenyl) + $21.5O_2 \rightarrow 18 CO_2 + 7 H_2O$ or for every 18 moles of oxygen consumed as carbon dioxide, there are 3.5 moles consumed as water) then this would imply 4-7% of the oxygen consumed at steady-state could be accounted for as water. From the analysis of the oxidized coolant it appears that polymerization may be an important reaction which could yield water by $2 RH + O_2 \rightarrow R-R + H_2O$. Based on the amount of water found in the traps after the oxidation, the water could account for up to 20% of the oxygen consumed.

Analysis of the gas samples showed only trace amounts of volatile organic compounds. Table IV gives some of the results found at steady-state conditions.

2. Coolant Species

Some coolant samples were analyzed for biphenyl and terphenyl content before and after oxidation (see Table V for results). The samples of unoxidized Santowax OM used in the runs contained $93 \pm 1\%$ terphenyls and about 1.0% biphenyl. The gas chromatographs showed only trace amounts of low boiler impurities and no high boilers were detected. The high boiler analysis for coolant used in Runs 83 and 87 showed no detectable amounts of high boilers. Therefore the remaining 5% of the coolant was mainly intermediate boilers. The gas chromatograph shows seven peaks between biphenyl and o-terphenyl and two peaks just after o-terphenyl. Compounds which have been identified were fluorene, fluorenone and alkylbiphenyls.

The samples of oxidized coolants show a significant decrease in the terphenyl isomers when oxidized at 580°F. There was only one new peak observed for the intermediate boilers (just preceding fluorenone) and the others, especially those just following biphenyl, showed a decrease. There were many peaks (20) observed for high boilers. Some

TABLE IV
Nonoxygen Containing Volatile Compounds

Moles % at Steady-State Oxidation*

<u>Run No.</u>	<u>H₂</u>	<u>CH₄</u>	<u>Butane</u>	<u>Pentane</u>	<u>Alkyl Benzenes</u>	<u>N₂</u>	<u>Comments</u>
77	.004		.003	.007	.005	.054	
78	.008			.160	.007	.239	
79	.008		.002	.018		.057	before irradiation
	.009		.007	.012		.004	during irradiation
81	.001		.001	.199		.249	low gas flow rate
	.002	.004	.002	.070		.235	high gas flow rate (34% increase)
82	.004	.002		.014		.031	
83	.04	.02	.03	.01		.27	
85	.01	.02	.03	.03		0.0	pump 90%
	.01	.01	.01	.01		.08	pump 30%
86	.05		.02	.02		0.82	
38				.31			at 400°F
89	.01		.01	.01		0.10	at 350°F
	.01		.01	.01		0.0	at 400°F
	.01			.01		0.0	at 480°F
	.01			.02		0.0	at 580°F
				.005		0.0	at 350°F

*Temperature is 580°F unless otherwise noted

TABLE V
Composition of Coolant Before and After Oxidation

Run No.	Coolant	Biphenyl	<u>o</u> -Terphenyl	<u>m</u> -Terphenyl	<u>p</u> -Terphenyl	Total of Biphenyl & Terphenyl	Low Boilers	High Boilers
82	oxidized	0.8	52.2	30.4	3.9	87.3		7.0
83	unoxidized	1.1	59.3	30.8	3.3	94.5	<.1	0.0
	oxidized	0.9	45.0	24.5	3.0	73.4		18.0
85	oxidized	0.8	55.5	27.7	3.4	87.4		8.5
86	oxidized	1.0	55.2	27.7	4.4	88.3		
87	unoxidized	1.0	63.6	26.5	2.9	94.0	<.1	0.0
	oxidized	1.1	57.7	28.9	3.1	90.8		1.1
88	unoxidized	1.1	63.2	26.1	2.9	93.3	<.1	
89	unoxidized	1.1	59.5	30.6	3.5	94.7		
	oxidized	0.9	52.2	25.4	3.3	81.8		13.0
90	unoxidized	< .05	63.4	34.5	2.5	100.4	<.1	
92	(unoxidized)*	< .01	63.0	34.4	2.4	99.8	<.1	
93	(unoxidized)*	< .01	63.2	34.8	2.4	100.4	<.1	
	oxidized	< .05	63.0	34.4	2.5	99.9	<.1	

Results are in weight %

* These coolants were previously exposed to oxygen in the preceding experiment.

of them have been tentatively identified as quaterphenyls, a quiquephenyl and a hexaphenyl (See Table VI). The gas chromatographic results indicated that 7-8% high boilers were formed in a typical 580°F oxidation. In Run 83, in which the oxidation rate was about four times the usual, there were about 20% high boilers in the oxidized coolant. The high boiler analysis of the oxidized coolants (see Table V) agree with the high boiler content estimated from the gas chromatographic analysis.

The experiments conducted with the pure OM mixture (Runs 90-93) showed no apparent change in the terphenyl isomers, thus supporting the other data indicating that terphenyls were not themselves oxidized at 580°F but that the presence of certain impurities could catalyze the oxidation at high temperature. In Run 93, in which 0.2% alkylbiphenyls were added, after oxidation less than 0.02% could be detected by gas chromatographic analysis.

Coolant samples taken during the oxidation period indicated that a steady-state production rate was reached for oxygen containing organic species. This was demonstrated from the analysis of coolant sample taken during Run 85 (see Table VII). In Run 85 the coolant was oxidized at 580°F. After about 2.5 hours of oxidation with 3.7% oxygen in argon, the coolant attained about 2950 ppm TBO which did not change during a further 3.5 hours' exposure to oxygen. This was also shown to be true for the carbonyl compounds analyzed in Run 85. Other runs also lend support for this observation of a steady-state production rate for phenols and carboxylic acids, as well as TBO and carbonyl compounds. At 580°F of the TBO (~ 3000 ppm) accounted for, 15-17% were carbonyl compounds, 5-10% were carboxylic acids and about 1% were phenolic compounds. The 72-79% not accounted for may be in the form of another type of compound (i.e., ethers), or the methods of analysis used may not detect all compounds of the above types. Summary of the steady-state concentration of oxygen compounds are given in Table VIII.

The fact that a steady-state TBO content does arise is very important, for this means that at the steady-state the rate of oxygen consumption must equal the rate of formation of volatile oxygen-containing species, plus the rate of film formation. Thus, if one knows the steady-

TABLE VI

Typical GLC Analysis of Coolant After High Temperature Oxidation

Peak	Retention Time from Air Peak (minutes)	Tentative Identification
1	0.13	benzene
2	0.38	-
3	0.56	-
4	0.63	-
5	1.19	biphenyl
6	1.56	-
7	2.00	-
8	2.19	-
9	2.44	fluorene
10	2.94	-
11	3.50	-
12	4.00	fluorenone + unknown compound
13	5.41	o-terphenyl
14	6.38	-
15	10.69	m-terphenyl
16	11.41	p-terphenyl
13	0.75	o-terphenyl
15	1.25	m-terphenyl
17	1.63	-
18	1.94	triphenylene (?, R. T. = 1.88)
19	2.38	1,2,4-triphenylbenzene (?, R. T. = 2.44)
20	2.75	-
21	3.25	1,3,5-triphenylbenzene (?, R. T. = 3.88)
22	4.75	-
23	5.19	3,3'-diphenylbiphenyl
24	6.13	-
25	6.81	p-quaterphenyl
26	8.13	-
27	9.75	-
28	11.56	-
29	14.00	-
30	15.94	-
31	17.94	-
32	21.88	-
33	25.50	m-quinquephenyl
34	32.81	-
35	39.88	4,4'-(2-xenyl)-biphenyl

Notes: Column - 5 ft, 1/4" stainless steel packed with 20% DC-11 Silicone Oil on 42/60 mesh firebrick. Injector temperature 325°C; detector temperature 300°C; detector filament voltage 80 ma. Sample size - 10 µl liquified coolant.

Operating conditions. Peak Nos. 1 to 16 inclusive: column temperature 250°C; helium gas flow 67 cc/min. Peak Nos. 13 to 16 (second set) and 17 to 35: column temperature 317°C, helium gas flow 120 cc/min.

TABLE VII

ANALYSES OF COOLANT SAMPLES FROM RUN 85

Sample Time (minutes)	ppm Oxygen in Sample as		
	Water	Bound Oxygen	Carbonyl Compounds
17	25	~ 0	109
18	34	92	112
O ₂ on 21			
53	155	646	345
84	48	1758	375
115	236	2048	470
171	441	2852	476
203	306	2880	507
2035	316	2893	472
204	373	2864	523
232	166	3007	503
293	182	2917	539
322	114	2880	477
355	172	2930	484
O ₂ off 378			
394	81	2914	512
395	67	3019	540
423	184	2959	540
450	79	3009	485
477	42	3086	484
510	73	3063	
531	374	2949	
532	172	2895	
566	84	2687	
565	171	2966	
593	123	2832	
594	59	3021	

TABLE VIII

SUMMARY OF OXIDIZED COOLANT ANALYSIS FOR BOUND-OXYGEN SPECIES

Run No.	Temperature	Steady-State Concentration of Oxygen Compounds (ppm as oxygen)				% TBO as		
		TBO	Carbonyl Compounds	Carboxylic Acids	Phenolic Compounds	Carbonyl Compounds	Carboxylic Acids	Phenolic Compounds
49	620	1300						
50	620	4050						
51	620	1400						
52	620	2550						
53	620	1500						
56	620	2150						
61	400	240						
62	620	2300						
63	620	2900						
82	580	2950	455	160	15	15.4	5.4	0.5
83	580	8180	2240	1655	127	27.4	20.2	1.6
85	580	2950	500	--	--	16.9	--	--
86	580	2825	--	164 305*	27 29*	--	5.8 10.8	0.9 1.0
88	350	< 200	--					
89	350	288	--	51*	42*	--	18.1	14.6
	400		--	61*	47*	--	21.8	15.6
	480		--	176*	73*	--	12.4	5.1
	580	3470	--	228*	27*	--	6.6	0.7
	620	3920	--	134*	36*	--	3.4	0.9
90	580	< 150						
91	580	< 200						
92	580	< 302						
93	580	528						

(continued)

TABLE VIII (continued)

SUMMARY OF OXIDIZED COOLANT ANALYSIS FOR BOUND-OXYGEN SPECIES

Note: The coolant samples for Runs 49-63 were taken from coolant drained from the reaction vessel and stored up to 9 months in sealed metal cans. All others were taken directly from the loop into polyethylene capsules and analyzed within one month.

*These analyses were performed in carbon tetrachloride instead of carbon disulfide.

state oxidation rate and the steady-state rate for formation of the folatile species, the rate of film formation can be estimated for that system under a set of given conditions. In this system, for example, at 580° the oxygen was consumed at 1×10^{-3} moles/min of which ~ 50% was accounted for as volatile oxygen compounds (CO_2 , CO , H_2O), so that ~ 5×10^{-4} moles/min of oxygen could result as film. The film (see Section III.F) deposited in the loop has an empirical formula $\text{C}_{18}\text{H}_{9.9}\text{O}_{1.3}$; therefore, film can form at a maximum rate of 0.2 g/min at 580°F during steady-state. This also means that there was an obtainable limit to the amount of bound oxygen species the coolant could have under certain conditions no matter how much oxygen was admitted.

As with the oxidation rate, the TBO initially builds up fast and then levels off. Results from Run 86, a typical 580°F run, indicate that to increase the TBO to 1000 ppm takes about 30 min., to 2000 ppm takes about 60 min., and to the steady-state amount 3000 ppm takes about 150 to 200 min.

It appears that the compounds which make up the TBO are fairly stable at 580°F. In Run 85, after the oxygen was turned off, the coolant was allowed to continue to circulate around the loop for an additional 3.6 hours at 580°F. There was no detectable change in the TBO during this time.

D. IRRADIATION EFFECT

Experiments were carried out to investigate the effect of Co^{60} gamma irradiation (about 3×10^6 rad/hr) on the oxidation rate of Santowax OM. The irradiation site was a coiled tube (see Figure 4 and Section II.A.1 for details on irradiation coil) in the loop about 1-1/2 feet from the reaction vessel (where the coolant was exposed to the oxygen-argon mixture). About 120 ml (~ 10%) of the coolant inventory was in the coil at any one time. The residence time for the coolant in the coil was about 3 sec, with a complete coolant inventory turnover time of 30 sec.

Experiments were conducted with irradiation at 400°, 580° and 620°F. In each case, the oxidation of the coolant was allowed to proceed until a steady-state oxidation rate was reached and then the coolant was irradiated. The results of the radiation are summarized in Table IX

SUMMARY OF Co⁶⁰ IRRADIATION EXPERIMENTS

Run	Temperature (°F)	Gas Flow Rate (mole/min)	Dose Rate (rad/hr)	Irradiation Time (min)	Steady-State Oxidation Rate (mole/min)		
					Before Irradiation	During Irradiation	After Irradiation
56	620	.00367 (O ₂) .360 (Ar)	3.4 x 10 ⁶	20	7.63 x 10 ^{-4*}	7.74 x 10 ^{-4*}	
61	400	.00367 (O ₂)	0.85 x 10 ⁶	42	1.92 x 10 ⁻³	1.98 x 10 ⁻³	
		.360 (Ar)	3.4 x 10 ⁶	41		1.98 x 10 ⁻³	2.01 x 10 ⁻³
79	580	.00583 (O ₂)	3.2 x 10 ⁶	53	1.54 x 10 ⁻³	(1.40 x 10 ⁻³)	
		.152 (Ar)				(1.32 x 10 ⁻³) 1.18 x 10 ⁻³	1.07 x 10 ⁻³

*These data are an average of two points.

(also see oxidation rate curve for Run 79, Figure 13).

In none of the experiments was there any large effect noted. In Runs 56 and 61 there was a very slight increase in the oxidation rate. However the change falls within the instrument error of $\pm 3\%$ absolute.

In Run 79 there was an apparent small decrease in the oxygen consumption rate when the coolant was irradiated and a further small decrease when the irradiation source was removed. Although these decreases could be real, the changes could be accounted for by a large instrument drift. As can be seen from the oxidation rate curve for this run, there were several small decreases before the irradiation and three during the irradiation period, suggesting that the instrument was unstable. Furthermore, irradiation would be expected to increase the oxidation rate and not, as observed, decrease.

It is reasonable that under the conditions of these irradiation experiments there could be no detectable affect on the oxygen consumption rate. Autoxidation of organic coolants is initiated by free radicals which, in turn, react with the molecular oxygen. Irradiation induces free radical formation in the organic coolant. However for these free radicals produced by radiation, to affect the oxygen consumption rate there must be molecular oxygen present to react with them before the radicals undergo other reactions that lead to unreactive species. This condition may not have been fulfilled in these experiments. Since the irradiation of the coolant was not near the oxygen inlet, either a sufficient amount of dissolved gaseous oxygen must survive until it reaches the irradiation coil or a sufficient amount of radiation-induced free radicals must survive until they reach the oxygen in the reaction vessel. The oxidation rate is very fast as shown by the low activation energy and, therefore, very little of the oxygen would be expected to survive to reach the radiation site. Evidence for this conclusion can be seen in the film formation data (see Section III.F). Likewise, the free radicals produced from Santowax OM should be extremely reactive and would thus react with the coolant or decompose before arriving in the reaction vessel.

Also, if the reaction between molecular oxygen and the coolant is diffusion controlled as some of the data suggests, then again it is possible there would be no observable rate enhancement. The rate of oxygen consumption would depend on the rate at which the oxygen can diffuse into the coolant to the reactive molecules and not on the number of reactive molecules present (unless there were a very large number of free radicals). Thus, although the number of reactive radicals is increased by irradiation, this would have little effect on the rate.

These results do not imply that there was no irradiation effect, but only suggest there was no observable change in the rate of oxygen reaction with the coolant under these conditions and short periods of irradiation. The radicals underwent other reactions which did not affect the oxidation rate. Had the radiation dose been many magnitudes greater (increasing the yield of radicals that would survive to reach the oxygen) or had the coolant which was in direct contact with the oxygen been irradiated, then the effect on the oxidation rate would probably have been observable.

E. CLAY EXPERIMENTS

Attapulugus clay has been found useful in removing from organic reactor coolants species which result in fouling, as well as inorganic impurities.^(15,16,17) The effectiveness of the clay was evaluated by such tests as the pyrolytic capsule fouling test (PCFT), membrane stain test (MST), ash analysis, iron analysis (x-ray fluorescence) and gamma spectrographic analysis. However, little is known about what types of organic compounds are being removed by clay.

It has been observed that the fouling rate in organic reactors increases rapidly when the coolant becomes contaminated with oxygen-containing organic compounds. These compounds can be introduced into the coolant by addition of fresh virgin coolant or from air leakage into the system. One possible method to remove these undesirable oxygen species is with Attapulugus clay. Little has been reported in the literature on the capability of clay in removing these species. In a report by Eichelberger⁽¹⁸⁾ it was mentioned that when 2500 grams of OMRE coolant was passed through 10 grams of Attapulugus clay the carbonyl

content decreased from 960 ppm to 640 ppm oxygen. The phenolic and carboxylic acid content did not seem affected by the clay treatment.

Several experiments were performed to investigate the capability of clay in removing oxygen species from both "fresh" Santowax OM and oxidized coolants containing various amounts of oxygen. The effect of the clay was followed by taking periodic coolant samples that were analyzed for total bound oxygen (TBO), carbonyls, phenols and carboxylic acids as well as by the usual monitoring of the effluent gas. A summary of these experiments and TBO results is given in Table X. Description of the clay column is given in Section II.A.1 and data for the clay bed are presented in Table XI. Attapulugus clay is a hydrosopic, hydrated magnesium-aluminum silicate and belongs to a "naturally" active class of adsorbents in which its adsorptive properties are developed by thermal treatment alone. The degree of activity is determined by the amount of water retained after thermal treatment. Generally the clay was used as received without any thermal activation. The clay column was purged of air by repeatedly (3 times) evacuating and filling the column with argon to 270 psig. The excess pressure was released just before use. However, in one case (Run 88), the clay column was thermally pretreated by heating at 600°F for 16 hours while purging with dry argon to remove sorbed water and gases.

The clay was most effective with the unoxidized Santowax OM. In three experiments (Runs 86-88) freshly distilled coolant containing 100-150 ppm TBO was treated with clay. In each case within two hours over 90% of the oxygen was removed yielding a very "clean" coolant containing about 5 ± 5 ppm TBO. Clay exhibited this ability even at lower temperatures as illustrated by the results of Run 88 in which the coolant and clay column were maintained at 400°F.

As the concentration of oxygen species increased in the coolant the effectiveness of the clay rapidly decreased. In two experiments (Runs 82 and 87) oxidized coolants containing 800 ppm and 2950 ppm TBO were treated with fresh clay, the TBO was decreased by 56% and 27%, respectively. In another experiment (Run 83) oxidized coolant containing 8000 ppm TBO circulated through the clay column used for the previous experiment

TABLE X
SUMMARY OF RESULTS OF THE CLAY EXPERIMENTS

Run	Temp. (°F)	Weight of Coolant (g)	Inventory Turnover Time (min)	Exposure Time (min)	Number of Turnovers	E/A	Total Bound Oxygen (ppm)		Oxygen Removed		Clay after Exposure ^a
							Before Clay	After Clay	g	% of O ₂	
82	580	1000	2.09	153 (62) ^b	73.2 (29.6)	1005 (407)	2950	2150	0.80	27	
83	580	1500	3.14	49	15.6	322	(660) ^c	630	-	-	
		1400	2.93	60 (41) ^b	20.5 (14.0) ^b	394 (269) ^b	8000	7500	0.70 (1.50) ^d	6 (15) ^d	Dark brown with fine brown mater- ial (inorganic)
86	> 700 ^e	470	2.03	148	72.9	972	140	5 ± 5	~ .13	~ 95	Very black; ^f weight gain 7.1 g
87	580	1135	2.38	123 (30) ^b	51.7 (12.6) ^b	808 (197) ^b	100	5 ± 5	~ .10	~ 95	
		1000	2.09	144 (21) ^b	68.9 (10.0) ^b	946 (138) ^b	800	350	.45 (.55) ^d	56 (61) ^d	Gray with fine brown material; weight gai 6.4 g
88	400	1140	2.18	120	55.0	863	100	5 ± 5	~ .10	~ 95	

a) Clay washed with benzene at room temperature until washes were colorless.

b) At time after which total bound oxygen (TBO) did not change.

c) Estimated from 1100 g coolant with 102 ppm TBO and 400 g oxidized coolant with 220° ppm TBO.

d) Calculated from the total oxygen removed by the clay column.

e) Clay column overheated (> 700); coolant in vessel ~ 600°F.

f) Calculated by assuming clay weighs 68.7 g due to loss of about 4.0 g water.

TABLE XI
CLAY BED DATA

Clay*	-	Type	Attapulugus
		Grade	AA - LVM
		Size	30/60 mesh
		Color	light tan
		Surface area	125 m ² /g
		pH	7.5 - 9.0
		Bulk density	0.48 g/cm ³
		Void fraction	0.20
		Water content	5 - 6% (600°F, 24 hrs)
		Weight used	72.7 g
		Volume	152 cm ³
		Void space**	30.4 cm ³
		Water in clay	3.6 - 4.4 g
Bed Dimensions		Height	25.7 cm
		Diameter	2.66 cm
Flow Rate			550 cm ³ /min
Coolant Contact Time			3.3 sec.
Space Velocity			218 hr ⁻¹

* Obtained from Minerals and Chemicals Division, Minerals and Chemicals
Philipp Corp., Menlo Park, N. J.

** Void space of total column is 450 - 500 cc.

(Run 82) with only a 6% reduction in TBO. However, taking into account the 0.80g already on the clay from Run 82, a more reasonable estimation of the effective removal capability of the clay is 15% (based on 1400g of coolant having an initial 8570 ppm TBO). Also for Run 87, taking into consideration the 0.10g oxygen removed by the initial circulation of the fresh coolant through the clay in the first part of the experiment would increase the TBO removal from 56 to 61%.

The above results suggest that the removal of oxygen compounds from the coolant is an adsorptive process and not a saturation process in which all available sites are being used. Thus the clay column which appeared "saturated" in Run 82 was still capable of further removal of oxygen from the coolant in Run 83. Also the grams of oxygen removed was not constant per weight of clay, but depended on the initial concentration of TBO. Adsorption processes follow the Langmuir isotherm:

$$\log \frac{x}{m} = K + \frac{1}{n} \log c$$

where x and m are the weights of substance adsorbed and of adsorbent respectively, c is the concentration of the solution when equilibrium is reached, and the K and n are constants characteristic for specific system, hence the weight of clay (m) is the same for each experiment. A plot of $\log$ (grams oxygen removed) vs $\log$ (ppm TBO at equilibrium) should give a straight line if it is an adsorptive process. The plot is shown in Figure 14. Considering the uncertainty in the data and the assumptions used, the results appear to give a straight line and, therefore, strongly suggest an adsorption process.

Since this is probably an adsorption process, it is possible for a given system to calculate the amount of clay that would be necessary to remove a given amount of oxygen species from a coolant having a known amount of TBO. This would be done by using the Langmuir isotherm equation given above. The constants in the equation would be determined for the system desired by preliminary experiments.

The purpose of these experiments was to demonstrate a reasonable capability of clay for removing oxygen species from organic coolant and not the maximum efficiency obtainable. No attempt was made to

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FIGURE 14. LANGMUIR ISOTHERM PLOT
OF CLAY RESULTS

obtain the optimum conditions for the clay column for removing oxygen impurities. To do this would have required expensive and time-consuming redesigning of the oxidation loop. Thus the minimum flow rate of coolant through the clay column obtainable with the pump was about 550 cc/min which gives a space velocity (volume of coolant per volume of clay per hour) of 218 hr^{-1} which is about 100-fold too great for maximum clay performance. The minimum bed height for optimum adsorption is 18.8 ft (height used 10 inches) which would have been impracticable with the present design.

The data shows that the optimum conditions were not obtained. The E/A (volume of coolant per volume of clay) for equilibrium was about 200-400. The number of coolant inventory turnovers was 10-30 to establish equilibrium. With more favorable conditions, it would not be unreasonable to expect a five-fold decrease in these values.

Even with these extremely fast coolant flow rates, Attapulugus clay still demonstrated a very rapid sequestering ability for oxygen compounds. In most experiments within 60 minutes the clay had reached the maximum removal capability. A more pronounced effect was observed with the coolant samples from Run 87 (see Table XII). When the clay was fairly fresh, coolant containing about 800 ppm TBO when entering the column was found to be reduced to ~ 100 ppm TBO at the exit of the column.

Coolant samples from Runs 82 and 83 were analyzed for carbonyl compounds and the samples from Runs 82, 83, 86 and 87 were analyzed for phenols and carboxylic acids. The decrease in these species does not parallel the decrease in TBO when the coolant is passed through clay. In fact, no noticeable change in concentration of these species was found in Runs 82, 83 and 86. On the other hand, there was a definite decrease in phenols and carboxylic acids in Run 87. To get a more accurate estimate of the decrease, the amount of coolant left in the clay column must be considered (as done for TBO in Table X). It is estimated that the column contains about 400g of coolant at 580°F . This value is then used to calculate the amount of dilution when the column is reopened. The concentration of TBO and of oxygen compounds in the coolant when the clay is valved out of the system is considered

TABLE XII

ANALYSES OF COOLANT SAMPLES FROM RUN 87

Sample Time (minutes)	ppm Oxygen in Sample as			
	Water	Bound Oxygen	Phenols**	Carboxylic Acids**
Feed Coolant	66	231		
Feed Coolant	43	189		
2	23	73	50	34
3	48	123	51	44
Clay in 24				
26 (b)*	77	107	42	42
26.5	43	314	37	43
29 (b)*	40	125	32	43
29.25	76	150	41	36
40	37	98	33	34
54	110	-23	33	29
84	38	-4	45	34
114	102	-33	35	34
146	31	1	33	44
Clay out 147				
180	129	-125	30	45
180.25	40	-36	31	34
O ₂ on 196				
207	30	34	35	34
212	44	70	38	60
O ₂ off 226				
257	47	1166	73	274
258	71	1159	71	224
Clay in 273				
275 (b)*	124	773	37	75
275.5	91	114	46	79
276	128	38	48	89
279.5 (b)*	78	475	55	118
280	152	131	52	110
294 (b)*	40	337	50	120
294.25	113	343	51	108
304	33	340	50	104
337	106	345	50	114
Clay Column				
Bypass open 353				
Clay Column				
Bypass closed 387				
417	80	360	41	105
417.5	120	249	37	120
Pot Residue	103	236	41	115
Pot Residue	102	263		

*(b) means the coolant sample was taken at the entrance of the clay column; all other samples were taken at the exit of the clay column.

** Analyses performed in CCl₄ solution.

to be the concentration when the clay is again valved in. These results and the TBO for Run 87 are given in Table XIII. The TBO is reduced by 56% while the acid is only decreased by 37% and the phenols even less, about 18%.

The slight decrease in these species in comparison to TBO suggest that the principal oxygen compounds being removed by clay are of a different type. Another possibility is that the method of analysis is not sensitive for certain carbonyls, phenols or carboxylic acids which are, however, removed by clay. Further work in this area is needed.

The effluent gas stream was monitored during the clay experiments for oxygen, water, carbon dioxide and carbon monoxide. There was no detectable oxygen produced when coolant was passed through clay. However, the other species did show an increase in production when coolant was treated with clay.

As-received clay contained adsorbed water which was released when the clay was heated or came in contact with hot coolant. To determine the amount of removable water on the clay two samples of clay were heated in a muffle furnace at 600°F for 24 hours. The weight loss was 3.6 and 4.4%. The clay regained this weight when left exposed to air at room temperature overnight. This appears to be the amount of water also lost when a "fresh" clay column is valved in for the first time. This was shown from the analyses of the coolant samples taken in Run 82.⁽¹⁹⁾ The first coolant sample taken after the clay was valved in contained about 5500 ppm of water which is equivalent to about 4.5 grams removed from the clay.

The carbon monoxide could only be monitored by intermittent gas sampling. Although not enough data are available, the carbon monoxide production rate seems to follow the carbon dioxide production rate but is a factor of 2-3 less.

The carbon dioxide was monitored continuously and also intermittently with gas samples. The results (see Table XIV) suggested that as-received Attapulugus clay has sorbed carbon dioxide which was not removed by purging with argon at room temperature, but which could be removed upon heating to a higher temperature. In all experiments in which clay purged with argon

TABLE XIII

DECREASE IN TBO, PHENOLS AND CARBOXYLIC ACIDS DUE TO CLAY
FOR RUN 87

	ppm Oxygen as		
	TBO	Phenols	Acids
Coolant before clay (observed)	~ 1160	~ 72	~ 250
Coolant before clay as result of dilution (calculated)	~ 800	~ 57	~ 170
Coolant after clay (observed)	~ 350	~ 37 - 50 (47 aver.)	~ 75 - 120 (103 aver.)
Net decrease	~ 450	~ 7 - 20	~ 50 - 95
% decrease	56%	12 - 35% (18% aver.)	29 - 56% (39% aver.)

TABLE XIV

PRODUCTION OF CO₂ FROM COOLANT EXPOSED TO ATTAPULGUS CLAY

Before Oxidation						After Oxidation				
Run	Clay Treatment Before Run	Clay Temp (°F)	Clay In	CO ₂ Burst*	CO ₂ Steady-State [†] With Clay In ₄ (mole/min x 10 ⁴)	Clay In	CO ₂ Burst	CO ₂ Steady-State With Clay In ₄ (mole/min x 10 ⁴)	CO ₂ Steady-State With Clay Out [‡] (mole/min x 10 ⁴)	Total Bound Oxygen (ppm)
82	Purged with Ar @ R. T.	~ 580	No	-		Yes (2 times)	Yes (2 times)	1st 0.7 2nd 0.6	0.3	~2950
83	Contained oxidized coolant from Run 82	~ 580	Yes	No	0.15 to 0.25	Yes (3 times)	Yes (3 times)	1st 1.5 to 1.6 2nd 1.35 3rd 1.15	0.85 0.85 0.85	~8000
86	Purged with Ar @ R. T.	> 700	Yes	Yes	0.25 to 0.4	-	-	-	-	~ 140
87	Purged with Ar @ R. T.	~ 580	Yes	Yes	0.5 to 0.6	Yes	No	0.7 to 0.8 0.1 to 0.2 [†]	-	~100 (before O ₂) ~775 (after O ₂)
88	Purged with Ar @ 580°F for 16 hr until CO ₂ and H ₂ O evolution ceased	~ 350	Yes	No	~ 0.0	Yes	No	~ 0.0	0.0	~100

* A "burst" was a sudden, several-fold increase in CO₂ production rate which decreased to near-background in a few minutes.

† A CO₂ "steady-state" was the rate of CO₂ production in mole/min, at the specified conditions. In all cases, the CO₂ production rate of fresh coolant was zero before the clay was valved in, prior to exposure of coolant to O₂.

‡ Data calculated from gas sample bulbs; the infrared CO₂ analyzer probably was not working correctly (strong drifting in baseline) due to insufficient warm-up time.

at room temperature was used, the initial valving-in of the clay gave a burst of carbon dioxide. This was true even in Runs 86 and 87 where freshly distilled, unoxidized coolant that contained only about 100 to 200 ppm TBO was used. There was not enough oxygen in fresh coolant to account for the amount of carbon dioxide produced. Moreover, in Run 87, no burst of carbon dioxide was observed the second time the clay column was valved into coolant containing about 1000 ppm total bound-oxygen; nor was there a burst of CO_2 in Run 83 when a "used" clay column that contained oxidized coolant was initially valved in. Furthermore, when a fresh clay column was heated to 580°F (see Run 88) with an argon purge, large amounts of carbon dioxide were given off. When the same column was cooled, and then later exposed to coolant at 350°F, there was no detectable amount of carbon dioxide produced.

However, another source of carbon dioxide production in the presence of clay is decomposition of oxygen species in the coolant promoted by clay. Such a process is indicated by the results of Runs 82 and 83. In Run 82 (see Figure 15), after the initial burst of sorbed carbon dioxide, the production rate of CO_2 remained at a higher level than before the clay was valved in. Upon valving out the clay column, the carbon dioxide evolution rate again fell to a lower level. Valving in the clay column again produced another small burst of CO_2 and an increase in CO_2 steady-state production rate. The carbon dioxide production rate was low at the end of this run (about 3×10^{-5} mole/min). In the next experiment, Run 83 (Figure 10), this same clay column still contained about 400g of oxidized coolant which had been produced in the previous run (No. 82). After the fresh coolant and the "used" clay column were brought to 580°F, the column was valved in. No burst of carbon dioxide was observed, but there was a small steady-state production of carbon dioxide (about 2×10^{-5} mole/min). After the oxidation period, the clay column was again valved in. This time, there was a big burst of carbon dioxide and a subsequent increase in steady-state CO_2 production. The valving in and out of the clay column was repeated twice. In each case there was observed a burst and an increase in steady-state production (over thermal production) of carbon dioxide.

However, in each case the burst and steady-state rate of CO_2 production were always smaller than those of the immediately preceding in-valving (see Table XIII). This then suggested that clay promoted the decomposition of some kinds of oxygen species in the oxidized coolant, and was capable of removing a small fraction of total bound oxygen in this manner.

It also appeared that the steady-state production rate of carbon dioxide depended on the amount of total bound-oxygen in the coolant. Thus, in Runs 87, 87 and 88, when the total bound oxygen (TBO) was less than 200 ppm, the steady-state CO_2 production rate was 0 to 0.5×10^{-4} mole/min. Also in Run 87, after only 30 min. of O_2 exposure (TBO = 1000 ppm), there was not enough CO_2 precursor to produce a CO_2 burst on valving in clay after coolant oxidation, although there was a very small and steady CO_2 production ($< 1 \times 10^{-4}$ mole/min). In Run 82, the TBO was about 3000 ppm, and the steady-state CO_2 production rate was $\sim 3 \times 10^{-5}$ mole/min. In Run 83, when the TBO was about three times greater (8000 ppm), the steady-state CO_2 production rate was likewise three times greater ($\sim 9 \times 10^{-5}$ mole/min).

To summarize the volatile species production during clay experiments:

- 1) About 4g H_2O was released from as-received clay if not pretreated.
- 2) CO_2 evolution rates at greater than 3000 ppm of TBO appeared to increase 2 to 3 times in the presence of clay at 580°F .
- 3) Concentrations of CO_2 precursors capable of producing detectable CO_2 evolution rates in the absence of O_2 at 580°F were obtained only after several hours of exposure of coolant to O_2 .
- 4) Any CO_2 produced after the initial burst of sorbed CO_2 may have come from residual CO_2 still sorbed on clay, but the major fraction of CO_2 probably came from clay-promoted decomposition of oxidized organic species (CO_2 precursors) in the coolant at 580°F .
- 5) CO_2 production rate is dependent upon the concentration of TBO.
- 6) CO production rate seems to follow CO_2 production rate but is a factor of about 2-3 less.

F. FILM FORMATION

At various times the oxidation vessel was opened and inspected for corrosion and film formation. It was noted that after a series of high temperature runs ($\sim 620^\circ\text{F}$) patches of a thin flaky material were deposited on the walls. Thus, after Run 47, approximately one gram of hard brown film (Film I) had formed on the vessel walls and the baffle screens. The film was thickest in the areas near the oxygen inlet opening. At the end of Runs 52, 58, and 62 the vessel was examined and only a small amount of a very thin varnish-like film was found adhering to the wall and screens. After Run 68, there was again about one gram of a shiny black material (Film II) deposited in the same location as with Film I.

These films were washed thoroughly with benzene and analyzed. The films were then further treated to remove a possible entrapped coolant by heating for four days at 125°C and 50 Torr. Film I gave no sublimate but Film II gave a small amount ($< 1\%$) of white sublimate which was shown by G.L.C. analysis to be terphenyls. The films were reanalyzed and the results are shown in Table XV. Films I and II appear quite similar in chemical composition and also basically unchanged by the sublimation process. The properties, brittleness, high melting point ($> 500^\circ\text{C}$), insolubility in organic liquids, and the high C/H ratio indicate that the material is polymeric in nature. If one assumes the terphenyl carbon skeleton for the polymer, then the data corresponds to an empirical formula of about $\text{C}_{18.0} \text{H}_{9.9} \text{O}_{1.3}$ or that there was a loss of four hydrogens with a gain of 1.3 oxygen per terphenyl. Thus, the high oxygen content of these films formed from oxidation of unirradiated Santowax OM indicates that although irradiation may help film formation in an organic reactor, the presence of radiation is not necessary at high temperatures when the coolant has been exposed to sufficient oxygen.

The chlorine, sulfur and iron content of Films I and II suggest that all three of these species and possibly other inorganic species are selectively concentrated in the films. The original coolant contains less than 1 ppm of these inorganic contaminants. This might imply that inorganic species play an important role in film formation via oxidation of organic coolants.

TABLE XV

ANALYSES OF FILMS FROM OXIDATION VESSEL

Analysis	Before Sublimation		After Sublimation		Method of Analysis
	Film I	Film II	Film I	Film II	
Carbon (wt %)	87.00	87.49	87.00	87.22	Gravimetric
Hydrogen (wt %)	3.99	4.16	4.05	4.09	Gravimetric
Oxygen (wt %)	~ 8.7	~ 8.3	~ 8.3	~ 8.6	By difference
	6.7 ± 0.35	8.8 ± 0.3	-	-	Neutron Activation
Ash (wt %)	0.61	0.1	0.35	0.1	Gravimetric
Iron (ppm)	1600	500	500	2000	X-Ray Fluorescence
Chlorine (ppm)	250	30	50	150	X-Ray Fluorescence
Sulfur (ppm)	300	15	200	-	X-Ray Fluorescence

Deposits formed under reactor conditions have been found to have a high oxygen content (ranging from 0.5 - 13%) as well as a high concentration of inorganic impurities (depending on the collection site and sample history). Some films, mainly the out-of-core deposits of PNPF, have a composition similar to that of Films I and II. For comparison, Table XVI presents the analysis of out-of-core deposits from PNPF⁽²⁰⁾ found at the thermocouple plate (B-11 position) and in-vessel filter housing (E.6 position). The PNPF deposits have a much higher ash content and more hydrogen had been removed per oxygen addition to the carbon skeleton than either Film I or II.

After a series of low temperature runs (Runs 69-76 at 400°F) the oxidation vessel was re-examined and no film was observable. This is in keeping with the fact that at lower temperatures there is very little oxidation of coolant. After Run 82 the vessel was again found to have a shiny black film adhering to the sides. The vessel was cleaned by sandblasting (usual procedure) and then washed with dilute nitric acid (~ 2N) followed by water. In the next run (No. 83), in which a clay column containing oxidized coolant from Run 82 was used, there was a very high oxidation rate. When the vessel was inspected a small amount of a deposit had already formed. The major part of this film was removed by scraping. During the next runs the vessel was examined periodically but the film was not removed. By the end of the last run (No. 93) about 0.1 gram of a black deposit, similar to Film II, was found which again was thickest on the walls nearest the oxygen inlet (diffuser). There was also a film deposited on the walls at the level of the gas-liquid interface area. However there was no film observable on the walls in the 3-5 inch area in the middle of the vessel between the two filmed areas nor below the level of the gas disperser.

This observation indicates the possible type of species responsible for film formation in the oxidation loop. The middle area of the vessel which had no film is the hottest area of the vessel. Therefore it is unlikely that the film is a result of pyrolytic decomposition of stable, oxygen containing organic compounds. Instead, the film formers must be short-lived, highly reactive species that are produced from the initial

TABLE XVI

COMPARISON OF SOME PNPf DEPOSITS WITH OXIDATION FILMS FROM LOOP

Measurement	PNPF E-6 Position	PNPF B-11 Position	Film I	Film II
Wt % C	87.2	86.8	87.0	87.2
Wt % H	3.48	3.62	4.0	4.1
Wt % O	8.6	7.5	8.6	8.6
Wt % ash	3.6	2.8	~ 0.4	~ 0.1
ppm Fe	-	20,000	~ 1,000	~ 1,000
ppm Cl	-	130	~ 150	~ 100
ppm S	-	80	~ 250	~ 10
C/H atom ratio	2.1	2.0	1.8	1.8
C/O atom ratio	14	15	14	14

reaction between molecular oxygen and organic compounds. These species must be able to come in contact with the metallic surface rapidly before they decompose into more stable compounds. The areas in which these species could come in contact with the walls the fastest would be where the gaseous oxygen concentration is highest or near the oxygen inlet and the gas-liquid interface. Thus, the compounds which can be analyzed by usual techniques are not themselves the reactive species in film formation, although they could possibly react further with oxygen to give the reactive film formers.

An interesting observation is that film seems to be formed faster on another layer of film than on a metallic surface. The vessel walls were partially scraped to remove some film samples. After a few more runs, re-examination of the walls revealed that the film was growing on the old remaining film but had hardly formed on the clean (or scraped) areas.

Another observation, which might be expected, is that the more surface area exposed to the reacting oxygen-coolant mixture, the more film produced. Thus, in the earlier experiments with baffle screens placed above the oxygen inlet the major part of the film was on the screens and amounted to about one gram of film. Without the screens much less of the film was formed during longer exposure periods. This is a further indication that the film forming species are short-lived and do not form film unless a surface is nearby.

IV. SUMMARY AND CONCLUSIONS

Freshly distilled, commercial Santowax OM was oxidized with a gas mixture of oxygen and argon at various oxygen concentrations, gas flow rates, coolant flow rates and temperatures. It was found that under the conditions used:

- 1) At high temperatures ($\geq 580^{\circ}\text{F}$) the oxidation rate, after a small induction period, rapidly increases to a maximum, then slowly decreases to a steady-state rate.
- 2) The nonterphenyl impurities in Santowax OM cause the peaking in the oxidation rate curve.

- 3) The nonterphenyl impurities in Santowax OM greatly increase the steady-state oxidation rate. The steady-state oxidation rate of pure OM mixture having $< 0.1\%$ nonpolyphenyl impurities is tenfold less than observed with Santowax OM at 580°F .
- 4) At low temperatures ($\leq 400^{\circ}\text{F}$), the rate apparently does not peak but, instead, uniformly increases to a very low steady-state.
- 5) Oxidation rate has a first order dependence on oxygen concentration.
- 6) Oxidation rate decreases with increase in gas flow rate and with a decrease in coolant pump rate.
- 7) An activation energy for the oxidation was calculated at 13 ± 3 Kcal/mole.
- 8) The carbon dioxide production rate and probably the carbon monoxide and water production rates follow the oxidation rate curve.
- 9) At the steady-state oxidation rate at high temperatures, 20-35% of the oxygen being consumed appears as carbon dioxide, 5-12% as carbon monoxide and 4-20% as water, while at low temperatures 2% of the oxygen appears as carbon dioxide and possibly greater than 50% as carbon monoxide.
- 10) Trace amounts of hydrogen, methane and butane were produced during the oxidation.
- 11) The terphenyl isomers (particularly the ortho and meta isomers) are being consumed during oxidation. The HB content increases to about 8% after 4-5 hours oxidation at 580°F . Only one new intermediate boiler was detected in oxidized coolant, while 20 new products are easily detected in the HB.
- 12) The rate of formation of oxygen-containing species in the coolant also follows the oxidation rate curve.
- 13) A steady-state concentration is reached in oxygen-containing species in the coolant. At 580°F the steady-state concentration is 3000 ppm oxygen; at 350°F , < 200 ppm oxygen.
- 14) Most oxygenated species in the coolant were thermally stable at 580°F .

- 15) Certain impurities, such as fluorenone, show little effect on the oxidation rate, while others, such as alkylbiphenyls, greatly increase the rate.
- 16) Film is not readily formed in low temperature oxidation experiments.
- 17) Film is formed in high temperature oxidation experiments. Analysis of the film shows carbon ~ 87%, hydrogen ~ 4.1%, oxygen (by difference) ~ 8.5% and having a high content of iron, sulfur, chlorine in the 0.1-0.6% ash.
- 18) An irradiation dose of $\sim 3 \times 10^6$ rad/hr applied to 10% of the coolant in a coil outside of the oxidation vessel had little effect on the steady-state oxidation rate.

Some experiments were also performed with Attapulugus clay to determine if the clay can remove the oxygenated species found in the unoxidized and oxidized Santowax OM. The results are as follows:

- 1) The amount of oxygenated species removed depends on the initial amount of oxygen impurities present and appears to follow the Langmuir isotherm equation.
- 2) Clay removed well over 90% of the oxygenated impurities in unoxidized coolant even at 400°F.
- 3) Clay catalyzed the decomposition of some species to carbon dioxide.
- 4) Although the amount of total bound oxygen in the coolant decreased when circulated through clay, the particular types of compounds (carbonyls, phenols and carboxylic acids) analyzed for in the coolant did not decrease proportionally.

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APPENDIX A

CALCULATION OF DATA

1. Fraction of Oxygen ConsumedMethod A (RGA)

Due to the problem of peak height drift with the Veeco Residual Gas Analyzer discussed earlier in this report, the more reliable peak height ratio of oxygen to argon (O_2/Ar) was used to follow the change in oxygen with time. The oxygen concentration is proportional to the O_2/Ar or

$$[O_2] = K (O_2/Ar)$$

Assuming the amount of argon remains constant then the fraction of oxygen consumed, $f(O_2)_c$, calculated from the expression

$$f(O_2)_c = 1 - f(O_2)_{unreacted} = 1 - (O_2/Ar)_{out} / (O_2/Ar)_{in}$$

where $(O_2/Ar)_{in}$ is the ratio going into the vessel and $(O_2/Ar)_{out}$ is the ratio observed coming out of the vessel. The instability of the RGA required that the $(O_2/Ar)_{in}$ had to be determined for each experiment. The (O_2/Ar) could be obtained with about 5% (relative) precision.

Method A¹ (RGA and Gas Samples)

This method was used when the $(O_2/Ar)_{in}$ was not obtainable or was thought to be unreliable and when gas samples were taken during the run and for unexposed gas. A $(O_2/Ar)_{gs}$ was calculated from the gas sample data obtained with a CEC 103 mass spectrometer. Using the reliable $(O_2/Ar)_{RGA}$ values obtained during the run at the same time as the gas sample was taken, a $K(RGA/g_s)$ was calculated for each set of data.

$$K(RGA/g_s) = \frac{(O_2/Ar)_{RGA}}{(O_2/Ar)_{gs}}$$

From the average of these K's and the gas sample data on the unexposed gas an "RGA" $(O_2/Ar)_{in}$ was calculated

$$(O_2/Ar)_{in} = K(RGA/gs)_{aver.} (O_2/Ar)_{in} (gs)$$

The fraction of oxygen consumed was then calculated as in Method A.

Method B (Polarograph and Rotameter)

When the polarographic oxygen analyzer was used, the percent oxygen unreacted could be read directly off the scale or chart paper. The instrument was calibrated against air (assuming 20.0% oxygen in air) using the 0-25% scale and then switched to the 0-5% scale during the run. The oxygen concentration of the unexposed stream was calculated from the rotameter data. The expression used is:

$$f(O_2)_c = 1 - \frac{\%(O_2)_{out} \text{ (polarograph)}}{\%(O_2)_{in} \text{ (rotameter)}}$$

Method B¹ (Polarograph and Gas Samples)

The same method of calculation as above is used except the oxygen concentration of the gas sample data or

$$f(O_2)_c = 1 - \frac{\%(O_2)_{out} \text{ (polarograph)}}{\%(O_2)_{in} \text{ (gs)}}$$

Method B¹¹ (Polarograph and Premixed Gas)

When a premixed cylinder of oxygen and argon was used, the polarograph oxygen instrument was calibrated against the known composition of the premixed gas (3.80% oxygen) so that:

$$f(O_2)_c = 1 - \frac{\%(O_2)_{out} \text{ (polarograph)}}{3.80\%}$$

2. Conversion of Data to Rates

The water (from the Beckman electrolytic hygrometer), carbon dioxide (from the MSA infrared instrument), and gases analyzed for in-gas sample data are given directly in mole % (or volume %) of total gas stream. To convert this data to a rate the mole % is multiplied by the flow rate (in moles/min) of the total gas. The flow rate can be taken from the rotameters or the wet test meter data.

The oxygen data (from the RGA or polarograph instruments) are converted to fraction of oxygen consumed by the methods described above. This fraction is multiplied by the flow rate of oxygen (in moles/min) obtained from the rotameter to give the rate of oxygen consumed.

APPENDIX B

SUMMARY OF LOOP MODIFICATIONS

<u>After Run</u>	<u>Modifications</u>
5	Replaced exit valves with needle valves. Installed pressure gauge just upstream from exit needle valves.
12	Installed two U-tube cold traps packed with stainless steel wire mesh.
25	Installed valve at condenser exit. Put folded stainless steel ribbon in cold traps.
26	Changed argon rotameter from R-6-15B to R-2-15C.
38	Replaced static gas sampling manifold with a continuous leak system for RGA.
76	Removed baffle screens from reaction vessel. Replaced gas bubbling tube with more efficient gas disperser (40 μ). Improved condenser and trapping systems. Added gas sampling system for off-line analysis. Improved coolant addition and removal systems and techniques.
81	Added continuous monitoring instruments for carbon dioxide and water. Added coolant sampling system. Installed bypass line for clay column.
82	Installed a better designed gas disperser. Added continuous monitoring oxygen analyzer (polarographic).
86	Added an additional coolant sampling system.

SUMMARY OF RUNS 42 TO 93

Run No.	Temperature (coolant)°F	Pressure (psig)		Flow Rate (rotameter)		Steady-State		Peak Maximum		Mins of O ₂ Exposure
		Inlet	Outlet	O ₂ (moles/min)	Ar (moles/min)	O ₂ Consumption % Mole/min x 10 ³		O ₂ Consumption % Mole/min x 10 ³		
42	620	266	230	.00367	0.360	29	1.10			135
43	620	271	230	.00367	0.360	13	.48			130
44	620	270	232	.00367	0.360	42	1.73			205
45	620	270	230	.00367	0.360	46	1.76			165
46	620	270	250	.00367	0.360	32	1.18			170
47	620	270	250	.00367	0.360	10	0.37			175
48	620	271	240	.00367	0.360	8	0.30	85	3.12	315
49	620	271	253	.00367	0.360	23	0.86	73	2.69	160
50	620	271	252	.00367	0.360	24	0.88	80	2.93	175
51	620	270	252	.00367	0.360	19	0.71	82	3.00	200
52	620	270	250	.00367	0.360	24	0.91	71	2.60	170
53	620	271	252	.00367	0.360	20	0.73	78	2.85	240
54	620	271	252	.00367	0.360	20	0.73	69	2.53	200
56	620	270	252	.00367	0.360	23	0.86	83	3.05	210
57	620	270	245	.00400	0.655	20	0.80	70	2.78	180
59	620	270	248	.00400	0.655	13	0.51	76	2.95	220
60	620	270	245	.00400	0.655	-	-	61	2.43	85
61	400	270	255	.00367	0.360	53	1.95	None		225
62	620	270	254	.00883	0.360	25	2.21			155

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Run No.	Temperature (coolant)*F	Pressure (psig)		Flow Rate (rotameter)		Steady-State		Peak Maximum		Mins of O ₂ Exposure
		Inlet	Outlet	O ₂ (moles/min)	Ar (moles/min)	O ₂ Consumption % Mole/min x 10 ³		O ₂ Consumption % Mole/min x 10 ³		
63	620	270	260	.00583	0.360	18	1.02			245
64	620	270	255	.00583	0.360	18	1.06			210
65	620	270	253	.00483	0.360	27	1.30			210
66	620	270	255	.00483	0.360	34	1.66			290
67	620	270	255	.00483	0.360	35	1.70			220
69	400	270	255	.00483	0.360	4	0.19	None		215
72	400	270	255	.00367	0.360	~ 0	~ 0	None		250
73	400	270	255	.00367	0.360	38	1.39	None		270
74	400	270	255	.00367	0.360	31	1.14	None		240
75	400	270	255	.00367	0.360	8	0.29	None		305
76	400	270	255	.00367	0.360	4	0.15	None		180
77	580	269	257	.00583	0.280	≤ 19	≤ 1.11	65	3.79	125
78	580	268	258	.00583	0.160	33.5	1.95	87	5.07	225
	580	268	259	.00958	0.160	27.3 33.5	1.59* 3.21	-	-	50
79	580	268	258	.00583	0.152	17.8	1.04	79	4.61	335
				.00958	0.152	28.1	1.64*	-	-	75
81	580	270	260	.00583	0.152	33.3	1.94	90	5.25	200
				.00783	0.204	26.6	1.55*			
						13.7	1.07			75
82	580	270	260	.00583	0.152	14.7	1.15*			
						27.3	1.59**	77	4.50**	260
						24.5	1.43*			

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Run No.	Temperature (coolant)°F	Pressure (psig)		Flow Rate (rotameter)		Steady-State		Peak Maximum		Mins of O ₂ Exposure
		Inlet	Outlet	O ₂ (moles/min)	Ar (moles/min)	O ₂ Consumption % Mole/min x 10 ³		O ₂ Consumption % Mole/min x 10 ³		
83	580	270	262	.00583	0.152	85.2 4.97 85.6 (4.70)*		69 4.01		505
85	580	270	262	.00583	0.152	Pump at 90%:				
						18.0 1.05		71 4.12		
						21.3 1.24**		72 4.19**		
						21.4 1.25*				
						Pump at 30%:				
						11.5 0.67				263
						13.7 0.80**				
						10.8 0.63*				
86	580	270	262	.00583	0.152	18.2 1.06**		69 4.04** 69 4.02*		360
87	580	270	262	.00583	0.152	- -		64 3.76**		30
88	350	270	262	.00583	0.152	< 0.1 < 0.01		None		125
						< 1.0 < 0.06**		None		
						1.0 0-0.06*		None		
89	350	270	262	.00578	0.146	1.4 0.08** 0.5 0.03*		None -		127
	400	270	262	.00578	0.146	2.9 0.17** 8.5 0.5(Aver)*		None -		102
	480	270	262	.00578	0.146	16.0 0.93** 14.8 0.86(Aver)*		None -		90
	580	270	262	.00578	0.146	9.3 0.54** 11.7 0.68(Aver)*		> 80 > 4.67		296
	620	270	262	.00578	0.146	< 17.7 < 1.03**		30 ~ 1.76**		163
	350	270	262	.00578	0.146	1.4 0.08** - 0.8 - 0.05(Aver)*				75
	580 350	270	262	.00578	0.146	2.6 0.15** ~ 0 ~ 0**		None		502

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Run No.	Temperature (coolant)°F	Pressure (psig)		Flow Rate (rotameter)		Steady-State		Peak Maximum		Mins of O ₂ Exposure
		Inlet	Outlet	O ₂ (moles/min)	Ar (moles/min)	O ₂ Consumption % Mole/min x 10 ³	O ₂ Consumption % Mole/min x 10 ³	O ₂ Consumption % Mole/min x 10 ³	O ₂ Consumption % Mole/min x 10 ³	
91	580 350	270	262	.00578	0.146	1.0 ~ 0	0.06** ~ 0**	None		136
92	580 350	270	262	.00578	0.146	2.0 ~ 0	0.12** ~ 0**	None		115
93	580 350	270	262	.00578 .00578	0.146 0.146	≤ 3.3 ~ 0	≤ 0.19** ~ 0**	6.2	0.36	190

* These values are calculated from gas sampling data.

**These values are calculated from polarographic data.

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