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Studies of the Oxidation Dynamics of Turbine Oils—Initial Data from a New Form of the Rotating Pressure Vessel Oxidation Test

ABSTRACT: The importance of oxidation-resistant turbine oils in the various applications in which turbines are used is difficult to understate. Turbines in themselves are very costly energy-converting mechanisms which, among many other applications, provide much of the electricity for the power grids of modern society. Most critical to these turbines are the lubricants that are essential to their operation in long, dependable service. Equally critical, then, are the tests that determine the acceptability of these turbine oils and the understanding of the oxidation mechanisms that cause these oils to form deposits and otherwise lose their ability to properly lubricate the turbine. This paper is a first report on a new dry-bath approach to not only determine antioxidation characteristics of turbine oils in the well-known Rotating Pressure Vessel Oxidation Test (RPVOT) but to enable the direct study and modification of the oxidation process as it occurs. The instrument not only eliminates the hot oil-bath associated with the RPVOT but also allows the test fluid to be available for direct monitoring of temperature, chemical content, and the effects of injecting reactants. In the process of gathering the preliminary information for this paper, it was found that significant exotherms may develop in the turbine oil at a critical stage of oxidation response. These exotherms can vary in duration and temperature rise depending on the nature of the antioxidant system and other properties of the formulated turbine oil. Moreover, the fact that these exotherms seem to mark a certain level of the oxidation process, brings the opportunity to more thoroughly investigate and understand oxidation processes as well as the chemistries of other lubricants.

KEYWORDS: turbine lubricant, turbine oil, oxidation, Rotating Pressure Vessel Oxidation Test (RPVOT), Rotating Bomb Oxidation Test (RBOT), quantum oxidation test, dry-bath oxidation test, dry-bath RPVOT, ASTM D 2272

Introduction and Background

Dependence of Society on the Power Turbine

Societies of many countries of the world today are highly dependent on generally available electric power grids produced by various forms and sizes of turbine engines. This form of energy conversion is also the major form of aircraft propulsion and, additionally, is often used in powering ships and railroad engines.

Turbine engines have become so dependable and common that, as a whole, the societies they serve are unaware of how fundamentally dependent such societies are on the service and durability of these sources of power. It is only when some failure or accident occurs involving these power sources and their work output that society regains consciousness of its own vulnerability. Often, the society becomes highly disturbed by this sudden recognition of its degree of its dependence and the potential consequences of its loss of such an important mainstay of social structure and civilized life.

Growth of such dependence has rapidly accelerated over the past half century. This growth in a power-hungry civilization has been assisted by major engineering design improvements in the metallurgy and the manufacturing methods of turbine components and broadened use and refinement of this form of power.

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Dependence of the Power Turbine on Its Lubricant

Undergirding both the turbine and its service to society has been the development of the lubricants upon which the turbine must completely depend. Just as the turbine engine is indispensable to civilization, its lubricant is indispensable to the turbine engine.

The Turbine Engine Lubricant and Its Properties

As turbine engines have improved in efficiency, dependability, and range of applications, a considerable part of that development has been coupled with improvement in the base stocks and additives used in formulating the oils that enable and extend the turbine engine's power-producing function. In many ways, the co-relationship between the turbine engine and its lubricant is basic and very demanding. Essentially, it is lubrication at its simplest and yet most profound required level of dependability.

Desired Properties of the Lubricant—The two major and indispensable properties of the turbine lubricant are:

1. Provision of sufficient viscosity for hydrodynamic lubrication and hydraulic service, and
2. Resistance to oxidation with its accompanying burden of varnish and deposit formation as well as oxidation's concomitant effects on altering other properties of the lubricant.

In addition, vulnerability to foam and air entrainment, or both, is a serious concern accompanying the formulation of the turbine lubricant. Foam and air entrainment can drastically reduce the ability of the lubricant's ability to form as well as maintain hydrodynamic lubrication and, additionally, apply sufficient hydraulic pressure when required. Thus, a third desirable property of a turbine lubricant is the ability to:

3. Reduce or eliminate foaming tendencies and air entrainment.

Viscosity—Viscosity is a physical property that can be readily selected by the formulator of the lubricant from a range of base oils and synthetic oils available. The viscosity of the lubricant is best measured by simulation of the conditions of turbine operation using a high shear rate viscometer at the operating temperatures encountered.

Oxidation—Oxidation resistance of the lubricant is a chemical function of the effectiveness of the additive employed to counteract the various paths of oxidizing decomposition of a turbine lubricant exposed to air and perhaps water at sufficiently high temperatures and any catalyzing effect of the metals present in the turbine.

Foam—Foam, on the other hand, is a somewhat poorly understood physical response to agitation of the turbine lubricant in the presence of air. The molecular composition of the lubricant in conjunction with some additives or organic contaminants may predispose the lubricant to forming foam, particularly when pressure on the circulating lubricant is suddenly reduced. In addition, foaming tendency can be affected by the changes that can occur in viscosity and composition as an indirect result of lubricant oxidation.

To control foam, it is highly desirable to have a particular form of additive present that, because of its limited solubility in the turbine oil, encourages rupture of the foam cell membrane to cause rapid foam collapse or to indirectly block entrained air from developing into foam-forming voids.

Lubricant Formulation and Operating Volume—As a consequence of the evident need for continuous, acceptable service for long periods of time, turbine lubricants should be formulated with careful choices of base stocks and additives, particularly considering the three desired properties previously discussed. Moreover, to extend the lifetime of their acceptable service, the relatively limited areas in a given turbine engine requiring lubrication are served by considerable volumes of these carefully formulated lubricants.

Appraising Life Expectancy and In-service Conditions of Turbine Lubricants—A continuing challenge in the formulation and application of turbine lubricants has been to appropriately define their functionality for service life and rate of depreciation without the need to periodically run very expensive, long full-scale tests. Accompanying the need for prior-service lubricant screening tests is the related need for determining the in-service remaining life of a turbine lubricant. Both of these needs have led to several bench tests for

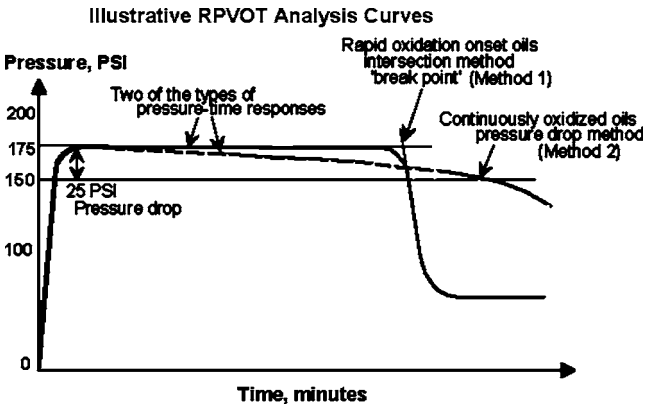

FIG. 1—*Illustrative plots of RPVOT analyses showing two types of oxidation curves and methods of interpreting the oxidation.*

appraising initial and in-service condition of turbine lubricants. Fortunately, the properties of viscosity, and foam formation can be (and have been) relatively simply reduced to bench tests. However, testing the oxidation resistance of turbine lubricants has been considerably more challenging.

One of the most widely used tests is the Rotating Pressure Vessel Oxidation Test (RPVOT) formerly known as the Rotating Bomb Oxidation Test (RBOT), ASTM Method D 2272 originally developed by Von Fuchs et al. [1,2].

The Rotating Pressure Vessel Oxidation Test (RPVOT) Laboratory Test

Test Method

For many years the Rotating Pressure Vessel Oxidation Test (RPVOT) has been applied to the need to appraise the oxidation resistance of new turbine lubricants as well as to measure their rate of depreciation in oxidation resistance while in use.

In essence, this test measures the length of time in minutes that the turbine or other lubricant can withstand the attack of pure pressurized oxygen gas at a relatively high temperature of 150°C while in contact with a coil of copper wire ostensibly serving as a catalyst. Correlation of relatively brief test time in ASTM D 2272 to the actual extended service time in the turbine engine has been established.

More specifically, the RPVOT exposes 50 g of the test lubricant and 5 mL of distilled water to an operating pressure of approximately 1240 kPa (180 psi) of pure oxygen gas in a sealed steel container in the presence of a 55.6 g coil of 99.9 % pure copper wire serving as a catalyst. Internal pressure of the steel vessel is continuously recorded. The special form of glass beaker (into which the lubricant, copper coil, and five mL of water are placed) is rotated at 100 r/min until the oxidation resistance of the lubricant reaches its so-called “break point” or reduced by 175 kPa (25.4 psi) at which time the bench test is ended.

During some period of test time (which may extend to several thousand minutes), the oxidation resistance of the test oil is affected by the oxygen. That is, the lubricant chemically reacts with the oxygen to bind the gas molecules into both organic and inorganic oxidation products. In this process some or much of the free oxygen gas responsible for maintaining pressure in the steel vessel is progressively chemically incorporated in these oxidation products. Consequently, the oxygen pressure is reduced and, if the rate of oxidation of the lubricant for some lubricants is rapid, the pressure may rapidly plunge to a fraction of its former value.

Both slow and rapid oxidation response of lubricants are shown in the simulated sketch of Fig. 1. The criterion of lubricant failure is the time in minutes required to reach either the so-called “break point” or to reach the 175 kPa pressure drop specified in ASTM D 2272. Some lubricants may, in replicate tests, show both forms of failure. In some cases, the failure time may be considerably different.

RPVOT Test Equipment Utilizing Oil Baths

Until recently, all RPVOT tests have been conducted using a technique of immersing the steel pressure vessel containing the prepared and loaded sample beaker into bath oil heated to an average temperature of

150°C to obtain the operating temperature of the required for the test. Some of these baths are capable of operating with four pressurized steel vessels simultaneously and may contain more than 75 L (20 gallons) of bath oil.

Under the test protocol, the necessary rotation of the steel pressure vessels at 100 r/min often is done by driving the rotating mechanism through the floor of the bath as shown in ASTM D 2272. Unfortunately, this approach is accompanied by problems of seal leakage and subsequently difficult cleanup and repair.

Moreover, these oils baths are normally kept at operating temperature continuously because of the length of time required to reheat the baths to operating temperature. As a consequence, the often expensive bath oil is oxidizing continuously and must be changed at relatively short intervals (unless the bath oil is silicone requiring special operator exposure control). In addition, the odor problem of oxidizing oil baths usually require these to be kept in hoods making bath oil change more difficult when the oxidized oil becomes too thick for effective circulation of heat and temperature control.

Four RPVOT tests are often started at the same time in some of these larger oil baths and the pressure vessels removed when their individual break points were obtained. However, new tests cannot be started until all four tests are completed since the addition of a new steel vessel upsets the critical constancy of the bath temperature.

Perhaps the greatest ongoing problem with any hot oil-bath dependent equipment is in the more or less frequent handling of the steel vessels and supporting equipment into and out of the hot bath oil and the attendant safety precautions.

These considerations of the limitations of present equipment led the authors and their associates to develop a new, nonliquid bath approach to the RPVOT method and this development is the subject of this paper.

A New "Dry-Bath" Approach to the RPVOT Protocol

Basic Considerations

The limitations of oil bath heating the RPVOT pressure chamber led to the concept of an electrically heated, dry-bath, fixed pressure chamber with magnetic drive of the test sample beaker. This approach permitted other simplifications and advantages which became apparent during development:

1. The stainless steel pressure chamber could be stationary and permanently connected to a source of high pressure oxygen as well as another permanent connection for venting the used gases of oxidation.
2. Instead of rotating the whole pressure vessel, only the sample beaker could be rotated at the appropriate speed with use of a magnetic cup.
3. The instrument could be operated outside of a hood although the reaction gases would have to be released into a hood or other intake.
4. The instrument would be most productive in the laboratory when made as single units having a small footprint. This would permit use of one or several units at a time since single units could be relatively quickly returned to analysis of another sample if desired.
5. The stationary pressure chamber and rotating sample beaker would make it readily possible to directly measure the test oil temperature as well as to sample fluid for other analyses by use of a high pressure sampling port.
6. Clean up of the apparatus after test would be reduced to the sample beaker, magnetic cup, and pressure chamber side wall and bottom.

Transition of the Concept into the Dry-Bath Instrument

As with almost all major changes in instrument design, the rendering of the concept into a practical instrument required considerable time. Recognizing its importance as a basic test method, attention was focused on the RPVOT protocol early in the developmental stage. Early prototype units of the dry-bath instrument—trade named the Quantum—were very helpful in teaching appropriate ways of handling the heating of the pressure chamber and control of heat radiation.

Similarly, use of a magnetic drive from the bottom of the pressure chamber led to several techniques

FIG. 2—*Bench top, dry-bath RPVOT and lid cover.*

for close-coupling the drive magnet and the driven magnet as well as effectively reducing the friction of the rotating cup within the pressure chamber with both the walls and bottom of the chamber. Forcing outside air flow through the interior of the cabinet through vents after test completion was found desirable for quick analytical turnaround.

One of the earlier designs of the electrically heated, dry-bath Quantum instrument is shown in Fig. 2.

Careful consideration was given to the pressures developed in the pressure chamber. Consequently, the pressure chamber was made of stainless steel with relatively thick walls. Other metals such as aluminum were avoided because of their vulnerability to distortion under heat and their response to the highly reactive oxidation conditions within the pressure chamber.

The stainless steel access lid to the high pressure chamber was designed to be easily closed and opened while retaining a complete pressure seal when closed. For this purpose, a specially designed O-ring sealing approach simplified the pressure-resistant closure and, as shown, requires only three finger-tightened nuts threaded onto three bolts protruding through the circular flange of the pressure chamber to completely seal the chamber for operation.

Above the pressure chamber lid are two valves for admitting high pressure oxygen (left) and releasing pressure (right). Below the lid are two electronically programmable control meters—temperature measurement, control, and recording on the left and pressure measurement and recording on the right. On the vertical panel are the main, heat and cup rotation switches accompanied by a warning light indicating when pressure chamber temperatures are low enough to avoid hot water spattering when the lid is removed.

The rear panel of the cabinet has connections for oxygen and vented gas as well as connections for data recording by either strip chart or computer program. Shown to the right of the dry-bath instrument in Fig. 2, is the insulated Teflon cover cap for the pressure chamber lid which is used during test to control heat loss and protect the operator from the hot flange and lid surfaces.

Although, as noted, a strip chart or other recorder can be attached to the dry-bath instrument, it is advantageous to use a special computer program placed on an accompanying laptop computer to track pressure and temperature data which can then be readily converted into spreadsheet programs for further analysis and reporting of the collected data, if desired. The combination of computer and program is capable of recording data from four instruments simultaneously.

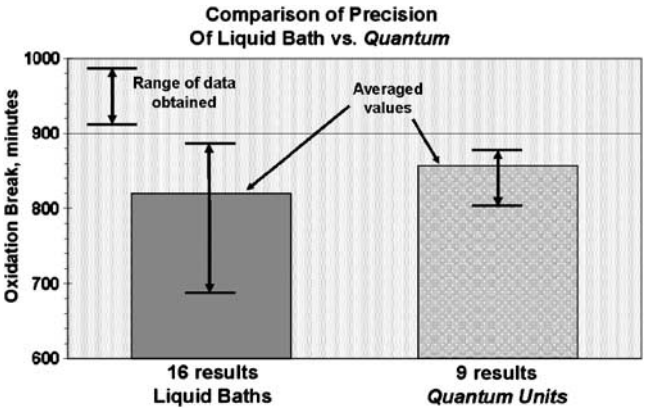

FIG. 3—*Comparative values and precision of oil- and dry-bath heating in the RPVOT protocol.*

Preliminary Experimental Results

Initial Repeatability Studies

Among the first questions of importance when developing a new instrumental approach to a long-standing method are the dual questions of agreement with the older technique and the precision of the newer technique.

For this study, test oil which had previously been used for comparative results in several laboratories was made available through the courtesy of Joseph Franklin, Chairman of the ASTM RPVOT Task Group of Committee D02, Subcommittee 9. Results are shown in Fig. 3.

For this study, data from two earliest prototype dry-bath instruments were used. The multiple runs on these two prototype instruments, as shown in Fig. 3, were obtained by interchange of operators.

In comparison, the oil-bath instrument data in Fig. 3 were obtained by combined multiple data on several instruments in different laboratories manned by different operators. While the comparison shown somewhat favors the dry-bath instrument, the data are not generated in exactly the same way. Thus, the contrast in precision shown in Fig. 3 is between the summed repeatability-reproducibility of the oil-bath data and the semi-reproducibility in the dry-bath units.

However, from the viewpoint of the first question regarding agreement and precision of older liquid-bath and the new dry-bath instruments, the data shown in Fig. 3 gave the following pertinent information:

1. Oil-bath and dry-bath modes of obtaining RPVOT values gave reasonably similar results (the band of values for the dry-bath units fell within the band of data obtained on the oil-bath units.
2. Precision of the prototype dry-bath instruments may be better.

Moreover, as anticipated in the conceptualization of the dry-bath instrument, it was found that return of the instrument to subsequent analyses was relatively rapid, particularly with use of more than one rotating cup.

Observation of Oxidation Exotherms

Unexpected information came to light during early investigations with the dry-bath instrument. Easy access to the rotating sample beaker permitted direct measurement of the sample temperature during a dry-bath RPVOT analysis. In the first experiment conducted using this technique, it was found that the oxidation process produced an evident exotherm of several degrees Celsius during the rapid oxidation step shown in Fig. 1. Moreover, as would be predicted, since the exotherm is a measure of the rate of energy released to the test fluid with oxidation of the fluid ($\Delta H/\Delta t$), the maximum in the exotherm occurs at the maximum of the rate of decreasing pressure change ($-\Delta P/\Delta t$). To assist in visualizing this phenomenon, an idealized re-sketch of the curve of rapid oxidation in Fig. 1 is shown with an accompanying temperature exotherm in Fig. 4.

These exotherms varied in height and breadth depending on the oils analyzed and were repeatable on reanalysis of the same test oil. It is thus evident that these exotherms may have value in identifying and understanding the relationship of type, amount, and effectiveness of oxidation inhibitors in relation to the process of oxidation. The more rapidly the oil oxidizes the more pronounced the exotherms.

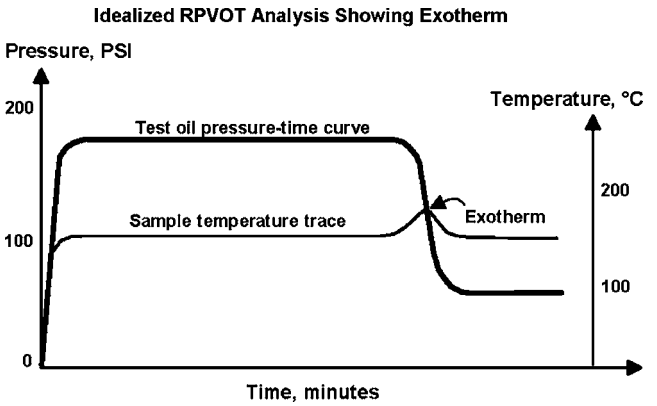

FIG. 4—*Schematic example of appearence of exotherm during analysis of sharply oxidizing oil.*

Analysis of the Process of Oxidation by Sampling During Test

The technique of measuring the sample temperature during RPVOT analysis in the dry-bath instrument led to the further technique of removing small samples of the fluid under test while the analysis was in progress. The authors consider this an important use of the dry-bath technique since the chemistry of oxidation with use of different oxidation inhibitors can be followed closely.

Only a fraction of a milliliter needs to be taken for such information given the sensitivity of today's analytical instruments, such as inductively coupled plasma (ICP) spectrometers, nuclear magnetic resonance (NMR), and Fourier Transform InfraRed (FTIR).

Technique for Sampling Sample During Test—The sampling technique is simple. A long, thin metal hypodermic needle is threaded through the graphite ferrule of a high pressure fitting and a three-way valve connected to the syringe end of the needle. The oxidation test can be performed and very small samples taken periodically and conveniently using this technique.

Figure 5 is a cut-away side view sketch of the pressure chamber of the dry-bath instrument showing this setup for sampling.

Trial Application of Sampling Technique—Fortunately, an opportunity developed to explore this sampling technique concept. During a meeting of the ASTM Committee D02 in June of 2006, a need was expressed during the Subcommittee 9, Section C, to determine whether and to what extent the copper catalyst coil was attacked in the process of catalyzing oxidation by the test oil—particularly when rapid oxidation of the sample was occurring.

This seemed to be an ideal use of the dry-bath instrument. A turbine oil provided for this test was exposed to the RPVOT oxidation conditions in the dry-bath instrument and periodic 0.1 mL samples were

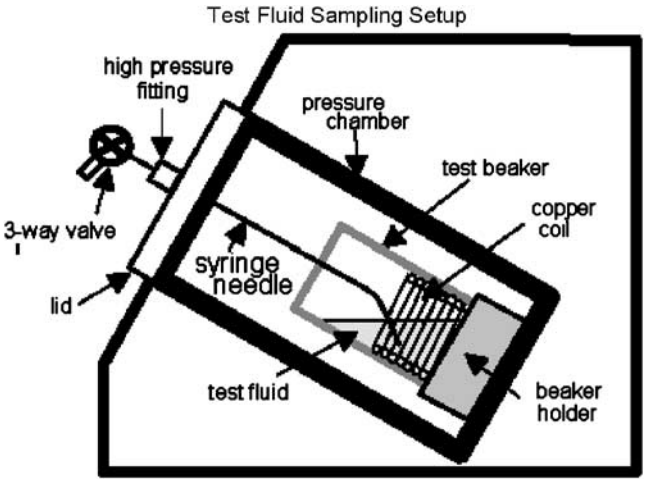

FIG. 5—*Schematic of sampling technique.*

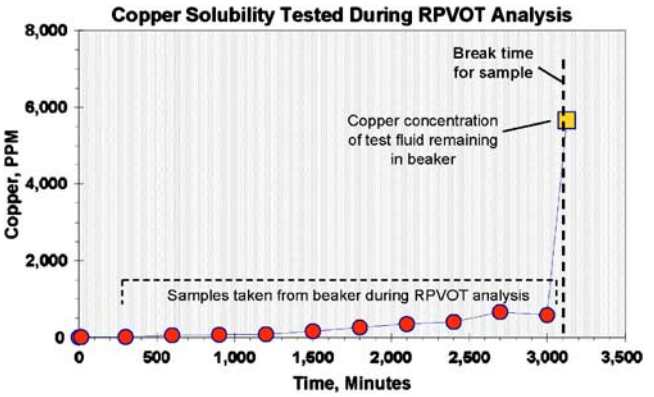

FIG. 6—*Copper dissolution in and RPVOT test protocol on a turbine oil analyzed in the dry-bath instrument.*

taken during the course of the test. These first results in a prototype instrument are shown in Fig. 6.

During the initial portion of the test, copper gradually increased from 6 ppm at 15 min to about 600 ppm in samples taken at 2700 and 3000 min. However, when the turbine oil oxidation break point occurred at just over 3100 min, the copper concentration in the residual fluid in the test beaker was found to be over 5500 ppm—almost ten times the prior sample.

Obviously, rapid attack of the copper catalyst coil occurs when the oxygen is rapidly assimilated into the test oil sample. What progression might occur under the slower oxidation process illustrated in Fig. 1, has not yet been examined but should be interesting.

Discussion

The long standing problems of RPVOT determinations in oil-bath equipment such as bath oxidation, odor, leakage, replacement of oil, and the difficulties of working with hot oil led to the development of a dry-bath instrument. In essentially all respects, the dry-bath instrument protocol was designed to be similar to the oil-bath apparatus regarding exposure of the test sample to the copper-catalyzed oxidation conditions as indicated in the table of Appendix I. However, it was very dissimilar in not having the attendant liquid bath problems previously mentioned, but more so in making simple access to the test fluid possible.

In preliminary studies using a reference oil on which considerable RPVOT data had been collected in liquid baths, two prototype dry-bath instruments have shown reasonable agreement with, and apparently better precision than, data collected on the same fluid in the oil-bath RPVOT equipment of several laboratories. Further work with more modern turbine lubricants is about to begin with production Quantum™ instruments.

It has also been found easier and faster to prepare and load samples in the dry-bath instrument and the elimination of the odiferous bath oil permits hood-free use of the instruments. Venting of the test gas to a hood through plastic tubing or use of a vacuum “snorkel” is a simple approach to the odor of this gas.

The technique of turning the test fluid beaker without turning the pressure chamber has made it possible to use the dry-bath instrument to produce information that, for all practical purposes, cannot be obtained from present oil-bath RPVOT equipment even with tedious and repetitive multiple analyses of a given oil. For example, it has been shown in this paper that by applying the dry-bath instrument, it is possible to follow the process of oxidation by thermal sensors in the fluid being tested or, if desired to sample the fluid for further information of interest.

Conclusions

Preliminary studies with the dry-bath instrument have shown that this approach can produce data that are similar to oil-bath equipment but early data indicate that it may be somewhat more precise.

Of considerable importance, moreover, is the ability to apply the instrument to the observation of the oxidation process through either or both temperature sensors in the test fluid and sampling of the test fluid by direct removal of small samples or conceivably by infrared using glass fiber optical waveguides.

Perhaps equally, or more importantly, is the ability to inject reactants into the test fluid and to observe the consequences.

Essentially, this approach has made the dry-bath instrument a more universal tool for the study of oxidation, nitration, chemical and physical reaction dynamics, and other associated uses in which it is desirable to monitor, alter, and sample, or a combination thereof, the material(s) being investigated.

It is anticipated that the dry-bath technology will produce new understanding of the oxidation processes occurring in the various oleaginous fluids used in lubrication and hydraulics. Moreover, this constant-temperature oxidation technique may have much broader applications in the study of other reactions of interest and importance.

Acknowledgments

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Appendix I

Comparison of Operational Parameters

Operational Parameter	Oil Bath	Dry Bath
Bath Temperature	150 ± 0.5°C	150 ± 0.5°C
Sample Size	50 ± 0.1 g	50 ± 0.1 g
Copper Coil	55.6 ± 0.3 g	55.6 ± 0.3 g
Water in Sample	5 g	5 g
Initial Oxygen Pressure	620 ± 5 kPa (90 ± 1 psi)	620 ± 5 kPa (90 ± 1 psi)
Pressure Recording	Round or Strip Chart Electronic Transmission	Strip Chart or Computer Interfaceand Program
Temperature Recording	Strip Chart or Electronic Transmission	Strip Chart or Computer Interface and Program
End of Test Signal	175 kPa (25 psi) pressure drop or "break point"	175 kPa (25 psi) pressure drop or "break point"

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