

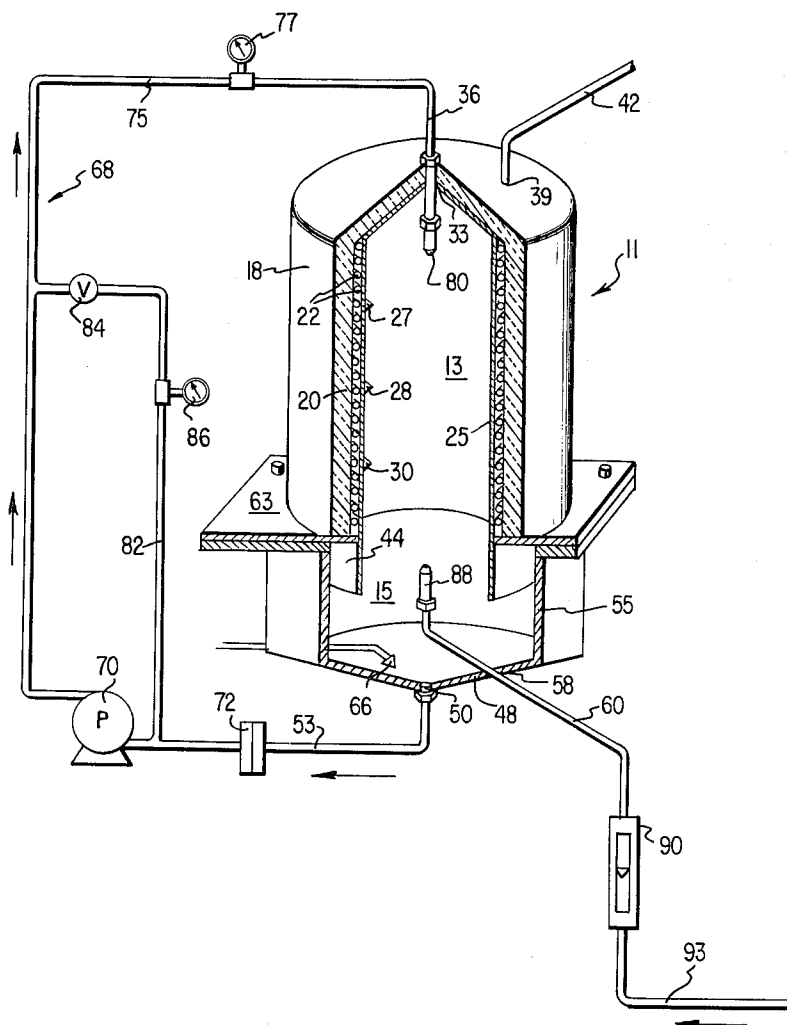
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COKING TEST

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3,248,927 COKING TEST

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This invention relates to a method for testing the coking and certain other properties of a lubricant or other potential coke-forming organic fluid and an apparatus which may be used to perform this method. In this invention the fluid to be tested is exposed as a thin film to the action of a coking gas under high temperature conditions, collected from this coking zone and recycled back to coking. The coking tendencies of the liquid are determined from the amount of coke produced, or the time required for coke to accumulate sufficiently to affect the flow properties of the liquid, or both.

Development of improved lubricants for use in high temperature service, for example at the high temperatures found in jet and jet-prop aircraft engines, has been hampered by lack of test equipment which correlates with the results obtained in the engine. This invention can evaluate fluids of varying quality and has a high degree of correlation with actual engine performance and is especially useful for the evaluation of ester-type lubricants.

In this invention a coking zone is provided wherein the fluid to be tested may be run along a surface as a relatively and substantially uniformly thin film while being exposed to a coking gas containing molecular oxygen, e.g., air, at an elevated temperature, e.g., the temperature of engine performance. The requisite temperature may be imparted to the fluid inside the coking zone or external to it. Preferably the coking zone is provided with heated walls onto which the fluid is sprayed and the fluid moves through the coking zone under the influence of gravity. The coking surface thus provided will be long enough to give the amount of exposure desired per pass through the coking zone. Advantageously, the test fluid is sprayed in a downward direction substantially uniformly against the walls of the coking zone and the air is sprayed upwardly, so that a collection zone for sprayed, partially-coked, fluid may be provided below the coking zone and excess air may be drawn off from above the coking zone.

As mentioned, after a pass through the coking zone, the fluid is collected and recycled back for further exposure to the coking gas. Generally a pump is employed for recycling and the fluid circulation, which may include a coarse filtration stage to prevent pump clogging, can be held constant throughout the test, as also may be the temperature, and the air flow rate.

Apparatus which may be used to perform the process of this invention comprises a coking chamber and a collection chamber, both advantageously being provided in the same vessel and recycle means. Preferably the coking chamber is arranged above the collection chamber and will be provided by an insulated vessel having spray means for the lubricant or other liquid more or less centrally located at its top. The heating means for the liquid sample preferably is provided in the walls of the insulated coking vessel and the spray is advantageously arranged so that substantially all of the liquid sample will impinge evenly on the walls and be heated by indirect heat exchange. The fluid sample spray means preferably is a nozzle which is conically shaped to direct test fluid against the walls of the coking chamber and will generally have a metal screen say, of about 50 to 250 mesh, preferably about 200 mesh. The upper coking vessel

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also will be provided with vent means for exit of the coking gas.

The collection chamber generally will be larger in cross-sectional area than the coking chamber so that partially coked liquid may drip from the walls of the upper chamber into the lower collection chamber. A spray means for coking gas is in the lower chamber, the nozzle being generally above the level of liquid which collects in this chamber. The collection chamber is ideally a sump with a tapered bottom provided with means, for example, a conduit, for removal of partially coked liquid. This conduit is connected by the recycle means, usually a pump, to the liquid spray means in the coking chamber.

The apparatus of this invention is illustrated by, but not necessarily limited to, the device shown in the accompanying drawing which is a more or less schematic view of the system with the coking-collection vessel partly cut away.

In the drawing, 11 represents a vessel in which the coking and collecting functions may be performed. The vessel has the upper or coking section 13 and the lower or collection section 15. The coking section 13 is preferably a closed-top cylinder 18 provided with insulation 20 at the sides and top. The walls also are provided with the heating elements 22 which may be placed between the insulation and the inner liner 25. It has been found that a length of about 10 inches or more, say about 15 inches, is desirable for the liner 25 in order for the fluid sample film, flowing by gravity down the liner, to spend enough time in intimate contact with air to give the most advantageous amount of coking per pass.

The preferred heating elements shown are built-in electric resistance elements but alternatively may be a coil for a heat exchange fluid, etc. The liner walls preferably are provided with top, middle and bottom thermocouples 27, 28 and 30, respectively, conveniently spaced for temperature observation and control. The top of the chamber 13 is provided with a preferably central opening 33 for the test fluid line 36 and with a usually offset opening 39 for a combustion-gas outlet or vent line 42.

As shown in the drawing, the lining 25 may have a lower section 44 which reaches down toward the collection chamber 15. This collection chamber may have the tapered bottom or sump 48 with a central opening 50 for reception of the test fluid exit line 53. The wall 55 of the chamber 15 has the opening 58 for passage of the combustion-gas line 60. Upper chamber 13 may be fixed in its relationship to lower chamber 15 by any convenient means, for example, the bolted flange 63 and the oil sump 15 is also usually provided with a thermocouple 66 for temperature observation and/or control. The test fluid or oil line 68 comprises the exit line 53 which leads to pump 70, which may be a Zenith pump, usually by means of the coarse filter 72. Line 75, which may be provided with pressure gage 77, joins the pump 70 to fluid entry line 36. Line 36 is provided, inside the combustion chamber 13, with the nozzle 80, which, as mentioned, has preferably a conically-shaped fine metal screen. The fuel line 75 is also preferably provided with the relief line 82 containing a relief valve 84 which generally is of the check valve type and a pressure gauge 86. When the nozzle 80 gets clogged with coke and other combustion products, relief line 82 provides for by-passing test fluid back to the pump.

Air entry line 60 leads to air nozzle 88 within the combustion chamber 13. This line may be provided with a flowmeter 90 and any suitable source of air, such as the line 93 leading to an air pump, not shown.

The operation of the apparatus is as follows:

The test fluid sample is placed in the collection chamber 15 below the tip of the nozzle 88. The pump 70 draws fluid from the collection chamber 15 and blows it through the nozzle 80 into the combustion chamber 13. The test fluid is sprayed downward countercurrent to the air spray emanating upwardly from the nozzle 88. Substantially all of the test sample is directed uniformly against the upper portion of the liner 25 and runs down this wall, being heated and exposed to the air in transit. The fluid drips from the lower portion 44 back into the collection chamber 15. The air rate may be held at, for example, 0.5 cubic ft. per hour while oil is pumped at the rate of about 13.5 liters per hour.

A temperature is maintained suitable for simulating the approximate temperature to which the fluid sample will be subjected under actual service conditions, for example, about 200–800° F. or even up at 1000° F. The test temperature is often about 400–600° F. in the case of jet engine lubricants. An off-on cycle for the test apparatus may be established to further simulate service conditions, for example, the apparatus may be operated for 21 hours at 500° F. and then put on a down status for about 3 hours. The operation is repeated, that is, 21 hours running with 3 hours down, until the 200 mesh metal screen plugs with products of oxidation. At this point pressure control equipment, responsive, for example, to gauge 86, may shut down the apparatus. The oil and oxidation products are then removed for analysis.

The method and apparatus of this invention are of special value in the testing of lubricants having as the major component a base oil which is an ester of lubricating viscosity which may be, for instance, a simple ester or compounds having multiple ester groupings such as complex esters, di- or other polyesters, and polymer esters. These esters are usually made from mono- and polyfunctional aliphatic alcohols or alkanols, and aliphatic mono- and polycarboxylic or alkanolic acids. Frequently, the alcohols and acids have about 4 to 12 carbon atoms. The reaction product of a mono-functional alcohol and a monocarboxylic acid is usually considered to be a simple ester. A diester is usually considered to be the reaction product of 1 mole of a dicarboxylic acid, say of 6 to 10 carbon atoms, with 2 moles of a monohydric alcohol or of 1 mole of a glycol, for instance, of 4 to 10 carbon atoms, with two moles of a monocarboxylic acid, e.g., of 4 to 10 carbon atoms. The diesters frequently contain from 20 to 40 carbon atoms.

A complex ester is usually considered to be of the type $X-Y-Z-Y-X$ in which X represents a monoalcohol residue. Y represents a dicarboxylic acid residue and Z represents a glycol residue and the linkages are ester linkages. Those esters, wherein X represents a monoacid residue, Y represents a glycol residue and Z represents a dibasic acid residue are also considered to be complex esters. The complex esters often have 30 to 50 carbon atoms.

Polymer esters or "polyester bright stocks" can be prepared by direct esterification of dicarboxylic acids with glycols in about equimolar quantities. The polyesterification reaction is usually continued until the product has a kinematic viscosity from about 15 to 200 centistokes at 210° F., and preferably 40 to 130 centistokes at 210° F.

Although each of these products in itself is useful as a lubricant, they are particularly useful when added or blended with each other in synthetic lubricant compositions. These esters and blends have been found to be especially adaptable to the conditions to which turbine engines are exposed, since they can be formulated to give a desirable combination of high flash point, low pour point, and high viscosity at elevated temperatures, and need contain no additives which might leave a residue upon volatilization. In addition, many complex esters have shown good stability to shear. Natural esters, such as castor oil may be employed and also be included in

the blends, as may be small amounts of a foam inhibitor such as a methyl silicone polymer, or other additives or lubricant components to provide a particular characteristic. For instance, extreme pressure or load carrying agents, corrosion inhibitors, etc., can be added.

The monohydric alcohols employed in these esters usually contain about 4 to 20 carbon atoms and are generally aliphatic. Preferably the alcohol contains up to about 12 carbon atoms. Useful alkanols include butyl, hexyl, methyl, iso-octyl and dodecyl alcohols, C_{12} oxo alcohols and octadecyl alcohols. C_8 to C_{10} branched chain primary alcohols are frequently used to improve the low temperature viscosity of the finished lubricant composition. Alcohols such as n-decanol, 2-ethylhexanol, "oxo" alcohols, prepared by the reaction of carbon monoxide and hydrogen upon the olefins obtainable from petroleum products such as diisobutylene and C_7 olefins, ether alcohols such as butyl carbitol, tripropylene glycol mono-isopropyl ether, dipropylene glycol mono-isopropyl ether, and products such as "Tergitol 3A3" which has the formula $C_{13}H_{27}O(CH_2CH_2O)_3H$, are suitable alcohols for use to produce the desired lubricant. If the alcohol has no hydrogens on the beta carbon atoms, it is neo-structured; and esters of such alcohols are often preferred. In particular, the neo- C_8 alcohol, 2,2,4-trimethylpentanol-1, gives lubricating diesters or complex esters suitable for blending with diesters to produce lubricants which meet stringent viscosity requirements. Iso-octanol and iso-decanol are alcohol mixtures made by the oxo process from C_3 – C_4 copolymer heptanes. The cut which makes up iso-octanol usually contains about 17% 3,4-dimethylhexanol; 29% 3,5-dimethylhexanol; 25% 4,5-dimethylhexanol; 1.4% 5,5-dimethylhexanol; 16% of a mixture of 3-methylheptanol and 5-ethylheptanol; 2.3% 4-ethylhexanol; 4.3% α -alkyl alkanols and 5% other materials.

Generally, the glycols contain from about 4 to 12 carbon atoms; however, if desired they could contain a greater number. Among the specific glycols which can be employed are 2-ethyl-1,3-hexanediol, 2-propyl-3,3-heptanediol, 2-methyl-1,3-pentanediol, 2-butyl-1,3-butanediol, 2,4-diphenyl-1,3-butanediol and 2,4-dimesityl-1,3-butanediol. In addition to these glycols, ether glycols may be used, for instance, where the alkylene radical contains 2 to 4 carbon atoms such as diethylene glycol, dipropylene glycol and ether glycols up to 1000 to 2000 molecular weight. The most popular glycols for the manufacture of ester lubricants appear to be polypropylene glycols having a molecular weight of about 100–300 and 2-ethyl hexanediol. The 2,2-dimethyl glycols, such as neopentyl glycol have been shown to impart heat stability to the final blends. Minor amounts of other glycols or other materials can be present as long as the desired properties of the product are not unduly deleteriously affected.

One group of useful monocarboxylic acids includes those of 8 to 18 or even 24 carbon atoms such as stearic, lauric, etc. The carboxylic acids employed in making ester lubricants will often contain from about 4 to 12 carbon atoms. Suitable acids are described in U.S. Patent No. 2,575,195, and include the aliphatic dibasic acids of branched or straight chain structures which are saturated or unsaturated. The preferred acids are the saturated aliphatic carboxylic acids containing not more than about 12 carbon atoms, and mixtures of these acids. Such acids include succinic, adipic, suberic, azelaic, and sebacic acids and "isosebacic" acid which is a mixture of α -ethyl suberic acid, α,α' -diethyl adipic acid and sebacic acid. This composite of acids is attractive from the viewpoint of economy and availability since it is made from petroleum hydrocarbons rather than the natural oils and fats which are used in the manufacture of many other dicarboxylic acids, which natural oils and fats are frequently in short supply. The preferred dibasic acids are sebacic and azelaic or mixtures thereof. Minor amounts

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of adipic used with a major amount of sebacic may also be used with advantage.

The following examples of tests run according to the process of this invention also are illustrative and not limiting. In Table I, below, results are given for tests performed on two jet engine synthetic ester lubricants using a conventional oxidation test rig. Sample 44 is a di-2-ethyl-hexyl sebacate based lubricant fluid having a viscosity of about 7.5 cs. at 210° F. and containing a polymethacrylate V.I. improver and other additives in minor amounts to retard oxidation and give extreme pressure characteristics.

TABLE I

Sample No.	44	34
Test Conditions:		
Wall Temp. at Point of Fluid Contact, ° F.	500	500
Air Rate, liters per hour	14.2	14.2
Fluid Rate (approx.), liters per hr.	13.5	13.5
Average Sump Temperature, ° F.	265	257
Test Duration, hours	59	59
Test Results: Wt. of Coke Formed, gms.	16	64
Used Oil Properties:		
Acid No. (pH 11)	0.31	0.11
KV at 210° F., cs.	3.610	5.329

It will be noted that in this conventional test, sample 44 lubricant had much better oxidation resistance. In actual service performance, however, sample 44 lubricant was found to give about three times as much coke as the sample 34 type lubricant, showing that the conventional test was of questionable value.

Table II, below, shows the results of testing samples 44 and 34 by the method of this invention and in the apparatus above described. In Table II, also, tests upon other synthetic-ester type lubricants (samples 29 and 64), are reported.

TABLE II

Run No.	1	2	3	4	5	6
Sample	44	44	34	29	64	34
Fresh Oil Properties:						
KV (cs.) 100° F.	34.88	34.88	38.05	39.41	39.31	38.05
Acid No. (pH 11)	0.14	0.14	0.14	0.28	0.34	0.14
Test Conditions, Liner Temp. (° F.):						
Top:						
Av.	500	500	500	500	500	500
Max.	500	505	505	505	505	505
Middle:						
Av.	400	400	410	385	380	360
Max.	410	410	415	390	390	370
Bottom:						
Av.	365	370	360	355	355	360
Max.	370	375	365	360	365	370
Collection Chamber Temp. (° F.):						
Av.	360	355	355	350	350	330
Max.	360	365	360	355	360	335
Air flow rate (liters/hr.)	14.2	14.2	14.2	14.2	14.2	14.2
Average pump pressure (p.s.i.)	100	100	110	100	100	100
Total test time (hrs.)	48	40½	120	159	168	144
Nozzle plugged	Yes	Yes	Yes	No	No	No
Wall deposits:						
Upper (coke)	(¹)	(¹)	Hard	Flaky	Flaky	Flaky
Lower (varnish)	100%	100%	Light	Light	Light	Light
Filter deposit (gms.)	.0541	.0461	.0577	.0278	.0249	.0170
Nozzle deposits (gms.)	20	10	6.5	14.5	12.0	9.0
Used Oil Properties:						
KV (cs.) 100° F.	23.89	23.48	49.39	49.89	53.06	37.86
Acid No.	0.27	0.29	18.9	16.7	15.7	6.84

¹ Thick/grainy.

As is clear from the data of Table II, the method of this invention, using the preferred apparatus, gives an indication of the coking propensities of samples 44 and 34 which is in far greater accord with the service performance of these lubricant fluids than the previously used test method, the results of which are given in Table I.

It is claimed:

1. A method for testing the coking tendencies of an

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organic fluid at an elevated temperature sufficient to give coking of the fluid which consists essentially of flowing the fluid at said elevated temperature along a surface as a relatively thin film flowing a molecular oxygen-containing coking gas countercurrent to said film thereby exposing the fluid to said molecular oxygen-containing coking gas, recycling exposed fluid back to said surface, continuing said flowing and recycling for a period of time and measuring the coke in the product.

2. The method of claim 1 in which the said surface is heated to said elevated temperature.

3. The method of claim 2 in which the fluid flows under the influence of gravity.

4. The method of claim 3 in which flow is achieved by spraying the fluid against a vertically arranged surface.

5. The method of claim 4 in which fluid is sprayed downwardly against said surface.

6. The method of claim 1 in which the recycling is continued until an accumulation of coke in the product interferes with the spraying.

7. The method of claim 1 in which recycle is continued for a predetermined period of time.

8. The method of claim 1 in which the oxygen-containing gas is air.

9. The method of claim 1 in which the fluid is a lubricant.

10. A method for testing the coking tendencies of an ester-based lubricant fluid which consists essentially of spraying the fluid substantially uniformly against a vertically-arranged surface held at a temperature approximating the service temperature to which the lubricant will be exposed in use and sufficient to give coking of the fluid, allowing the lubricant fluid to flow downwardly along the surface while exposed to air which is sprayed upwardly along said surface, collecting the partially coked lubricant in a collection zone beneath the said surface and recycling collected lubricant to spraying, continuing the

spraying and recycling for a period of time sufficient to simulate a period of actual use and measuring the amount of coke in said partially coked lubricant.

11. The method of claim 10 in which the temperature is about 400 to 600° F.

12. An apparatus for producing coke in an organic liquid which comprises a vessel having an insulated upper chamber provided with heating means, a vertically-arranged cylindrical inner surface, means for spraying liquid

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substantially uniformly against the upper portion of said surface and means for removal of coking gas, a lower collection chamber provided with means for spraying coking gas upwardly into said upper chamber and means for removal of partially coked liquid, and recycle means connecting said removal means with said liquid spray means.

13. The apparatus of claim 12 in which the liquid spray means comprises a nozzle having a metal screen.

14. The apparatus of claim 13 in which said nozzle is conical.

15. The apparatus of claim 13 in which said recycle means includes a by-pass liquid circuit.

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16. The apparatus of claim 12 in which said recycle means is provided with a pump and a filter means to prevent pump clogging.

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