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Report

on

A New Method for the Study of the Oxidation
Stability and Corrosiveness of Lubricating Oils

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ABSTRACT

The new method of analysis of oils for the presence of polar compounds has been described in NRL Reports Nos. P-1595, P-1621, and P-1640. Because the spreading oil drop method is very sensitive to the presence of organic acids, is rapid in operation, and requires only one drop of oil for a test, it is especially well suited for the testing of the heat, light, and oxidation stabilities of oils. This is the first report on results obtained by this method on the oxidation stability of typical lubricating oils, two highly refined white oils, and Dupont Cetane, the standard for rating diesel fuels.

It was found that the earliest products of the oxidation of the oil are volatile compounds. These were found to be low molecular weight polar molecules such as ketones, alcohols and acids. Later in the course of the oxidation process, higher molecular weight non-volatile polar compounds are formed. The time of commencement of the production of these compounds is sharply defined and is shown to be the same as the "induction period" or "induction time" so familiar in oil and gas analysis. From then on, the amount of high molecular weight compounds produced increases with great rapidity. In fact, a graph of the logarithm of the total amount of high molecular weight polar compounds vs. the time of oxidation is found to be a straight line. When the oxidation has progressed considerably, oil insoluble substances begin to form. This point is reasonably well defined by a sharp kink in the above described graph and by the onset of hole formation in the oil films when spreading on water.

The most significant results of these tests on oil oxidation are:

1. The formation of volatile polar substances due to cracking is shown to occur considerably earlier than the induction period.
2. The early volatile products include highly corrosive organic acids. The importance is shown of providing a good "breather" system in minimizing engine corrosion and in increasing the induction period of the oil.
3. The induction period and the point of formation of insolubles are each readily and conveniently determined by this new method.
4. The mathematical relation between rate of formation of polar compounds and time of oxidation is shown to be a simple exponential function. This permits calculation of the energy of activation of the oxidation reaction -- a result of value in studying stabilities of pure hydrocarbons.

5. The cause of the corrosive action on metals of short chain acids and of the protective action of long chain acids are outlined.
6. The cause of engine corrosion in the case of new engines operating on new oil, and the avoidance of such corrosion in breaking-in engines on oxidized used oil, or oils with especially selected additives are readily understood in terms of the results obtained.
7. The spreading oil drop method is suggested as a standard Naval test for qualitative detection of acids and polar substances in lubricating and fuel oils.

INTRODUCTION

(a) Authorization

1. This project was authorized by a Bureau of Ships Project 1121/42.

(b) Statement of Problem

2. The thermal stability of lubricating oils in internal combustion engines is of fundamental importance in the development and selection of lubricants, and hence, is of concern to the Navy. This is the first report of an investigation of the thermal stability of lubricating oils and the study of the products of their oxidation.

(c) Known Facts Bearing on the Problem

3. Mineral lubricating oils, when used in internal combustion engines and turbines, do not long remain in their original condition but become contaminated by the oxidation products of the lubricant, as well as those of the fuel and extraneous materials. These contaminants may influence the stability of the lubricant under service conditions. This first report is solely concerned with the oxidation of the oil, and no attempt is made to describe any catalytic effects of extraneous materials.

4. Hydrocarbons heated in contact with air oxidize to form more chemically reactive polar compounds which are often objectionable. Some products are active acids and cause corrosion of metal parts, especially the bearings. Others are good emulsifying agents which stabilize emulsions of the oil with water. Such emulsions may hold particles of carbon and metal in suspension with subsequent abrasion of the bearing surfaces and are sometimes so viscous as to cause the clogging of oil passages. Other polar materials may react with each other to form polymers which settle out of the oil as gums or resins, forming at least part of the so-called "lacquer" found coating the surfaces of an engine.

5. Lubricants differ markedly in their relative abilities to resist oxidation, that is, in their stabilities. It is well known that white oils are less stable than ordinary lubricating oils, and that, in general, over-refining tends to reduce the oxidation stability. The accepted conclusion is that over-refining removes something from the oil which is used to protect it from rapid oxidation. However, little is known of the nature and the mode of action of such oxidation "inhibitors" or "stabilizers". It has been suggested frequently that these inhibitors may act as negative catalysts retarding the oxidation of the oil, or they may be preferentially oxidized instead of the oil. Of course, the oxidation products of the inhibitors must be less objectionable than that of the oil or they are valueless.

(d) Theoretical considerations

6. The hydrocarbon molecules in oil are often complicated in structure and all the possible structures to be found in a given oil sample are not known. They are believed (references 1 to 6) to consist of systems of condensed rings, the 5 and 6 membered rings being most probable. These ring systems show various degrees of condensation and unsaturation. Aliphatic side chains varying in number, length, and branching are common.

7. The oxidation of these hydrocarbon molecules can result in any of the following products: alcohols, aldehydes, ketones, acids, and peroxides. It is possible that compounds containing two or more polar groups may be formed. The presence of unsaturated bonds will increase the rate of oxidation. The oxidation of the cyclic nucleus itself is less probable than that of its side chains. Larsen (7) found that aromatic nuclei were more stable to oxidation than the naphthenic. It is also possible for the oxygenated products to react with each other to form new products. For example, aldehydes may polymerize to form high molecular weight oil-insoluble compounds. Such compounds or resins are probably one source of lacquer. Also, acids and alcohols can condense to form esters which (8) may be in the monomeric or polycondensed form, depending upon the reactants and conditions.

8. NRL Reports Nos. F-1595, F-1621 and P-1640 have shown that the study of the spreading of oil drops on water is a highly sensitive means of measuring the amount and nature of the polar materials in the oil. This spreading is proportional to the amount of polar material present. It was found possible to differentiate acids from other polar groups which are not ionized by the difference in spreading on acid and alkaline water. The acids are ionized on alkaline water, and thus all the molecules are adsorbed at the oil-water interface. On acid water the ionization is repressed, and hence only part of the acid molecules are adsorbed at the oil-water interface.

9. When the solubility in the oil of any polar material is exceeded, holes are formed in the spreading oil disc due to the arrival at the oil-water interface of particles of undissolved material. The time required for the holes to form, and the total number of holes, give a qualitative indication of the size and number of particles of undissolved material in the oil. As such insoluble material will in time settle out as a sludge or lacquer, this highly sensitive test can be used to determine when such insoluble materials are first formed during the oxidation of the oil.

10. Short-chain polar materials, that is, compounds containing less than ten carbon atoms in the molecular chain, cause the oil drop to skate around over the surface of the water. This skating motion is due to "edge-diffusion" or the two-dimensional leakage or escaping of the polar molecules from the rim of the drop to the water. Small quantities of short-chain polar molecules can be detected by putting the oil drop on a tray which has been covered by a film of grease-free talc or sulfur powder. The escaping molecules push the layer of powder particles away from the disc forming a circular ring. As the length of the carbon chain increases, there is a gradual transition from the phenomenon of edge diffusion to that of

spreading. At a chain length of twelve carbon atoms, the spreading effect is the more pronounced.

(e) Narrative of the Original Work Done at this Laboratory

11. The oils tested were oxidized by bubbling clean air through each at various temperatures, and the progress of the oxidation reaction was followed by spreading the drops upon a tray of acid and one of alkaline water. The amount of non-volatile polar material formed, being proportioned to the spreading of the drop, was obtained by measuring the maximum diameter of spreading.

METHODS

(a) Apparatus

12. The oil was oxidized in pyrex glass cells of two sizes, 100 ml. and 33 ml. capacities. These cells are described in Plate 4. The larger cell was used in a liquid bath, thermostatically controlled to $+ 0.05^{\circ}$ C. Because of the danger of contamination of the oil sample by the vapors from any available liquid bath when operated at temperatures above 100° C. a solid metal cylinder of duralumin was used instead. This was electrically heated and thermostatically controlled to $+ 0.1^{\circ}$ C. The smaller pyrex cell closely fitted a hole in the block.

13. The necessary air was supplied to the cells by a small diaphragm pump. This air was first filtered through cotton to remove dust, then dried in a calcium chloride tower, and next run through a combustion furnace to oxidize any organic material and carbon monoxide which was present. The resultant carbon dioxide and water were removed by suitable adsorbers and the air again filtered through cotton. Therefore, the air used for the oxidation of the oil was essentially oxygen and nitrogen, the oxygen content of which was 23% by weight or 21% by volume. The air flow was determined by calibrated orifice-type flow meters. The effluent gas from each cell was carried by pyrex glass tubing drawn down to a fine tip into the bottom of a test tube containing 25 ml. of water. A stream of the purified air was similarly run through water at the same rate thus serving as a "blank" or check run. The pH of the water is a measure of the volatile acids formed in the oxidation cell.

(b) Materials

14. The samples marked with the asterisk (Table 1) were obtained at this Laboratory from opened containers. The "Crystal" petrolatum is a low viscosity white oil manufactured by L. Sonneborn, Sons, Inc. (see report NRL 1595) while the "Squibbs" petrolatum is a higher viscosity medicinal white oil of excellent quality. Because the sample of Texaco #2190 oil spread some when first tested, it was cleaned by contacting with clay, filtered through paper, and finally through a Norton Company alundum thimble, RA 84 whose porosity is such that it retains particles of 0.1 micron or larger. These thimbles were treated as described by Bulkley (9) as they are alkaline after firing. The filtered oil was stored in clean glass bottles in the dark. The cetane was used as obtained from the Dupont

Company. It had a slightly yellow color and a very faint odor. It is used as primary standard for the determination of cetane numbers of diesel fuels.

15. Although the newly cleaned oil did not spread on water indicating its freedom from polar molecules, it did not stay in this condition, for when tested three months later it spread on alkaline water and this spreading increased with time of storage. Therefore, some breakdown during storage had occurred. When the Gulf Pride SAE 30 oil was removed from the sealed container, it did not spread on water. It was also stored in a clean glass bottle in the dark. Yet this oil also began to exhibit spreading properties during storage. As great care was taken in cleaning the storage bottles, it is concluded that the spreading observed was caused by oxidation or deterioration at room temperature and not by contamination. After it was found that the stored Gulf Pride SAE 30 oil had developed polar material, a new sample was purchased for tests. A drop of this sample spread completely over the trays demonstrating that the oil manufacturer had recently begun to add polar material to the oil.

(c) Experimental

16. The oxidation runs at 75° C and 100° C were made using the large cell except on Dupont cetane. The small cell was used for all runs at 125° C and 150° C. Small samples of oil were removed at intervals, generally every hour, and tested on the water contained in glass hydrophil trays, one solution being alkaline (sodium hydroxide at a pH of 12 or greater), and the other acid (hydrochloric acid at a pH of 3 or less). The amount of spreading, edge diffusion, and hole formation were observed for each sample.

17. The area of spreading was computed from the diameter of the disc of spread oil. To get the results of spreading on a comparable basis, the area of the spread drop was determined per unit mass ($\frac{\pi r^2}{m}$). After the oxidation had reached the point that the spreading of the drop became too great for convenient measurement of the area, it was necessary to dilute the drop with the original oil and determine the spreading of the diluted drop.

18. The amount of acid polar material in the oil was calculated from the spreading area on alkaline water. As all the long-chain acids when adsorbed at the oil-water interface on alkaline water occupy a molecular cross-sectional area of approximately 100×10^{-16} sq. cm., the area of the drop in sq. cm. divided by 100×10^{-16} is, therefore, the number of molecules of acid present. The number of molecules divided by 6.06×10^{23} times the gram molecular weight of the acid is the weight of the acid in the drop. From the weight of the drop the weight concentration can be calculated. As the molecular weights of the acids formed in a commercial oil are not known, the weight concentration given here, Table 1, has been calculated in terms of the stearic acid molecule; that is, the weight is calculated on the assumption that the molecular weight is the same as that of stearic acid.

19. The pH of the water was determined frequently during the run using a Beckman pH meter.

20. At the end of the daily run the cells were removed from the bath and covered to keep out the light. The run was resumed the next day. This procedure was followed until the test was completed.

DISCUSSION OF RESULTS

(a) Volatile Polar Materials and Corrosive Acids

21. All samples showed edge loss after the first hour of oxidation except the Crystal and Squibbs petrolatums at 75° C. As it was conceivable that this edge loss could be due to the evaporation of short chain hydrocarbons from the cracking of the oil, a check was made with a hydrocarbon, hexane, dissolved in Crystal petrolatum. The spreading on water of solutions of this material in weight concentrations up to 8×10^{-3} were tested, and no evidence of edge loss could be detected. Samples of normal valeric, isovaleric, and isobutyric acids showed edge loss when present at a weight concentration of 2×10^{-4} . Acetic acid solutions required roughly twice this concentration before edge loss could be detected. Concentrations of the same magnitude as that of the hexane solution, i.e., 8×10^{-3} , of normal valeric or isovaleric acid caused spreading and edge loss to such an extent that the drop seemed to explode when placed on water. No tests were made on the short chain alcohols as the similarity of their spreading behavior to that of the corresponding acids has been shown in NRL Report No. P-1595. Thus, it is evident that the edge loss observed in the oxidation of the oils was due to polar compounds produced and not to hydrocarbon fragments from cracking.

22. The short-chain polar substances produced are quite volatile at room temperature for it was found that the rate of edge loss of any given sample diminished in intensity with the length of time between sampling and testing.

23. As the volatile material causing edge loss is polar, it was considered probable that some would be acid. Furthermore, such short-chain acids would be expected to be fairly strong. Any organic acid formed by the oxidation of an oil molecule is a weak electrolyte whose strength in aqueous solution is proportional to its hydrogen ion concentration. Thus, a determination of the pH of an aqueous solution of these volatile products should be a measure of the strength or corrosiveness of the acids formed. Of course, such a determination is not a measure of the total acidity, but of the effective hydrogen ion concentration. The pH of pure water is 7.0 while when saturated with carbon dioxide, it drops to 5.7. Hence, in these experiments only those pH determinations resulting in values of less than 5.7 can be considered as demonstrating the presence of organic acids. It was found that the pH of the blank rose from 5.7 to approximately 7. This was due to displacing the dissolved carbon dioxide by the oxygen and nitrogen of the purified air. It was very difficult to get consistent results on the blank due to the redissolving of the carbon dioxide from the air during the pH determinations; however, the values ranged from 6.5 to 7.

24. From Table 2 it is seen that no acids were formed from Crystal petrolatum when oxidized at 100° C during the first 14 hours. Neither were any formed by the Dupont cetane at 100° C during the first 46 hours, Table 3. Thus, the polar material formed during the first stages of the oxidation of these oils is non-acidic, probably consisting of alcohols, aldehydes, or ketones. The Crystal petrolatum and Dupont cetane when oxidized at higher temperatures formed acids during the first day. The Texaco 2135, Texaco 2190, and Gulf Fride AM 30, when oxidized at 100° C, showed the formation of acids during the first day, Table 4.

25. The amount of acids formed increases with the temperature for the oils studied. From Tables 2 and 3 it appears that the pH of the aqueous solution more or less approaches a steady state. This effect is probably due to the solubility and volatility of the acids in water at room temperature. The three lubricating oils formed short-chain acids before the petrolatums, but the strength of the acids was not as great. Of the materials studied, Dupont cetane is the most resistant to the formation short-chain acids.

26. It is well known that the metal parts of engines, especially the bearings, are pitted and corroded by the acids formed in the oxidation of oils. This corrosive action has also been noted in turbines (10) and (11), particularly in the installation of new ones. The results of Dantsizen (11) would indicate that the lower molecular weight acids were the rust producers. Under the conditions of his experiments he found that complete corrosion protection was afforded to iron in the presence of water by hexanoic acid and all acids of greater chain length. Alloy bearings, however, are probably much more readily corroded by acids than iron and may be attacked by acids of longer chain length than hexanoic.

27. The corrosion in engines and turbines due to the oxidation of the oil involves two principal mechanisms:

A. Corrosion of metal parts not ordinarily covered by oil.

This type of corrosion obviously is due to volatile acids. The early formation of short chain acids in the course of the oxidation of lubricating oils having been demonstrated here, it is now evident where and why these troublesome corrosive effects originate. If water or water vapor is present, due to the dissociation of these acids, the corrosion and pitting effects will be greater. Evidently, the concentration of these volatile acids can be reduced by a suitably designed breathing or ventilating system.

B. The corrosion of metal parts covered by oil.

The acids dissolved in the oil are responsible for this type of corrosion. The concentration of the volatile acids dissolved in the oil will also be reduced if the engine has an adequate breathing or ventilating system. These dissolved acids will migrate to the metal-oil interface. The rate of migration of the acids will depend upon the

viscosity of the medium and the chain length and configuration of the acid, the shorter chain acids migrating at the greater rate. When the acid molecules reached the metal-oil interface, they will orientate so that the hydrocarbon portion is in the oil and the carboxyl group on the metal. The reaction of the acids with the metal to form soaps will vary with the strength of the acid and the degree of ionization. It is well known that the shorter chain acids are stronger; hence, their rates of reaction will be greater. The resulting soaps may dissolve in the oil, depending upon the solubility, or be worn off through friction and washed away by the oil stream. Thus, the reaction of acids and metal can continue with the resultant accumulative pitting and corrosion. On the other hand, the longer-chain acids will migrate to the metal interface at a slower rate. Their rates of reaction with the metal to form soaps will be somewhat slower since the strength of such acids decreases as the chain length increases. Finally, they will be worn off and washed away much less readily because they form much better thin film lubricants.

C. Protection from Corrosion

The long-chain acids will also orient at the metal-oil interface but will be more permanently adsorbed due to the effect of van der Waals forces acting to form cross linkages between adjacent hydrocarbon chains. The hydrocarbon portions of the molecules being hydrophobic and closed-packed will serve to protect the metal surface from further contact with either water or other acid molecules. Thus, a protective coating of oriented acid molecules will be formed whose permeability may be considered roughly proportional to the chain length for any homologous series.

(b) Spreading Tests

28. The graph obtained by plotting on semi-log paper the spreading area per unit mass (πr^2) against the time of oxidation is of considerable interest (see plates 1, 2 and 3). The differences in the spreading on acid and alkaline water are due to the effect of pH or adsorption of fatty acids. The early portion is always a straight line, that is, the reaction is at first in accordance with the exponential law. It is well known that unimolecular reactions and bimolecular reactions in which one constituent is present greatly in excess obey such a law. As the oxidation progresses, the curve deviates at an accelerating rate from its original linear course suggesting that the nature of the reaction is becoming more complex. This would be expected since side reactions such as polymerization, esterification, and fission of the chain become more probable as the concentration of the polar oxidation products increase.

29. It was noticed that holes first began to form in the oil film approximately at that point in the oxidation-time curve where deviation from linearity occurred. Hole formations in the film are due to the arrival of insoluble materials at the oil-water interface. Since this insoluble material is developed during the oxidation of the oil, it must be either an insoluble oxidation product or a polymerized material formed by the reaction of the soluble oxidation products with each other or the

point where the solubility limit has been exceeded. Further work is in progress on the study of polar and non-polar polymers and resins on the spreading of oil on water. The time for first formation of insolubles is given for each oil in Table 5.

30. The induction period as determined by the time of first spreading on alkaline water was less at 100° C for the lubricating oils than any of the other oils studied. However, once started, the oxidation of these oils proceeded at a slower rate than for the petrolatums or cetane. The curves also bent over earlier and tended to flatten out. This suggests the presence of an oxidation inhibitor in the lubricating oils. As the unoxidized Texaco 2135 and Gulf Pride SAE 30 oils did not spread, and the Texaco 2190 oil showed only a slight spreading, it is possible that the inhibitor is a component of the crude oil and not an additive. Larsen (7) believes that the auto-retardation of the oxidation of lubricating oils is due to the presence of aromatics which are oxidized to form inhibitors. The rate of the oxidation reaction is influenced by the formation of these inhibitors. The petrolatums, which are highly refined oils with a very low aromatic content, show little evidence of any inhibitory action. This is also true of the commercial cetane. The induction period of the various oils at the three temperatures studied are given in Table 5.

31. A preliminary oxidation test on Texaco 2135 oil at 125° C resulted in a very erratic curve. A second test was made in which a portion of the sample was tested immediately and the remainder not tested until after storage in the dark at room temperature for 11 days. The difference in spreading are shown in Plate 3. It was also found that the oxidation continued overnight when the cell was removed from the bath, the gain in spreading being equivalent to 2 1/2 hours oxidation at 125° C.

32. Because of these differences in spreading of the Texaco 2135 oil on standing, a similar test was made on Crystal petrolatum. No difference in the spreading of this oil on standing could be detected.

33. Often the drops of oxidized oil spread to a maximum and then began to shrink slowly. This shrinking could have been only in small part due to the solubility of the polar material in the water. The interfacial films were plastic or very viscous as evidenced by the fact that it took some time for the fragments to assume a circular shape, when the disc was cut with a clean platinum wire. This shrinkage may be due to a reaction taking place in the film at the oil-water interface. When the drop was spread the polar material migrated to the interface thus increasing the effective concentration of the reactants. The orientation of the polar groups at the interface also increased the probability of a reaction. The reaction taking place between the polar groups caused a film condensation by reducing the total number of polar molecules of the reactants.

34. An oxidation test was made at 100° C on Crystal Petrolatum containing a weight concentration of 2×10^{-3} of hexanoic acid (see Table 2). An acid of this chain length in the unoxidized petrolatum caused only edge diffusion when present in such concentration. The induction period of the Crystal petrolatum containing hexanoic acid was then found to be 6 hours, whereas that of the pure petrolatum was 17 hours. It is seen in Plate 1 that the two curves are practically parallel, therefore, the speed of the

latter stage of the oxidation reaction is approximately the same. Apparently, the presence of the short-chain acid acted as an accelerator of the oxidation by reducing the induction period. The extension of this conclusion to the catalytic influence of other short-chain acids is obvious. Clearly the induction period of an oil will be less in an engine not provided with a good "breather" system to keep down the concentration of volatile acids generated, in the oil system.

35. Tests were made using a cell equipped with a condenser maintained at 0° C in order to determine the effect of the condensation of the volatile products on the induction period and speed of reaction (see Table 2). No differences were found. However, the cell having been opened frequently for sampling purposes, the volatile acids may have escaped, thus preventing the concentration of these products from building up sufficiently to influence the reaction.

36. Duplicate determinations resulted in induction periods which agreed to within + 1 hour for an induction period of 28 hours. The oxidation was independent of the rate of air flow over the range of 20 to 100 ml. per minute. Raising the temperature of oxidation greatly reduced the induction period and increased the speed of oxidation reaction, see Table 4.

CONCLUSIONS AND RECOMMENDATIONS

(a) Facts Established

37. The induction period as determined by the formation of volatile polar materials took place within the first hour of oxidation, at temperatures of 100° C or higher, for all samples investigated.

38. Corrosive acids are one of the constituents of the volatile material. The amount generated varies with the nature of the oil tested.

39. The induction period as determined by the time required to get the first spreading of the drop occurs considerably later, depending upon the nature of the oil. This induction period agrees approximately with that found by other oxidation stability tests.

40. It is concluded that the excessive corrosion noted in new installations is due to the formation of short-chain acids in the first stages of the oxidation of the oil.

41. The speed of the oxidation reaction is less for the lubricating oils than the petrolatums or cetane. It is believed that this is due to the oxidation of certain non-polar molecules in the oil which serve to form inhibitors.

42. The first formation in the oil of insoluble oxidation products can be determined by the commencement of hole formation in the films. This is a test of great sensitivity.

43. After exposure to heat the oxidation and the reaction of the oxidation products can continue even at room temperature.

44. Short-chain acids accelerate the oxidation of the oil examined by reducing its induction period, but do not accelerate the rate of oxidation.

45. Reactions are believed to take place at the oil-water interface. This is due to the orientation of the polar groups so that the chance of interaction is greater than in their random distribution in the oil. The formation of lacquer or varnish at the oil-metal interface and the metal-air interface above the oil level in engines may be due, at least in part, to such reactions resulting from the adsorption of orientated and hence activated polar molecules.

(b) Recommendations

46. It is proposed that this technique be extended to the study of the oxidation of certain main types of pure hydrocarbons. A report on the oxidation of highly purified cetane is in preparation. As oil is a mixture of many different kinds of molecules, it is at present impossible to determine which components of the oil contribute the properties of oxidation stability and instability.

47. The investigation should be extended to known mixtures of pure hydrocarbons.

48. The effect of catalysts in accelerating and in inhibiting oxidation needs investigation and the general technique described here would appear to be especially suitable.

49. Further studies should be made of the effect of polymers on oil spreading in order to permit the use of the spreading drop method as a means of testing oils for their varnish and sludge forming tendencies.

50. An oxidation consumption technique should be developed suitable for measuring the oxidation stabilities of oils containing polar additives.

51. The spreading oil drop method should be adopted as a sensitive and reliable test for the presence of acids and polar additives in lubricating and fuel oils purchased for Naval use.

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TABLE I

RESULTS OF TESTS ON OIL SAMPLES AS RECEIVED

Oil Tested	Spreading Behavior		Conclusion
	On Acid Water	On Alkaline Water	
Crystal Petrolatum	none	none	no polar material present
Squibb Petrolatum	none	none	no polar material present
*Texaco 2135	none	none	no polar material present
Dupont Cetane	none	none	No polar material present
*Texaco 2190 5-16-41	None	none	No polar material present
Texaco 2190 8-28-41	slight	1.9 cm	6.6×10^{-6} wt. conc. of acid
Texaco 2190 11-6-41	9.3 cm	10.6 cm	2.0×10^{-4} " "
Gulf Pride SAE 30 5-16-41	none	none	no polar material present
Gulf Pride SAE 30 8-28-41	slight	2.1 cm	8.2×10^{-6} wt. conc. of acid
Gulf Pride SAE 30 11-6-41	6.2 cm	8.1 cm	1.2×10^{-4} " "
Pennzoil SAE 30	none	slight	trace
*Sinclair 3150	slight	2.8 cm	1.5×10^{-5} wt. conc. of acid
Good Penn SAE 30 Western Auto	none	3.0 cm	1.7×10^{-5} " "
Super Good Penn SAE Western Auto	none	1.8 cm	6.0×10^{-6} " "
*Texaco 3080	7.2 cm	11.4 cm	2.4×10^{-4} " "
*Texaco 1080	6.8 cm	8.2 cm	1.2×10^{-4} " "
*Mobiloil 1080	completely over tray	completely over tray	probably contains polar additive
*Sinclair 1080	completely over tray	completely over tray	" "
Quaker State SAE 30	completely over tray	completely over tray	" "
Kendal SAE 30	completely over tray	completely over tray	" "
Esso SAE 30	completely over tray	completely over tray	" "
Gulf Pride New Sample purchased 9-16-41	completely over tray	completely over tray	" " is different from sample obtained 5-16-41

TABLE II

DETERMINATION OF VOLATILE ACIDS PRODUCED FROM CRYSTAL
PETROLATUM:

Oxidation at 100°C. Large cell used with air flow of 60 ml/min

Total oxidation	pH of 25 ml. of aqueous solution from		
	Normal Run	Run with Reflexing	Run with Additive Hexanoic acid
7.0	6.4	6.4	3.59
14.0	6.4	6.3	3.64
21.0	5.14	5.18	3.60
27.0	4.34	4.55	3.53
34.0	3.83	3.96	3.50
40.0	3.98	4.05	3.72

TABLE III

DETERMINING OF VOLATILE ACIDS PRODUCED FROM DUPONT
CETANE SMALL CELL USED WITH AIR FLOW OF 20 ml/min.

Total oxidation Time in Hours	pH of 25 ml of aqueous solution from:	
	Cetane at 100°C.	Cetane at 125°C.
7.0	6.7	5.72 in 9 hours
14.0	6.7	
21.0	6.8	
31.0	6.6	
39.0	6.6	
46.0	6.4	
54.0	5.49	

TABLE IV

DETERMINATION OF VOLATILE ACIDS PRODUCED

* The value given is the pH of 25 ml water after bubbling through it the volatile oil oxidation products for the indicated length of time.

Oil Oxidized	Temperature of Oil °C.	Length of time oil was oxidized	pH*
Crystal Co. Petrolatum	100	7.0	6.4
	125	7.0	3.4
	150	3.0	3.3
Squibbs Petrolatum	100	7.0	—
	125	7.0	3.9
	150	3.0	3.3
Texaco #2135	100	7.0	5.0
	125	7.0	4.5
	150	—	—
Texaco #2190	100	7.0	4.2
	125	7.0	4.1
	150	—	—
Gulf Pride SAE 30	100	7.0	5.3
	125	—	—
Dupont Cetane	100	9.0	6.6
	125	9.0	5.7

TABLE V

SUMMARY OF OXIDATION STABILITY DATA ON OILS
TESTED

Oil	Induction Periods (In Hours)			Time of Appearance of Insoluble (in Hours)		
	at 100°C.	At 125°C.	at 150°C.	at 100°C.	at 125°C.	at 150°C.
Cetane(Dupont)	32.0	2.0	under 1.0	over 52.	over 8.	under 1.0
Crystal petro- latum	17.0	1.5	0.5	25.0	2.5	0.5
Squibbs petro- latum	48.0	3.5	0.5	58.0	4.3	0.5
Texaco #2135	12.5	2.5	---	34.0	12.5	---
Texaco #2190	--	---	---	34.0	---	---
Gulfpride SAE 30	13.0	---	---	23.0	---	---

LARGE CELL
100°C. AND 60 MI/AIR/MIN.

- △ --- TEXACO 2135, ALKALINE WATER
- --- GULF PRIDE S.A.E. 30, ALKALINE WATER
- △ --- TEXACO 2190, ALKALINE WATER
- --- CRYSTAL PETROLATUM, ALKALINE WATER
- x --- CRYSTAL PETROLATUM, ACID WATER
- --- SQUIBB PETROLATUM, ALKALINE WATER
- x --- SQUIBB PETROLATUM, ACID WATER
- --- CRYSTAL PETROLATUM, HEXANOIC ACID ADDED,
ALKALINE WATER
- --- DUPONT CETANE, ALKALINE WATER
- ↓ HOLES FORM

SPREADING AREA PER UNIT MASS

$$\left(\frac{I \cdot t^{0.2}}{M}\right)$$

OXIDATION STABILITY
CURVES AT 100°C.

OXIDATION TIME HOURS

1000

1000

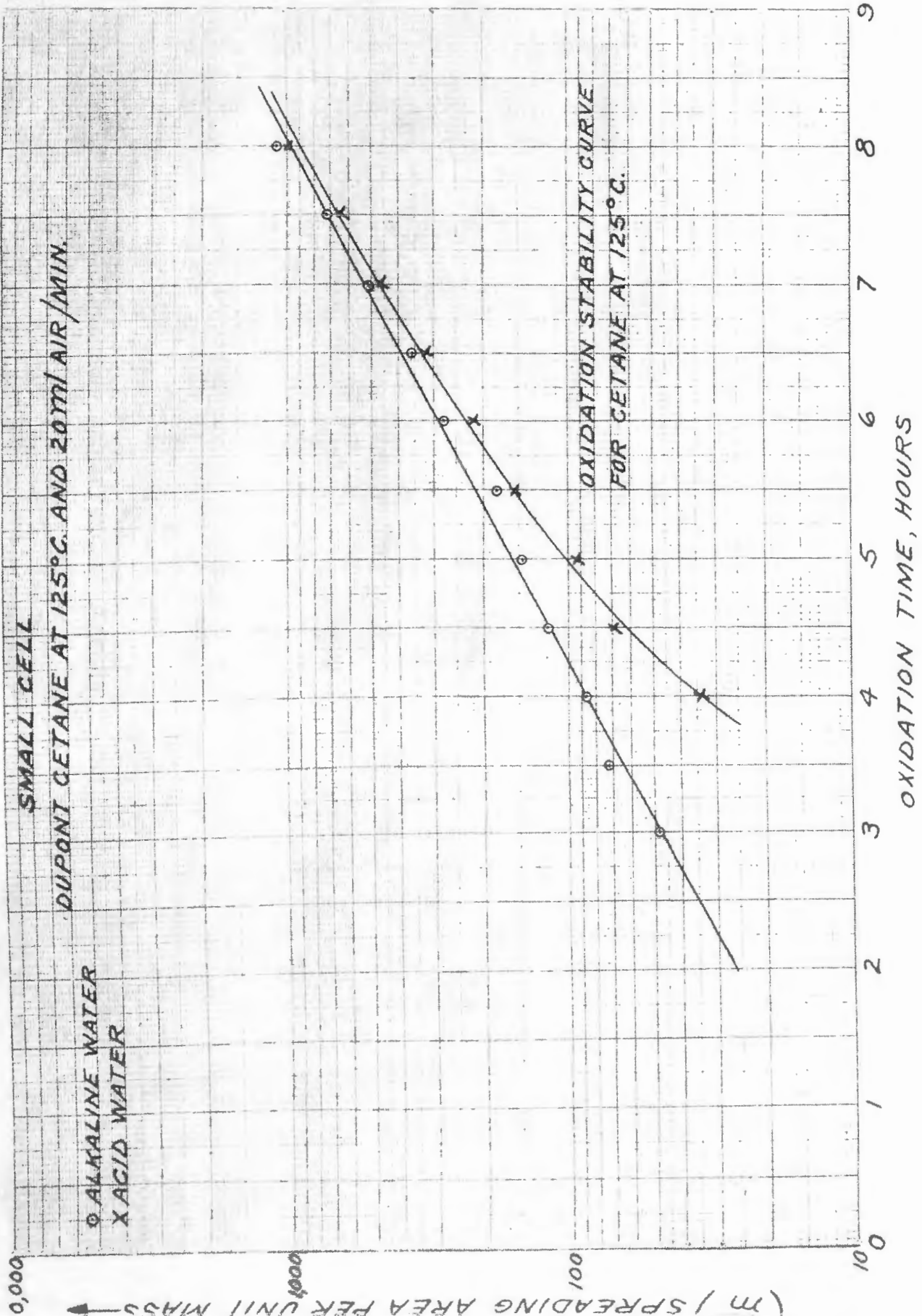
1000

1000

100

112

0 8 16 24 32 40 48 56 64 72 80 88 96 104 112



7702

10,000

$\left(\frac{\pi r^2}{m}\right)$ SPREADING AREA PER UNIT MASS

100

1,000

SMALL CELL

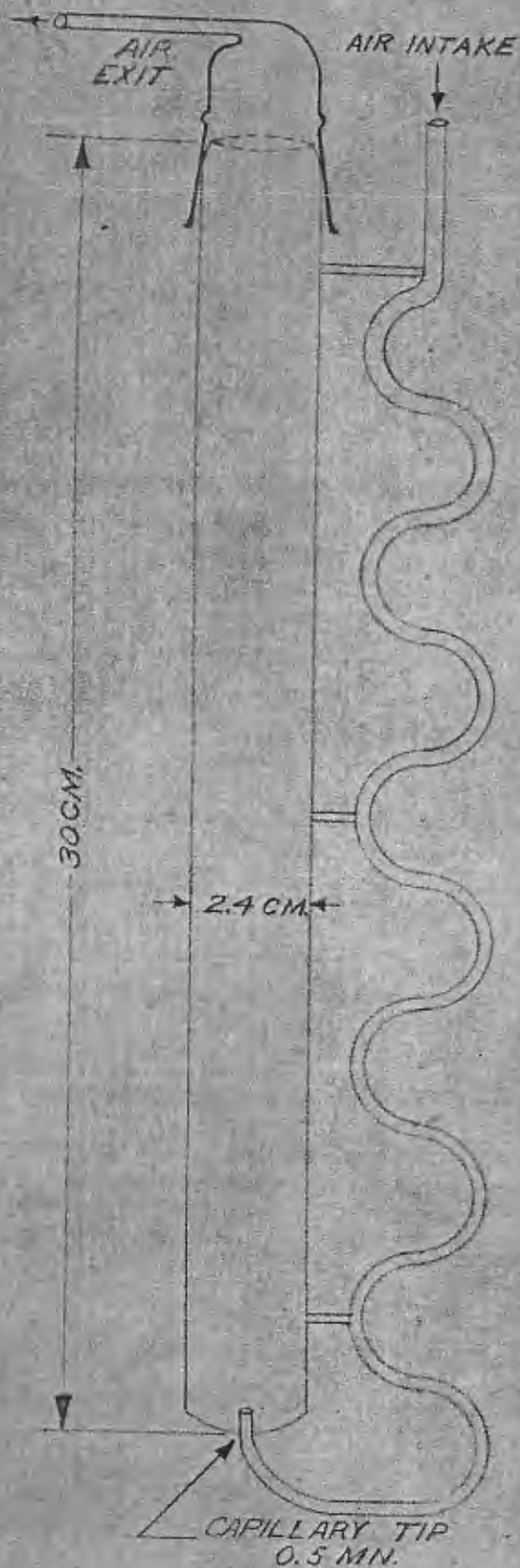
TEXACO 2135 AT 125°C. - 20 ml AIR / MIN.

- — ALKALINE WATER, TESTED IMMEDIATELY
- × — ACID WATER, TESTED IMMEDIATELY
- — ALKALINE WATER AFTER STANDING 11 DAYS
- × — ACID WATER AFTER STANDING 11 DAYS
- ↓ HOLES FORM

EFFECT OF STORAGE ON AN OXIDIZING LUBRICATING OIL



LARGE CELL



SMALL CELL

