

GEORGIA SCHOOL OF TECHNOLOGY

DEPARTMENT OF CHEMISTRY

SOME PRODUCTS OF THE OXIDATION OF STEAM TURBINE OIL

A Thesis submitted in partial fulfillment of the
requirements for the Degree of Master of Science
in Engineering Chemistry.

Submitted by:

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Foreword

The first thirty years of this century have seen a remarkable development of the steam turbine. It has grown enormously in size, in efficiency, and in the scope of its usefulness. Hand in hand with this growth has gone an increase in the complexity of the problem of lubricating these turbines. This has come about partly because of the extremely hard service to which the lubricant is put in a large modern turbine and partly because of economic reasons. The dependence that is placed on a turbine driving a 70,000 Kva. generator is of such magnitude as to render it imperative that a cessation of operation due to lubrication trouble shall not come to pass.

Turbine oils have come to be regarded as the highest quality lubricants that the refiners are called upon to supply. But after all these oils are only mixtures of chemical compounds of more or less unknown constitution and stability, and these oils do change and deteriorate in service. It was in the hope of shedding some light on the nature and causes of this deterioration that the work described in this paper was undertaken. The writer wishes to acknowledge his indebtedness to Dr. A. E. Flowers of The De Laval Separator Company for furnishing the samples of material for investigation, and for permission to publish the results, also to Professors Chipman and Wroth of Georgia School of Technology for their assistance and guidance in the work.

General Discussion of the Problem.

The changes which steam turbine lubricating oils undergo during use may be qualitatively stated to be as follows:

1. The color becomes darker.
2. The viscosity increases.
3. The acidity increases.
4. The resistance to emulsification decreases.
5. Oil-insoluble solids are formed.

The first of these changes may be dismissed without further comment since no quantitative relation between color, per se, and quality has been established, although it has been pointed out by Mead (20) in his studies of oil oxidation that the color change is an index of the amount of oxidation. The increase in viscosity which the oil undergoes may serve as an index of its suitability for continued use (1) since the makers of a turbine may specify the viscosity limits for the oil to be used in its lubrication. It is quite possible that the oil in service might become so viscous as to be unsuitable for use although this would be an extreme case.

The increase in the acidity of the oil is one of the most interesting features of the problem. The term acidity is misleading since the chemical individuals have not for the most part been isolated and identified as true acids. However these substances react as acids

(20) Numbers refer to Bibliography.

to phenolphthalein and are neutralized by potassium hydroxide. The comparative rarity of instances of severe corrosion traceable to these acidic bodies has led to the belief that their corrosive action is slight (4) and the lack of knowledge of their constitution has led to the use of the term "neutralization number" (2) rather than "acidity" for designating the figure expressing the quantity present in any oil. The neutralization number is defined as the number of milligrams of potassium hydroxide required to neutralize one gram of oil. The work described in this paper has to do with these acidic bodies and will show that some of them are true acids and that their potential possibilities for causing corrosion are great.

The decrease in the resistance to emulsification of the oil becomes, when sufficiently great, an index of the quality of the oil. The oil in many turbine systems becomes contaminated with water through steam seal leaks, and this water should be continuously removed by settling, centrifuging or filtering. It is desirable that the tendency of the oil to emulsify with this water be slight. The resistance of the oil to emulsification may be measured by the "Steam Emulsion Number" (3) a low S.E. number being characteristic of an oil from which admixed water separates readily.

The formation and precipitation of solids in the oil is of course objectionable to the turbine user since

these solids may cause clogging of oil passages and by depositing on the tubes of the oil coolers may cause the oil to be fed to the bearings at too high a temperature. These solids are generally continuously removed from the oil of turbine systems by a filter or centrifuge. The solid matter plus some emulsified water and entrained oil is spoken of as sludge.

The following tabulation gives figures for these changes just discussed as they were observed in an actual turbine lubricating system (6)

	: New Oil	: Oil after	: Maximum
	:	: 3 years 2	: value ob-
	:	: months ser-	: served dur-
	:	: vice	: ing test
	:	:	: period
Neutralization number	:	:	:
(mg. KOH per gm of oil)	: .06	: .43	: .57
Steam Emulsion Number	:	:	:
(seconds)	: 90	: 240	: 380
Viscosity, Saybolt	:	:	:
Universal at 100 deg. F.	:	:	:
(seconds)	: 237	: 263	: 266
	:	:	:
	:	:	:

The amount of oil in this system was about one hundred gallons. Makeup oil to the amount of five or six gallons per year was added as necessary. The centrifugal purifier operating on this oil removed about 300 grams of sludge and from 10 to 35 liters of water per month. It is pointed out in the paper describing this test that this removal probably accounts for the fluctuation of the

neutralization number of the oil during the test since as is well known some of the acidic bodies of used oils are appreciably water soluble. The article further states that at the time the oil showed the maximum neutralization number practically no water was being removed from the system.

It may be remarked that the above figures represent very moderate values, that is to say, they show but slight deterioration of the oil. As representative of fairly severe deterioration the writer recalls having observed used oils which showed neutralization numbers as high as 1.8 mg. KOH per gm. oil and steam emulsion numbers of 600--900 sec. The extreme in turbine oil deterioration occurs when the oil "goes to liver", that is, the entire body of oil becomes a semi-solid mass of sludge and emulsion. Needless to say this phenomenon is rare; no cases of it have come under the direct observation of the writer.

The principal cause of these various changes in turbine oils is generally conceded to be oxidation, which is hastened by heat, moisture, and contact with metals. Light (7) and electric currents (4) have also been cited as having the effect of hastening deterioration of the oil. These last two factors however need hardly be considered in connection with turbine oil deterioration since the construction of modern turbine systems is such as to practically preclude any action by either of these agencies.

It thus appears that turbine oil deterioration is in reality a special case of hydrocarbon oxidation and a consideration of the work of previous investigators in this field is in order.

Review of the Work of Previous Investigators.

The subject of hydrocarbon oxidation is one of great diversity and the literature on the subject voluminous. For the most part the work done falls naturally into two classes, the first being work done on controlled oxidation with the idea of producing valuable products, e.g. alcohols, and fatty acids, the second class comprising research work on the uncontrolled oxidation which causes deterioration of oils in service. This type of work may be further subdivided into (a) efforts to establish the mechanism of the reactions and, (b) efforts to identify the products. Taking up these various phases of the subject in the order given it is seen that as early as 1880 Schaal (7) devised a process for converting petroleum distillates into saponifiable acids. As far as is known this process never attained any practical success probably for economic reasons. Brooks (8) states that it was in 1896 that Byerly and Mabery first described their now well-known process for manufacturing "artificial asphalt" by blowing air through heavy high boiling petroleum residues for four to five days at 230 deg. C. Water is formed during this process and the final products contain but little oxygen leading Brooks to the belief that oxidized

bodies which are at first formed finally polymerize or condense with the elimination of water. At lower temperatures these condensation reactions occur to only a slight extent and the primary oxidation products may be recovered as such.

In 1905 Walther (9) claimed a process for the vapor phase oxidation of petroleum hydrocarbons to produce useful products. It has, however, been shown by James (5) that Walther's process due to the high temperatures and high air ratios used could hardly have produced any great quantity of materials of commercial value.

James (5)(11) has described his own work on oil oxidation leading to the development of a process for the vapor-phase, low temperature, catalytic oxidation of the aliphatic hydrocarbons of petroleum. He has found the oxides of such metals as uranium and molybdenum to be especially useful as catalysts for the oxidation reaction, the uranium oxide having the specific property of catalyzing to a marked degree the aldehydic stage of oxidation. In his process the temperature of the catalyst "screens" through which a mixture of air and hydrocarbon vapor is passed is maintained at from 280 to 380 deg. C. He states that below 240 deg. C very little oxidation takes place while above 500 deg. C. no results of industrial value are obtained. It may be noted here that the lowest of these temperatures is considerably higher than encountered in problems of oil deterioration or in the laboratory aging tests.

As to the products obtained by this oxidation James states that they represent in general all the stages of the oxidation of aliphatic hydrocarbons from alcohols acids. These acids, he adds, are not true fatty acids but are oxygenated and respond to all the aldehyde reactions. He further points out a fact which appears to bear on the writers work viz. that the partially oxidized hydrocarbons thermally decompose to form both hydrocarbons of lower molecular weight and oxidized bodies of lower molecular weight.

In a later publication (10) Bitler and James describe a commercial plant for carrying on this oxidation process. In oxidizing a Pennsylvania kerosene an alcohol denaturant as "alcohol" is prepared, enough formaldehyde being formed as a by product to warrant its recovery as hexamethylenetetramine. Water soluble acids are also formed the recovery of which has not been worked out. Formic acid has however been identified.

Another worker in this field Marks (12), cites the formation of carboxylic acids by oxidizing with air a petroleum hydrocarbon mixture at a temperature of 100 to 160 deg. C and a pressure of 100 to 350 pounds per square inch.

Egloff and Schaad (13) recently published a comprehensive review of the work done to date on the oxidation of gaseous paraffin hydrocarbons. They list among the oxidation products which have been identified; methyl and ethyl alcohols, formaldehyde, acetaldehyde, formic and

acetic acids, hydrocarbons (both saturated and unsaturated) of lower molecular weight than those originally submitted to the oxidation reaction, resins (which are probably aldehyde polymers) and even traces of hydrogen peroxide. They also present a list of possible research problems in this field and a bibliography of 120 references. A large percentage of the work which they report has been done on methane with a view to developing commercial processes for the manufacture of formaldehyde.

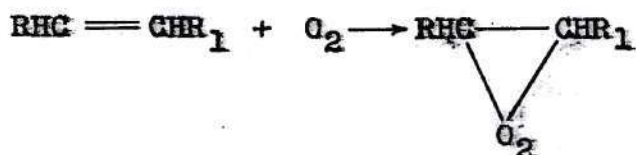
Passing now to the work which deals with the mechanism and products of the oil deterioration reactions one is at once struck by the enormously increased activity in this field in the last five years.

Gurwitsch(7) wrote in 1924 that "the mechanism of this oxidation process and the behavior of individual hydrocarbon groups have, unfortunately never been accurately investigated, so that the little work done on this subject provides only vague indications but no certain data."

This statement should not however be taken as indicating a complete lack of knowledge up to that time for Brooks(8) states that in 1904 Engler and Weissberg established their theory of the mechanism of organic oxidations. To quote Brooks;

"It has been shown by the well known work of Engler and Weissberg (19) that organic substances, which alone are not appreciably affected by air or oxygen, may readily

be oxidized in the presence of a second substance which is capable of direct oxidation. They have shown that the latter class of substances form peroxides and their hypothesis is that these peroxides may then effect the oxidation of substances which by themselves are inert to oxygen. Thus, paraffin wax is only very slowly affected by air or oxygen at 150 deg. but the oxidation is very much accelerated if a small quantity of previously oxidized material is introduced. Unsaturated hydrocarbons which are capable of forming peroxides, according to Engler's theory



may in this way bring about the oxidation of saturated hydrocarbons."

That this theory was based on careful experimentation and sound reasoning seems to the writer to be evidenced by the way in which the findings of subsequent investigators have supported it. For example Digby (8) states that the iron and copper soaps which he found in transformer oil sludge "probably act catalytically in promoting the oxidation." Likewise, Waters (17) (18) observed the formation of resinous substances in oxidized oils and in the course of his work was led to the belief that these resins promoted further oxidation by acting as oxygen carriers.

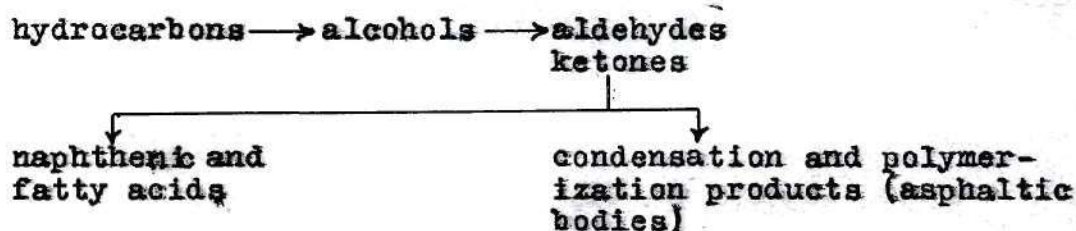
Waters also investigated the effect of unsaturation and of sulfur content (23) on oxidation of oils and found that, of several oils investigated by him, the one having the highest percentage of unsaturation, showed the least oxidation. Apparently he did not regard this as evidence against Engler's theory since he explained it as perhaps being due to greater amounts of catalysts or oxygen carriers in the more highly oxidized oils. With reference to the sulfur content of the oils he found that increase in sulfur content increased the amount of oxidized material formed and that the sulfur content of the oxidation products was higher than that of the original oil.

During the World War intensive research was conducted in Germany on the synthesis of fatty acids. Much of the work was based on oxidation of paraffin wax and according to Brooks "the most complete results published indicate that the best yields were obtained without the addition of any catalytic material other than a small amount of previously oxidized material added to initiate the reaction."

It is readily seen from the foregoing that Engler's theory at least as regards the idea of "autoxidation" has abundant evidence in its favor. It is also apparent that there is excellent foundation for the belief, generally held by turbine engineers, that the presence of sludge in oil causes the rapid formation of more sludge.

As an example of more recent work on the mechanism of oil oxidation may be cited the work of Haslam and Fröhlich (16) and that of Mead and collaborators (20).

These workers were primarily interested in the deterioration of transformer oils, and its prevention by the use of antioxidants or negative catalysts. Haslam and Fröhlich propose the following scheme as representing the oxidation process.



They also point out the further possibility of continued oxidation of the acids followed by condensation to asphaltic bodies. (Cf. James loc. cit.) They show that the alcohols and aldehydes formed have but little stability and are further oxidized almost as fast as formed. The action of the negative catalyst is to delay the initial step i.e. the formation of alcohols.

Mead and his coworkers determined the effect of temperature on the reaction rate and give the temperature coefficient as 2.4 per 10 deg. C between 120 deg. C and 130 deg. C. They found that the rates of sludge and acidity formation were low at the start but increased as the experiment progressed. The rate of oxygen absorption increased with the unsaturation of the oil at least for oils from the same base crude. (Cf. Waters, loc. cit.) In addition they give the following conclusions:

- *1. The acidity development in commercial transformer oil is autocatalytic at low initial acidity,

but not at relatively high initial acidities which are obtained by additions (up to 5 per cent) of deteriorated oil.

2. Sludge formation seems to be greatly influenced by the initial acidity of the oil, much more sludge being formed at high initial acidities (obtained by additions of deteriorated oil) than at the low acidity of the new oil.*

One of the most recent publications dealing with the mechanism of oxidation reactions is that of Pope, Dykstra and Edgar (21) who have studied the vapor phase oxidation of octane and its isomers. They interpret their data as leading to the following conclusion.

The oxidation of the hydrocarbons proceeds in the main by the following steps: (a) Oxygen attacks the methyl group at the end of the longest open end straight chain of the molecule forming an aldehyde. (b) This aldehyde is further oxidized to an aldehyde of the next smaller number of carbon atoms by a 'chain' reaction in which CO is formed and by a side reaction in which CO_2 is formed. These reactions continue until a branch in the hydrocarbon chain occurs at which point the oxidation slows down markedly; or (in the case of very long chains) until a secondary explosive reaction sets in.

Passing now from the work which has been primarily concerned with the mechanism of oxidation to that which has been chiefly at identification of the products it is seen that there has been no lack of effort along this

line. Several workers have made proximate or ultimate analyses of turbine or transformer oil sludges, the proximate analyses being based for the most part on the selective action of certain solvents.

For example Blakeley (14) reports the analysis of a turbine oil sludge as follows:

	Per Cent
Water	.5
Oil (Petroleum ether soluble)	43.3
Ethyl ether soluble	50.4
Chloroform soluble	2.2
Insoluble (mostly metallic iron)	<u>4.4</u>
Total	100.8

These various solvents were applied to the same portion of sample in the order named, i.e. the ethyl ether extract did not include any petroleum ether soluble material.

Similarly, Salathe (15) cites a turbine oil sludge that contained 42.5% water and 13.6% acids. (Aliphatic and naphthenic acids calculated on an oil free basis). This sludge gave a positive test for acetaldehyde and had a high saponification number.

Winchester (22) has analysed a considerable number of turbine oil sludges and cites the following as an example:

	Per Cent
Water	53.5
Oil (Petroleum ether soluble)	18.4
Soaps (Ethyl Ether soluble)	19.7
Asphaltenes (carbon tetrachloride soluble)	2.7
Insoluble	<u>2.9</u>
Total	97.2

His scheme of analysis involved successive extractions with the solvents listed and ash determinations on the

original sludge and the various extracts. He also analysed the ash. For the example cited he found 1.49% of ash based on the water-free sludge. This ash consisted of:

	Per Cent
Fe_2O_3 and Al_2O_3	47.1
Cu O	32.3
Si O_2	11.2
Undetermined	<u>9.4</u>
Total	100.

While it is quite true that this pioneer work on proximate analysis is difficult of interpretation, enough of it has already been done to show that it may conceivably become a method of great value in the diagnosis of lubricating oil troubles.

A similar scheme of analysis has been used by Chernojockov (1) who gives the following values for a turbine oil sludge:

	Per Cent
Water	35.5
Oil (gasoline soluble)	29.5
Gasoline insoluble	35.0

He found the gasoline insoluble portion to consist of 16.5% of alcohol soluble material 72.6% of benzol-soluble and 11.2% of insoluble residue. The alcoholic extract contained organic acids and organic salts of iron. The benzine extract contained asphalts and organic salts of iron and copper. The insoluble portion contained free iron and copper also some silica and carbon.

As to the nature of the sludge forming reactions Chernojakov distinguishes three kinds of sludge, to wit:

- "(1) Sludge formed through the polymerization and oxidation of tarry substances and having the appearance of the so called asphaltenes. This sludge is never formed in properly refined oils.
- (2) Sludge of a distinctly acid character formed through the oxidation and polymerization of unsaturated compounds and the basic hydrocarbons of the oil. This sludge is usually a sticky and viscous mass of a brownish color.
- (3) Sludge composed of iron and copper salts of organic acids. These are formed by reactions of the organic acids with the metals especially when water is present to promote rusting."

In a later paper (24) the same writer apparently revised somewhat his opinions as to the mode of formation of the second variety of sludge for he states "The saturated hydrocarbons form, by oxidation, high molecular weight acids or 'sludge of the second kind' which cannot be dissolved in petroleum ether and has an acidity which varies between 60 and 110 milligrams of KOH per gram of acid."

An example of sludge analysis which is interesting on account of the high sulfur content found is cited by Stadnikov and Vozzinskaia (25) who found in a transformer oil sludge 13.16% of ash in which they identified iron, copper, lead, and tin. The ultimate analysis of the sludge

on a water and ash free basis was, Sulfur 78.03%, Hydrogen 9.29%, Nitrogen .83% and Oxygen (by difference) 11.48. They further state, citing experimental evidence in support of their belief, that the sulfo-acids (and the sodium salts of these acids) which may be present in oils which have been sulfuric acid treated and insufficiently washed, play an important part in catalyzing the condensation reactions which largely account for sludge formation.

Frank (26) in a general discussion of the changes taking place in insulating and lubricating oils during use cites those commonly observed (See page 1) and in addition states that the tar number of the oil increases and the iodine number decreases. This last especially, indicates to him that unsaturates play an important role in oxidation. He suggests the use of methyl alcohol for extracting the acidic bodies from used oils so that these acids may be isolated and identified. He mentions the reported formation of acetic acid by oxidation of heavy oils (Cf. Brooks loc. cit.) but contends that stray current phenomena have probably more to do with its formation than has direct air oxidation.

In a later paper (27) Frank describes the analysis of a turbine oil sludge. He extracted the sludge with acetone and ethyl ether, obtaining from the acetone extraction 11.4% of material and from the ether extraction 14.2% based on water and oil free sludge. The

acetone extract had the appearance of an organic iron salt. By treatment of these extracts with hydrochloric acid he separated the organic acids from which he obtained the following data:

	Acetone-HCl extract	Ether-HCl extract
Acid value	86.6	171.5
Saponification number	125.2	180.
Mean molecular weight	448.3	310.
Carbon	75.7	68.8
Hydrogen	8.3	7.4
Oxygen	16.0	23.8
Empirical formula	$C_{28}H_{37}O_4$	$C_{18}H_{25}O_5$

In commenting upon these results Frank suggests that the divergence in acid and saponification numbers may indicate that the acid obtained from the acetone extract was transformed to a lactone soon after its formation. However, the hazard of such theorizing is perhaps best shown by quoting his own conclusion: "I forbid myself to make further deductions and recommend that the figures given be regarded as material for further work rather than as explanations."

The writers own experience with sludge analyses leads to the observation that the splitting of the iron soaps with HCl is very difficult to accomplish on account of the gummy resinous nature of the materials.

It is apparent from the foregoing review of the literature that many gaps in our knowledge of oil deterioration products still exist, further that the study of water soluble products which are probably the most aggressive, especially in the case of turbine oil has

been rather neglected.

Basis of the Present Work.

In view of the demonstrated importance and far reaching effects of oil oxidation reactions, it is quite natural that considerable effort has been spent on the development of tests for measuring the oxidizability or aging tendency of mineral oils. A recent review (28) listed not less than fifteen such tests and it is quite possible that as many more have been proposed but have not gained wide acceptance.

There are five tests which are in more or less common use in this country, these being as follows:

1. The Waters Carbonization Test (17).
2. The Sligh Oxidation Test (29).
3. The Snyder Life Test (30).
4. The Funk Sludge Accelerator Test (31)(32).
5. The Stability Test of Rogers and Miller (33).

In each of these tests the oil is subjected to oxidation under controlled conditions, after which the extent of oxidation is judged by some convenient criterion such as the sludge content or neutralization number. The first three tests are used for both turbine and insulating oils, the last two being designed for turbine oils in particular. Of these two the Funk test most nearly approaches duplication of the actual turbine conditions. In 1926 the writer had occasion to make a series of tests on some turbine oils using the Funk apparatus and at the

conclusion of the tests decided to attempt the identification of some of the oxidation products formed in the oils during the tests. This paper has to do with the results of this work. For the sake of furnishing a background for this present work a description of the apparatus and the test results is included at this point.

The Sludge-Accelerator test was originally developed by Mr. N. E. Funk of the Philadelphia Electric Company for use in testing the turbine oils purchased by his company. The test subjects the oil to the action of heat, air, water and metals (iron and brass).

The apparatus used by the writer differed from Funk's design only in minor details and is known and marketed as "The Funk Sludge Accelerator." Its constructional detail is shown on Enclosure "A". Essentially it consists of a cast iron box-like container or tank 48 cm long by 38 cm deep and 26 cm wide (inside measurements). The top is closed by a cast iron lid fastened with cap screws so as to make a water and air tight joint. Across the inside of the container four baffle plates extend from side to side. Two of these baffles extend from near the top to within 4 cm of the bottom the other two extending from the bottom to within about 7 cm from the top. The container is thus divided into five communicating compartments. Mounted on the outside of it is a motor which drives a pump and blower. The pump takes suction from the compartment at one end of the container and dis-

charges into the compartment at the other end. The blower forces air into the container at a point below the surface of the oil under test the air then escaping through a vent pipe to which is connected a gas meter for recording the volume of air passed. The apparatus also carries a thermometer, gage glasses and sampling valves.

To make a test thirty liters of the oil and three liters of distilled water are poured into the apparatus, and the cover fastened down. The pump and blower are started and heat applied by means of two Meker burners set under the container. The temperature is brought to 96 deg C (205 deg. F) and maintained at that point. The oil and water are thoroughly admixed by the pump and forced to travel through the apparatus in a tortuous path due to the baffles previously mentioned. The rate of circulation of the oil-water mixture is about 35 liters per minute and the supply of air to the apparatus is kept at 40 liters per hour.

About fifty to seventy five hours of operation are usually required to test an oil. This operation need not be continuous, in fact a rest period of eight hours or more out of each twenty four is recommended. The rate of deterioration of the oil is gaged by means of samples drawn at five-hour intervals as the test progresses. The content of sludge and emulsion in the sample is determined by centrifuging, and the neutralization number

is determined on the oil and water separately. The sludge content of the oil is also determined by precipitating the sludge with a mixture of ethyl alcohol and petroleum ether and then centrifuging.

In the series of tests run by the writer two Funk Sludge Accelerators were used. One of these was as described above. The other differed only in that it had a sheet of stainless steel (U-loy) inserted under the cast iron lid so as to eliminate from the sludging effect of the oil the influence of loose scaly rust which had been found to form on the lid in previous runs. These machines were operated about nine hours per day. The test period was seventy-five hours so that about a week was required for each test.

Three oils were tested, two runs being made on each oil, one run in each machine. The oils were high quality turbine oils being described as light, medium and heavy grade. These oils were made from naphthenic base crude by a high vacuum distillation process.

The characteristics of the oils before and after being tested are shown on Enclosure "B". It will be noted that the changes in viscosity, steam emulsion number and neutralization number are quite appreciable. It is generally believed that the effect on the oil of one hour in the Funk Sludge Accelerator is comparable to that of 100 hours of actual turbine service. While the results of this test are of interest here only as a

background to the present work it may be pointed out that these oils tested would all class as very good oils for turbine use.

When the sludging test on an oil was completed the mixture of oil, water and sludge was drained from the Funk machine and passed through a De Laval Centrifugal Oil Purifier. This separated the mixture into its components, which were reserved for further examination. The work described above was carried on in the Process Laboratory of the De Laval Separator Company. The examination of the water samples and identification of the acids dissolved therein was done at the Georgia School of Technology.

Examination of the Water from the Funk Sludge Accelerator.

It will be noted on Enclosure "B" that the neutralization number of the water at the end of each sludging test was from four to eight times the neutralization number of the oil from that test. Since a little over three liters of water from each test was available, it was considered that the total content of acidic bodies in the water was sufficient to warrant an extended investigation. An examination of these water samples was therefore undertaken.

These samples being very dilute solutions no tests, even for the common acids, were attempted at the start. It was decided to attempt to concentrate the solutions by means of fractional distillation, so apparatus was set

up as described below. A 5 liter round bottom flask was used as the still body. This was surmounted by a Hempel column made of 25 mm. o.d. Pyrex tubing 90 cm. long. The first filling tried in this column was 5 mm glass balls but the hangup of liquid in this packing was so great that the balls were removed and replaced with 5 mm. o.d. glass tubing cut into pieces 6-7 mm. long. The depth of packing was 71 cm. and the column was lagged for a distance of 56 cm. from the bottom, the upper portion serving as a dephlegmator. The distilling flask was also lagged except on the bottom where it was fitted with an electric heater. The six samples of water were distilled separately in this apparatus, the heat input being adjusted so as to give a ratio of reflux to distillate of about 1:1. The distillates were collected in 250 ml. portions, and titrated with .050 N potassium hydroxide solution, using phenolphthalein as indicator. As each distillation progressed the neutralization number of the distillate as shown by these titrations gradually increased. When the neutralization number reached a value of about 0.2 the distillation was discontinued, and the residue in the still, usually about 500 ml., was set aside for further investigation. Most of the acid content of the six water samples was by this procedure concentrated in the still residues, thus reducing the volume of liquid from about 22 liters to less than three. The amount of acid which had passed over with the distillate was almost negligible in comparison with the total; nevertheless, an attempt

was made to concentrate the neutralized distillates and recover the potassium salt for examination. This proved to be a rather difficult proceeding, and was finally abandoned.

It is thus seen, that these distillations did not throw much light on the problem. The vapor temperatures did not differ appreciably from the boiling point of water. It was however noted that at the beginning of each distillation a gelatinous gray-green precipitate formed in the water, indicating the presence of easily hydrolyzed salts.

The residues remaining from these six distillations were then combined and filtered. This combining of the residues was considered to be justified by the fact that the three original oils were successive fractions from the same base crude. Their constituent hydrocarbons should therefore have partaken of the nature of an homologous series, moreover, since commercial oils are not closely-cut fractions, some of the same hydrocarbons may have been present in each oil. Thus, even if the acids in the water were products of direct oxidation, rather than decomposition, practically no more contamination than already existed should have resulted from combining the samples.

A considerable amount of red-brown precipitate, substantially hydrated ferric oxide was removed by the filtration of the combined residues. The filtrate was found

to have a neutralization number of 3.45 mg. of KOH per gram. As the total volume of this filtrate was over 2500 ml. its total acid content was therefore equivalent to about 8.6 grams of KOH.

This filtrate was then distilled in the same apparatus as used for the first distillations but at a slower rate so as to increase the ratio of reflux to distillate and thereby secure better fractionation. Even this increased fractionation, however, was not sufficient to prevent the distillation of some of the acid with the water. As in the previous distillations the acidity of the distillate increased as the distillation progressed. The distillate was at first collected in 250 ml. portions, this amount being later reduced as the acidity increased. These samples were titrated with .050 N potassium hydroxide. The potassium salt of the unknown volatile acid was then recovered by evaporation, followed by drying to constant weight at 105 degrees C. Four or five weighings were usually necessary for each sample as the potassium salt was very hygroscopic. From the weight of potassium hydroxide required for the neutralization of a sample and the weight of potassium salt obtained, the combining weight of the unknown acid was calculated for each of the samples, on the assumption that the acid was monobasic.

The results of this work are tabulated on Enclosure "C". These results, viewed as a whole, make apparent at once the fact that was brought out only gradually as the work was done, namely:

The volatile acidity of the water samples was not, as supposed, due to a series of acids of increasing molecular weight, but was probably all due to the same acid the combining weight of which was about 60. (It will be noted that the marked deviations from this figure are shown by the samples of low acid content. The results from these samples are therefore liable to larger percentages of error than the others.)

The combining weight of 60 and the observed hygroscopicity of the potassium salt indicated acetic acid, so some portions of the potassium salt were tested with sulfuric acid and ethyl alcohol, strong positive tests for acetic acid being thereby obtained. The assumption of a monobasic acid, made use of in calculating the combining weights referred to above was therefore justified.

The finding of this rather large amount of acetic acid (presumably present in the water samples as ferrous acetate) was so surprising that it at once raised the suspicion that some bacterial decomposition of the sample might have taken place during the time (about one year) which elapsed between the Sludge Accelerator tests and the examination of the samples. This suspicion however was put at rest by the fact that the samples were in sealed tin cans during that time, and that when opened they showed no evidence of mold or bacterial action. As final proof the neutralization numbers for these water samples determined at this time were substantial checks on the values obtained at the time of the conclusion of the sludge accel-

erator tests.

The distillations so far described had reduced the volume of the "combined residues" to about 50 ml. The deposition of solids (ferric oxides) was beginning to cause bumping in the flask so no further distillation of the residue was attempted in that apparatus. In order to continue the work a micro-fractionating column was set up, modeled after the one described by Cooper and Fawcett (34). Instead of the vacuum jacketed column described, this column was lagged with mineral wool. By means of an electric heating coil wound over the lagging a thermometer buried in the lagging was maintained at the temperature of the outgoing vapor, thus making the column practically adiabatic. A 100 ml. flask was used as the distilling vessel. The residue from the larger still was filtered (to remove iron oxides) giving about 42 grams of liquid which was put into the flask of the micro-still. This liquid was dark brown in color. By careful heating twenty ml. of distillate were taken off, a reflux ratio of three to four being maintained during this distillation. This sample was principally water as shown by the vapor temperature (99degrees C. at 738 mm. pressure.) and the neutralization number (5.14 mg KOH per gm.). The weight of potassium salt from it gave a combining weight of 55 for the acid radical and addition of sulfuric acid gave a strong acetic acid odor so it was not further tested.

Attention was again turned to the residue which had become a pasty semi-solid mass on cooling in the distilling flask. A portion of this pasty residue was taken up with water and slowly evaporated on a watch-glass. There resulted some pale green crystals mingled with a dark brown gummy material. The crystals were readily soluble in water, the brown gummy material was much less so but very soluble in alcohol. The appearance of the crystals suggested iron salts, (confirmed by qualitative test for ferrous ion) and the first thought was to attempt to split these salts with sulfuric acid, and then distill the liberated acids under vacuum. Fortunately this treatment was not immediately applied. Instead a small portion of the pasty residue was heated in a test tube. It gave evidences of decomposition, the odor when first heated being reminiscent of burning celluloid. On continued heating the smell of oxides of sulfur was detected. Following this clue another portion was taken up with water and tested for sulfates with barium chloride and nitric acid. A strong positive test was obtained.

Inasmuch as distilled water only had been used in the previous work including the Funk Sludge Accelerator runs, these sulfated could only have come from sulfuric acid formed by oxidation of the sulfur compounds present in the original oil.

To check this point sulfur determinations were made (peroxide bomb method) on some of the original oil and the oil (water and sludge free) after the Sludge Accelerator tests. These determinations were not made on each sample

separately but on two composite samples, one made up of the three original oils and the other of the six oils from the sludging tests. These showed, (average of two determinations on each),

New Oil .0084 % sulfur

Oil after sludging test. 0048 % sulfur

Thus there was a disappearance of .0036 % of sulfur from the oil, which for the 90 liters of oil originally subjected to test would amount to about three grams of sulfur. This is equivalent to nine grams of sulfuric acid, which if converted to ferrous sulfate would more than account for the mass of crystals in the "pasty residue" previously mentioned. Attention was accordingly centered on the "brown gummy material" of the residue. As stated, it was readily soluble in alcohol. The solution was acid to phenolphthalein. Efforts to crystallize it for melting point and combining weight determinations were unsuccessful. Treatment of the green crystals from the residue with sulfuric acid yielded no further quantity of this gummy material but merely checked their previous identification as ferrous sulfate. Finally owing to gradual dissipation of the small quantity (possibly one gram) available of this gummy material, work on it was necessarily abandoned.

Examination of the Sludge Samples.

Concurrently with the work on the water samples, an examination of some of the samples of sludge resulting from the Funk Sludge Accelerator tests was begun. A little over one hundred grams of sludge was available from each of the two tests on "Light" oil and somewhat less from the "Medium" and "Heavy" oil tests.

Preliminary examination of the sludges from Runs "A" and "B" (see Enclosure "B") showed them to be emulsions of the water-in-oil type. This was to be expected since the emulsifying agent was presumably a heavy metal soap. The sludge from Run "A" was light brown, that from Run "B" was much darker.

These two sludges were freed of water by adding light naphtha and distilling, repeating this until no more water came over. The volume of water collected was noted. The residue was transferred to an extraction thimble and extracted with light naphtha until oil free. The residue was then weighed. In this way there was found:

	Sludge from	
	Run "A"	Run "B"
Water	69 %	67 %
Dry oil-free sludge	1.6%	1.2%
Oil (by difference)	<u>29.4%</u>	<u>31.8%</u>

The surprisingly small amount of actual oil oxidation products available in these sludges could hardly be considered sufficient to justify further work. Moreover the time allotted to the problem was practically exhausted and the examination of the samples was discontinued.

Conclusions and Discussion of Results.

1. In turbine oils which are subjected to conditions closely approximating those of actual service, appreciable quantities of acetic acid may be formed. In the presence of water and iron this acid becomes combined as ferrous acetate. Under oxidizing conditions this may be converted to ferric acetate. Either of these salts may hydrolyze at temperatures near the boiling point of water and precipitate iron oxides or hydroxides. If then, these oxides of iron should become combined with other acids, some acetic acid would be left free to accomplish further corrosion.

2. Turbine oils, under conditions simulating those of use may develop appreciable quantities of sulfuric acid. This acid is formed by the oxidation of the sulfur compounds which are present in small amounts, even in highly refined oils.

3. This work offers but little basis for conclusions as to the mechanism of the formation of the acetic acid found. Previous investigators have detected it among the oxidation products of oils, but the conditions of its formation were always such that thermal decomposition (cracking) might conceivably have played a part in it. In this case such a possibility seems remote. At no time during the work was the oil subjected to a temperature higher than 100 deg.C, and it is generally held that cracking temperatures are of the order of 300 deg.C. Thus there is reason to believe that an oxidized side chain e.g. an ethyl group, is more

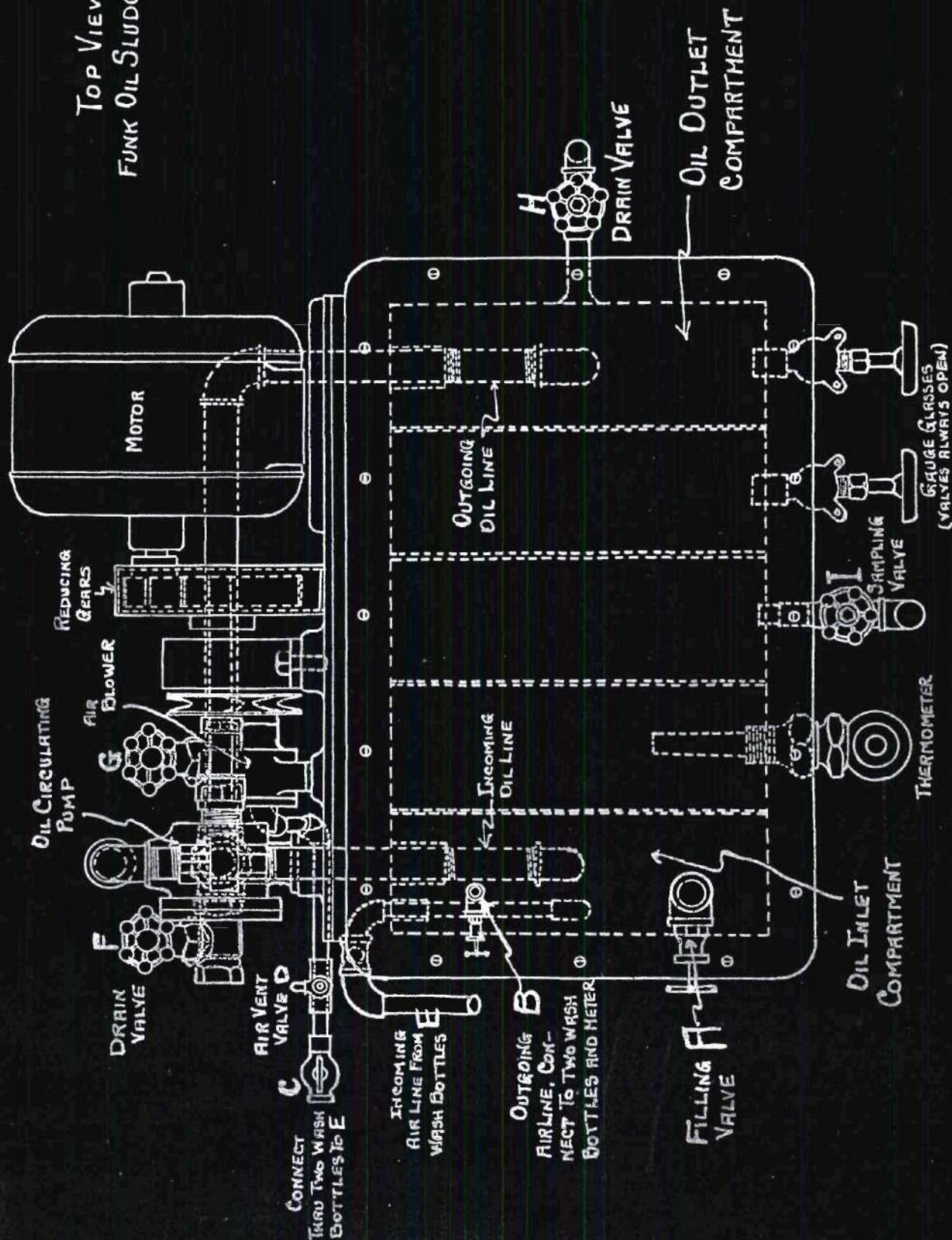
easily split off from the hydrocarbon molecule than is the same side chain before oxidation.

4. The evidence as to the mechanism of sludge formation is somewhat confusing. It is plausible to suppose that the hydrous oxides of iron, set free as mentioned above by the hydrolysis of iron acetates, might combine with organic acids of high molecular weight, thereby promoting sludge formation. Iron "soaps" have been noted in sludges by other investigators, (e.g. Frank, loc. cit.).

This theory however is opposed by the fact that the Funk Sludge Accelerator runs made with a non-rusting lid on the machine developed more sludge than did the corresponding runs made with a rusting lid. (See Encl. "B").

Thus it must be concluded that acidity is a more potent factor in sludge formation than is the nature and condition of the metals present.

TOP VIEW OF
FUNK OIL SLUDGING APPARATUS



SOME PRODUCTS OF THE OXIDATION OF STEAM TURBINE OIL - ENCLOSURE "C"
DATA SHEET - DISTILLATION OF COMBINED RESIDUES FROM WATER SAMPLES.

SAMPLE NUMBER	VOLUME OF DISTILLATE TITRATED	ML. OF .05N KOH REQUIRED	EQUIVALENT GRAMS OF KOH	NEUTRAL- IZATION NUMBER	GRAMS OF POTASSIUM SHLT	COMBINING WT. OF ACID RADICAL	REMARKS
1	250 ml.	25.94	.0728	.291	—	—	
2	250	34.65	.0972	.389	.1741	61	
3	100	12.90	.0362	.362	.0682	66	
4	100	14.70	.0413	.413	.0741	61	
5	100	18.05	.0507	.507	.0900	60	
6	100	18.23	.0512	.512	.0937	64	
7	100	19.00	.0534	.534	.0959	61	
8	100	23.95	.0672	.672	.1181	59	
9	100	25.30	.0710	.710	.1259	60	
10	100	27.59	.0775	.775	.1370	60	
11	50	4.85	.0136	.272	.0279	75	HEAT INPUT TO STILL REDUCED
12	100	18.42	.0518	.518	.0967	65	
13	50	11.05	.0310	.621	.0594	68	
14	50	7.01	.0196	.394	.0383	70	
15	50	7.54	.0211	.423	.0400	67	
16	50	6.31	.0177	.354	.0344	70	
17	50	18.70	.0525	1.05	.0916	59	
18	50	30.31	.0850	1.702	.1471	58	
19	50	37.08	.1040	2.08	.1820	59	
20	50	67.01	.1880	3.76	.3181	56	
21	50	96.90	.272	5.44	.4650	57	

ENCLOSURE C

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