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THE INSTITUTE OF PETROLEUM.

GENERAL DISCUSSION ON TRANSFORMER OILS.

A MEETING of the Institute of Petroleum was held in the lecture theatre of the Institution of Electrical Engineers, London, on Tuesday, April 9, 1946. MR E. A. EVANS (Vice-President) was in the Chair.

THE CHAIRMAN, in his opening address, said : This is the first meeting of the Institute devoted solely to transformer oil. As the subject is one which is of interest to electrical engineers, it is fitting that it should be held in the headquarters of the Institution of Electrical Engineers and under the shadow of the British Electrical and Allied Industries Research Association. The presence of so many distinguished electrical engineers serves to remind us of the links which attach together two great professional bodies.

This discussion has been organized to bring together oil suppliers, transformer makers and users, to express their respective thoughts and observations, and to enable each section to appreciate the plans and problems of one another. Although eight papers are being presented and discussed, comments on any phase of transformer oil usage or testing is welcome. The results of this meeting will doubtless be of considerable value to the British Standards Institution when it reconsiders the British Standard Specification for Transformer Oil.

I should like particularly to pay a tribute to the work of Michie, Everest, Rayner, and Parker, who have done so much to advance our knowledge of transformer oil in Great Britain. We have the pleasure of Dr Rayner being with us, and I have endeavoured to encourage some of our overseas friends who have been associated with transformer oil for many years to be here. We are able to welcome two overseas friends in Dr Salomon of Strasburg University, whose name has been associated for many years with that of Dr Wien, and also M. Rogieres of Ghent, who has devoted much time to the question of viscosity.

The following eight papers were presented in summary :

OLI

THE CONTRIBUTION OF THE E.R.A. TO INTER-NATIONAL RESEARCH ON TRANSFORMER OILS.

By P. W. L. GOSSLING and A. C. MICHIE.

SUMMARY.

This paper deals with the research on sludge and acidity in transformer oils, which has been carried out by the E.R.A. over a long period.

INTRODUCTION.

RESEARCH work sponsored by the E.R.A. and designed towards, firstly, a better understanding of the mechanism of deterioration of transformer oil in use, and secondly, the development of an improved specification for this oil has been carried out under the responsible direction of Panel E/Aa: Research for the International Electrotechnical Commission, and of Sub-Committee E/A: Chemical and Physical Tests.

It had been arranged, at a meeting in New York in 1926 of Advisory Committee No. 10 of the I.E.C., that comparative tests on samples of identical oils should be carried out by the various standard national methods at two temperatures—namely, that normally used and 110° C, the object of the work being the ultimate development and standardization of a research test for the examination of insulating oils from different sources. The national tests selected were those of Germany, Sweden, Switzerland, and the U.S.A., and chief consideration would be given to the relative importance of sludge and acidity development, and also to the effect of acidity on electrical insulating materials. The British test was not included in the official I.E.C. programme, the view being held that it was purely an acceptance test, but the British investigators considered it very desirable to be able to compare the results obtained with the British test with those yielded by the other four national methods, and Michie sludge tests were included in the British programme.

A report of the work of the British group was published by the E.R.A. in 1930,* and, after a critical discussion of the American, German, Swedish, and Swiss tests, recommended that the British test should, with the addition of procedure for determining the total acidity and the separate proportions of the latter volatile and non-volatile under the conditions of the test, be put forward as a research test for the consideration of the I.E.C.

At the Stockholm meeting of Advisory Committee No. 10 in 1930 the National Committees of Great Britain, France, Germany, Italy, and Sweden were asked to appoint delegates for a sub-committee to study systematically the factors influencing the oxidation of oils, so that a test method suitable for international use might be devised. The E.R.A. was requested to carry out the investigations on behalf of the British National Committee.

* Reference E/T39.

The resultant very considerable programme of work was shared by four laboratories in this country, and was fully reported in 1935.*

PROGRAMME OF RESEARCH 1932.

The oils used in this research had been distributed to the laboratories of the five collaborating countries, and were representative of four sources— Venezuelan, Russian, Pennsylvanian, and Texan. Oil from each source was submitted in grades representing three degrees of refinement designated slightly, medium and highly refined, so that twelve oils in all were examined.

1. General characteristics of the oils according to the B.S.I. specification;

2. Sludge, acidity and saponification values obtained from tests of 45 hours at temperatures of 110° , 130° , and 150° C;

3. Sludge, acidity and saponification values obtained after carrying out the tests at periods of from 12 hours to 96 hours in 12 hour steps, at temperatures of 110° , 130° , 150° , and 175° C;

4. The time of first appearance of sludge, taking periods of 12 hours;

5. Sludge, acidity and saponification values, using different rates of air flow;

6. The effect of moist air on sludge and acidity;

7. Investigation of the chief products produced at 150° C to determine the manner of breakdown.

Results of Tests and Conclusions.

The main conclusions affecting the course of subsequent work were the following :---

The results obtained in respect of the first appearance of sludge were too indefinite for the drawing of clear-cut conclusions, and it was decided to defer further work on this point, but there did appear to be a tendency for the period before the first appearance of sludge for oil from a given source to be greater the higher the degree of refinement of the oil.

In all tests for 45 hours at 110° , 130° , and 150° C the quantity of sludge followed inversely the order of the degree of refinement, except in the case of the Venezuclan and Russian oils, where the medium refined oils, when tested at 130° C, gave higher figures than the less refined oils of their series.

In all cases the development of acidity was highest in the most highly refined oils and lowest in the medium refined oils, with the exception of the Russian series, where the medium refined oil gave a higher acidity than the least refined of this series.

In the meantime the other national committees had carried out their respective programmes, and a meeting of Advisory Committee No. 10 was then held at Scheveningen in 1935. It is important to note that, during the progress of the work the collaborators had found it necessary to widen

^{*} Reference E/T47.

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the scope of study regarding the mechanism of the reactions of ageing so that more attention was being given to correlation of laboratory oxidations with the actual behaviour of oils in transformers. One factor, which was particularly stressed at the meeting and had considerable influence upon the course of subsequent work by the British Committee, was the suggestion that the phenomenon of alteration of oils may not be the same for different types of oil; there was a different kind of alteration in the case of the highly refined oils. Further, there was general agreement that determination of acidity development in ageing tests was necessary.

QUESTIONNAIRE TO NATIONAL COMMITTEES.

As a result of the discussions at the meeting and before proceeding with further programmes it was decided to submit a questionnaire to the National Committees for their replies after consultation with competent authorities in the respective countries.* The document listed the following questions :—

I.A. Which of the following alterations in the oil cause most trouble?

1. Formation of sludge;

2. Formation of soluble material, giving rise to corrosion;

3. Formation of soluble material, deteriorating the electrical properties of the oil (breakdown strength, power factor, etc.);

4. Formation of soluble material, which in addition evaporates and condenses on the colder parts of the transformer or case (volatile acids, water);

5. Formation of gaseous material (methane, carbonic acid, etc.).

B. Is it the opinion of the electrical engineer that, during service, the oil can come in touch with unlimited quantities of air, or is this quantity tied down to a maximum, even in the most unfavourable conditions?

II. Dr B. Anderson, representing Sweden, had been carrying out work in which the apparatus used for ageing oil constituted an experimental transformer. Mr Anderson was anxious to be assured that his investigations would be regarded as being valid for all normal types of transformers and that his method of treatment was in accordance with that which occurs with oil in practice.

Replies to Questionnaire.

Replies to these questions were received from the National Committees of Australia, Belgium, France, Germany, Great Britain, India, and Italy.

It is usually difficult to give positive and clear-cut answers to items in questionnaires of this type, and this difficulty was clearly reflected in most of the replies to this questionnaire. The British reply is given in full below :---

British Reply.

Question IA: 1. Prior to the introduction of B.S. No. 148, transformer breakdowns associated with oil deterioration were mainly attributed to sludge, but since its introduction this type of breakdown has been practically eliminated.

2. No trouble has been experienced due to the formation of soluble material giving rise to corrosion.

3. Even after long use the electrical breakdown strength remains considerably in excess of the minimum to meet the British Standard Specification for electric strength. With regard to power-factor, no importance has been attached to this, and there is little data available.

4. Some trouble has been experienced from the condensation of volatile acids and water on the colder parts of the transformer tank, causing corrosion, especially when the lids of the transformer have been zinc coated, but this practice is no longer followed in this country. This type of trouble has not been met with in transformers having conservator tanks.

5. The formation of methane, carbonic acid, and moisture are concomitant with oxidation of transformer oils, and in the presence of the moisture the carbonic acid causes corrosion.

Question IB: The quantity of air entering a transformer varies greatly with the design of the transformer. In all cases attempt is made to reduce the introduction of air to a minimum and, where size of plant permits, attempts at complete elimination of air are made by the use of a conservator.

Question II: We shall be pleased to see Dr Anderson continue his experiments in transformers, which we have considered with interest, but at the stage reached at present we are unable to accept the transformer method of test as being applicable to all types of transformer.

Replies from other Countries.

With regard to the other countries, the difficulty arose that in some cases the national association did not attempt a reply based on discussion in committee, but invited the opinions of individual interests, whose replies could not fairly be bulked into a single answer because they were too conflicting. The Belgian Committee reported, in connection with question I A, that "the diversity of views expressed does not permit of answering this question. . ." India returned separately the replies of three individual engineers, while Australia furnished the replies of two engineers. However, the replies can be briefly, if freely, summarized as follows :---

Question I A—Australia: (a) Sludge is most troublesome; (b) No serious trouble ever experienced.

Belgium: The effects of various ageing phenomena are discussed. Sludging is the one most feared.

France : Medium refined oils are largely used, and sludge causes most trouble.

Germany : Sludge formation is regarded as troublesome.

Italy : Sludge formation is the most dangerous.

India: (a) Sludge and soluble matter deteriorating the electrical

properties cause most trouble; (b) Deterioration of electrical properties is the chief trouble (but this engineer also refers to considerable quantities of sludge having to be removed, after two years, from some transformers); (c) Sludge causes most trouble.

Question I B—Belgium : On the whole, the answer is in the affirmative. France : Yes—but with qualifications.

Germany : Indefinite.

India: (a) Yes; (b) Indefinite; (c) Indefinite.

Italy : Indefinite.

Question II—Australia: Do not agree with Dr Anderson's test methods. Belgium: Individual replies contradictory—transformer design and operating conditions as important as oil quality—tests therefore required with all sorts of transformers and under all sorts of conditions.

Germany : Favours continuing the work.

India: (a) Approves methods, but would like more consideration to the effect of insulating materials.

Italy : Indefinite.

It is probably fair to summarize majority opinion as stating that sludge formation was the worst feature of transformer oil ageing, or at least the one most to be feared, that there was considerable contact of oil with air in practice, but that it could be restricted by suitable design, and that Dr Anderson's investigations were of sufficient interest to be worth continuation, although considerable doubt was fairly generally expressed with regard to the validity of acceptance of the results obtained as indicative of those in transformers generally, owing to the considerable variations in design and materials of construction in practice.

In their own review of the replies the I.E.C. Advisory Committee in October 1936 concluded that it was important, for technical purposes, to know the tendency of oils to form sludge and soluble products susceptible to being changed into sludge or to producing corrosive effects, and that studies of other manifestations of ageing should be pursued only with a view to elucidating the mechanism of ageing. It also took the view that the only way of taking account of the opinions expressed would be the making of two sets of tests for artificial ageing, one applying to highly refined oils and the other to less refined oils, thus allowing for the very different mechanism of ageing of these two groups of oils. The British Committee, however, asked the I.E.C. in April 1937, that development of international test methods of two types should be held in abeyance pending completion of a new programme of work they were putting in hand for the purpose of determining whether it was desirable to retain the two categories of oils, classes "A" and "B," or only class "B" by the complete suppression of class "A." The British Committee were in agreement with the general conclusion of the majority of members of the I.E.C. Advisory Committee that the most important factor to be taken into consideration was the formation of sludge; they considered that the formation of acid and saponifiable products and the quantity of water formed should be taken into account and, further, that the nature of the volatile or fixed acids should, if possible, be determined.

At a meeting of the Sub-Committee of the I.E.C. held in Paris in June 1937 the British proposal to defer the separate investigation of class "A" oils pending the further work of the British Committee was approved. As far as the other national committees were concerned, a programme of work was agreed on with five oils prepared from Russian crude at various degrees of refinement. Ageing tests were to be carried out at varying temperatures for different periods by the appropriate national method, with measurement of sludge formation and acidic products and, in some cases, saponifiable products. Investigations would also be made of the effects on ageing of electric fields, of air as compared with oxygen and of the quality of sheet steel in contact with the oil, and of the effect of ageing on dielectric losses. In addition, there was a programme of work involving the periodic examination of samples from test transformers.

PROGRAMME OF RESEARCH 1937.

The programme of work started by the British Committee in 1937 was directed towards providing information upon many of the foregoing points with, however, an emphasis upon the study of acidity formation having regard to experiences with class "A" oils. Further, it was recognized that the types of oil available under the designation class "B" varied considerably in respect of acidity development during the sludge test at 150° C. It was felt necessary to collect data upon the behaviour of these oils in long period tests at comparatively low temperature—for example 100° C—and it was envisaged that this study might well lead directly to modifications of the British specifications, possibly by rejection of the present class "A" oil and the introduction of suitable clauses to restrict class "B" oils to those forming less acidity than those commonly used.

The oils chosen for study were as follows :--

Reference "A"-a typical class "A" oil.

Reference "B"-a B.30 oil with a sludge value well below the maximum permitted.

Reference "C"—a B.30 oil with a sludge value at the upper limit (the actual figure reported was slightly above the maximum permitted).

Reference "D"—a B.30 oil of medium sludge value and known to give low acidity formation in the standard sludge test.

The oils, tested against the requirements of B.S. No. 148—1933 by Dr Michie, gave the following figures :—

Oil.	А.	B.	C.	D.
Flash point (closed), ° C	160	162	157	160
Specific gravity at 15.5° C.	0.8654	0.8739	0.8798	0.8815
Evaporation (5 hrs. at 100° C), per		200 A 10 A	dis. Directly	1 10 P
cent	0.88	0.86	1.15	0.88
Moisture	Absent	Absent	Absent	Absent
Acidity	Absent	Absent	Absent	Absent
Viscosity (Redwood seconds) at-		1000	a dana	
60° F.	162	176	158	198
100° F.	68	71	65	75
140° F.	45	46	44	47
Freezing point, ° C.	-44	-49	-52	-49
Colour	Water	Pale	Pale	Dark
	white	vellow	vellow	vellow
Total sulphur per cent	0-039	0.040	0.080	0.066
Conner discoloration test	Nil	Nil	Nil	Nil
Sludge (45 hrs. et 150° C)	0.06	0.30	0.01	0.63
Sundo 120 mo. av 100 0)	0.00	0.50	0.01	0.00

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Each oil was to be oxidized at three temperatures— 100° C, 120° C, and 150° C—for periods of 48, 72, and 96 hours under the otherwise standard conditions of B.S. No. 148/1933. The oxidized oils were to be examined for sludge formation, acid value, and saponification value. The collaborators in this part of the work were Dr A. C. Michie, and Mr A. A. Pollitt of the Metropolitan-Viekers Electrical Co., Ltd., while Mr W. B. Parker of the British Thomson-Houston Co., Ltd., extended the work to the determination of acidity, volatile and non-volatile under the conditions of the test, water-soluble acidity, and carbon dioxide and water formation. Dr Michie included variations of the rate of flow of air and long-period tests up to 1000 hr, and part of the programme was duplicated in the laboratories of W. B. Dick and Co., Ltd.

The conclusions which can be drawn from the work carried out under this programme can be summarized as follows :—

General Observations.

The results supported statements previously made at I.E.C. Advisory Committee meetings that the mechanism of the ageing of highly refined oil is different from that of oil less refined.

The difference may be described as a tendency for sludge formation to occur concurrently with development of acidity in the case of the class "B" type oils, while the class "A" oil tested developed acidity in amounts increasing with time without substantial sludge formation.

It is noteworthy that these comments apply in general to the results obtained at the lower as at the higher temperatures.

The statement frequently made that class "B" oils of comparatively low sludge test are necessarily prone to greater acidity formation than oils of higher sludging value is found to be incorrect, since the sludge test of the low-acidity-type class "B"oil (Reference "D") is intermediate between those of the comparatively high acidity oils (Reference "B" and "C").

Comparison of Acidity Formation of Class " A " and " B " Oils.

The acidity development of the three class "B" oils was in general lower than that of the class "A" oil, and this comparative tendency was especially pronounced in the case of the low-acidity-type class "B" oil for all the temperatures and periods used. These comments apply equally whether the term acidity is used to cover the Neutralization Number of the oxidized oil after separation of the sludge formed, or the total acidity including that of volatile fractions collected.

The validity of conclusions based only upon the relative acidities of the residual oxidized oils might have been considered suspect on the grounds of a lack of correspondence of the test conditions with those of the comparatively totally enclosed systems which result in major retention of acidic compounds in transformers. For this reason, the extension of the work to cover the collection and estimation of the acidity of the material volatile under the conditions of the test was of great value.

Comparative Formation of Products Likely to be Important in Respect of Corrosive Tendencies.

An attempt to draw conclusions from the proportions of acids volatile under the conditions of the tests might possibly be criticized on the grounds that the degree of fractionation into volatile and non-volatile material in the standard sludge test condenser used was insufficiently precise. It is, however, generally considered that corrosion is mainly caused by the lowermolecular-weight acids, and the proportions of these formed in these experiments can probably be approximately assessed by considering the totals of volatile acidity and water-soluble acidity in the oxidized oils, this procedure largely eliminating any objection based on imperfect fractionation of the lower molecular weight volatile material. A comparison of the proportions of corrosive products on this basis showed differences between the class "A" oil and the two class "B" oils References "B" and "C" at the varying temperatures and periods of test used, but the differences were not sufficiently clear-cut to allow of any generalization. However, the proportions formed in the case of class "B" oil Reference "D" were substantially lower than those of the other three oils for all temperatures and periods considered.

Detailed Comparison of Class " B " Oils.

The results obtained are very illuminating with regard to the possible wide difference in types obtainable as class "B" oils. The sludge formation at 120° C of class "B" oil Reference "D" for the three periods used averages approximately one-fifth of those for oils "B" and "C." The amounts of sludge formed in the tests at 100° C were too small for strict comparisons to be made for periods less than 192 hours, at which a definite superiority was shown by the "D" oil, but after 1000 hours at this temperature the "D" oil showed three- and five-fold superiority over oils "C" and "B" respectively.

Oil "D" was found to be superior to oils "B" and "C" in respect of total acidity formation (non-volatile and volatile under the conditions of the tests) for all temperatures and periods used, with one minor exception, where, in any case, a very low figure was concerned, so that a high proportional experimental error might be expected. The ratios of total acidity formation of oils "B" and "C" to that of "D" averaged approximately 2 to 1 at 100° C and 150° C, whilst at 120° C the ratio for "B" to "D" averaged approximately 10 to 1 and for "C" to "D" approximately 6 to 1.

Similar conclusions can be reached in respect of the Neutralization Number of the oxidized oil after separation of sludge formed, with again the striking similarity in the ratios at 100° C and 150° C and the rather higher ratios at 120° C.

Reference has already been made to the distinctive superiority of oil "D" in respect of formation of materials likely to be suspect for their corrosive tendency.

PROPOSED AMENDMENT TO B.S. NO. 148/1933.

The work reported above was completed in 1939, and would have provided the basis for an early recommendation but for the outbreak of war, but amendment of B.S. No. 148 to incorporate tests aiming at selection of class "B" transformer oils of low-acidity-forming type is now the subject of a recommendation to the British Standards Institution.

Information is available that the outstanding characteristic of the

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"D" oil—namely, relatively low acidity formation both in the standard test and in tests carried out at lower temperatures—is shared by other class "B" oils showing similarly low acidity in the standard test. The proposal under consideration is the retention of the present test and limit for sludge formation of class "B" oils with the addition of a clause limiting acidity development in the residual oil in the standard sludge test to a figure based upon that of the "D" oil.

An important consideration is that the amendment, by keeping within the framework of the present specification, avoids the necessity for awaiting completion of the lengthy work involved in a programme of correlation with practice which would be considered essential in the case of a fundamental departure from the present system, while at the same time eliminating the type of oil which must be regarded as suspect in respect of responsibility for such corrosion as has occurred in practice.

The future work of the Committee envisages the inclusion of a programme of correlation with practice using a number of units sufficiently large to provide statistical information, and it is planned that this work will be carried out in conjunction with further work upon the separation from the products of laboratory oxidation of the types especially tending to cause corrosion.

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SOME DEVELOPMENTS IN THE REFINING OF TRANSFORMER OILS.

By J. C. WOOD-MALLOCK.

INTRODUCTION.

THE stresses of war have forced the petroleum refining industry to modify and improve many of its products to meet the ever-increasing demands made on them by the engineer, and it is undeniable that technical progress in fuels and lubricants has been enormously stimulated.

Such progress has in times of emergency generally to be made at the expense of less vital problems, and it is not therefore surprising that the technical press records, during the past five years, no radical changes in the methods used for refining transformer oils, and few contributions to the literature of its chemical and physical history in service. It is hoped, however, to show in this paper that some progress in the former direction has in fact been achieved, and that, while no completely new method of producing transformer oil has been discovered, the effect of various methods of treatment and production are now more clearly understood, and can consequently be applied to the manufacture of a transformer oil of satisfactory physical and chemical properties.

REQUIREMENTS.

Before considering the means employed in producing a finished product, it is essential clearly to understand what are the properties required of that product. A transformer oil, being required to act simultaneously as a dielectric and a coolant, must possess many mutually incompatible properties, and the final product is invariably a compromise, but a compromise in which the preferred properties will vary according to the use to which the oil is to be subjected. Some of these required properties are :---

High insulation resistance.
High dielectric strength.
High specific inductive capacity.
Low loss factor.
High heat conductivity.
High heat capacity.
Low freezing or set point.
Low volatility.
Low viscosity.
Low water tolerance.
High resistance to chemical or physical change, particularly under oxidizing or hydrolysing conditions.

Passivity to copper and cellulose.

WOOD-MALLOCK :

These properties can, for hydrocarbon oils, be divided into three groups:

(a) Properties specific to petroleum oils, controllable to some degree by selection of distillate, but incapable of major variation by selection of refining method;

(b) Properties specific to fully refined petroleum insulants, and incapable of improvement beyond that point;

(c) Properties dependent solely on degree and method of refining, improvement to which no limit can at present be set.

Group (a) includes viscosity, volatility, heat conductivity and capacity, specific inductive capacity, freezing or set point.

Group (b) includes insulation resistance, dielectric strength, loss factor, water tolerance.

Group (c) includes resistance to chemical or physical change, passivity to copper and cellulose.

From this grouping it follows that in working out a production programme for transformer oil manufacture we can do so in two stages, as follows :---

(a) Selection of distillate of suitable viscosity, volatility, heat conductivity, heat capacity and specific inductive capacity, and of suitable chemical constitution to form a base for the refining processes available.

(c) Selection of refining methods capable of giving in the finished oil the desired degree of resistance to chemical and physical change, and neutrality or passivity to copper and cellulose.

No consideration need be given to fulfilment of Group (b) characteristics, as a properly carried out refining process will yield an oil having the maximum properties obtainable in these respects.

SELECTION OF DISTILLATE.

Viscosity.

Low viscosity is desired in transformer oil in order to ensure adequate circulation of oil within the windings and ducts of the transformer. As the absolute viscosity of petroleum hydrocarbons is a function of chemical constitution and molecular weight, increasing with the complexity of the molecule and its size, it follows, therefore, that, all other considerations being equal, the refiner would choose a distillate fraction largely composed of straight and branched chain hydrocarbons of the lowest practicable molecular weight. As such distillates almost invariably contain solid paraffins in solution which would need removal at considerable expense, this type of distillate is preferably avoided in favour of a naphthenic/ aromatic fraction of the lowest practicable viscosity.

Volatility.

Volatility is, presuming efficient distillation methods, inversely related to viscosity, and priority to low volatility can be given only at the expense of increase in viscosity, and vice versa. A satisfactory compromise can usually be achieved.

Thermal Conductivity.

Is low for all petroleum liquids and related to specific gravity and temperature in accordance with the following equation plotted in Fig. 1.

$$K = \frac{0.813}{d} \left\{ 1 - 0.0003 \ (t - 32) \right\}^{-1}$$

where K is thermal conductivity in B.T.U./hr/sq. ft./°F/in, d = specific gravity at 60° F/60° F and t = temperature in °F. Since the oil's



FIG. 1.

Specific gravity/thermal conductivity relation for petroleum oils at 60° f.

effectiveness as a coolant is largely derived from the presence or otherwise of convection currents within it, the slight difference in favour of the lowergravity paraffinic oil as against the naphthenic is in most cases unimportant.

Thermal Capacity (Specific Heat).

Oils of similar viscosity which differ in specific gravity possess different specific heats by virtue of their differing chemical composition.

Fig. 2 shows the relation between specific heat and density in accordance with the equation

$$C = rac{1}{\sqrt{d}} \left(0.388 + 0.00045t \right)^2$$

where C = specific heat in B.T.U./lb/°F, and d and t defined above.



SPECIFIC GRAVITY/SPECIFIC HEAT RELATION FOR PETROLEUM OIL AT 60° F

Specific Inductive Capacity.

The S.I.C. of an oil may vary very considerably in accordance with its chemical composition, roughly within a range 2.0 for highly paraffinic oils to 3.5 or even 4.0 for highly aromatic oils. While transformer design is not affected to the same extent as condenser design by the permettivity of the insulating liquid, a high S.I.C. is desirable for several reasons. When materials of differing permettivities are placed in series, the voltage stresses on them are inversely proportional to their S.I.C. This for the materials normally used generally means that the insulant with the lowest breakdown voltage is most highly stressed-e.g., when oil and air are in series the air has about 2.2 times the stress of the oil applied across it. Similarly with oil and solid dielectrics, the oil is usually the more highly stressed of the two, although its breakdown voltage is lower than that of the solid insulator. Reduction of voltage stress on the oil, as the result of using an oil of high S.I.C., correspondingly reduces the possibility of insulation breakdown, and this would be desirable. While efforts have been made in this direction and transformer oils of S.I.C. 3.5 produced, their stability to heat and oxygen is not yet adequate, and much more work is required before distillate fractions with S.I.C. in excess of 2.5 can be considered as suitable bases for transformer oil manufacture.

Freezing (or Set) Point.

Should the distillate selected become solid when held at a temperature of -30° C under the conditions of the B.S.S. 148—cold test, it will be necessary at some point in the refining process to remove the paraffin wax which causes this solidification. While this is a technically simple process, it is, owing to the heavy refrigeration cost, an expensive one, and, in general, wax-bearing distillates are avoided for this reason. The insistence on transformer oils of lower than -30° C pour point has no justification under the atmospheric conditions prevailing in Great Britain, and while more often than not a pour point of this order is fortuitously obtained in the end, occasionally a suitable distillate is rejected for transformer oil manufacture, or, alternatively, heavy increase in cost is incurred, due to the necessity of dewaxing to a -30° C pour.

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In selecting a distillate as above, stress will naturally be laid on those properties most desired for the particular service in view, since little or no change will be effected in the properties mentioned above by the refining process described below.

EFFECT OF REFINING METHOD UPON PROPERTIES OF FINISHED OIL.

We have already stated that the purpose of the refining treatment is to produce an oil with the desired degree of resistance to chemical or physical change, and neutrality or passivity to the copper and cellulose used in construction windings. Unfortunately for both manufacturer and user, no unanimity exists in this country as to the degree of change permissible, or the relative importance of the degradation products resulting from such change. Production of an oil meeting the requirements of the B.S.S. 148 specification, Class B, can be achieved by a variety of methods, each of which yields a product differing considerably in its performance in service from its neighbour. We must, therefore, unable as we are to produce the perfect dielectric which would have the desired characteristics when new, and remain unchanged except for mechanical contamination throughout its life, discover methods of controlling the tendency of an oil to oxidise or to corrode, and to produce, as a result of its oxidation, volatile acids or solid sludges, or to change electrically from a good insulator to a poor conductor. With such knowledge the required balance of properties can be established, and suitable limits set for the extent to which any phase of deterioration can be allowed to proceed.

In our work on this subject the effect of various refining methods has been studied upon: (a) the tendency of the refined oil to form soluble acidic degradation products; (b) the tendency of the oil to form solid degradation products (sludge); and (c) the tendency of the oil to lose its insulating properties.

All the above are essentially oxidation phenomena, and the question therefore arose as to whether a single method of test could by suitable choice of conditions evaluate an oil in all three respects. It is sufficient for the purpose of this paper to record that this was not found possible, the conditions conducing to adequate comparison of acid-forming tendencies being too mild for comparison of sludge-forming tendencies and vice versa. Two tests, one with stagnant oil at 120° C, for acidity development and insulation stability (the Pirelli test),³ and one with aerated oil at 150° C, for sludge formation (the Michie test),⁴ were found to be of suitable range and sensitivity for our purpose. Both tests have the advantage of comparative simplicity of apparatus and are in use commercially, hence cross check with other laboratories has been possible.

Development of Acidic Degradation Products.

Discussion in recent years has raised the question of acidity formation in service to a position of first importance. While it is probably true that most oils, if used in well-designed transformers under normal loads, will rarely show abnormal acidity development even when used over a period of fifteen years,⁵ a heavy continuous overload or a poorly designed transformer may cause a normally satisfactory oil to break down in a comparatively

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short time, with consequent production of volatile or non-volatile acids. For this reason, and because all oils to-day can be produced if required to be sludge-free in normal service, we consider acidity development to be of prime importance.

Treatment with Sulphuric Acid.

Sulphuric acid is still the classical method of refining electrical oils, and the majority of transformer oils marketed have been treated with this reagent. The effect of acid treatment on acidity development is consistent and well understood. Fig. 3 shows the effect of increasing the quantity



DEGREE OF ACID TREATMENT AGAINST ACIDITY DEVELOPED ON OXIDATION.

of acid used in treatment on the acidity of the oil after ageing. While the slope of the curve varies for different oils, if sulphonation is carried sufficiently far a substantially constant value is achieved for most oils.

It has been found, by examination of the fraction left after complete sulphonation in this way, that while the ratio of combined paraffinnaphthene content to aromatic content in different fractions is roughly constant, irrespective of the crude source, considerable differences can exist in the paraffin/naphthene ratio. If variation in this ratio does not cause marked change in the rate of acid formation, it appears reasonable to conclude that the saturated hydrocarbons behave similarly on oxidation, forming soluble acids rather than insoluble sludge. It follows, as a further corollary, that the reduced tendency of the unrefined oil to produce acids on oxidation is due to the inhibiting action of the sulphonatable com-

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ponent of the distillate. This component can be subdivided into (a) aromatic hydrocarbons and (b) sulphur compounds, both aryl and alkyl. It is well known ⁶ that sulphuric acid increases in its effectiveness as a remover of sulphur compounds from hydrocarbon distillates as its strength is increased, and that oleum (20 to 60 per cent SO₃) is considerably more effective than concentrated (98 per cent H_2SO_4) acid. Unfortunately the stronger acids also react more readily with the hydrocarbon constituents, and it is therefore not possible to say, without further data, which of these effects predominates.

Solvent Treatment with Liquid SO.

Removal of aromatic hydrocarbons and their derivatives can, however, be selectively obtained by the use of solvents, of which liquid SO_2 is one of the most effective. When extraction by this solvent is substituted for



DEGREE OF SOLVENT TREATMENT AGAINST ACIDITY DEVELOPED ON OXIDATION.

sulphuric acid treatment it is found that, for a given distillate, solvent refining yields an oil with much-reduced tendency to acid formation, even when the degree of treatment is carried sufficiently far to give an oil of higher saturated/aromatic ratio than is given by the optimum acid treatment. Furthermore, increase in solvent dosage does not give marked increase in acid-forming tendencies, as is shown in Fig. 4, where the value of the acidity after ageing for the various solvent refined oils is shown to be dependent more on the distillate than on the degree of extraction.

It appears, therefore, that removal of increasing amounts of aromatic hydrocarbons has no great effect on acidity formation. In investigating the converse proposition, however, it was found that whereas removal of an aromatic extract from an oil by solvent treatment had only a limited effect on acidity development, addition of the same extract to a highly refined oil reduced a high acidity index to a very low one indeed. It appeared possible, therefore, that it was not the aromatic hydrocarbons of the extract fraction which were responsible for the inhibition of acid formation so much as sulphur compounds which were only partly removed in the extraction procedure.

As a first approach to confirmation of this theory, the effect of various extract additions on oils of differing degrees of refinement was tried.

Base oil A Extract B		Compositio	Neut. No.	
	Distance Di	Parts A.	Parts B.	ageing.
B.30/1 "" ". A.30/2 "	Nil AEC AET AEPS LAEPS Nil E.1 E.2	100 90 90 90 90 100 90 90	Nil 10 10 10 10 Nil 10 10	$\begin{array}{c} 0.93 \\ 0.86 \\ 0.24 \\ 0.42 \\ 0.60 \\ 1.42 \\ 0.08 \\ 0.34 \\ 0.56 \end{array}$
33 95	AET	90	10	0.26

TABLE I.

Effect of Aromatic Extract on Acidity after Oxidation.

It was found (Table I) that extracts varied considerably in their ability to suppress acidity formation, but that all possessed the property to a marked degree.

Primary extracts—*i.e.*, those most soluble in SO_2 —were more effective than secondary and tertiary extracts of lower specific gravity, but no relationship between effectiveness and viscosity-gravity-constant, specific refractivity or unsaturation (as shown by Iodine No.) could be discovered. Acid-treated extracts were produced by conventional refining methods and their effect examined. It was found that light treatments of the order of 5–10 per cent of acid decreased the effectiveness of the extract, but did not change its effectiveness relative to other similarly treated extracts. Heavy treatments up to 160 per cent weight of 95 per cent acid which might have been expected on the analogy of the heavy acid treatment of distillates to effect substantial removal of sulphur compounds left the extract still approximately 50 per cent effective as an acidity inhibitor.

Owing to the case with which the aromatic extract was sulphonated by sulphuric acid stronger than 95 per cent concentration, it was not practicable to use oleum in an endeavour to obtain a sulphur-free extract. Recourse was therefore made to the synthetic method, and the effect of adding pure aromatic hydrocarbon was studied. Naphthalene, anthracene, and diphenyl were chosen as representing aromatic rings in various states of combination. From the results recorded in Table II it will be seen that no significant reduction in acidity development was observed. It seemed probable, therefore, that the inhibition obtained by the use of extracts was due to the sulphur compounds present therein rather than to the aromatic hydrocarbon content as such. Similar conclusions have been reported by Lassen *et al.*⁷ and Denison ⁸ in studies of lubricating and whiteoil oxidation.

As the effect of pure benzenoid hydrocarbons was negative, attention

Base oil A.	Additive B.	Per cent. by wt. of additive B in oil A as tested.	Acidity of oil after oxidation mgKOH/gm.
B.30/3 "' "' "' "'	Nil Naphthalene Diphenyl Anthracene "	Nil 0·5 1·0 0·5 1·0 0·5 1·0 1·0	0.55 0.45 0.49 0.60 0.52 0.49 0.56

TABLE II.

was directed to their derivatives, particularly those containing sulphur, whose stabilizing effect on the oxidation of hydrocarbons has frequently been reported.^{9, 10} The results of these experiments, given in Table III,

TABLE III.

Effect of Sulphur and Sulphur Compounds on Acidity after Oxidation.

Base oil A.	Additive B.	Per cent. wt. of additive B in oil as tested.	Acidity after oxidation, mg. KOH/gm.
B.30/4 	Nil Sulphur Nil Dibenzyl disulphide """"	Nil 0-01 0-10 1-00 Nil 0-10 0-25 1-00	0.17 0.15 0.01 0.01 1.08 0.16 0.10 0.11

show that not only does elemental sulphur afford almost complete protection against oxidation to a transformer oil under the conditions of our tests, but that almost equally effective suppression of acid formation is obtained by the addition of comparatively small amounts of aryl sulphur compounds, as for example dibenzyl disulphide.

Similar experiments were carried out with substituted amines, cresols, and other compounds largely used in the petroleum and chemical industries as oxidation inhibitors. In no case, however, was the effect on acidity development marked.

Development of Solid Degradation Products.

While we have already stated our belief that the tendency of an oil to produce organic acids during oxidation is of prime importance, it remains true that the consumer's criterion is still the tendency to form solid highmolecular weight products under the conditions obtaining in the B.S.S. (Michie) sludge test. It cannot be too strongly emphasized that production of a transformer oil of low sludging value presents no serious difficulty to the refiner. As is shown in Fig. 5, progressive reduction in sludging value is obtained by increasing the degree of acid treatment, and only in the case of high unstable or sulphurous distillates must the treatment be carried to impracticable lengths. We have already shown, however, that heavy



DEGREE OF ACID TREATMENT AGAINST SLUDGING VALUE OF TRANSFORMER OIL.



FIG. 6.

DEGREE OF SOLVENT TREATMENT AGAINST SLUDGING VALUE OF TRANSFORMER OIL.

acid treatment gives an oil prone to acidity development, and our problem is therefore one of producing an oil of low sludging tendency by means other than heavy acid treatment.

As is shown by Fig. 6, solvent treatment with liquid SO₂ is again un-

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predictable in its effects, certain oils responding almost linearly to increased extraction, while others show little change with varied dosage of solvent. The good results are moreover usually difficult to reproduce by the operation of a commercial plant, for reasons not at present clear, and it is believed that there is no substantial production of transformer oil of medium sludge value (0.4–0.6 per cent sludge in the Michie test) by the use of solvent processes alone. It has been found, however, that a light acid or oleum treatment following solvent extraction produces an oil of satisfactory sludge value with high overall yield, but the oil produced has in general the organic acid-forming tendencies of an acid-treated oil of equivalent sludge value.

In view of the effect of aromatic oils and aryl sulphur compounds on oxidation as shown by acid development, their effect on sludging value has

where the	Composition of blend.		Shudao	
Base oil A.	Extract B.	Per cent. by wt. of A.	Per cent. by wt. of B.	per cent. wt.
B.30/4 ,, ,, ,, ,, ,, ,, ,, ,, ,, ,	HCTLS/A.21	100 98:33 96:60 95 90 99:25 98:5 97:75 97	Nil 1.66 3.33 5 10 0.75 1.50 2.25 3	$ \begin{array}{c} 1 \cdot 16 \\ 1 \cdot 03 \\ 0 \cdot 91 \\ 0 \cdot 93 \\ 0 \cdot 95 \\ 1 \cdot 07 \\ 0 \cdot 94 \\ 0 \cdot 78 \\ \end{array} $

TABLE IV. Effect of Aromatic Extracts on Sludging Value of Transformer Oils.

TABLE V.

Effect of Sulphur and Sulphur Compounds on Sludging Value of Transformer Oils.

Base oil A.	Additive B.	Per cent. wt. of additive B in oil as tested.	Sludge, per cent. wt.
B./30/5 ,, ,, ,, ,, ,, ,, ,, ,, ,, ,	Nil Dibenzyl disulphide """" Mercaptobenzthiazole """""" Nil Dibenzyl disulphide """"""" Mercaptobenzthiazole """""""	Nil 0.0001 0.001 0.01 0.001 0.025 Nil 0.0001 0.0001 0.001 0.00000000 0.0000000000	$\begin{array}{c} 0.29\\ 0.53\\ 0.43\\ 0.69\\ 0.20\\ 0.43\\ 0.41\\ 1.03\\ 0.90\\ 0.50\\ 0.50\\ 0.70\\ 1.07\\ 1.41\\ 1.15\end{array}$

also been investigated, with the results shown in Tables IV and V. It will be observed that although the result may be either to increase or to decrease the sludging value of the oil so modified, it is possible in many cases to add useful quantities of aromatic acidity inhibitors without increasing the sludging value beyond the permissible limit.

The effectiveness as inhibitors of sludge formation of the conventional anti-oxidants previously mentioned was, contrary to the findings made in the acidity inhibition experiments, very varied. Aryl substituted amines e.g., paraphenylenediamine, diphenylamine, phenyl-a-naphthylamine gave limited protection at low concentration, as did nitrobenzene and nitrocresol. The practical value of these findings was largely negatived by the influence of the chemical composition of the oil on the result. Table VI shows the effect of paraphenylenediamine upon: (a) oils of different origin; (b) oils of different degrees of refinement; and (c) oils containing more or less traces of metallic soaps from the refining process.

TABLE	VI.
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Effect of paraPhenylenediamine on Sludging Value of Transformer Oils.

Base oil A.	Per cent. wt. paraPhenylenediamine.	Sludge, per cent. wt.	Text reference group.
B.30/2	Nil	1-19	8
	0-01	0.87	8.
	0-05	0.62	a
B.30/1	Nil	0.83	a, b
	0-01	0.87	a, b
	0-05	0.83	a, b
A.30/3	Nil	0-50	b, c
,,,	0-001	0.47	b, c
,,	0.01	0-50	b, c
	0-05	0.36	b, c
A.30/4	Nil	1.39	C
11	0-01	0.91	c
,,	0-05	0.77	С

It is evident that the anti-oxidant effect is dependent not only on the presence or otherwise of certain hydrocarbon groups, but on the presence or absence of pro-oxidants. With few exceptions, therefore, sludge inhibitors are specific to a given oil in a given state of refinement, and it follows that they may cease to protect should the oil become contaminated in any way—e.g., by mixing with another oil of dissimilar composition.

The possibility of pro-oxidants being introduced into an oil during the refining process has been demonstrated in a previous paper,¹¹ and the necessity for complete removal of metal soaps stressed. It has recently been found, however, that the tolerance of transformer oil for such compounds is much less than that of the more viscous oils used for lubricants and cable impregnation, and that acknowledged oxidation catalysts, such as calcium sulphonates, must be almost completely absent if the oils is to pass the B.S.I. sludge test. This conclusion was arrived at after use of both the synthetic and analytic methods. In the former case calcium sulphonate was prepared by sulphonation of a suitable distillate, extraction of the β -sulphonic acids, preparation of the calcium salt therefrom, and addition of this salt to a suitable transformer oil. Fig. 7 shows that 0-01 per cent of this soap is sufficient to put the oil off-grade. Confirmation that calcium was similarly effective in a plant produced oil was sought by comparing two

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EFFECT OF CALCIUM SULPHONATE ON SLUDGING VALUE.

transformer oils of widely different sludge values, both of which had, however, been produced from the same distillate by the same acid and clay refining process, in the same plant.

The metallic soap content was in each case concentrated by distillation, the residual oil ashed, and the ash submitted to spectrographic analysis in the electric arc. The results are given in Table VII, and show

TABLE '	V	II.
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Inspection results.	Low ash content oil RD. 18.	High ash content oil RD.39.
Sp. gr	0.876 118 0.96 0.6 * * * * * * * * * *	$\begin{array}{c} 0.877\\ 113\\ 1.71\\ 14.0\\ 4\\ 0.005\\ 0.05\\ 0.05\\ 0.005\\ 0.005\\ 0.003\\ <0.001\\ 0.005\\ <0.001\\ <0.001\\ <0.001\\ <0.001\\ \end{array}$

Characteristics of High and Low Ash Content Oils.

* Below lower measurable limit.

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that while the high sludge oil contained 0.0014 per cent ash consisting principally of calcium sulphonate, the low sludge oil contained only 0.00006 per cent ash consisting principally of iron oxide.

Loss of Insulation Resistance.

Although dielectric deterioration accompanies oil oxidation and is to some extent related to the accumulation of oil-soluble acids and insoluble sludges,



FIG. 8.

DEGREE OF ACID TREATMENT AGAINST INSULATION RESISTANCE AFTER OXIDATION.



FIG. 9.

DEGREE OF SOLVENT TREATMENT AGAINST INSULATION RESISTANCE AFTER OXIDATION.

neither acidity nor sludge-forming tendencies are suitable criteria of the suitability of an oil for some high-voltage services. In view of the use of transformer oils for condenser and switch service, it is obviously desirable that the loss of insulating properties on oxidation should be kept to a

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minimum, and the measurement of such deterioration can usefully be made on oils oxidized under the standard conditions of the 50-hour ageing test. The D.C. resistivity of the oil is measured at 70° C before and after ageing.

Typical results on a number of insulating oils produced by various methods are shown in Figs. 8 and 9, and it is apparent that high insulation stability is normally achieved only by oils which have received heavy acid treatments. While careful choice of distillate is of value in minimizing acid requirements, during the past six years such freedom of choice has been impossible, and heavy acid treatment has occasionally had to be employed. The oils so produced were prone to acidity development, and aromatic fractions were added to retard such formation. The effect of such aromatic fractions on insulation stability was not marked at the concentrations employed, but usually reduced the stability somewhat. As shown in Fig. 10, however, there was often a critical concentration around $2\frac{1}{2}-7\frac{1}{2}$ per cent,



EFFECT OF ADDITION OF EXTRACTS ON RESISTIVITY AFTER OXIDATION.

within which range the addition of extract improved the insulation stability of the blended oil. Further experiment with aromatic fractions obtained from a variety of distillates disclosed that although this effect was to be observed to a slight extent in most extract/oil blends, a limited number of extracts, when blended in certain oils only, caused very large improvements in the insulation stability of the oxidized oil. Typical results of this kind are shown in Fig. 14, where the effect of four aromatic extracts of varying origins and degrees of refinement on heavily treated transformer oils of the class A.30 type can be seen to be at a maximum when the concentration of the former is between 5 and 10 per cent of the blended oil. In the case of Extract AET in oil A. 30/2 the resistivity after oxidation can be increased from 4.3 to approximately 40 ohms $\times 10^2$ /cu. m., which means that the loss of insulation resistance under the conditions of test is, judged from the practical standpoint, negligible. This blend represents the blending of extreme types-i.e., a highly aromatic oil in a highly refined oil-and it has been proved by repeated experiment that the maximum improvement is obtained when such oils are combined.

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CONCLUSIONS.

It has been attempted, within the limitations imposed, to show that wide variation in the character of a transformer oil can be obtained by careful selection of both distillate and refining method. While progressive reduction in the sludge-forming tendency of a given oil can be achieved by increasing the quantity and strength of the sulphuric acid used in treatment, the invariable result of this process is a corresponding increase in the tendency of the oil to form acidic degradation products. It is suggested that the auto-catalytic type of oxidation, typical of such highly refined oils, which is known ¹² to proceed to an end-product of soluble acids rather than insoluble condensation products, results from the removal of aromatic sulphur compounds, and that by re-introduction of such sulphur compounds in controlled quantities, retardation of the acid forming reaction can be achieved. Such sulphur compounds may be synthetic, of known constitution, or natural and present in the aromatic fraction obtained by solvent extraction of suitable distillates.⁴

Control of the sludge-forming tendency of the oil is effected by acid treatment, but inhibition of the normal kind—that is, by the extension of the induction period—can be obtained by introducing small amounts of aryl amines. The action of such inhibitors is not only temporary, the reaction proceeding at its normal velocity at the end of the induction period, but is liable to neutralization by more powerful pro-oxidants. Removal of such pro-oxidants is an essential part of the refining process

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the presence of, for example, a few parts per million of calcium sulphonate, a reaction product of the sulphonic acids produced in acid-refining and the alkaline earth present in the clay used for bleaching, violently accelerating sludge formation.

In view of the frequent use of transformer oil as a pure dielectric, a high degree of insulation stability is desirable. It is shown that substantially complete suppression of increase in conductivity on limited oxidation can be obtained by the incorporation of from 5 to 10 per cent of a suitable aromatic extract, and that the maximum improvement is effected when the base oil has been heavily refined with acid. The range of this phenomenon is critical, and it appears probable that only a limited amount of unstable aromatics is tolerable.

It is therefore apparent that the present commercial specification, concerned as it is with the sludging aspect of oxidation alone, allows the production of oils of very widely varying characteristics in other respects. That some further limitations should be imposed, particularly in acidforming tendency, appears desirable, and it is suggested that such limitation is not incompatible with present methods of production.

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A REVIEW OF THE MECHANISM OF THE OXIDATION OF LIQUID HYDROCARBONS.

By PHILIP GEORGE and ALAN ROBERTSON.

SUMMARY.

In the oxidation of liquid hydrocarbons the primary intermediate is a peroxide. If a C-H bond is attacked a hydroperoxide is formed. Conjugated olefins yield ring peroxides by 1:4 addition of the oxygen, and also more complicated polymeric peroxides. Polycyclic aromatic hydrocarbons give transannular peroxides.

After the primary formation of a hydroperoxide the course of the oxidation is governed by its decomposition. Although this is a complex reaction there is much evidence that the ketone is the key decomposition product from which the more highly oxidized compounds are derived.

Hydroperoxide formation in both the thermal and catalysed reactions proceeds by a chain mechanism. Whilst the catalyzed reactions involve free radicals as the chain carriers, there is some evidence that in the thermal reaction the chain carriers can be free radicals or energy rich molecules, depending on the particular hydrocarbon which is oxidized. In the uncatalyzed oxidation the autocatalytic increase in the rate is due to a hydroperoxide catalysed reaction developing side by side with the thermal oxidation. This phenomenon has been observed in many gas phase chain reactions and is known as degenerate chain branching.

THE SEQUENCE OF OXIDATION PRODUCTS.

In the last twelve years many of the complex reactions occurring in the oxidation of liquid hydrocarbons have been elucidated. The main advance has been the discovery of the peroxidic compounds which result from the primary reaction between the hydrocarbon and oxygen. Thus the oxidation of liquid hydrocarbons proceeds by a peroxidation mechanism of the type originally suggested by Bach and Engler rather than by the successive hydroxylation reactions proposed by Bone and others.

Four distinct types of organic peroxide have so far been distinguished in the oxidation of hydrocarbons in the liquid phase or in solution :

1. Hydroperoxide.

This is the most important type, for it is the product of the attack of an oxygen molecule on a C-H bond. Hydroperoxides are formed, and can be isolated in the oxidation of alkyl benzenes such as ethylbenzene and tetralin, and mono-olefines and unconjugated polyolefines such as *cyclo*hexene and ethyl linoleate. It is extremely probable that saturated hydrocarbons also yield hydroperoxide as the primary oxidation intermediate. These saturated hydroperoxides have been prepared by other means and studied by Rieche¹ and others, but even though it is possible to detect them analytically in an oxidation, it is extremely difficult to isolate them because they are unstable and their stationary concentration is very low.

2. Monomeric Peroxides of Conjugated Dienes.

The peroxide of α -terpinene which occurs naturally is a monomeric compound of this type.

3. Polymeric Peroxides of Conjugated Dienes.

All the peroxides of conjugated olefinic compounds, such as sorbic ester, elaeostearic ester, and *cyclohexadiene*, which have been formed artificially have been shown by Farmer and Sundralingam² to be polymeric compounds with up to eight monomer units containing little or no monomeric component.

4. Transannular Peroxides.

These can be formed by the photo-oxidation of many polycyclic aromatic hydrocarbons. There are two distinct classes: those polycyclic hydrocarbons with anyl groups joined to the meso carbon atoms of an anthracene system yield peroxides which on heating dissociate to give the hydrocarbon and oxygen, whilst those polycyclic hydrocarbons without this structure yield photoperoxides which decompose to give products with the oxygen incorporated in the molecule (Bergmann and McLean).³

Of these four types of peroxide, the hydroperoxide is by far the least stable, and it is only in exceptional cases, as in the oxidation of tetralin that yields of hydroperoxide amounting to nearly 100 per cent of the absorbed oxygen can be obtained.

The course of the oxidation thus consists of peroxide formation followed by peroxide decomposition, and it is here that much of the complexity of the reaction arises. As yet there has been comparatively little work on the peroxide decomposition. At least three types of reaction can occur even with a saturated hydroperoxide; alcohols, ketones, and products of chain fission are all formed, and in the case of olefin peroxides. Farmer and Sundralingam ⁴ have shown the reaction to be still more complicated involving interaction between the hydroperoxide group and the carboncarbon double bond to give epoxides. Some of these points are discussed and elaborated in the recent papers by Farmer,⁵ Walsh,⁶ and George and Walsh.⁷

In the oxidation of oils, fats, and many natural and synthetic polymers it is the attack of oxygen on a C-H bond which is the predominant reaction, and so it is the hydroperoxide decomposition products which are important in determining the further sequence of reactions. As far as any generalization can be made, the following scheme describes the course of the reaction when the chain fission reaction of the hydroperoxide does not occur :----

Hydrocarbon \longrightarrow Hydroperoxide \longrightarrow Alcohol

Ketone \longrightarrow Acid \longrightarrow Further Oxidation Products

The important point is that the key oxidation product from which all the more highly oxidized materials derive is the ketone, and this is not formed by the oxidation of the alcohol, but directly from the decomposition of the hydroperoxide.

The chain fission reaction of the hydroperoxide which is most common with the tertiary hydroperoxides has been shown by George and Walsh⁷ to consist first of the splitting of the O-O bond to give an alcohol radical followed by the breaking of the weakest adjacent C-C bond to give a ketone and a hydrocarbon radical. Hence a very similar scheme to that outlined above describes the sequence of oxidation products if the chain fission reaction of the hydroperoxide predominates :---

Hydrocarbon \longrightarrow Hydroperoxide \longrightarrow Alcohol radical \longrightarrow Alcohol

Ketone + Hydrocarbon radical \longrightarrow Hydrocarbon or | Hydroperoxide

Acid \longrightarrow Further oxidation products

Again the ketone is the key oxidation intermediate from which the more highly oxidized products are derived.

Evidence that the oxidation proceeds via ketones rather than alcohols is provided by the experiments of Farmer and Sundralingam,⁴ who in studying the oxidation of *cyclo*hexene found it impossible to oxidize *cyclo*hexene-3-ol to *cyclo*hexenone. George, Rideal, and Robertson ⁸ also found that long-chain saturated alcohols inhibit the metal catalyzed oxidation of long-chain saturated hydrocarbons, and so this particular oxidation cannot proceed through the alcohol as a primary intermediate, otherwise the reaction would be autoretarding, and alcohols would predominate in the oxidation products, which was not found to be so. Larsen, Thorpe, and Armfield ⁹ have analyzed the products in the uncatalyzed oxidation of aliphatic, naphthenic, and aromatic-naphthenic hydrocarbons at 110° C. Some of their experimental results are listed in Table I, where the percentage of absorbed oxygen occurring as peroxide, alcohol, and ketone is given for oxidation over periods of 10–50 hours.

TABLE I.

Hydrocarbon.	Hydroperoxide,	Alcohol,	Carbonyl com-
	per cent.	per cent.	pounds, per cent.
Aromatic-naphthenic	4·3	8-5	27·2
Naphthenic	13·5	8-9	51·4
Paraffinic	4·1	1-9	46-0

Analysis of Oxidation Products (Larsen, Thorpe and Armfield *).

These results are significant, for they show the large preponderance of ketones over alcohols. George, Rideal, and Robertson ⁸ found that alcohols oxidize very slowly compared with ketones, and so the ketone formed in these oxidations cannot have been produced by the oxidation of alcohols, but must have been derived from an earlier oxidation intermediate—the hydroperoxide. These results confirm the sequence of oxidation products outlined above.

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The mechanism of ketone oxidation has not yet been investigated. The recent papers by Farmer and his collaborators all argue against the direct attack of oxygen on an isolated carbon-carbon double bond. This would exclude ketone oxidation as proceeding by the attack of the oxygen molecule on the double bond of the enolic form of the ketone. The most likely course of ketone oxidation is the production of a keto α -hydroperoxide on the methylene group joined to the activating >C=0, followed by the decomposition of this peroxide into acid and aldehyde.

The decomposition of a keto- α -hydroperoxide is formally very similar to that of a tertiary hydroperoxide-fission of the O-O bond followed by the breaking of the C-C bond. The aldehyde formed would be very rapidly oxidized to its corresponding carboxylic acid through the intermediate formation of the peracid. With the possibility of so many peroxidic compounds being present in ketone oxidation, the detection of keto a-hydroperoxides is extremely difficult, especially since alkoxy-peroxides, the addition compounds of ketones and hydroperoxides which were investigated by Egerton, Smith, and Ubbelohde 10 and Medvedev 11 could be formed too. The mechanism for the ketone oxidation outlined above accounts for the experimental fact that in the oxidation the original >CO group stays with the shorter chain. For, as has been well established in a great many reactions of organic compounds, the hydrogen atoms on the α -carbon atom of the longest chain are the most reactive, and so hydroperoxide formation will occur in this position, and the subsequent decomposition gives the observed products. Hence in the oxidation of hydrocarbons there are two main reactions which can lead to the fission of the carbon chain: the decomposition of the hydrocarbon hydroperoxide and the ketone hydroperoxide. Both these reactions depend first on the splitting of the O-O bond, and then the breaking of the weakest adjacent C-C link.

To complete the oxidative degradation of a liquid hydrocarbon the oxidation of the carboxylic acid must be considered. The production of carbon dioxide in this reaction can be readily understood if hydroperoxide formation again occurs on the α -carbon atom :—

$$\begin{array}{ccc} H & O & H \\ R \cdot C \cdot C & OH \longrightarrow R \cdot C \cdot C & OH \longrightarrow R \cdot C + CO_2 + H_2O \\ H & OOH & O \end{array}$$

Thus the main features of the liquid phase oxidation of hydrocarbons are readily explained by the initial formation and decomposition of hydroperoxides. Walsh ⁶ has recently discussed the gas phase oxidation of certain specific straight-chain and branched-chain paraffins, and has shown, too, how the many complex features of the low-temperature combustion of fuels can be explained by the hydroperoxidation mechanism.

In the next two sections of this paper the nature of the reactions by which hydroperoxides are formed in the thermal and in the catalyzed oxidation is discussed.

THE MECHANISM OF HYDROPEROXIDE FORMATION.

The complexity of the kinetics of the thermal and catalyzed oxidations and the marked sensitivity to inhibitors show that these reactions proceed by a chain mechanism. Two distinct types of chain mechanism have been formulated. The chain carriers might be either energy-rich molecules or free radicals, and so one of the main problems is to decide which type of chain mechanism is operative. In seeking to elucidate this problem kinetic methods have been employed. There is, of course, the possibility that the type of mechanism may vary from one hydrocarbon to another, and furthermore that the thermal and catalyzed oxidations of the same hydrocarbon may not proceed by the same mechanism. Too few reaction systems have been studied for any general conclusions to be reached. The choice of such systems is necessarily limited because few hydrocarbons on oxidation give predominantly the hydroperoxide; however, tetralin and certain olefins can readily be made to yield nearly pure hydroperoxide, and it is with these hydrocarbons that the major kinetic investigations have been carried out.

Bolland and Gee ¹² have studied the kinetics of the oxidation of representative mono-, 1: 4-, and 1: 5-olefins, and have found that a free radical chain mechanism best explains the features of the thermal oxidation and the hydroperoxide catalysed oxidation. The double-bond displacement, shown by spectroscopic analysis, which occurs in the course of the oxidation is strong evidence for the participation of free radical chain carriers. Medvedev 11 examined the thermal oxidation of tetralin and assumed it to proceed by an energy chain mechanism; however, as George and Robertson ¹³ have shown from a consideration of various model reactions, no unique choice of mechanism is possible on the sole basis of the kinetics of the uninhibited reaction. From their study of the kinetics of the inhibited thermal oxidation of tetralin they have been able to show that certain free radical mechanisms which can explain the kinetics of the uninhibited reaction are not applicable to the inhibited reaction, and they argue that their experimental results are in favour of an energy chain mechanism. They also examined the oxidation of tetralin catalyzed by benzoyl peroxide, various powders and soluble heavy metal catalysts and proposed a free radical chain mechanism. It was impossible to analyze these reactions further by studying the kinetics or the inhibited system because of direct interaction between the catalysts and the inhibitor.

In examining the evidence for these suggested mechanisms for hydroperoxide formation, it will be convenient to discuss first the thermal reaction and then the catalyzed reactions.

I. THE THERMAL REACTION.

(a) Olefins.

Bolland and Gee ¹² have found that the empirical rate equation for the oxidation of ethyl linoleate is of the form :—

$$-\frac{dO_2}{dt} = k_u [RH]^{3/2} [O_2]^{1/2} \frac{[O_2]}{[O_2] + \lambda [RH]} \quad . \quad . \quad Equ. \ I.$$

where k_u and λ are constants and (RH) and (O₂) the hydrocarbon concentration, and the oxygen pressure, respectively. The appearance of fractional powers of the reactant concentrations, as in many photochemical

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reactions is strong evidence for chain termination by the neutral reaction of chain carriers. The following chain mechanism was proposed :--

The chain carriers are the alkyl and the alkyl hydroperoxide radicals.

(b) Tetralin.

George and Robertson ¹³ found that the initial oxidation rate was proportional to the square of the tetralin concentration and independent of the oxygen pressure.

$$-\frac{d\mathcal{O}_2}{dt} = k_0 [\mathrm{RH}]^2 \cdot \cdot \cdot \cdot \cdot \cdot \mathbf{Equ. 2}.$$

Free radical chain mechanisms involving termination by neutral reaction of alkyl radicals or alkyl hydroperoxide radicals can be immediately dismissed, for these lead to reaction rates proportional to fractional powers of both hydrocarbon and oxygen concentrations. Chain termination by interaction of alkyl and alkyl hydroperoxide radicals is also inapplicable, because then the rate is proportional to the first power of both reactants. The question thus arose as to whether this reaction was homogeneous, for if the chains were initiated and terminated on the surface of the vessel, these experimental results could be accounted for. An examination of the surface catalyzed reaction showed this rate equation to be completely different and similar to that of the benzoyl peroxide and heavy metal catalyzed oxidations (see later), and so there is no doubt that the above expression relates to a true homogeneous thermal reaction. The study of the inhibition of the reaction to elucidate the mechanism can be summarized in the following manner.

The overall rate of a chain reaction is made up of the following terms :---

$Overall rate = Initiation rate \times \frac{Propagation rate}{Termination rate}$

The second term is an expression of the chain length of the reaction being the probability of the further propagation of the chain divided by the probability of its termination. Thus the uninhibited rate can be represented by :—

$$-\frac{dO_2}{dt} = \frac{\alpha p k_c}{b x k_c} \quad . \quad . \quad . \quad Equ. 3.$$

where a, pk_c , and bxk_c are the rates of chain initiation, propagation, and termination respectively: k_c is the chain carrier concentration and x the concentration of the entity with which it reacts in the termination reaction : a and p thus contain reactant concentrations, whilst b is a reaction velocity constant. The chain length is given by P/bx.

In a chain reaction an inhibitor reacts with one of the chain centres. FF If its concentration is I and the velocity constant of its reaction with the chain carrier c, then the initial inhibited rate is given by :—

$$-\left(\frac{dO_2}{dt}\right)_i = \frac{\alpha p k_c}{b x k_c + c I k_c} \quad . \quad . \quad Equ. 4.$$

Four distinct types of inhibitor were used, β -naphthol, *p*-phenylenediamine, *p*-benzoquinone, and iodine, and in all cases the kinetics of the initial inhibited rate were found to be identical with those of the uninhibited rate.

$$-\left(\frac{dO_2}{dt}\right)_i = k_i [RH]^2$$
 . . . Equ. 5.

By an analysis of equation 4 it can be shown that the entity x is independent of the hydrocarbon and oxygen concentrations. It is known that the surface of the vessel plays no part in the reaction; and so the concentration of xdoes not depend on any reactant present. It can be concluded, therefore, that x does not exist and the chain termination is a unimolecular reaction of the chain carrier.

From equation 4 it can be shown that the induction period—the time taken for the rate to reach the uninhibited value within experimental error is given approximately by :—

$$t_i = I_0/a$$
 Equ. 6.

where I_0 is the initial inhibitor concentration. t_i was found to be independent of the oxygen pressure and inversely proportional to the hydrocarbon concentration. Thus the chains are initiated in a first-order reaction of the hydrocarbon.

By observing the variation of the inhibited rate with time, the chain length of the uninhibited reaction can be evaluated, and by determining the temperature variation of the chain length and the overall reaction rate, the activation energy of chain initiation can be estimated. It was found to be 28 ± 2.5 k.-cal.

Thus in the thermal oxidation of tetralin the chains are initiated in a first-order reaction of the hydrocarbon which has an activation energy of about 28 k.-cal, and the chains are terminated in a unimolecular reaction of the chain carrier. These three points exclude a free radical mechanism, and George and Robertson ¹³ suggested the following energy chain mechanism :—

 P^* and RH^* are energy rich molecules. A further study of the relevant activation energies shows that the process of inhibition must not only be regarded as an additional means of terminating the chains, but as a competition for the chain carrier between the hydrocarbon and the inhibitor in which the reaction with the inhibitor is greatly favoured.

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II. THE CATALYZED REACTIONS.

(a) Olefins.

Bolland and Gee ¹² have studied the oxidation of ethyl linoleate catalyzed by its own hydroperoxide and the benzoyl peroxide catalyzed oxidation of ethyl linoleate, methyl oleate, and squalene. The observed rate equations are respectively :--

$$-\frac{dO_2}{dt} = k_a[RH][RO_2H] \frac{[O_2]}{[O_2] + \lambda[RH]} \quad . \quad Equ. 7.$$

and

$$-\frac{d\mathcal{O}_2}{dt} = k_a \left[\mathrm{RH}\right] \left[\mathrm{B}z_2 \mathcal{O}_2\right]^{\frac{1}{2}} \frac{\left[\mathcal{O}_2\right]}{\left[\mathcal{O}_2\right] + \lambda \left[\mathrm{RH}\right]} \quad . \quad \mathrm{Equ. \ S.}$$

There is thus in this case a very marked similarity between the thermal and catalyzed oxidations, and Bolland and Gee have shown that an identical chain mechanism is operative, the only difference being the manner in which the chains are initiated. Whereas in the thermal oxidation the chains are initiated by a direct reaction between the hydrocarbon and oxygen, in these catalyzed oxidations it is the decomposition of the peroxide that yields the free radical chain carriers. The different powers of the peroxide concentrations in the equations given above (7 and 8) arise from the fact that the decomposition of ethyl linoleate hydroperoxide and benzoyl peroxide are second and first order, respectively.

(b) Tetralin.

George ¹⁴ and George and Robertson ¹³ have examined the oxidation of tetralin catalyzed by benzoyl peroxide, powders containing sub-analytical amounts of transition element impurities, and soluble heavy metal catalysts. Similar kinetic behaviour was found in all cases, and the following rate equation was found to be obeyed approximately :---

$$-\frac{dO_2}{dt} = a \frac{[\mathrm{RH}][O_2][X]}{b[O_2] + c[X]} \cdot \cdot \cdot \cdot \mathrm{Equ. 9.}$$

where a, b, and c are numerical constants and X is the catalyst concentration. Thus in the case of tetralin there is no correspondence at all between the rate expression for the thermal and the catalyzed oxidations: the oxidation rates are proportional to the square and the first power of the hydrocarbon concentration, respectively. This is very strong evidence for there being a true homogeneous reaction, and it is extremely improbable that this oxidation is caused by minute traces of soluble catalysts or by the surface of the vessel.

In formulating a mechanism for the catalyzed oxidations, George and Robertson ¹³ have agreed that the free radical character of the decomposition of benzoyl peroxide and the similarity of this oxidation to the autoxidation of hexaphenyl ethane both favour the choice of the alkyl radical and the alkyl hydroperoxide radical as the chain carriers. The proposed chain initiation by a direct reaction between the catalyst and oxygen, and chain termination by reactions of the alkyl hydroperoxide radical with oxygen and with the catalyst. Chain termination by reaction with oxygen offers one explanation for the appearance of the oxygen concentration in the denominator of equations 1, 7, 8, and 9. Bolland and Gee ¹² accounted for this by the several mutual radical reactions possible. It is very difficult to suggest a plausible chemical reaction for the oxygen chain termination reaction, and the explanation given by Bolland and Gee is to be preferred. On the other hand, it is very difficult to formulate a mechanism which accounts for the kinatic behaviour at both low and high catalyst concentrations. The constant rate observed at high catalyst concentrations of radicals. In this case the assumption of chain termination by reaction with the catalyst is inevitable. This is supported by the marked inhibition noted with some metallic compounds in catalyzed oxidations. Two examples are given showing the action of copper stearate as an inhibitor in oxidations catalyzed by cobalt and iron stearate.

(a) The oxidation of a mixture of long-chain paraffins $(C_{15}-C_{25})$ catalyzed by 0.5 per cent cobalt stearate at 110° C.

Copper concentration	Oxidation rate
(per cent by weight).	(cc O2 per cc per hour).
0	3.7
0.15	2.2
0.20	0.7

(b) The oxidation of tetralin catalyzed by 0.5 per cent ferric stearate at 110° C.

This is shown in Fig. 1.



A further most striking case of inhibition is found with cobalt stearate in the oxidation of oenanthaldehyde, where 0.15 per cent of cobalt stearate reduces the oxidation rate from its uncatalyzed value of 720 to 30 cc oxygen per cc aldehyde per hour respectively.

The conclusion to be drawn from this work on the catalyzed oxidation
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of hydrocarbons is that there is very close correspondence between the oxidation of tetralin and olefines under similar conditions and between the several different catalyzed systems. Further experimental work is needed to establish whether or not there is an identical chain mechanism.

III. THE DEVELOPMENT OF THE UNCATALYZED REACTION WITH TIME.

It is now possible to explain the increase in the rate observed in the oxidation of many hydrocarbons as time goes on. This is the phenomenon which Semonov ¹⁵ called degenerate chain branching. It entails the production of a relatively stable intermediate as the product of the primary chain reaction which subsequently reacts independently to give the final product. Sometimes, however, either at the cost of the energy of this secondary reaction or by virtue of free radicals formed in it, further chain centres are produced. In these hydrocarbon oxidations the hydroperoxide and its decomposition products fulfil the role of stable intermediate and final product respectively. The thermal oxidation thus accounts for the initial rate, and the hydroperoxide catalyzed oxidation for the increase in the rate with time.

George and Robertson ¹³ have shown that the equation derived from the variation by Semenov,

$$Rate = Ae^{-\phi t}$$

where A and ϕ are constants is applicable to the slight autocatalysis observed in the oxidation of tetralin.

Further support for this mechanism lies in the fact that it is those hydrocarbons with a tertiary carbon atom that show the most marked accelerating rate. For instance, it is much more noticeable with decalin than with tetralin. It is precisely these hydrocarbons whose hydroperoxide cannot decompose intramolecularly to yield ketone and water but decompose yielding free radicals as George and Walsh 7 have shown.

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OXIDATION AND ANTI-OXIDATION.

By E. A. EVANS (Vice-President).

THE oxidation of transformer oil is probably not materially different from that of other petroleum hydrocarbons, therefore whatever research has been done on the oxidation of any one set of hydrocarbons from petroleum bears some relationship to what would occur with another set. It is insufficient to examine the work on transformer oil and conclude that our knowledge of its oxidation reactions are scanty. Differences do exist which must be studied separately, but it would be unfortunate if all the results which have been obtained with all organic compounds were neglected. Not only is it desirable to consider the whole family of hydrocarbons, but it is essential to trespass on to other fields of organic structures, whether they be fatty oils or synthetic chemicals. No apology will therefore be made for any reference to substances which are not used for cooling electrical transformers, nor is it necessary to evade chemical changes merely because they are not obviously associated with transformer oil. The time is at hand when broad principles must be introduced, studied, and applied. Caution can be observed, provided it does not decelerate progress.

Oxidation of transformer oil produces solid sludge and acidic compounds, both of which are objectionable. Any method by which either or both can be reduced is worthy of consideration. The fear that the method is transitory is insufficient to condemn it. Shyness is not in the tool-kit of the research worker. Refining and uses of different petroleum crudes are ever open. But another approach by chemical additives has been introduced, and is now standardized in many industries.

Oxidation does not necessarily imply the donation or acceptance of oxygen. It can equally well apply to the removal of hydrogen from a compound. Without resorting to the theory of electrons it is difficult to define an oxidizing agent as it would appear that almost any substance containing oxygen can, under proper conditions, oxidize another substance. Ordinarily, carbon dioxide and water are not regarded as oxidizing agents, yet under suitable conditions carbon dioxide can oxidize hydrogen, and water can oxidize carbon monoxide. In this particular reaction temperature is the controlling factor :---

$$CO_2 + H_2 \implies CO + H_2O$$

One of the simplest cases of dehydrogenation is the removal of hydrogen from hydroquinone to form quinone :---



Another well-known example is the oxidation of mercaptans to disulphides :---

2R·SH -2H R·S·S·R

The direct introduction of oxygen into an organic compound occurs only at an unsaturated bond. An ethylenic compound will absorb oxygen at the double bond to form a glycol, ketone or ozonide.



As the oxidation of hydrocarbons is often described as proceeding via an aldehyde to a carboxy-acid, a little caution is required at this stage to prevent any confusion between $-\dot{C}$ —OH and the orthodox aldehyde grouping —CHO. Actually an alcohol is converted into an aldehyde by dehydrogenation.

$$\begin{array}{cccc} R & \stackrel{H}{\longrightarrow} & 0H & \stackrel{-2H}{\longrightarrow} & R - C = 0 \\ H & H & H \end{array}$$

The change from aldehyde to acid is written :--

 $\stackrel{\mathrm{R-C-H}}{\stackrel{\mathrm{H}}{\mathrm{O}}} \rightarrow \stackrel{\mathrm{R-C-OH}}{\stackrel{\mathrm{H}}{\mathrm{O}}}$

in spite of the fact that anhydrous aldehyde is not oxidized to acid by silver oxide. The change is much more likely to occur by dehydrogenation in the presence of water which may form an aldehyde hydrate :—

$$R \cdot C \xrightarrow{H} OH \xrightarrow{-2H} R \cdot C \longrightarrow OH$$

When air or oxygen is brought into contact with a hydrocarbon, oxygen adds on at an unsaturated bond to form a peroxide, or, if there is no unsaturated bond, but a labile hydrogen, it will add on to form a hydroperoxide which is mentioned in the paper by George and Robertson :---

 $RH + O_2 \longrightarrow R \cdot O \cdot O \cdot H$

A chemical oxidation test which relies upon electrical impulses to dissociate the oxygen into atoms is referred to by Pollitt.

The much-spoken-of triphenyl methyl behaves slightly differently :---

$$2(C_6H_5)_3 \cdot C + O_2 \longrightarrow (C_6H_5)_3 C \cdot O \cdot O \cdot C(C_6H_5)_3$$

$$\begin{array}{ccc} C_{6}H_{5}\cdot \bigcirc = 0 + O_{2} & \longrightarrow & C_{6}H_{5}\cdot \bigcirc = 0 \\ H & & 0 - OH \\ C_{6}H_{5}\bigcirc = 0 & + C_{8}H_{5}\cdot \bigcirc = 0 \\ O - OH & H & \longrightarrow & OH \end{array}$$

Benzaldehyde when perfectly pure does not combine with oxygen. Also

 $R \cdot SH + O_2$ does not yield $R \cdot S \cdot S \cdot R$. So, when oxidation takes place a starter must be present, but how it functions probably nobody knows.

Pro-oxidants are substances which donate oxygen directly or indirectly to an accepter of oxygen. There are a number of substances which enter into the construction of engineering projects which fall into this category, notably iron and copper. The influence of iron and copper and their compounds in accelerating oxidation of mineral oils cannot be over-emphasized. It is often assumed that such metals act catalytically, passing from the monovalent to the divalent condition in the case of copper, and with iron from the divalent to the trivalent condition. For the purpose of this paper it matters little whether the iron acts in the metallic state, monovalent, or divalent condition. It is sufficient to know that oxygen is activated by bare iron or copper. The activity can be reduced or stopped by coating the metal face with an inert film. Soluble iron and copper compounds may be inductive, and not catalytic; therefore they are probably different and require different treatment.

Thus, it will be seen that as soon as the oxygen is implanted a potential oxidizing agent is *in situ* to develop what is frequently termed autoxidation. What happens after that is difficult to explain, as the process is complicated and the products which result are numerous, some gaseous, some acidic, and some solid.

Anti-oxidants are substances which check or stop oxidation. Probably they inhibit the formation of the primary oxidant, or destroy it before it can react with its neighbour. Anti-oxidation is not a new subject. It is well known to all workers on corrosion, biology, foods, and many other branches of science. Now it is being applied freely to mineral oils in their many fields of activity in electrical and mechanical engineering.

Gum formation in petrol probably gave the impulse to find anti-oxidants for petroleum products. Egloff and his co-workers, possibly inspired by the work of Moureu and Dufraisse, stepped into the arena and pointed to the inhibitory effects of phenols and aromatic amines. Simplicity was the keynote to those pioneer days immediately after World War No. 1. Catechol, hydroquinone, pyrogallol, and α -naphthol were characteristic of those chosen hydroxy-compounds. *p*-Phenylenediamine was a sample of the simple amine. The co-presence of a hydroxy-group and an amino-group found a natural sequence in such compounds as *p*-aminophenol, methylaminophenol, and benzyl *p*-aminophenol. These assiduous workers found it difficult to obtain good repeatability with petrols, so they suggested that *cyclo*hexene should be used for evaluation. To illustrate the effect of chemical structure numerical values or *cyclo*hexene numbers are given for a selection of antioxidants :—

p-Aminophenol	. 1400
Benzyl-p-aminophenol	935
Dibenzyl-p-aminophenol .	915
Pyrogallol	845
a-Naphthol	. 610
p-Phenylenediamine	475
2:6-Dimethylphenol	175
Resorcinol	55
β-Naphthol .	35

Other additives became necessary to combat colour stability. Sorg¹

showed that the normal aliphatic amines, up to and including the amyl amines, possess stabilizing properties. While the amino group is probably responsible, its effectiveness is modified by the length and number of alkyl groups attached. Primary and secondary amyl amines are effective, and tributyl and triamyl amines have found practical application. To delay oxidation under the influence of metallic catalysts in general, and copper in particular, Clarkson and Pederson² discovered that disalicylalethylenediamine neutralizes its action. And Quimby and Oosterhout³ suggested lecithin as a preventive for haze in petrol.

From these beginnings it will be seen how the development of antioxidants for petroleum oils progressed. There was nothing unnatural in profiting from previous experiences, particularly when the mechanism of oxidation inhibition was little or not understood. Oxygen was a foe which had to be reduced in its activity by any means at the disposal of the chemist. Hence it will not be surprising if quaint compounds are suggested in the patent literature; compounds which do not fit snugly into modern chemical theories. Perhaps chemical theories will benefit by the results obtained by some of them. Certainly those compounds which do reach the flood of usage can be observed on a scale which would shade laboratory experiments.

The oxidation of transformer oil is probably not materially different in mechanism from that of petrol, therefore it is comprehensible that compounds similar in essential features should be used for both distillates. The effective concentrations may be so different that special steps have to be taken to modify a compound to increase its solubility. Sometimes the steps taken to achieve satisfactory solubility robe the fundamental structure so completely that it is almost hidden from view. Let it not be supposed that all adorned compounds are synthesized with this object in view. They may be prepared to differ from a relation protected by patent rights. That pyrogallol can be converted into more soluble forms such as the 5-alkyl pyrogallol-1:3-dimethyl ethers according to Scheumann and Haslam ⁴ well illustrates the case :—



Aliphatic amines 5 which were available made an early appearance in the patent literature, especially for colour stabilization. Preference was given to the secondary and tertiary varieties, starting with tributylamine, and extending the selection to those with a hydroxy-substituent as found in diethanolamine :—

(CH₃·CH₂·CH₂·CH₂)₃N

H·N<CH2·CH2·OH CH2·CH2·OH

The alkylenediamines ⁶ were no doubt introduced to multiply the amine influence. The R, R' can be hydrogen, alkyl, or aryl groups :---

$$\begin{array}{ccc} H & H \\ H_2 N - & - & - \\ Q - & - \\ R & R' \end{array}$$

or they may be substituted. Even the hydrogen atoms attached to the carbon or nitrogen atoms can be replaced. So the dominant feature is the nitrogen suitably placed. The length of the molecule can be extended by treating cracked wax with hypochlorous acid, and the resultant product with ammonia.⁷ By this procedure hydroxyl and amine groups are linked to adjacent carbon atoms.

The simple aromatic amines are represented by the naphthylamines and the substituted naphthylamines 8 :---





a-Naphthylamine.



By the elimination of water and hydrogen from α -amine aldehydes pyrazines are prepared :—

$$2H_2N \cdot CH_2 \cdot CHO \longrightarrow 2H_2O + H_2 + N$$

which, when reduced with sodium and alcohol, are converted into the hexahydro-derivatives or piperazines. It is claimed that diphenyl-piperazine⁹ is superior to phenyl- α -naphthylamine. Bruson ¹⁰ condensed $\beta\beta$ -dichlorodiethyl ether with $\alpha\alpha\gamma\gamma$ -tetramethylbutylphenol, and refluxed the product with aniline at 120° C to obtain :—

$$(\mathrm{CH}_3)_2 \cdot \mathrm{CH} \cdot \mathrm{CH}_2 \cdot \mathrm{C}(\mathrm{CH}_3)_2 \longrightarrow \mathrm{O} \cdot \mathrm{CH}_2 \cdot \mathrm{CH}_2 \cdot \mathrm{O} \cdot \mathrm{CH}_2 \cdot \mathrm{CH}_2 \cdot \mathrm{NH}$$

The success achieved with α -naphthylamine apparently suggested the use of $\alpha\beta$ -dinaphthylamine.¹¹



Compounds with nitrogen in the benzene ring have not escaped attention. *n*-Alkyl pyrrole, *n*-alkylpiperidine, pyridine, or quinoline, and $\alpha\alpha'$ -dipyridyl are claimed as antioxidants,¹²



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Among the nitrogen compounds must be mentioned NN'-diphenyl-pphenylenediamine,¹⁴



and the bicomponent mixture diphenylamine and ditert.-butyl-4-methyl phenol¹⁵:--





2:6-Ditert.-butyl-4-methyl phenol.

OH

In place of the diphenylamine may be used benzyl-p-anisidine 16 :--



or N-tetrahydrofurfuryl-p-aminophenol 17 :---

CH₂-CH₂ CH₂ CH-CH₂-NH

The simple phenols which are active antioxidants usually suffer from their comparative insolubility in mineral oil. A method by which pyrogallol has been rendered more soluble has already been mentioned. *tert.*-Butyl cresol ¹⁸ is miscible and effective, probably by virtue of its aliphatic groups and its phenolic character.

A combination of a phenolic group and an amine group in the same compound is found in disalicylal ethylenediamine.¹⁹



With the general dislike for sulphur in transformer oil it would seem to be bold to suggest the addition of a compound of sulphur to improve it. The antagonism to sulphur goes back to the days when deleterious sulphur was not always removed and was a potential danger to bright copper surfaces. As an extra guardian to safety it was decreed that all sulphur compounds should be reduced as far as possible irrespective of their stability. Now it is necessary to consider afresh this subject when we find that the addition of dibenzyl disulphide and β -naphthol²⁰ reduces oxidation of the oil and does not stain copper within the temperature range of usage.

OH



Aromatic thioethers and polysulphides have been suggested of which hydroxyaryl thioethers 21 are an example :----



In the aliphatic range we find amyl mercaptyl diethyl ether ²² :---

$$0 < \stackrel{\mathrm{CH}_2 \cdot \mathrm{CH}_2 \cdot \mathrm{S} \cdot \mathrm{C}_5 \mathrm{H}_{11}}{\mathrm{CH}_2 \cdot \mathrm{CH}_2 \cdot \mathrm{S} \cdot \mathrm{C}_5 \mathrm{H}_{11}}$$

or diethyl xanthyl ethyl ether 23 :---

$$\begin{array}{l} \mathrm{S=C} < \mathrm{CC_2H_5} \\ \mathrm{S=CH_2CH_2CH_2} \\ \mathrm{S=C} < \mathrm{CH_2CH_2} \\ \mathrm{CC_2H_5} \end{array}$$

Then there are the compounds containing both nitrogen and sulphur in which the amino-group and the thioether or disulphide group are incorporated 24 :---

Tetramethyl thiuram disulphide.

$$C_{6}H_{11}$$

 $C_{6}H_{11}$
 $N-S-S-N < C_{6}H_{11}$
 $C_{6}H_{11}$
 NN' -Dithiobisdicyclohexylamine.

and the heterocyclic type thiomorpholines 26 :---

$$\begin{array}{c} \mathrm{S} < & \mathrm{CH}_2 - \mathrm{CH}_2 \\ \mathrm{CH}_2 - \mathrm{CH}_2 \\ & Nn - \mathrm{CH}_2 \cdot \mathrm{CH}_2 \cdot \mathrm{CH}_2 \cdot \mathrm{CH}_2 \cdot \mathrm{CH}_2 \cdot \mathrm{CH}_3 \\ \\ & Nn \cdot \mathrm{Amyl \ thiomorpholine.} \end{array}$$

In conclusion, it is interesting to see how the study of the stabilization of fats and fatty foods can be turned to account with petroleum products. In 1923 Bollman 27 patented the use of lecithin, which consists of two fatty radicals esterified to glycerol, and a phosphoric radical attached to a nitrogenous base group choline. It was later shown that it is really :---

$$\begin{array}{cccc} \mathrm{CH}_2 \cdot \mathrm{OOC} \cdot \mathrm{R} & \mathrm{CH}_2 \cdot \mathrm{OOC} \cdot \mathrm{R} \\ \mathrm{CH} \cdot \mathrm{OOC} \cdot \mathrm{R}' & \mathrm{CH} \cdot \mathrm{OOC} \cdot \mathrm{R}' \\ & & & & \\ \mathrm{OH} & & & \\ \mathrm{OH} & & & \mathrm{OH} \\ \mathrm{Lecithin.} & & & \mathrm{Cephalin.} \end{array}$$

or 25

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the cephalin fraction of the phosphatide that is the active compound.²⁸ The phosphatides attracted the attention of Eckey²⁹ who protected by patent the use of the phosphoric acid fragment in the β -position to the amino group. Similarly Epstein and Harris³⁰ obtained the molecule minus the cholamine and one of the fatty acid radicals.

Lecithin³¹ has been patented for use in petroleum.

This list of compounds does not cover the whole field of possible antioxidants, nor does it attempt to evaluate them. It only indicates the various types which might be used or form a basis for extended study. It is clear that the subject has been the subject of considerable research.

As we have studied oxidation in the past so we shall study anti-oxidation in the future.

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THE INFLUENCE OF STRUCTURE ON THE OXIDATION REACTIVITY OF HYDROCARBONS.

By PHILIP GEORGE and ALAN ROBERTSON.

In the preceding paper it has been shown that the oxidation of liquid hydrocarbons at low temperatures proceeds by a chain reaction, the first isolatable product, both in the catalyzed and uncatalyzed reactions, being in the majority of cases a hydroperoxide of the form ROOH. Obviously in a consideration of the oxidation of oils, themselves complex mixtures of hydrocarbons and alicyclic compounds, it is of great value to know the relative rates of oxidation and the nature of the final reaction products formed by the various types of hydrocarbon. This question has been attacked many times before, the most comprehensive series of experiments having been carried out by Larren, Thorpe, and Armfield.¹ In general, however, it can be said with truth that owing to the complex nature of most oils and to the uncertainty as to the correlation between laboratory experiments and the actual deterioration in use, any such work can only hope to point out useful lines of development.

REACTION PRODUCTS.

The first isolatable product in those cases which have been thoroughly investigated has been the hydroperoxide. These have been obtained in the case of *cyclo*hexene,² tetralin,³ and ethyl linoleate 4 :--



CH₃(CH₂)₄CHOOH(CH=CH)₂(CH₂)₇COOC₂H₅

The point of attack in the various molecules will be discussed in more detail later in the paper. This peroxide then decomposes (the decomposition being catalyzed by the soaps of metals such as copper, cobalt, iron, etc.) to give in the main a mixture of ketone and alcohol as follows :---

and

RR CHOOH \longrightarrow RR CO + H₂O. 2RR CHOOH \longrightarrow RR, CHOH + other products.

In addition, in the oxidation of unsaturated compounds there is to some extent during the decomposition an attack on the double bond to give the peroxide. The relative proportion of the different products depends obviously on the oxidation conditions. Sully ⁵ has found 20 per cent alcohol and 80 per cent ketone in the oxidation of ethylbenzene using copper catalysts. As has been mentioned in the previous paper, the decomposition of the tertiary hydroperoxides follows a slightly different

course, as the simple ketonic breakdown is structurally impossible, but the final products are basically the same.

The main end products are therefore mainly acids, formed from the subsequent oxidation of the ketones, and alcohols, partly in combination as esters. Although the acids are the main source of trouble as the cause of corrosion in practice, the polymeric products, which have not so far been touched on, are also of considerable importance. Although much work has been done on them, their chemical nature and the mechanism of their formation remain obscure. It can be shown, however, that polymeric substances are formed in the decomposition of peroxides, particularly at higher temperatures. A solution of tetralin hydroperoxide in tetralin was passed in a current of nitrogen down a glass tube heated at 220° C. It was found that a brown non-volatile product was formed which was soluble in benzene. The weight of polymer formed corresponded to about 5 per cent of the peroxide decomposed. It was found that the inclusion of olefines in the solvent caused an increase in the amount of polymer formed, presumably due to induced polymerization. The use of peroxides for the catalysts of polymerization is, of course, well known, as in the use of benzoyl peroxide to polymerize styrene.

STABILITY TO OXIDATION.

The point of attack in a hydrocarbon is invariably at the weakest C-H bond, and the rate of oxidation is roughly dependent on the strength of that bond. The strength of such a bond can be most easily measured by the energy required to remove the hydrogen atom. Such a removal to give a free radical can be considered in two steps :---

(a) Removal of the atom without alteration of the electronic structure of the radical. This will require energy roughly equal to the strength of the C-H bond in methane (102 k.-cals.).

(b) Rearrangement of the radical if extra resonance is possible, giving out the excess resonance energy.

This can be most easily illustrated by the case of toluene. In step (a) the H atom from the methyl group is removed and the valencies of the carbon atom remain tetrahedral. In step (b) the carbon valencies become planar in the plane of the ring, and the π electrons of the ring can now pass into the orbitals of the side-chain carbon, giving an extra possibility of resonance, and therefore extra resonance energy. The gain in energy in this case would be expected to be of the order of 10 k.-cal. and in the case of a methylene group next to a double bond to be about 14 k.-cal.

Thus in any hydrocarbon the strength of a bond RH will depend on the resonance energy of the R radical. In the following cases the weakening of the bond due to this effect is obvious :--





This, of course, explains why the hydrogens in the carbon atom of ethylbenzene are attacked and also those in the methylene group next to the double bond in *cyclo*hexene.

In the case of paraffins and naphthenes the position is not quite so obvious. But the work of Polanyi⁶ and others has shown that the strength of the RH bond in the simpler hydrocarbons can easily be calculated from experiments on the rate of pyrolysis of alkyl iodides, and that these results are in agreement with those calculated from the resonance energy of the various radicals and also from the dipole moments. The results show that the resonance energy will increase along the series

$$CH_3 \cdot CH_2 \leq CH_3 \cdot CH \cdot CH_3 \leq CH_3 \cdot CH_3 \cdot CH_3$$

Thus the tertiary hydrogen atoms will be the most reactive, then the secondary, and then the primary. This receives confirmation from the work of Chavanne and others ⁷ on substituted *cyclo*hexanes, where the point of the attack is the tertiary carbon atom in the ring.

It is therefore not too difficult to predict the stability to oxidation of a pure hydrocarbon of known structure. In the uncatalyzed oxidation the overall picture is complicated by the fact that the decomposition of the tertiary hydroperoxides gives rise to radicals which act as chain starters. The rate of oxidation when catalyzed by metal soaps should therefore give a clearer picture of the effect of structure. Table I gives some examples of the rates of oxygen uptake of various hydrocarbons, when catalysed by 0.5 per cent copper stearate at 110° . The results are given in cc of O_2 per cc hydrocarbon per hour.

TA	BLE	I.
----	-----	----

Aromatic Hydrocarbons.			
Naphthalene		ext	0
Tetralin	5-135	1013	125
Ethylbenzene	1.10	1 . 171	7.5
isoPropylbenzene			6-0
p-Methylisopropylbenzene			7.6
tertButylbenzene			0-02
Mesityleno		1.00	4.8
Naphthenes.			
Dekalin .	- 101 -	1000	4.3
Ethylcyclohexane	0	1.	1.5
isoPropylcyclohexano			2.2
1. Methyl-4-isopropylcyclohexane			5.7
tertButylcyclohexane	0,414,0		0.35
1:2-Dimethylcyclohexane	0-1		6.6
1:4-Dimethylcyclohexane			6.0
1:3:5-Trimethylcyclohexano		2.5	11.2
Paraffins.			
Straight-chain paraffin (C15-C25 mixture)			0.25

Consider, for instance, the oxidation of naphthalene and its hydrogenation products. In naphthalene itself all the hydrogen atoms are attached directly to the ring, and it is therefore very stable. However, when one of the rings is hydrogenated, two methylene groups activated by a benzene ring have been introduced into the molecule. The result is a very reactive compound with an oxidation rate of 125. Further hydrogenation to tetralin, however, removes the activation, but gives two tertiary carbon atoms. The net result is a decrease in the oxidation rate to 4.3, still, however, much greater than the rate of naphthalene.

A further interesting series is *iso*propylbenzene, *tert.*-butylbenzene, and *tert.*-butylcyclohexane. Here substitution of the H atom on the α -carbon atom of the former leaves no active hydrogen, and the rate becomes extremely slow. But hydrogenation provides a new tertiary carbon atom and gives an increase oxidation rate, though still a small one.

In the case of mesitylene and its hydrogenation product 1:3:5-trimethyl*cyclo*hexane, it can be seen that the introduction of three tertiary carbon atoms has more than compensated for the loss of the three activated methyl groups in the side-chains and the oxidation rate is increased by more than two.

SPECIFICITY OF CATALYSTS.

Hydrocarbons also vary very markedly in their response to different metallic catalysts. Copper stearate, for instance, is an excellent catalyst for tetralin, but a very poor one for long-chain paraffins. Cobalt and iron stearates are equally good for both. Some results are given in Table II.

Hydrocarbon.	Catalyst.	Rate.
Long-chain paraffin	None	0.25
	Copper stearato	0.25
	Iron stearate	4.9
	Cobalt stearate	4.6
Tetralin	None	12
	Copper stearate	125
39	Ferric stearate	190
Steario acid	None	0.5
	Copper stearato	1.2
	Cobalt stearate	7.4
	June Storature	

т	AB	LE	II.
		-	

Rates of Oxidation in cc O₂/cc/hr at 110° C using 1 per cent Catalyst.

In addition, as has been mentioned in the previous paper, if copper stearate is added to a long-chain paraffin catalysed by cobalt stearate, the rate falls to that due to copper stearate alone.

OXIDATION OF MIXTURES.

The overall rate is in fact made up of the rates of the separate reactions participating in the chain. In fact, the overall rate can be written as follows:

Oxygen uptake = Chain initiation rate
$$\times \frac{\text{propagation rate}}{\text{termination rate}}$$
.
(where chain length = $\frac{\text{propagation rate}}{\text{termination rate}}$.)

The reaction rate can therefore be affected by changes in all these three. The phenomenon of induced oxidation (essentially due to an increase in the G G chain initiation rate) and inhibition (due to increase in termination rate) are too well known to need further comment.

Any hydrocarbon may be unreactive for either of two reasons :---

- (a) Because the chain initiation rate is low.
- (b) Because the chain length is low.

A hydrocarbon of type (a) if added to a normally reactive hydrocarbon would be expected to act purely as a diluent, whereas one of type (b) might retard the reaction. The rate of oxidation of 50 per cent mixtures of ethylbenzene and other hydrocarbons catalyzed by copper stearate was therefore measured. The figure in parentheses gives the rate to be expected on purely diluent action.

Naphthalene . . 0 10 (3.8) Anthracene . . 0 (3.8)	Added hydrocarbon.	Rate.		
Anthracene (2 per cent.) 0.50 (7.2) Phenanthrene (20 per cent.) 4.1 (6.0) tertButylbenzene 3.8 (3.8) Ethylcyclohexane 4.0 (4.5) Long-chain paraffin 3.7 (3.9) n-Octane 3.8 (4.3)	Naphthalene	$\begin{array}{c} 0.10 \ (3\cdot8) \\ 0 \ (3\cdot8) \\ 0.50 \ (7\cdot2) \\ 4\cdot1 \ (6\cdot0) \\ 3\cdot8 \ (3\cdot8) \\ 4\cdot0 \ (4\cdot5) \\ 3\cdot7 \ (3\cdot9) \\ 3\cdot3 \ (3\cdot9) \\ 3\cdot8 \ (4\cdot3) \end{array}$		

TABLE III.

It is obvious from the above figures that whereas the naphthalenes and paraffins behave almost completely as diluent, the polycyclic aromatics showed a very considerable retarding effect. As phenanthrene shows a much less marked effect than anthracene, it would seem likely that the retarding effect is due in some way to the active hydrogen atoms in the 9, 10 positions. In fact, anthraquinone could be detected in the mixture after oxidation, although it was not itself an inhibitor.

Further investigation showed that, in fact, the retardation by anthracene is most marked in the case of alkyl benzenes with copper catalyst as the following results show.

Hydrocarbon mixture.	Catalyst.	Rate.
Ethylbenzene + 2% Anthracene ;; + 2% Anthracene I-Methyl-4-isopropylcyclohexane + 2% Anthracene	1% CuSt ₂ 1% FeSt ₃ 3/10% CuSt ₂	7.5 0.5 8.8 3.2 5.7 1.0

TABLE	\mathbf{I}	Y	
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(St = stearate.)

Surprisingly enough, anthracene was found to have almost no effect on the uncatalyzed reaction, which lends weight to the argument previously advanced on kinetic grounds that the uncatalyzed and metal-catalyzed reactions are of fundamentally different type, although leading to the same product by similar steps.

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The effect of the introduction of side-groups into the ring of ethylbenzene was touched upon to some extent. A mixture of ortho- and paranitroethylbenzenes was prepared by direct nitration, although the isomers were not separated. The result of the introduction of the nitrogroups was the almost complete cessation of the oxidation reaction, although in a 50:50 mixture with ethylbenzene the nitro-compound behaved as a diluent and showed no retarding effect. Here obviously the rate of chain initiation has been considerably cut down by the introduction of the nitrogroup.

INHIBITION.

An inhibitor may function in two ways :--

- (a) By reacting with a chain carrier.
- (b) By reacting with the catalyst in a catalyzed reaction.

In the investigations of the uncatalyzed oxidation of tetralin which have been published previously use has been made of β -naphthol in order to clucidate the various parts of the chain mechanism. Assuming that each inhibitor molecule stops one chain, it was calculated that the chain length in the oxidation of tetralin was of the order of a few hundred at about 100° C, and that the chain length decreased as temperature increased. Similar experiments on the reaction catalyzed by copper stearate lead to no clear result because of complex formation between the catalyst and inhibitor. This was shown by an obvious colour change in the more concentrated solutions. Thus in this case the inhibitor fulfils both the above functions. This seems to be the case with the majority of inhibitors normally used.

A few experiments were carried out on the effect of inhibitor structure on efficiency. Various substituted phenols were used and the decrease in oxidation rate found for various concentrations. Table V shows the relative efficiency of the inhibitors in arbitrary units.

Inhi	Efficiency.				
p-Nitrophenol p-Chlorophenol Phenol p-Methylphenol	•	••••••	•••••	•	0-07 0-57 1-11 5-10

TABLE V.

(Tetralin-uncatalysed 110°.)

As the efficiency of an inhibitor is a rough measure of its ease of oxidation, it is interesting that once again the introduction of a nitro-group decreases the tendency to oxidize as in the case of nitro-ethylbenzene.

THE OXIDATION OF OILS.

The problem of the oxidation of oils in actual use is an exceedingly complex one. Considering the problem from a purely academic viewpoint, the number of unknown factors in the deterioration in use is so great that laboratory results may bear little relationship to those, say, in an engine.

Considering the deterioration of aircraft engine lubricating oil, to tackle the problem *a priori* the following factors would need to be known :—

(a) The conditions under which the major part of the oxidation takes place;

(b) The nature and method of production of the undesirable oxidation products;

(c) The constitution of the oil concerned and its effect on oxidation rate;

(d) Metals likely to go into solution in the oil in the engine.

The line of attack which has been adopted here is to attempt to answer (b) and the second half of (c) on the basis of assumptions as to (a) and (d). It is possible on the foundation of the previous results to predict in some measure the stability of an oil under known catalyst and temperature conditions if its structure is known. But an elucidation of the structure sufficiently detailed to make the prediction is exceedingly difficult. We require to know :—

(a) What proportion of the oil is of non-aromatic character (considering, for instance, the ethyl group of ethylbenzene in this category);

(b) What percentage of the non-aromatic carbon atoms are primary, secondary and tertiary;

(c) To what extent are these carbon atoms activated by aromatic rings;

(d) Are there any potential oxidation retarders in the oil, considering here both polycyclic hydrocarbons such as anthracene, and also possible nitrogenous and sulphur-containing inhibitors.

Precise knowledge of these matters is obviously difficult to obtain. It is possible, however, to get a certain amount of indirect information. For instance, the natural retarding powers of the constituents of an oil can easily be evaluated by determining the oxidation rate of a mixture with a pure hydrocarbon of known oxidation rate. Also ultra-violet spectra should yield valuable information on the concentration of polynuclear aromatics, especially when combined with a study of the spectra of pure compounds and their alkyl derivatives. Experiments on one oil showed that mixture with ethylbenzene in equal parts gave an oxidation rate corresponding to the addition of about 1 per cent of anthracene. Now examination of the ultra-violet absorption spectrum in the region 3500-3800 Å (where anthracene has a marked series of bonds) showed an absorption coefficient corresponding to approximately this concentration of anthracenes. This comparison is made simpler by the fact that the addition of paraffinic side-chains to polynuclear aromatics does not greatly alter the position or intensity of the absorption. Similarly it is possible that the examination of oils in the infra-red region might yield information as to the types of carbon atoms in the oil, similar to the examination recently made of polystyrene to determine the proportion of phenyl groups attached to the chain.

The question of the correlation of laboratory results on oxidation rates with the actual stability in practice is also a complex one. Presumably,

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in this case an oil starts to oxidize almost uncatalyzed, and gradually dissolves away various catalytic metals as acids are produced. It is fairly certain that in the low-temperature oxidation (say below 200° C) the greater part of the oxidation takes place in solution, and not on metal surfaces. Experiments with metallic copper at 150° C indicate that the oxidation rate of an oil is much less than that catalyzed by copper stearate at 110° C. Under working conditions it is not merely the rate of formation of oxidation products, but also their nature which is important.

To sum up, the laboratory investigation of the oxidation of pure hydrocarbons has yielded considerable insight into the mechanism of oil deterioration by oxidation. Complex oxidation conditions and the complex nature of oils mean that the problem has only been touched upon as far as concerns the practical aspects. However, it would seem that some useful knowledge is to be gained from such investigations, especially along the lines of the correlation of infra-red and ultra-violet spectroscopic results as a means of determining those structural characteristics of an oil which affect oxidation stability.

We are indebted to Professor E. K. Rideal for many interesting and valuable discussions during the course of this work, and we wish to thank the Department of Scientific and Industrial Research (P. G.) and the directors of the "Shell" Refining and Marketing Co. Ltd., for financial assistance in the experimental work.

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THE SLUDGE TEST FOR TRANSFORMER OILS.

By C. H. BARTON.

INTRODUCTION.

THE test generally used in Great Britain (for controlling the stability of transformer oils towards oxidation) is the Institute of Petroleum's test I.P.-56/45 for sludging value, which is essentially the same as the test included in the British Standards Institution's specification B.S.S. No. 148, 1933, for transformer oils. The test, frequently referred to as the B.S.I. Sludge Test, is based on one put forward by Michie about forty years ago.* The test was recognized by the Institute of Petroleum in 1924.

In the sludge test the oil under examination containing copper foil is held at 150° C for 45 hours, and a current of dry, purified air is passed through the oil at a controlled rate. At the conclusion of the oxidation treatment the percentage of solid oxidation products—the so-called sludge insoluble in light petroleum (L.P.) spirit, is determined. According to the British Standards Institution's classification of transformer oils, Grade A oils should give sludge values not greater than 0.1 per cent, and Grade B oils not more than 0.8 per cent.

The test has been widely criticized in the past, chiefly on the grounds that (a) the testing temperature—namely, 150° C—is far higher than that to which oils are subjected in transformers, and (b) no account is taken of the development of acidity, increase in viscosity, or other changes which take place in the oil as a result of the oxidation treatment. In the present paper it will be shown that a third criticism may be brought against the method namely, that the test results suffer from poor reproducibility and repeatability.

HISTORICAL REVIEW OF EXPERIENCE WITH THE SLUDGE TEST.

Until 1930 the sludge test was regularly applied to transformer oils in only one of the Shell Laboratories. The test was known to give erratic results, but serious difficulties did not arise until results were compared with those of other laboratories.

In 1931 the sludge-test apparatus built from British parts was installed at the laboratories of Rhenania-Ossag in Hamburg. These laboratories were equipped to carry out all the important oxidation and stability tests for transformer oils applied in Europe, such as those of the V.D.E. (Germany), A.S.E.A. (Sweden), Brown-Boveri (Switzerland), etc., and the staff had acquired great experience in the testing of transformer oils.

The results of the Hamburg laboratory were compared with those of the "Shell" Central Laboratories in London, but agreement was poor. Every precaution was taken in exchanging samples, which were packed in special stoppered and sealed brown glass bottles. A representative of Central Laboratories therefore visited Dr Michie's laboratory at Newcastle. As a result of this visit minor amendments were made which brought the Central Laboratories' equipment and technique into line with Dr Michie's on all essential points of detail.

By 1932 fair agreement had been attained between the two Group laboratories as far as B class transformer oils were concerned, but correlation on A class oils had not been reached. Representatives of these laboratories therefore arranged a meeting, and spent a month studying the test. Details of apparatus, materials, and technique were thoroughly explored and discussed, a joint report being issued in which, *inter alia*, the following points were clarified :—

1. Minor differences of technique were traced down and their effect examined. Their influence was shown to be negligible, but they were nevertheless eliminated, and a standard technique was agreed.

2. Apparatus differences were examined and eliminated. One laboratory used Jena glassware, whereas the other used Pyrex. Check experiments showed that this difference was of no significance. Variations in the methods used for controlling the rate of air-flow were also investigated, but it was shown that lack of agreement could not be attributed to this cause. The arrangements for air purification, bath heating, temperature control, etc., were found to be satisfactorily uniform.

3. The petroleum spirit used by the two laboratories for precipitation differed to some extent, although each complied with the specified requirements. Check experiments revealed that the two spirits gave identical results.

Two operators carried out parallel series of experiments using the unmodified techniques previously adopted at the two centres, with the following results :---

	Rhenania	Technique.	Central Labs	s. Technique.
	German	English	German.	English
	operator.	operator.	operator.	operator.
Oil A	0.06	0-09	0-04	0-03
Oil B	0-07	0-11	0-06	0-07
Oil C	0-02	0-04	0-02	0-04

The final conclusion stated in the joint report was that "anomalous results recorded here must be due to factors beyond ordinary control."

In 1933, difficulties still continuing, it was decided to carry out an investigation of the progress of the oxidation reaction as shown by development of acidity, saponification value, and specific gravity in the samples being oxidized. The results confirmed published work in showing that the oxidation is approximately linear with time, and that autocatalytic effects are negligible. They also showed that oils giving low sludge values yielded higher acid values than less highly refined oils.

By 1935 concordant results had still not been attained, and a further

investigation was carried out on the effect of using different precipitation spirits, with aromatic contents varying up to the maximum permitted by the specification. The conclusion arrived at was that variation in aromaticity within this specified range had no significant effect on results.

In 1936 the London laboratories were called upon to examine four samples in order to clear up a disagreement between three centres in Mexico. The figures obtained on these samples by one of the Mexican laboratories were available, the comparison with the parellel London figures being :---

Sample.					London Labs.	Mexican Labs.
A B C D	•	• • • •		• • • •	0.77 0.91 1.08 0.90	0.78 0.72 0.81 0.86

By this time it had been arranged that all copper foil used in Shell laboratories for this test should be supplied from one central source, a large uniform stock of the foil being purchased for distribution as required. Two sources of precipitation spirit existed, but a check investigation on a number of transformer oils of widely different types had shown that these were interchangeable as regards the results they yielded.

MORE RECENT RESULTS.

In 1942 results reported by different laboratories on current "Pool" grades of transformer oil led to a programme of correlation work in which a number of laboratories co-operated. The results obtained in this programme are tabulated in Table I, which also incorporates the results of similar programmes carried out in 1943 and 1944.

The figures quoted represent the results of the correlation work up to the present date, and thus constitute an index of the present state of the test. They show :---

(a) That of the three laboratories submitting duplicate figures on the same samples, one laboratory only (No. 1) appears to have achieved repeatability in the reported figures. This conclusion, however, is vitiated by the remark of this laboratory that "it has been our experience that at least 10 per cent of the results obtained by the B.S.I. test have been 'sports' *i.e.*, anomalous results for which no reasonable explanation can be offered. When these 'sports' occur it has been the recognized practice to repeat the test and offer results which appear more reasonable."

(b) Correlation between different laboratories has not been achieved, in spite of inter-laboratory visits and consultations and the enforcement of the most rigid precautions to ensure that apparatus, materials, and technique correspond in every detail with those specified in the B.S.S. Specification and used in Michie and Davidson's laboratory.

(c) The ten figures determined by Messrs. Michie and Davidson permit comparison with twenty-two results determined in the laboratories of the various petroleum companies. With three exceptions

Sa	mple	Ref.		Oil Co. Lab. No. 1.		Oil Co. Lab. No. 2.	Michie and Davidson.	Oil Co. Lab. No. 3.	Oil Co. Lab. No. 4.
(1942)	A B C	- - -	•	0.85 0.80 1.10			0·39 0·45 0·60	111	111
	C ₁ *			$ \begin{cases} 1.00 \\ 1.10 \\ - \\ 1.10 \end{cases} $		I I I	0.65	$1.05 \\ 1.36 \\ 1.19$	$ \begin{array}{r} 0.99 \\ 1.02 \\ \end{array} $
(1943)	E	•	•	$ \begin{cases} 1.00 \\ 1.10 \\ (0.93) \end{cases} $	0.6 1.3 0.6	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	-	-	-
	г G	•	•	$ \begin{array}{c} 1 \cdot 11 \\ {0.94} \\ {0.96} \end{array} $	0.6 0.5 0.7	$\begin{array}{ccc} 5 & 0.82 \\ 7 & 0.79 \\ 0 & 1.03 \\ \end{array}$	-	_	-
	H I	•	•		1.1	$ \begin{array}{c} 0.85\\ 4 0.99\\ 0.55\\ - 0.55 \end{array} $		-	
Blend	E-H			$ \begin{cases} 1.19 \\ 1.03 \\ 1.14 \end{cases} $	0.85	$ \begin{array}{c} 0.35 \\ 2 \\ 0.98 \\ 3 \\ 0.97 \\ 1.01 \\ + \end{array} $	-	-	-
Blend	E-I			$_{\{1\cdot10\atop1\cdot13}$		1.02 0.74 0.75	-	-	-
(1944)	J K T	•		0.52 0.65			0·28 0·47	0.32	0.47
	M N	•		0.50		0.31 0.43 0.44	0·24 0·33 0·33	0.43	Ξ

TABLE I.

* C_1 was a separate sample from the same batch as C.

† Filtered through sintered glass filter.

only, the figures of the petroleum companies' laboratories are considerably higher than those of Michie and Davidson. Averaging all twenty-two ratios gives the figures of 1.50, so that, on the average, the figures reported by the petroleum laboratories are 50 per cent higher than those reported by Michie and Davidson. No explanation can be given for this discrepancy, but its seriousness in a product specification test is in no need of emphasis.

DISCUSSION.

The correlation work described above demonstrates that reproducibility of results obtained by different laboratories with the B.S.I. sludge test is extremely poor. Not only is this so, but satisfactory repeatability in individual laboratories has not been attained even after many years of experience with the test. During this time repeated investigations of apparatus and technique have been carried out in attempts to place the test on a more satisfactory footing, but all such attempts have been fruitless.

These facts strongly suggest that the principal reason for the variable results is not to be sought in minor details of apparatus, materials, and technique, but in the specified conditions for the test. In particular, there is material evidence that the specified oxidation temperature of 150° C is too high, and lies at or very near to a critical temperature in the oxidation process for the type of oil concerned. Thus the Electrical Research Association (J. Inst. elect. Engrs., 1923, 661) has shown in a sludge test carried out at 100°, 110°, 120°, and 150° C that many of the oils examined showed disproportionately large increases in sludging rate with temperature in the range 120° C to 150° C. Monkhouse quotes the case of a "B class" transformer oil which behaved excellently in a transformer, but which showed a 20 to 30 per cent variation in sludge content for a variation in oxidation temperature of 0.5° C at 150° C. The test is carried out with a specified tolerance of \pm 0.5° C for bath temperature, so that a difference between laboratories of 1° C (maximum) is possible within the terms of the specification.

Stark (Science of Petroleum, vol. 2, 1445) remarks that :

"It will be observed, firstly that the temperature chosen by the B.S.I. is considerably higher than that of any other authorities, and that sludge insoluble in petroleum spirit is the only criterion considered. . . .

"An exceptionally highly refined oil is necessary to meet the A specification, and almost invariably these oils develop a much higher acidity in an oxidation test than the B class oils. Since the temperature of oxidation chosen is probably 50-60° C higher than will be encountered in practice, sludge may be shown in the laboratory test in a short time, and yet never appear in practice, because of the lower temperatures occurring.

"The extent to which alterations in results can be obtained by performing the B.S.I. test in the normal manner and at the average temperature of the other tests quoted above is demonstrated in the following table :—

" B.S.I. classification	Temp. of	Per cent sludge	Acidity formation,
of oil	test, ° C.	formation.	mg. KOH/gm.
A.30	150	0.04	3·1
	110	Negligible	2·4
B.30	150	0-75	1.9
	110	Negligible	0.3

"Thus at 110° C, a temperature still above average service conditions, no differentiation is obtained in sludge formation between two typical A and B class oils. It will be observed that in these tests the B class oil is shown to develop less acidity at both temperatures. It is therefore obvious that if these two oils, which are typical of the two classes, were listed by such methods at the S.E.V. and B.B. and C methods, which employ a lower temperature than the B.S.I. test, allow a comparatively large asphalt formation but place a low limit on acidity formation, then there would be a great tendency for the A class oils to be rejected and the B class oils to be accepted. . . .

"This is a very anomalous situation, calculated to cause much inconvenience to suppliers of transformer oils." One of the chief criticisms of the B.S.I. Sludge Test from a survey of the literature of the subject is, in fact, that the temperature of 150° C is too high. The Report of the International Electro-Technical Commission Advisory Committee No. 10 on Insulating Oils states that 100° C is undoubtedly the highest permissible temperature of oxidation for transformer oils (*Science of Petroleum*, Vol. 2, 1446). A review of the accelerated oxidation tests which have been adopted by various leading authorities suggests that such a test should combine the following features : testing temperature, 100° C; use of oxygen; copper catalyst; use of reflux; determination of acidity and sludge.

The test has also been criticized on the grounds that sludging tendency is the sole criterion adopted to determine the degree of deterioration of the oil, and that the result so given may bear no relation to the practical suitability of a transformer oil. This aspect has been discussed by A. W. Thompson and J. C. Wood-Mallock (J. Inst. elect. Engrs., 1943, 90 (13), 35); also by A. A. Pollitt in the same journal; these authors conclude that the test does not line up well with actual practice. It has already been remarked (see also the I.E.-T.C. Committee Report cited above) that the more highly refined oils, whilst producing less sludge, develop greater acidity than the less highly refined oils upon oxidation, and that the situation arises in which "a highly refined oil such as a British 'A' class oil fails to pass those specifications which stipulate maximum acidities developed during oxidation, whilst less highly refined oils meeting many continental specifications fail to meet even the B.S. 'B' grade requirements on account of the high sludges obtained in the British test. Yet satisfactory results are obtained with both types of oil in their respective countries." It should be remarked in this connexion that British and Continental practices as regards transformer design have coincided for some thirty years in using sealed tanks, where sludging is not marked even with less highly refined oils.

CONCLUSIONS AND RECOMMENDATIONS.

(a) The results quoted in this paper demonstrate the unreliability of the B.S.I. Sludge Test and supporting the view that the reason for the unsatisfactory repeatability and reproducibility does not lie in details of technique, materials, and apparatus, but in the specified conditions of the test;

(b) The lack of repeatability and reproducibility are sufficient to disqualify the test as a basis for specification figures, apart from the fact that the soundness of basing such specification figures on sludge alone is open to serious question;

(c) Since, in its present form, the B.S.I. Sludge Test is unsuitable as a control on the quality of transformer oils, the test should either be abandoned or completely revised.

OXIDATION TESTS FOR TRANSFORMER OIL.

By A. A. POLLITT.

The American, British and chief European procedures for carrying out oxidation tests on mineral insulating oils are described and criticized.

FROM time to time criticism has been directed against the mineral oil oxidation test (*i.e.*, the so-called sludge test) specified by Britain in B.S.S. 148, 1933, and it is felt that a description of alternative test procedures and equipment, accompanied by a critical examination of these, and including a similar treatment of the British procedure, may serve a useful purpose.

Those who have contributed to the development of the British test equipment and procedure are fully aware that it is not in every respect an ideal test, but they are equally aware of what may not be so apparent to others—namely, the difficulty in developing an oil-oxidation test which shall be beyond criticism.

Considerable thought and experiment have been and still is being directed to improving the British procedure, which, in the opinion of many well qualified to judge, is fundamentally sound in conception. Some of those who have collaborated in the work from which the British equipment and procedure is at present specified have had the opportunity of carrying out experimental work with the alternatives which are described here, and have been able, therefore, to make a practical comparison between these several procedures.

TEST REQUIREMENTS.

It is well to consider at the outset what are the basic desiderata for a test which is to be applied in the main to the examination of new oils for acceptance purposes. These are: simplicity—both of equipment and procedure, speed, and repeatability, including reproducibility.

In consideration of the several factors which play their part in the initiation and progress of oil oxidation, extreme simplicity cannot be hoped for, whilst in order to evolve a procedure which will enable a test result to be obtained within a reasonable time, it is inevitable that the test shall become an acceleration test. This in turn necessitates that one at least of the dominant factors in oil oxidation shall be intensified in the test conditions, thus destroying the proportionality between these factors as experienced in service. Acceleration tests can always be criticized on these grounds, and all of the tests here reviewed have this feature in common, even if in varying degree. Experience alone, as attained by correlation of test and field behaviour, can enable the results of an acceleration test to be translated into terms of service and show whether the test is so designed and carried out as to provide the desired information.

Finally, in order to secure good repeatability and reproducibility, the necessary precision of control of the various physical factors of the test makes for complication both in equipment and procedure, but it is desirable

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that elaboration shall not be introduced unless unavoidable. It is also desirable, in view of the nature of the material concerned—mineral oil that the equipment shall lend itself with a minimum of modification to investigational work, for which it may be necessary to collect, isolate, and examine the several types of oil oxidation products and to study the influence of various independent factors upon oil oxidation.

DOMINANT FACTORS IN OIL OXIDATION.

These may be considered to be three in number—namely, air (*i.e.*, oxygen), temperature, and metal catalyst. After oxidation has commenced, other factors appear which influence the rate of oil deterioration, such as metal salts of organic acids and the formation of bodies of varying degrees of solubility in the oil under service conditions and resulting from condensation between or polymerization of oil oxidation products.

TEST PROCEDURES.

In describing these, attention is directed only to the methods and equipment adopted to secure oil oxidation, since it is against these that eriticism is mainly directed. The treatment and examination of the oil on the conclusion of the oxidation period are of relatively minor importance. The mechanism and progress of oil oxidation under the test conditions should ideally be identical with those which are responsible for oxidation in service, but, as already made clear, this ideal is not attainable. Nevertheless, radical departure from average service conditions, such as the omission of a dominant factor or the introduction of factors not normally encountered in service, should be avoided in test conditions.

THE AMERICAN TEST (PRIOR TO 1942).

Equipment and Procedure.

In this test, oxidation of the oil is effected by exposure to air in open glass vessels at 120° C. A circular oven with a motor-driven bottom accommodates eight samples of oil simultaneously. The oven is thermostatically controlled and is fitted with a cover provided with small holes for inspection and for withdrawing small samples (10 ml) of oil by pipette for examination. Air is passed through the oven at "about" 1.5 cu. ft. per hour, and its purification is advised, alkaline and acid washes being suggested. It is stated that the air supplied to the oven may vary from 1.0 to 2.0 cu. ft. per hour without influencing the test results. The oil sample, 500 ml, is contained in a 600-ml glass beaker, the dimensions of which are unspecified. No metal catalyst is used.

Each day a 10-ml portion of the oil is withdrawn by pipette through the hole in the oven cover for visual examination until, when sludge formation appears to have commenced, the 10-ml sample is centrifuged. The number of days elapsing from the commencement of the test to the appearance of the first trace of sludge in the centrifuged aliquot of the oil is recorded as the time required to produce sludging.

Criticism.

The equipment is simple in construction and in operation, the only fine control being on the temperature. The air supply—to the surface of the oil—though specified at 1.5 cu. ft. per hour, is not regarded as a critical factor. The test conditions compared with those of some of the other tests described may be considered as "mild." Hence, the test may take many days—up to 45-50 days has been recorded in experiments carried out with this test in Britain. This time is definitely disadvantageous.

A second point of criticism is the absence of any metal catalyst; such is invariably present in service, and is known to influence the rate of oxidation of the oil. A dominant factor is thus omitted from the test conditions.

The long duration of the test may occasion very considerable loss of sample by evaporation—e.g., some oils may lose as much as 40 per cent in volume by evaporation at 115° C in 14 days.

The test result is merely a statement of the number of days to the first isolation of a trace of sludge. This time, or period, especially when obtained under the American test conditions, may be no criterion whatsoever of the service life of the oil.

Since up to eight samples of oil may be tested together in the oven specified, it is possible for mutual contamination by volatile oxidation products to occur, and so a "long" life oil tested in company with other oils of shorter life may show up less favourably than should be the case.

Except for the daily agitation by the pipette when extracting aliquot samples of oil for inspection, there can be little or no agitation of the oil under test, and therefore oxygen supply to the bulk of the oil will be dependent on diffusion. This may be in some measure responsible for the long test times experienced. In service thermal convection and circulation do ensure some degree of agitation of the oil and assist in oxygen distribution.

No account is taken of acidity development, nor does the equipment permit this, since all acidity which is volatile at the test temperature will be lost. The equipment is not readily adaptable, therefore, for investigational purposes.

In view of the foregoing, it is of no moment whether the procedure has good repeatability and reproducibility or not. Work done in this country has not, however, indicated that the test is in any way commendable on these counts.

THE AMERICAN TEST (SUBSEQUENT TO 1942).

The use of a copper catalyst in mineral-oil oxidation tests was criticized by the Americans for many years, but it is significant that the A.S.T.M., at its annual meeting in June 1942, accepted two "Tentative Methods of Test for Sludge Formation in Mineral Transformer Oil" for inclusion in the A.S.T.M. Standards for Petroleum Products and Lubricants, and that one of these tests specifies the use of a copper catalyst. It may reasonably be inferred, therefore, that experience with the method of test, specified prior to 1942 and dealt with above, has shown the need for modification of the test conditions and procedure.

In order to present an up-to-date review of test methods, these two "Tentative" American procedures are now outlined and discussed.

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The first of these, called the "Sludge Accumulation Test," is specified as applicable to :---

" new mineral transformer oils except those which have been stabilized by the addition of retarders, stabilizers and negative catalysts"

and is suggested as suitable for "studying the sludge forming propensity of a new grade of mineral transformer oil before commercial application."

Procedure.

25 ml of filtered oil are oxidized in a glass vessel of test-tube form and of specified dimensions and which is provided with a loosely fitting glass cover having a central hole which admits an air-supply tube. This tube is adjusted so that its end is approximately $\frac{1}{2}$ in above the surface of the oil sample. Air is not passed through the oil, but over its surface, and the volume of air is specified at 0.5 litre \pm 0.1 litre per hour. The copper catalyst takes the form of a 12-in length of 0.040-in-diameter copper wire wound into a helical coil of diameter slightly less than the internal diameter of the glass reaction vessel.

Oxidation is carried out at $120^{\circ} \text{C} \pm 0.5^{\circ} \text{C}$ on three separate 25-ml portions of the sample for periods of 72, 168, and 336 hours respectively, so that some measure of the rate at which sludge deposition increases with time may be obtained.

Criticism.

Apart from the use of copper catalyst, this test in its main essentials is a more rigidly specified version of the procedure standard prior to 1942. The rate of air supply is specified, but a wide tolerance ± 20 per cent is allowed, but since the air is not blown through the oil, this may be of minor significance. The air is dried only, not purified, so that the test equipment is not suitable for use in a general laboratory, where the purity and composition of the atmosphere are liable to change. As in the earlier test, oxidation products volatile at 120° C escape, and although the specification does not call for an acidity determination on the oxidized oil, the possible influence of these products on the course of oxidation is lost, and the test may be criticized on this point.

The duration of the test—a total of two weeks—would be inconveniently long if the test were used as an acceptance test, but many would regard the temperature—120° C—as a point in its favour.

In the light of British experience, the copper catalyst and its treatment are too loosely specified—namely, "commercial" copper wire is "prepared" by polishing with No. 00 emery cloth or "its equivalent," and wiped free from abrasive with a clean dry cloth. It has been found necessary in this country to exercise great care with respect to both the quality of the copper and to the method of its preparation, and an appreciable amount of investigational work has been devoted to this matter.

Since covers are fitted to the oxidation vessels, mutual contamination of samples by volatile products is minimized, and is a point in favour as compared with the older American test, but high evaporation losses can still occur.

The equipment is relatively simple, and so is its control, but it is not well suited for investigational purposes.

The second "Tentative" test is specified as applicable to :---

"new mineral transformer oils except the so-called highly refined white oils of zero iodine value, and mineral oils containing retarders, stabilizers and negative catalysts,"

and is "considered of value in checking the sludge forming characteristics of a standard grade of oil in order to control the continuity of this property from shipment to shipment." This is, therefore, the real American acceptance test.

Procedure.

50 ml of oil sample, contained in a heat-resisting glass tube of specified dimensions, are oxidized in a rigidly specified stainless-steel bomb at 140° C for 24 hours under pure oxygen at a pressure (initial) of 250 lb./sq. in. No catalyst is employed.

Criticism.

The equipment, procedure, and control of the test are simple, and the time short. On the other hand, the use of pure (100 per cent) oxygen is open to criticism in the light of British experience—cf., the German and Swedish tests—and the gas pressure is a factor not encountered in service conditions. Also, though the initial gas pressure is 250 lb/sq. in., this will decrease as the test proceeds at a rate dependent on the susceptibility of the particular oil under test to oxidation, and will not therefore be the same in all tests.

All products of oxidation are retained, and the oxidized oil sample could therefore be given a more complete examination than that called for by the specification—namely, the weight of sludge only.

It is possible that some correlation between the data provided by this "rapid" bomb test, the long Sludge Accumulation Test, and service experience may eventually be established, and in this case the bomb method may become of service as a general acceptance test.

The A.S.T.M. point out in an explanatory note that no data are yet (October 1944) available which correlate the test results with the commercial use of transformer oil, but express the hope that continued use and study of these two tests may ultimately enable a true ovaluation of oils to be made.

THE BRITISH TEST.

Equipment and Procedure.

Though familiar to all concerned in Britain, a brief survey of the equipment and procedure must be included for ease of comparison with the alternatives described.

In this test 100 g of oil are subjected to a temperature of 150° C for a specified period of forty-five hours, during which time purified air is passed through the oil at the rate of two litres per hour, whilst in the oil is placed a piece of copper foil fashioned into a cylinder and disposed round the end of the air inlet tube. The reaction flask is fitted with a water-cooled

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reflux condenser, and the apparatus includes a thermostatically controlled oil heating bath, air-purifying equipment and air-flow control and measurement equipment.

Criticism.

The test is generally criticized on the score of the temperature employed. This, at 150° C, is considerably in excess of the maximum temperature likely to be reached in service. In general, the effect of increase in temperature on chemical reaction is to increase the rate, which as a general rule is considered to be doubled for each 10° C rise in temperature, so that in order to obtain test results in reasonable time, temperature is perhaps the safest factor to intensify. For investigational purposes, the temperature of the test can be, and is, set at any desired level. The test duration (oxidation period) of 45 hours is the shortest but one of those here considered, and is a point in its favour.

The equipment and procedure are rigidly specified, and because of this no great degree of simplicity can be claimed, but, by very reason of this rigidity of specification, it must be acknowledged that serious attention has been given to the development of a test which shall have good repeatability and reproducibility. Rigidity of specification is applied to temperature ($\pm 0.5^{\circ}$ C), the material and dimensions of the glass reaction vessel and condenser, the method of air purification, the air-flow control and measurement, the quality of the copper used as catalyst, its dimensions, and the method of its preparation.

Because of the provision of a reflux condenser, all but the most volatile products of oxidation are returned to the oil under test—as occurs, of course, in very large measure in service—so that the influence of oxidized oil products on the progress of oxidation is not lost. The oxidized oil can be examined for total acidity, and some measure taken also of the main types of acidity (e.g., the so-called volatile and non-volatile acidity, and watersoluble acidity, etc.). Further, for investigational purposes, additional equipment can readily be incorporated with the specified equipment, and this is in favourable contrast with the alternative procedures dealt with.

The test is acknowledged to be an acceleration test, and no claim is made that the data provided by it will enable an *accurate* estimate to be made of an oil's service life. Transformers differ in design, and service conditions and environment differ, but experience has shown that the test does enable oils to be graded in terms of their oxidation resistance, both with respect to sludge formation and to acidity development. The test includes a catalyst, and endeavour is made to ensure that this factor is as constant a one from test to test as are the temperature and rate of air flow. Mutual contamination of concurrently tested samples by volatile oxidation products cannot occur in the British test.

THE GERMAN TEST.

Equipment and Procedure.

In this test 150 g of oil are heated in a 300-ml glass reaction vessel (Erlenmeyer type) for 70 hours at 120° C with oxygen bubbling through the oil from a delivery tube of 3 mm internal diameter at the rate of "two

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bubbles per second." The oxygen is first passed through caustic potash (1.32 sp. gr.) and then through sulphuric acid (1.84 sp. gr.). The reaction flask is fitted with a cork to support the oxygen inlet tube, and the cork is notched to permit escape of volatile matters. No further specification is given as to equipment and no catalyst is used.

Criticism.

The equipment is certainly simple, but it is inadequately specified. No catalyst is used, and all oil-oxidation products volatile at the temperature of the test can escape. The test temperature of 120° C compared with that of 150° C in the British procedure will be accounted as a point in favour by many. The duration of the test-70 hours-cannot be criticized as unduly long for a test of this type, and might in fact be too short, in view of the absence of a catalyst, to give easily measurable results in 70 hours. The use of neat oxygen in place of air no doubt compensates for this in some measure, since by increasing the partial presence of this gas by five times (as compared to air O: N = 20: 80) the quantity of oxygen in solution in the oil during the test will be proportionately increased. Neat oxygen is not encountered in service, however, and criticism can be made on this score, since it is known that when oils are oxidized under neat oxygen, sludges of a type not met with under service conditions are produced, indicating that oxidation may follow a different course (cf., Swedish test).

Poor specification, absence of catalyst, use of oxygen in place of air, loss of volatile products during test, together with the subsequent treatment of the oil—a lengthy and involved procedure—are the main objections to this test. Experience with it in this country has revealed lack of consistency in results, and the test is clearly ill-suited for investigational purposes.

THE SWEDISH TEST.

Equipment and Procedure.

To describe this test in detail would require far more space than can be allocated to it. It is, however, characterized by the elaboration of the reaction vessel occasioned by the application during oxidation of 10,000 volts electric stress between two dissimilar metal electrodes submerged in the oil. The provision of this electrical stress adds to the amount and complexity of the equipment required.

60 g of oil are heated at $99-101^{\circ}$ C for (" normally ") 100 hours, and pure oxygen at the rate of 1 litre/hour is passed through the oil. The reaction vessel is of glass (dimensions not specified), and is provided with a bakelite or porcelain cover through which pass two conductors (the central one being hollow and serving also as the oxygen delivery tube), terminating respectively in an inner cylindrical copper electrode and an externally concentric cylindrical mild-steel electrode, each specified with respect to surface area. The surface of the copper electrode is prepared by heating to redness and plunging immediately into alcohol to ensure complete freedom from oxide. The copper is specified as " electrolytic." The mild-steel electrode—composition unspecified—is prepared by pickling in sulphuric acid, 1.2 sp. gr.

Criticism.

This is the least attractive of the tests considered. The only point in its favour is the specified temperature of 100° C, which is not far removed from the maxima which may be reached in service. The time of 100 hours is longer than is desirable for acceptance tests. Two catalysts are present, iron and copper, the latter specified as electrolytic copper, the former merely as mild steel. These, which also serve as electrodes, are used for test after test, after being prepared before each test as described; their surfaces will therefore be subject to progressive change, as they are repeatedly used. This is a bad feature. Further, experience in this country has shown that it is extremely difficult to obtain a uniform surface on the copper by the specified procedure. Local flaking of partly reduced oxide is a major defect. These flakes can cause concentrations of field and an increase of the total area of the copper surface, whilst if they become detached during the test they will add to the weight of sludge recorded.

Any departure from concentricity between the copper and iron electrodes will destroy uniformity of field. The condensation of volatile products on the cover of the reaction vessel can result in corona discharge and the production of ozone which increases the oil oxidation rate and deteriorates rubber connections.

Soft solder is used in the electrode mounting assembly, and though this solder is silver plated, it is clearly an undesirable feature. Collection of volatile acidity under the cover can cause short circuiting of the electrodes leading to fusion of the solder.

Actual experiment in Britain has failed to show conclusively that the imposition of the electric stress on the oil during oxidation has any significant influence on the quantity of sludge produced, and this irrespective of whether the test is carried out with oxygen or with air. The inclusion of this factor has therefore yet to be justified, and its omission would greatly simplify both equipment and procedure.

The use of two dissimilar metal catalysts is an unnecessary complication, particularly in view of the common knowledge that the specification with respect both to quality of the metal and the mode of its preparation must be rigid.

The use of neat oxygen in place of air has already been given comment in connection with the German test, and, like the latter, the Swedish test allows volatile oxidation products to escape.

In spite of the comparatively low test temperature, the Swedish test is too drastic. This is due to the fact that, compared with the British test, two and a half times the amount of oxygen is supplied to an oil volume of 60 per cent that used in the British test and for a period of time more than twice as long. Under these conditions some oils become so heavily sludged that subsequent separation of oil from sludge is difficult, with inevitable reflection upon the quantitative value of the results obtained. The test does not always grade oils in line with their service behaviour as ascertained by field experience—in fact, it can place oils in the reverse order of sludging tendency to that shown by the British and other tests.

The Swedish test is elaborate as regards equipment and manipulation and, by comparison, it includes a greater number of factors requiring accurate control over a long period. It is not adaptable for research purposes.

THE SWISS TEST.

Equipment and Procedure.

The reaction vessels in this test are specified a sspun copper cylindrical beakers of 100-mm internal diameter and 210-mm deep, with a wall thickness of about 0.6 mm. The quality of the copper is not specified. The only instruction as to their preparation is "to wash with benzine, then dry, and immediately before use, rinse out with the oil to be tested."

1000 ml of oil are used per test and maintained at 115° C ($\pm 2^{\circ}$ C) for a total period of 336 hours—two weeks. Cotton threads, wound on glass rods, are immersed in the oil during test. No air is passed through the oil, but the oil surface in the copper beakers is open to the laboratory atmosphere.

At the expiration of the first 168 hours, 20 ml of oil and one of the lengths of cotton thread are removed; the oil is examined for sludge and the acidity determined, and the mechanical strength (tensile) of the thread is measured. This procedure is repeated at the end of the second 168-hours' period. Limits for sludge and acidity and for decrease in strength of the cotton are prescribed for 168 and for 336 hours of test duration.

Criticism.

The temperature of the test is relatively low, but the duration is too long. All volatile products are lost, and measurement of acidity as specified records only that which is non-volatile at the test temperature. The equipment is simple, but the quality of the copper should be specified, as also should a more rigid procedure for cleaning or preparing the surface which is in contact with the oil. In view of the area of copper involved, however, it is obviously impossible to secure uniformity of surface condition for repeat tests, and experiment has shown that the results obtained on the same oil differ according to whether a new or an old copper vessel is used. For these reasons the use of copper reaction vessels is to be deprecated. The decrease in the volume of oil during test due to evaporation losses can be of serious magnitude—up to 40 per cent or more—but varies greatly with different oils.

The specification is lacking in detail and rigidity. The inclusion of cotton threads is novel, but since the acid development is a fairly direct index of the "tendering" of the cotton, the inclusion of cotton is of doubtful value.

In general, and from the point of view of sludge formation, the Swiss test grades oils similarly to the British test, but the repeatability is poor, due, no doubt, in large measure to the difficulty in securing uniformity from test to test in the comparatively very large area of copper catalyst employed, and in lesser measure to the lack of control of other factors associated with oil oxidation.

The test is not suited for investigational work.

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Metropolitan-Vickers Electrical Co., Ltd., Manchester.

SLUDGING VALUE OF TRANSFORMER OIL. INFLU-ENCE OF CONDENSER WATER TEMPERATURE.*

By P. W. L. GOSSLING and J. ROMNEY.

SYNOPSIS.

It is shown that the influence of condenser water temperature on sludge value is such that the permissible variation in this factor in the standard method is itself sufficient to make possible relatively large differences in sludge values obtained.

It is submitted that adoption of new limits for condenser water temperature suggested would result in a considerable improvement in precision.

The condenser water temperature also influences the acidity development during the test.

REFERENCE is frequently made to difficulties in obtaining good duplication of results in sludge tests. This has been recognised in the Precision Clause included in the standard method (I.P. 56/45), a maximum deviation of 15 per cent from the mean of duplicate determinations being indicated for Reproducibility, though 5 per cent is given for Repeatability, a figure no higher than that quoted for many other standard tests.

This note is restricted to a discussion of one factor in these difficulties namely, the temperature of the inlet water to the condenser, the standard method postulating limits of 15° C and 20° C (59° F and 68° F). The authors are not in a position to state whether limits were fixed owing to a definite recognition of the influence of this factor on the results of the test, or whether this provision was made on account of a natural desire to standardize the conditions of the test; however, the work now reported indicates that the variation in test results, arising from the use of condenser water at the allowable extremes of temperature, can be considerably greater than may be generally realized, and that a narrowing of the range between the allowable limits should result in considerably increased precision.

It is believed that the influence of this factor was first satisfactorily appreciated by the late J. C. Jennings, and Table I gives the actual sludge values obtained some years ago on a series of oils at various condenser water temperatures, some inside, others outside the permitted range. The figures represent averages of the closely agreeing results of not less than two tests put on at the same time. The condenser water temperatures used were those of the mains water available at the times of test, which were in various seasons of the year, except in many of the cases of temperatures above 70° F, when water from a roof tank, exposed to the sun, was used, and a general review of the results leaves little doubt about the errors which can arise as the result of failure to observe the requirements of the standard method in respect of condenser water temperature. This is also clearly illustrated in Fig. 1 by curves obtained by plotting

* Paper received April 19th, 1945.

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the sludge values against temperatures for oils "A" and "I" in the higher range of sludge values, and oil "C" in the lower range. The tendency for increase in sludge value with condenser water temperature is pronounced, particularly in the range of temperatures above the upper limit of the standard test.



More recent work in connection with a programme of research for the E.R.A., designed to yield information leading to the improvement of B.S. specification 148 in the direction of securing greater freedom from acidity formation in service of transformer oils, suggested the necessity for investigating the influence of condenser water temperature on acidity development during the sludge test as well as on the actual amount of sludge formed, and a selection of results is given in Table II. In this table the results of individual tests as well as the mean values are shown. The tendency for increase in sludge value with condenser water temperature

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is confirmed, but an interesting additional feature is the tendency revealed for acidity development, too, to increase with the water temperature, in spite of the fact that raising the temperature of the cooling water would have been expected to facilitate the escape of the more volatile acids. It should be mentioned that the oils in Table II were all deliveries of "Pool" transformer oil, and that acidity determinations were carried out on measured proportions of the spirit solutions of sludged oils after filtration for removal of sludge, so that the acidity which might be contributed by the sludge itself was ignored. However, other work has shown that inclusion of sludge has little effect on the acidity, and, in any case, in considering the increase in acidity which occurs in most cases with increase in condenser water temperature, it must be borne in mind that this higher acidity exists in spite of the preliminary removal of a larger proportion of sludge.

The importance of the results to which reference is made above is emphasized for two reasons :---

(1) It is probable that this detail of the standard test has not, in the absence of an appreciation of its influence, been strictly complied with in some laboratories in which the test is carried out.

(2) Even if the provision is rigidly observed, the results indicate the possibility of variations in results within the permitted condenser water temperature range greater than those reflected in the Repeatability section of the I.P. Precision Clause.

It is conceded that the first reason involves no criticism of the test itself, but it is a valid point in a discussion of practical experiences in respect of the reproducibility of the test.

With regard to the second reason, it is evident that the effect of condenser water temperature on the sludge value is not the same, quantitatively, for all oils. At the same time, it may be mentioned, as a matter of interest, that a careful study of a large series of results some time ago suggested that a variation of 2 per cent in the sludge value for each one degree Fahrenheit deviation from 63° F-roughly the mean of the permitted condenser water temperature range-represented a general average approximation, this suggesting that tests carried out at 59° F and 68° F respectively would, on average, give results 8 per cent too low and 10 per cent too high as compared with the result of a test carried out with condenser water at a temperature of 63° F. In Table III are assembled the sludge values reported in Table I and the mean sludge values from Table II, to show the effect of adjustment of the figures to estimated values at a condenser water temperature of 63° F on this basis. It is evident that the figure of 2 per cent per 1° F does not apply with accuracy to all oils, but a general narrowing of the range between the extreme values for various oils takes place, and this is, naturally, particularly marked where tests have been carried out on oils with condenser water temperatures below 59° F and above 68° F. For instance, in the case of oil "A," extremes of 0.76 and 1.17 per cent, with a deviation from their mean of 21 per cent, become extremes of 0.79 and 0.91 per cent with a deviation of 7 per cent. Corresponding changes for some other oils are as follows :--
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Oil	"B"				23.to	8	per	cent
Oil	"C"		1.		33 to	9	,,	>>
Oil	" D "			·	32 to	10	,,,	

These changes are very impressive partly because they are based on determinations with condenser water temperatures outside the standard range, but there is an obvious case for the narrowing of that range. It is possible to heat the incoming water or to cool it, but from the point of view of simplicity and economy of apparatus, the former is much the easier. In the authors' laboratories, provision has been made for some time past for the maintenance of the condenser water temperature at 63° F $\pm 0.5^{\circ}$ F, when mains water has been at a lower temperature, and the arrangement is described below. When mains water has been above this temperature no special stops have been taken to arrange for cooling, the water being run straight through the condensers and to waste, but careful records have been kept of temperatures throughout the test and the average temperature taken into consideration in assessing for comparative purposes the probable value for a condenser water temperature of 63° F, based on data of the effect of the temperature on the results for the oil in question, if available, or on the average effect on oils in general. For most of the year, in normal years, this assessment has not been necessary, but it would be more satisfactory to adopt a temperature even less likely to present difficulty. To ensure that, in Britain, no arrangement for cooling would ever be called for, it would be necessary to fix a temperature above the upper limit of the present range, but in order not to complicate the present situation with regard to specification limits for transformer oils, the adoption of 68° F, with an allowable deviation of 1° F on either side, is suggested.

The condenser-water-temperature control arrangement used in the authors' laboratories is shown diagrammatically in Fig. 2, and eighteen tests, in three baths, are supplied. The water runs to the condensers by gravity from an overhead tank, of 10 gallons capacity, fitted with an immersion heater controlled through a relay by a mercury-toluol regulator immersed in a tank below sludge bath level into which the return water from the condensers runs. The regulator is placed in the lower, rather than the upper tank, to facilitate attention and maintenance, but a suds pump in the lower tank returns the water to the upper tank, from which much of it runs back to the lower tank through a wide-bore overflow, at such a rate that it is found that the temperatures in the two tanks and the temperature recorded in the line to the condensers show no appreciable differences. The small rise in temperature through the condensers is slightly over-compensated by a flow of cold water from the mains into the lower tank, the rate depending on its temperature. A ball cock in the upper tank ensures water supply to the condensers in the event of failure of the pump, and a change-over cock enables supply of water from a roof storage tank if there should be a failure of the mains water.

The authors acknowledge with thanks the permission of the Directors of Messrs. W. B. Dick & Company, Ltd., to publish the results in this note.



F10. 2.

								TABLI	s I.									
								Oil".	A."									
Condenser water temp., Sludge value, % .	°F.	:	1	:	55 0·77	57 0·78	57 0·78	60 0·76	60 0-79	66 0·84	66 0-89	$70.5 \\ 1.01$	70·5 1·01	$74 \\ 1.02$	74 1·09	74 1-17	74 1·11	75 1·10
								Oil "	<i>B.</i> "									
Condenser water temp., Sludge value, %	°F.	:	1	1	48 0·54	$\begin{array}{c} 51 \\ 0.54 \end{array}$	51 0·53	68 0·69	70 0·70	73 0·87	74 0·80	74 0·78						
								Oil "	<i>c.</i> "	-								
Condenser water temp., Sludgo value, % .	°F.	:	:	:	44 0·097	46 0·095	48 0·100	48 0·105	58 0·115	$\begin{array}{c} 61 \\ 0{\cdot}127 \end{array}$	$\begin{array}{c} 66 \\ 0.143 \end{array}$	69 0·156	73 0·190	73 0·190				
								Oil "	D."									
Condenser water temp., Sludge value, %	°F.	:	1	:	38 0·36	39 0·39	44 0·44	44 0·40	57 0·56	58 0·46	58 0·56	$\begin{array}{c} 63\\0{\cdot}62\end{array}$	69 0·70	73 0·70	-			
								Oil *	E."									
Condenser water temp., Sludge value, % .	° F.	1	•	1	48 0·59	74 0·84												
Condenses water temp	0 77				50	73		Oil '	' <i>F</i> ."									
Sludge value, % .		1	•		0.99	1.32												
								Oil '	' <i>G</i> .''									
Condenser water temp., Sludge value, % .	° F.	1	:	;	$\begin{array}{c} 53 \\ 0.05 \end{array}$	53 0·06	71 0·10	71 0·07										
								Oil "	<i>H</i> ."									
Condenser water temp., Sludge value, % .	°F.	;	:	.:	51 0·109	$\begin{array}{c} 52 \\ 0.109 \end{array}$	53 0·113	57 0·110	62 0·133	69 0·139	$\begin{array}{c} 72 \\ 0.151 \end{array}$	$72 \\ 0.168$						
								Oil	" I."									
Condenser water temp. Sludge value, % .	,°F.	2	:	111	49 0·42	55 0·53	55 0·52	58 0·54	68 0·58	68 0·55	72 0·70	73 0·74	73 0·71	73 0·69				

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TABLE II.

Sludge value figures are percentages. Acidity figures are in mg. KOH/gm.

Oil " J."

Condenses water terms	59'	° F.	59'	°F.	63	F.	68	F.	68° F.		
Condenser water temp.	Sludge.	Acidity.	Sludge.	Acidity.	Sludge.	Acidity.	Sludge.	Acidity.	Sludge.	Acidity.	
	0·38 0·39 0·45	3.6 4.0 3.8	0.42 0.36 0.47	3.7 3.8 4.0	0.58 0.50 0.55	$4 \cdot 2 \\ 4 \cdot 0 \\ 4 \cdot 4$	0.56 0.64 0.78	$4.3 \\ 4.5 \\ 4.2$	0.62 0.66 0.69	4.6 4.5 4.1	
Mean	0.41	3.8	0.42	3.8	0.54	4.2	0.66	4.3	0.66	4.4	

Oil " K."

Condenser meter terms	59	° F.	59° F.		63	F.	63	F.	68	° F.	68° F.		
condenser water temp.	Sludge.	Acidity.	Sludge.	Acidity.	Sludge.	Acidity.	Sludge.	Acidity.	Sludge.	Acidity.	Sludge.	Acidity.	
Mean	0.87 0.78 0.76 0.80	1.8 1.8 1.6 1.7	0.75 0.83 0.80 0.79	$ \begin{array}{r} 1.7 \\ 1.5 \\ 1.7 \\ 1.6 \end{array} $	0.89 0.92 0.86 0.89	1.8 2.0 1.9 1.9	0.91 0.88 0.84 0.88	$ \begin{array}{r} 2 \cdot 0 \\ 2 \cdot 2 \\ 1 \cdot 7 \\ 2 \cdot 0 \end{array} $	0.89 0.94 0.96 0.93	$ \begin{array}{r} 1 \cdot 9 \\ 2 \cdot 0 \\ 1 \cdot 8 \\ 1 \cdot 9 \end{array} $	0.92 0.98 1.01 0.97	$2 \cdot 2$ 1 · 9 2 · 1 2 · 1	

				TAI	BLE II (co Oil "	ontinued). L."	1.1.10		1	5	13	
	49°	F.	50°	F.	50°	F.	63	° F.	70	° F.	80	°F.
Condenser water temp.	Sludge.	Acidity.	Sludge.	Acidity.	Sludge.	Acidity.	Sludge.	Acidity.	Sludge.	Acidity.	Sludge.	Acidity.
Mean	0-69 0-69 0-69	1·3 1·3 1·3	0.74 0.75 0.70 0.73	1.7 1.6 1.4 1.6	0.66 0.72 0.70 0.69	$ \begin{array}{c} 1 \cdot 1 \\ 1 \cdot 2 \\ 1 \cdot 3 \\ 1 \cdot 2 \end{array} $	0.82 0.84 0.82 0.83	$ \begin{array}{r} 1.7 \\ 1.6 \\ 1.6 \\ 1.6 \\ 1.6 \end{array} $	1.03 1.08 1.04 1.05	$ \begin{array}{r} 1 \cdot 8 \\ 2 \cdot 0 \\ 2 \cdot 0 \\ 1 \cdot 9 \end{array} $	1.48 1.50 1.43 1.47	$ \begin{array}{r} 2 \cdot 1 \\ 2 \cdot 4 \\ 2 \cdot 1 \\ 2 \cdot 2 \end{array} $
	Roll			a unit	Oil "	М."						
Condensation	46	F.	48°	F.	63	F.	70	° F.				
Condenser water temp.	Sludge. Acidity.		Sludge. Acidity.		Sludge. Acidity.		Sludge.	Acidity.				
Mean	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		$\begin{array}{ c c c c c c c c c c c c c c c c c c c$		0-69 0-70 0-68 0-69	$ \begin{array}{r} 3 \cdot 9 \\ 4 \cdot 0 \\ 4 \cdot 0 \\ 4 \cdot 0 \\ 4 \cdot 0 \end{array} $	0.98 0.89 1.05 0.97	$ \begin{array}{r} 4 \cdot 5 \\ 4 \cdot 5 \\ 4 \cdot 1 \\ 4 \cdot 4 \end{array} $				
and the second					0il " 1	v."		1				
Condenser water temp	50	°F.	63	· F.	80	° F.						
condensel water temp.	Sludge.	Acidity.	Sludge.	Acidity.	Sludge.	Acidity.						
Mean	$ \begin{array}{c} 0.9 \\ 1.0 \\ 1.0 \\ 1.03 \end{array} $	0.83 0.79 0.78 0.80	$ \begin{array}{c} 1 \cdot 2 \\ 1 \cdot 3 \\ 1 \cdot 1 \\ 1 \cdot 2 \end{array} $	1.30 1.08 0.96 1.11	$2.1 \\ 1.7 \\ 1.6 \\ 1.8$							

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TABLE III.

Amendment of Sludge Values to a Condenser Water Temperature of 63° F.

									Oil "	A."									
Condenser water t Sludge, % . Amended sludge,	tomp., %	°F.		:		55 0·77 0·89	57 0·78 0·87	57 0·78 0·87	60 0·76 0·81	60 0·79 0·85	66 0·84 0·79	66 0·89 0·84	70.5 1.01 0.86	$70.5 \\ 1.01 \\ 0.86$	74 1·02 0·80	74 1·09 0·85	74 1·17 0·91	74 1·11 0·87	75 1·10 0·86
									Oil "	B."									
Condenser water t Sludge, % . Amended sludge,	emp., *	° F.	:	:	•	48 0·54 0·70	51 0·54 0·67	51 0·53 0·66	68 0·69 0·62	70 0·70 0·60	73 0·87 0·70	74 0·80 0·63	74 0·78 0·61						
									Oil "	C.''									
Condenser water t Sludge, $\%$. Amended sludge,	emp., '	°F.		:	•	44 0-097 0-134	46 0-095 0-128	48 0·100 0·130	48 0·105 0·137	58 0·115 0·127	61 0·127 0·132	66 0·143 0·134	69 0·156 0·137	$73 \\ 0.190 \\ 0.152$	73 0·190 0·152				
									Oil "	D."									
Condenser water t Sludge, % . Amended sludge,	emp., %	°F.	•	•	•	38 0·36 0·54	39 0·39 0·58	44 0·44 0·60	44 0·40 0·55	57 0·56 0·63	58 0·46 0·51	58 0·56 0·62	63 0·62 0·62	69 0·70 0·62	73 0·70 0·56				
									Oil	E."									
Condenser water t Sludge, % . Amended sludge,	emp., ' %	°F.	:	:	:	48 0·59 0·77	74 0·84 0·65		011 "	F ''									
Condenser water t Sludge, % . Amended sludge,	emp., *	°F.	:	•	• • •	50 0·99 1·25	$73 \\ 1.32 \\ 1.06$		011	<i>av</i>		uner!							
Condenser water t Sludge, % . Amended sludge,	emp., 9	°F.	:	•	• • • •	53 0·05 0·06	53 0·06 0·07	71 0·10 0·08	71 0.07 0.06	G."									

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TABLE III (continued).

Oil " H."

Condenser water temp., ° F. Sludge, % . Amended sludge, %	: :	:	51 0·109 0-135	52 0-109 0-133	53 0·113 0·136	57 0·110 0-123	62 0·133 0·134	69 0·139 0·122	$72 \\ 0.151 \\ 0.124$	72 0·168 0·137		
					0	il " I."						
Condenser water temp., ° F. Sludge, % . Amended sludge, %	: :	•	49 0·42 0·54	55 0·53 0·61	55 0-52 0-60	58 0·54 0·59	68 0·58 0·52	68 0·55 0·50	72 0·70 0·57	73 0·74 0·59	73 0·71 0·57	73 0.69 0 53
					0	il " J."	11.2					
Condenser water temp., ° F. Sludge, % . Amended sludge, %	: :	:	59 0·41 0·44	59 0·42 0·45	63 0·54 0·54	68 0-66 0-59	68 0.66 0.59					
					0	il " K.						
Condenser water temp., ° F. Sludge, % Amended sludge, %	: :		59 0·80 0·86	59 0-79 0-85	63 0·89 0·89	63 0-88 0-88	68 0·93 0·84	68 0·97 0·87				
					0	il " L."	,					
Condenser water temp., ° F. Sludge, % Amended sludge, %	: :	•	49 0·69 0·88	50 0·73 0·92	50 0·69 0·87	63 0-83 0-83	70 1.05 0.90	80 1·47 0·97				
					Oi	l" M.						
Condenser water temp., ° F. Sludge, % Amended sludge, %	11	÷	46 0·48 0·65	48 0·47 0·61	63 0·69 0·69	70 0·97 0·83						
					0	il " N.	••					
Condenser water temp., ° F. Sludge, % Amended sludge, %	: :		50 0.68 0.85	63 0·80 0·80	80 1·11 0·73							

GENERAL DISCUSSION.

MR E. T. NORRIS (Ferranti Ltd.): I am speaking as a transformer designer of many years experience, and my remarks concern sludge and acidity formation in oil-immersed power transformers.

Dealing first with the development of suitable oils and methods of assessing their performance, I think oil suppliers are not working on the right lines.

With modern oils, whether Grade "A" or Grade "B," the sludge and acidity formation due to temperature, time, and exposure to air is relatively negligible. On the other hand, both characteristics, if a very small quantity of unpolymerized varnish or other insulating compound is added, are several orders of magnitude worse.

A normal power transformer consists of fibrous insulation, copper, iron, and varnish. Since metals have a catalytic effect, it has become customary in sludge tests to insert a piece of copper foil. A small amount of insulating varnish and, in fact, a very small amount of any unpolymerized varnish has a relatively enormous effect. It is astonishing that in all sludge tests this has been entirely neglected. It is somewhat absurd to consider carefully the effect of copper foil and ignore entirely the much larger effect of varnish.

I suggest it is a pure supposition—and probably an incorrect one at that —to assume that there is any significant connection between the effect of copper and the effect of varnish and that the effect of the former is any guide at all to the effect of the latter. I seriously suggest that sludge and acidity tests and investigations which take no account of insulation compositions or varnishes have little practical application to power-transformer operation.

I have given these conclusions rather bluntly—I will now offer the evidence in support of them.

It happens by chance, in fact purely as a coincidence, that I can present the results of a wide operating experience over more than twenty years of two unusual practices in power-transformer construction. I do not claim they are unique, since that is too absolute, but they certainly have not been in general practice. Both cases result in experience which is, I suggest, very pertinent to our present discussion. I call them (a) and (b).

(a) Over twenty years ago my firm became concerned in the building of high-voltage testing transformers. I designed, in fact, the first 500,000-volt transformer built in Great Britain and the first 1,000,000volt equipment. Insulation was naturally the first consideration, and I decided that the best combination was transformer oil and paper. The windings and high-tension insulation were vacuum impregnated in transformer oil, and no other insulating composition was used. This combination proved so satisfactory that in due course it was extended to high-voltage power-transformers. For the last twenty years every power-transformer we have built, including all those on the Grid for voltages of 66kV and upwards, have been insulated in this way. The accumulated experience is astonishing. There has been no instance of even mild acidity, and sludge formation has been, practically speaking, absent. It is true that in every case conservators have been fitted, but since most of the power-transformers are forcedoil cooled, this has not prevented hot surfaces being exposed to the air. The transformers have in very many cases been heavily loaded for long periods, and presumably, since the whole of the copper in the windings is in contact with transformer oil, its catalytic effect will be at a maximum. In one particular case recently a 20-mVA transformer, the first to be put into service on the Grid in 1929, was returned to the works in 1944 for a change of voltage ratio. The acidity value was only 0.044. Not only was sludge negligible, but the insulation and bakelized tubes still had the same polished appearance as when new. This is just a typical example. The oil was Grade "B."

(b) Over twenty years ago, for reasons not connected with either sludge or acidity, we decided to abandon varnish impregnation, and we used solely a pure composition of linseed or tung oil. The main difference between this material and the usual varnish and insulating compounds is that there were no solvents and no driers or oxidizing agents. Wide operating experience in all parts of the world has been quite exceptional. We have not had a single report or instance of serious acidity formation, and no instance of corrosion or other ill effects due to acidity. This, I submit, is a quite exceptional experience, judging from the publicity and concern that have been given to this problem in recent years.

Both these experiences (a) and (b) suggest that sludge and acidity are not practical problems with modern transformer oils as they have been supplied over many years. An endeavour to check the obvious deductions from these experiences was made experimentally in a simple manner. Three beakers of ordinary Pool transformer oil were taken, and a piece of bare copper foil was immersed in each. In one sample 1 per cent of pure linseed oil was added, and in a second sample 1 per cent of undried baking varnish. These were all heated to a constant temperature for a fixed time. After the tests the acidity of the linseed oil sample was 0.38 mg and of the varnish sample 2.2. The acidity of the plain oil was somewhat higher than with the linseed oil added. This was a surprising result, but was obviously due to the fact that with the linseed oil the copper foil soon became coated with a deposit, and its action thereby nullified. It does, however, indicate that pure linseed oil has less affect on acidity than copper foil. With both linseed oil and varnish considerable quantities of sludge or deposit were produced, which indicated that sludge and acidity do not go together. These experiments were of a crude war-time nature, and must not be regarded as conclusive. They do, however, indicate the effect of incomplete polymerization, and support experience in showing that the characteristics of a transformer oil are not the only, and certainly not the most important consideration.

This necessity for considering varnish is fortunate, since the structure of these varnishes is probably quite as complex and variable as that of the transformer oil itself. There will, however, be no difficulty in devising a test giving ample quantitative results without excessive accentuation of conditions or prolonged duration.

II

I suggest this is a matter which oil suppliers, in conjunction with makers of insulating varnishes, should study. It may lead to conclusions as to the part played by solvents or metallic driers; further study would consider varnishes polymerized by heat instead of by oxidation. It does seem to be established that the effect of completely polymerized varnish with the solvent completely removed is relatively small or negligible. This is not, however, a condition which occurs in transformer windings in commercial production, when one bears in mind the large effect of the very small amount of the raw material as illustrated in the experiment just described.

MR D. P. SAYERS (Birmingham Corporation Electricity Department): This contribution to the discussion is mainly concerned with the experience of electricity supply undertakings as to the practical factors which effect the formation of acid in transformer oil and the results of such acid formation.

Most of the information was obtained recently by the Incorporated Municipal Electrical Association through a questionnaire issued to twentytwo large municipal undertakings. The replies received show that these undertakings have some 10,000 transformers in service, ranging in size from 5 kVA to 45,000 kVA, aggregating in all well over six million kVA of plant, and they were asked to provide detailed information of any transformers in which excessive acidity had been experienced. Six undertakings reported no trouble or had no information and sixteen undertakings gave particulars of 170 transformers where acidity of the oil had necessitated special attention.

It is a significant fact that in only 170 cases, or less than 2 per cent of the 10,000 transformers in use, has any acidity trouble been sufficient to merit record.

A careful analysis of the data supplied in respect of these 170 units gives the following results :

Make of Transformer.—Seventeen different makes of transformer were involved, the largest number of any one make being thirty-one.

Date of Installation.—Forty-five transformers were installed prior to 1930; eighty-one in the years 1930-35; twenty-eight in the years 1936-40; and five subsequent to 1940.

More of these transformers were installed during the years 1930-33 than at any other time. This may be due to a higher rate of installation of transformers, or it may be due to some change in the oil. Perhaps the oil suppliers can say whether any new brand of oil or new process was introduced about this time, which would account for the higher number of transformers on which trouble has subsequently developed.

Type of Transformer.—Over 80 per cent of the transformers were of the indoor type with free oil level, and not provided with conservator vessel. The majority were not fitted with de-hydrating breathers.

Insulation.—There was a popular idea at one time that the varnish used by some transformer makers acted as a kind of catalyst, and promoted acidification, and one question asked was whether the windings were oil or varnish impregnated. The answers received indicated that the majority of the transformers were varnish-impregnated, but it is doubtful whether this question has been correctly understood and answered, as many of the undertakings gave the same answer irrespective of the make of transformer. It will be interesting to have some information on this point from transformer manufacturers.

Class of Oil.—Over 90 per cent of the troublesome transformers were filled with Class "A" oil. As to the particular brand of oil, it is not usual for the purchaser to specify oil supplied from a particular source, and it is safe to assume that some of the oil will have been supplied from all the recognized suppliers. At one time Class "A" oil was usually specified, but it appears that the majority of undertakings changed over to Class "B" shortly after 1937, presumably when acidification troubles with Class "A" oil first come into prominence.

Degree of Acidity.—As to the values of acid, most of the figures given are less than 8 mg/KOH, but ten cases were cited with values ranging up to 20.2 mg/KOH.

The information received as to the effect on the transformer of high acid values in the oil is far from consistent. The principal effect is rusting on the underside of the lid and tank sides above oil level, resulting in some cases in complete wasting of the metal and holes appearing. In some cases this deterioration has progressed to a serious degree, with acid values between 0.5 and 1.0 mg/KOH. On the other hand, one undertaking reported no serious deterioration in a number of cases where acidity had reached very high values, ranging from 12 to 20 mg/KOH. Where the design of the transformer has provided good ventilation to the air space above oil level, the rusting of the tank steel has been less noticeable than the formation of a sticky varnish like sludge on the windings. Hence it is clear there are still some unknown factors affecting the process which are not clearly understood.

Effect on Insulation.—In the majority of cases the acid appears to have had no direct deleterious effect on the solid insulating materials or copper windings of the transformer, but indirectly the transformers have suffered through accumulations of sludge and deposit fouling the windings and cooling slots. One undertaking only reported serious deterioration to the cotton insulating materials, but this may have been associated with rather excessive operating temperatures.

Generally speaking, values of acid up to 1 mg/KOH are not considered seriously harmful.

Water-Soluble Acids.—One undertaking suggests that the organic acids are comparatively harmless and it is only the water-soluble acids forming 5 to 10 per cent of the total acid which cause corrosion. This has led to the development of a water-washing process for removal of the watersoluble acids to which further reference will be made.

Transformer Breakdown Due to Acidity.—Only four undertakings have recorded actual breakdowns of transformers due to oil acidity. Seven transformers of four different makes were involved. In one case the tankcover corroded so badly that the cover eventually fell in, short-circuiting the terminals. In another case the corrosion produced a stalactite which ultimately caused a short-circuit. In the former case the oil was found to have an acidity of 6.96 mg/KOH, but in the latter case it was 2.2 mg/KOH or less.

Relationship between Electric Strength and Acidity.—The results do not show any consistent relationship between electric strength and acidity. It seems probable that the electric strength is affected more by the amount of rust and other secondary products than the actual amount of acid in the oil.

Growth of Acidity.—Most undertakings have found that once acidification has started the process continues, and tests taken at regular intervals show a progressive increase in acid value, but the rate of increase varies considerably. The period between tests on different undertakings varies from about three months to ten years or more, and after two or three tests the future increase can usually be predicted with reasonable accuracy.

Effect of Operating Temperature.—Most of the undertakings emphasized that high operating temperatures, particularly in basement substations where the ventilation is bad, are one of the principal causes of acid formation. In most of the cases cited the maximum temperature was estimated between 50° and 80° C. A few cases mentioned 90–95° C, and in one of the cases where actual breakdown occurred the temperature was estimated at 130° C.

Methods of Treatment.—It is generally accepted that acid cannot be removed by centrifuge or filter, but the rate of acid formation may be retarded if such methods are used frequently to remove any accumulation of sludge or moisture.

Three undertakings have attempted treatment with activated alumina. The results appear to have been moderately successful, but the economics of this process are doubtful owing to the relatively large amount of alumina required.

One undertaking has experimented with dehydrated lime, but found that the reduction in acidity was accompanied by a large increase in saponification value. In another case the oil was treated with trisodium phosphate, but the effect on other chemical and electrical properties of the oil is not known.

The water-washing process to remove water-soluble acids is used on a large scale by one undertaking with very successful results. The method used is to mix the oil with about 25 per cent of its volume of water at 170° F and pass the hot mixture through a centrifuge in which the oil and water are thoroughly mixed together, the water carrying away the soluble acids. Up to reasonable acid values 90 per cent of the water-soluble acids can be removed in one or two passages through the centrifuge, and the oil is then passed through the centrifuge arranged as a clarifier to remove the last trace of moisture. It is claimed that oils containing acidity have been treated in this way for a number of years, after which they have behaved in a normal manner and given many more years of useful service.

SUMMARY.

The results show that the principal causes of acid formation are :--

- 1. Use of Class "A" oil;
- 2. Running transformers at high temperatures;
- 3. Insufficient ventilation in the substation;
- 4. The use of non-conservator type transformers.

The information referred to above indicates, however, that the number of transformers where acid trouble is known to have seriously affected the operation of transformers is extremely small, being less than 2 per cent of the transformers installed.

MR A. G. ELLIS (Metropolitan-Vickers Electrical Co., Ltd.): As one who has been concerned for many years with the manufacture and supply of transformers, I should like to offer some general observations on the specification and operating behaviour of insulating oils. Experience has shown that there is no need for six grades of oil as specified in B.S. 148, and that these could be reduced to one grade having characteristics similar to those of grade B. 30.

While the cold test point of -30° C is quite adequate for general use, there has been some demand for oil with an even lower cold test, down to -40° to -50° C, for operation in Arctic climates. This is of importance for the oil in transformer tap changers, for automatic voltage regulation, in which the incidence of high viscosity of the oil when cold may prevent the proper operation of the mechanism, with possible disastrous operating results.

Is it possible for the oil suppliers to produce, without any difficulty, an oil with such a low cold test point as standard ?

During and since the war, Pool oil having characteristics approximating to B. 30 grade has been used with generally satisfactory results, though operating experience has only extended over five or six years. B. 30 oil was adopted many years ago by a number of leading electricity supply authorities, including the C.E.B., for use with their transformers, a choice since justified by operating experience.

While the sludge-test figure according to B.S. 148 is higher for B than for A oil, little actual sludge trouble has been experienced with B oil in transformers properly designed and operated. B oil has, in fact, proved itself, in service, superior to A oil with respect to acid development, which, though often associated with sludge formation, has proved to be the more serious factor.

Acid trouble has been restricted practically exclusively to A oils, and it has not been confined to any one, or few, of the oil suppliers or transformermakers.

The prime cause of high acid development appears to be still obscure. While it is known that certain factors in the design and operation of the transformer—such as a poorly ventilated winding design, giving rise to hot spots, and excessive overloading and overheating of the transformer in service—are contributory causes, the fact remains that properly designed and operated transformers have given oil-acid trouble. Analysis of design and operating records has shown that no general conclusions can be drawn pointing to any definite cause of the trouble in the transformer itself.

For instance, cases have occurred of several transformers of identical design and manufactured at the same time, and installed in the same substation, showing oil trouble on one unit and not on the others.

To take another example, acid development is not dependent on whether the transformer windings are coated or impregnated with varnish, properly applied, or are unvarnished; transformers with both types have shown acid development—and the majority of transformers of both types have, in fact, shown freedom from abnormal acidity. The acid appears sometimes associated with sludge and sometimes without sludge; the sludge appears in various forms, ranging from the slimy to the sticky variety. The transformer manufacturer is still anxious to know what is the cause of the erratic behaviour of A oil and what, if anything, can be done commercially to render it as reliable as B oil.

If the answer is the use of an inhibitor, this would need to be supplied as a normal constituent of the oil, or the tendency of transformer makers and users would probably be to prefer B oil. If inhibitors are used, the transformer maker and the operator would require to be assured that they would have no deleterious effect on the other properties of the oil, such as di-electric strength and sludge formation, in service, and on the insulating materials.

The alternative is, as suggested above, to delete A oil from B.S. 148 and standardize on only one grade of B oil.

In the revision of B.S. 148 it would be well if tests could be devised and included which would give a more certain indication of the service behaviour of the oil as regards both acidity and sludge.

I think there is some scope for investigation of the actual effects of acidity in oil on the insulating materials in the transformer. Differentiation should be made between acidity, *per se*, and the corrosive effects of the acid fumes on the transformer tank and cover and constructional steel work above the oil level. The latter can be mitigated by the provision of an oil conservator on the transformer, or by adequate ventilation of the space above the oil level. Cases are known where transformers have continued to operate at very high acid values with no apparent detriment to the transformer windings (provided there was no sludge formation), and I should be glad to know whether any investigational work has been done in Great Britain on the effects of acid on insulation over long periods.

MR C. W. MARSHALL (Central Electricity Board): The quantity of transformer oil used by the C.E.B. at the last official balance was approximately 3,500,000 gallons. Some of the oil dates back to 1929, and a large proportion of it is at least twelve years old. All the oil is B. 30 grade and, until the constitution of the Lubricating Oil Pool at the beginning of the war, supplies were obtained from the usual commercial sources. Great care was taken to avoid mixing of oils from different sources.

Almost all the Board's transformers are installed outdoors, and the oil is consequently operated under comparatively low temperature conditions for most of the year. Practically every unit is, however, periodically operated at the maximum allowable temperature during the period of peak load.

Experience till now has been good, and it is almost superfluous to extend the measures adopted to safeguard the quality of oil, and therefore the transformer insulation. Much patient work has, however, had to be done to keep track of the condition of the oil and to restore it if for any cause the characteristics were impaired. Filtration plants are installed at each major Grid substation, and portable plants are available to deal with the less important ones.

Dielectric strength, moisture tests, and acidity tests are made at regular intervals, and form the routine guides to oil condition. In addition, special electrical tests are made by Schering Bridge or high-resistance measuring equipment, since, being electrically-minded, we prefer to use electrical rather than chemical methods of diagnosis.

Further indications of oil condition are obtained on each occasion when a transformer is opened up for overhaul. At such inspections we have almost invariably found that the amount of sludge formation is negligible. Slight sludge deposits have occasionally been found, particularly where substitute varnishes had to be used during the war in conjunction with cotton coverings on high-voltage windings.

Although our experience has been favourable, we are naturally on our guard against any possible evidence of senility in the oil, and welcome the highly scientific approach which is being made to the study of quality and its restoration by oil technologists.

It would be particularly valuable to us if we could obtain a more direct measurement of acidity, which is the most evident enemy of insulation.

A detail point of considerable importance is that the oil in high-voltage bushings is liable to deteriorate much more rapidly and to a more dangerous extent than in the main body of a transformer. The replacement of bushing oil is liable to be an expensive operation, and while it may be that the practical solution lies in modification of bushing designs to alleviate the stresses on the oil, it is also possible that the oil experts could help by providing special oils.

MR L. H. WELCH (Central London Electricity, Ltd.): I am concerned with large and small transformers. The large one—like Mr Marshall's on the grid—give no trouble with acidity.

Mr Norris has said that by using a particular type of insulation no acidity occurs, but that does not help the user who already has many transformers.

Mr Sayers said only 2 per cent of some 10,000 transformers actually broke down. I would prefer not to have any breakdowns. I find that small transformers with no conservators and Class "A" oil are going acid at varying rates. They must be looked after, and it is our practice to change the oil when the acidity exceeds I. This is a purely arbitrary figure, and I should like opinions on it. As there are some 600 transformers, there are always some having their oil changed.

Let us keep the chemists on the right path. Can they give us an oil—or even an addition to the present oil—which will obviate this work on existing transformers which have many years of useful life ?

I shall not be satisfied until an oil is produced which will last the life of a transformer (say, 30 years at a conservative estimate) without exceeding a reasonable acidity, even if there is no conservator on the transformer. I shall keep on coming to the chemists until this has been done.

DR E. H. RAYNER: I simply came to learn, but I do appreciate the opportunity of saying something. First of all I should like to say how much, in the years that have passed, we who have been interested in oil from the electrical point of view have owed to Michie, Everest, Parker, and others. When we had to produce a specification for oil, the tests were done very thoroughly by these people, with the result—I am thinking of years gone by—that a Class "A" and a Class "B" oil was put into the specification, "A" being supposed to be better than "B" and would be used where it was suitable. But in course of time nobody would look at Class "A" because it was inferior in long-time durability, and it has amused me ever since to reflect that we people who did our best to produce a specification were completely led up the wrong street. Then trouble with transformers arrived due to lids falling in. We had some of these brought to the National Physical Laboratory, and were asked why it happened. However, it was not exactly the N.P.L.'s job, but we did what we could to advise people how to avoid it.

There are one or two points of interest in connexion with transformers. I hope that from the point of view of the excellence of transformer oil, you will be able to get down to one specification for oil for all general purposes. There is now a tendency to produce high-voltage transformers of very small size for X-ray work, etc., and other apparatus has been developed during the last five or ten years, in which a very high voltage and a small current are used, for which smaller space and weight requirements are very desirable. About twelve years ago I was at Cambridge talking to Lord Rutherford when high voltages were becoming important in the Cavendish Laboratory. He said, "Cannot you produce something which will give 100,000 or 200,000 volts a foot or so in size ? I am sure you can if you think about it." That has actually happened. Transformers are now becoming of very small size for this work, and it may be that something better than commercial oils are required where you need only a very small quantity of oil for expensive apparatus, and the oil would be worth a good deal more than the ordinary commercial oils.

With regard to oil in big transformers, I had a very striking instance near Milan some years before the war. I went to a substation of the local supply authority and saw a transformer of about 40,000 kW or more being assembled. It was being dried. The amount of the water which came out of the insulation was recorded hour by hour, and when the rate was down to zero it was assumed that the transformer was sufficiently dried out. Something like 100 lb of water came out of it in three or four days in Italy, where there are no London fogs, so that what the manufacturers in Great Britain may sometimes put into their transformers in the matter of water, I do not know. It was a striking instance, but it emphasized the usefulness of measuring the water as it comes out of a transformer when it is being assembled under field conditions.

DR T. SALOMON (University of Strasbourg): The papers before us raise several questions in which we have been very interested. Firstly, we have the two papers dealing with the mechanism of oxidation. The authors say how oxidation happens after the period of inhibition. The mechanism of oxidation begins by the formation of peroxides. But what happens during the period of inhibition? Some time elapses before we can observe any change in the oil and any evidence of the beginning of oxidation. We have reason to believe that there is dehydrogenation. We know that cable oils will break down due to the formation of hydrogen, the hydrogen coming from the oil by reason of high electrical stress. The same thing was observed by Dr Bruckman, who died during the war and whose work was not completed. When he was measuring the dielectric losses in an oil for a given stress he obtained a curve (Fig. 1) showing a very small stable value after long exposure.



This very small stable value did not change when the stress increased, but with a very high stress (80–100 kV/cm) Bruckman observed a breakdown in the gaseous atmosphere, constituted by nitrogen under a pressure of 20 atm. This breakdown can only be explained by formation of free hydrogen in the gaseous atmosphere; the hydrogen must be liberated by dehydrogenation of the oil.

If you are admitting dehydrogenation as the first step in the modification of the oil, then you must admit the existence of free radicles. I agree on this matter with Dr George and Dr Robertson.

The various attempts which have been made to avoid oxidation have not been completely successful. We must take steps to avoid the dehydrogenation, and so far we have no means of doing that. The cable men add certain substances which absorb the hydrogen product.

With regard to sludge tests, I think the difficulties experienced in obtaining correct and reproducible results are not always due to the methods employed, but rather to the nature of the oils. We have been obliged in certain cases to modify the method by first extracting the oxidation products by acetone and separating the acetone; then we deal with the residue and add the precipitating medium. There is immediate separation of all the sludge. But it is necessary to take it at once, and not delay for a day.

THE CHAIRMAN : I think you will agree that dehydrogenation is accepted as a form of oxidation ?

DR SALOMON : Yes, I do.

THE CHAIRMAN : Your suggestion that oxidation starts after the induction period is interesting. I do not know whether many people will agree with that.

MR W. HILL (West Gloucestershire Power Co., Ltd.): I should like to make a plea for an oil not so refined as we have to-day. I do not mean that we should keep to Class "B" instead of Class "A," but that we should go back to the oils we had in the period around 1925. My evidence for that is that, from 1923 to about 1930, my company bought a good number of transformers, and we always specified a Class "A" oil, usually a Russian white oil. There has not been a single case of acidity in any of those transformers. Some of the transformers had conservators; I think the biggest is of 5,000 kVA, and there are small ones, non-conservator, down to 25 kVA. There are small ones working at 33 kV.

I think that experience proved that the older Class "A" oil was sound. I believe the later Class "A" oils do give us acidity, as do also some of the later Class "B" oils.

I do not quite agree that varnish is necessarily the cause of the acidity trouble, because we had a good deal of varnish trouble on some of the earlier transformers, even with the older Class "A" oil. Even to-day, with filtering and getting rid of the varnish trouble, we have still no acidity on those transformers.

It seems that we have to examine the matter further in order to find the cause of the acidity trouble. We have had instances of two sister machines, working in parallel in the same substation, where one is perfectly sound and the other develops acidity. I cannot attempt to explain that.

The conditions we have to meet in Great Britain are very different from those obtaining in America, because the price of oil in America is less than it is here, and the Americans will scrap an oil more readily than we do because of its lower price to them. Therefore, when examining the structure of an oil and giving it a specification, we should not be guided too much by American experience.

THE CHAIRMAN : What are the temperatures at which the transformers you mention are operating ?

MR HILL: They should operate within the usual B.S.I. specification. But we have always found that acidity is tied up with some form of overheating. We have had transformers choked by overheating or overload. But overload does not mean acidity. There was one breakdown of a small transformer of 30-kVA capacity; it was carrying about 70 kVA, and it broke down after some months.

THE CHAIRMAN : Are there breathers on the transformers?

MR HILL: There are usually on the outdoor transformers. But we always tie up breakdowns with overheating. We do not like metal kiosks; there is always likely to be overheating in them during the summer, and they seem to be a source of trouble.

DR E. W. J. MARDLES (Royal Aircraft Establishment): I should like to speak about the mechanism of oxidation and the oxidation test. The programme of research of Kettering (U.S.A.) a little over twenty years ago led to the discovery by T. Midgley of lead tetra-ethyl as an anti-knock.

This, in turn, led to numerous investigations on the mechanism of oxidation and combustion, especially on the function of inhibitors.

Moureu and Dufraisse of Paris, at the time, found hydroquinone and other phenolic bodies could, in minute quantities in a liquid system, inhibit oxidation over a long period of time until consumed. These inhibitors differed from negative catalysts in the sense that they did not remain unchanged; when consumed, the oxidation proceeded in its normal course. Mr Evans has mentioned many modern oil inhibitors, including sulphur and metal compounds. It is still not known how these inhibitors act precisely, except in the broad sense that they, by reacting with the first traces of peroxides and destroying them, delay the course of oxidation. Some substances have the double function of behaving both as oxidant and anti-oxidant, according to circumstance; in other words, every anti-oxidant is chosen by trial and error, and it is important to our subject to have more precise knowledge on the organic chemistry of the mechanism of oxidation inhibition.

It is now well known that ordinary oxygen or air is relatively inert as an oxidizing agent because the oxidation of hydrocarbons proceeds by autoxidation via peroxides. The oxidation tests using a vigorous stream of air bubbling through the oil appear to be based on the misconception that the rate of oxidation is proportional to the rate of bubbling; but the oxidation of oils in flat dishes, without bubbling, proceeds at a rate not much less than that with vigorous bubbling. Possibly the rate of oxidation is proportional to the solubility and diffusion of oxygen through the oil, and not to the area of oil actually in contact with gaseous oxygen.

It would be very valuable to establish whether bubbling, with its consequent loss of sample by spray and vapour, is really necessary and correct.

In research work it is much more simple and straightforward to carry out oxidations in small flat dishes or rotating bulbs without bubbling, so that the amount of oxygen consumed can be measured directly. It appears to be important to inquire not only about the amount of change after an agreed interval of time, but also on the rate of change after different intervals; this is apparent after studying the acidity and sludge values which have been given after various times of oxidation for various grades of transformer oils.

So much depends on the correct interpretation of the specification test results, and the question may well be asked, are there other measurements that can be made in addition to the usual acidity, sludge, viscosity, etc., determinations? The sludge test is empirical, and might well be amplified. It is possible that the new science of rheology and the latest developments of colloidal chemistry could be used with advantage in studying an oxidized oil, so that the oxidizing tests be carried out at lower temperatures and the development of structure in the oxidizing oil identified earlier. We have found the deterioration of an oil is associated with increased cohesion and lowering of spreading coefficient on surfaces; this appears to be due to the development of rigidity and structure which must play an important part in loss in insulation.

George and Robertson have surveyed the field of oxidation, and have shown the course from hydroperoxides through alcohols and ketones, the decomposition products of the primarily formed peroxides.

Originally Callendar and colleagues (*Engineering*, February 4, 1927) were aware that alcohols oxidize and burn in an engine distinctly differently from hydrocarbons, and debated the manner of peroxide formation. They found hydroperoxides caused detonation in an engine, and suggested the mode of formation from straight-chained hydrocarbons. It would be an extremely valuable piece of academic work if using a pure single long-chained hydrocarbon the sequence of oxidation and concomitant polymerization could be worked out. Rheology, chromatography, and the identification of colloidal products by infra-red spectroscopy or X-ray photography would come into the problem as research tools.

MR R. WEAVING (The British Electric Transformer Co., Ltd.): I am afraid that, after all these learned papers have been presented to us, my remarks will be extremely practical.

I think it is the general wish now that we should have one class of oil only; and that class should be probably something between the present classes "B" and "A."

More than twenty years ago there was a spasm of oil acidity, very much the same as there is now, and after a considerable number of very rough experiments I began to advocate the use of Class "B" oil. Apart from the fact that Pool oil is all of Class "B," the majority of specifications now call for Class "B."

But I feel there is something a little wrong with the specifications. I cannot say what that is, but what we would like is a specification which will tell us what the oil will be like two or three years hence, rather than its actual chemical composition at the moment it is delivered. I know that that is asking a great deal, but I do think that if the oil technologists could work on those lines they would be approaching somewhere near the practical case.

In at least one of the papers before us, and I think in two of them, sludge is mentioned as being a most important feature in an oil specification. That is not my experience, for I find that very rarely do we see any evidence at all of sludging nowadays, though that was certainly not the case twenty years ago. I think the reasons for the change are that improvement has been effected in the quality of the oil so far as sludging is concerned, and that there has been some improvement in the design of transformers. The thought running through my mind is that, by refining to eliminate sludge, we get a better oil from the point of view of sludging, but definitely we have a worse oil so far as acidity is concerned.

Very few transformers are operating at full load continuously and it is unusual to have a root mean square load factor of greater than 50 per cent. Even with 80 per cent full load, as the copper losses go down as the square load, the temperature goes down very considerably. I think that in testing the oil at 150° C we are rather overdoing it. I speak purely from the practical point of view, and I would prefer testing at, say, 110° or 120° C, which measures roughly the extreme limit of temperature likely to be attained in a hot spot under extreme overload conditions. It does seem to me, generally speaking, that present specifications over-emphasize sludge to the detriment of other qualities in the oil.

The problem of acidity has been revived after a lapse of some twenty years. In 1921–23 we had trouble with acidity just as we have now. It died out, and we had a very good oil. It seems to me now that in many cases the crude is such that in the course of refining it does not become too acid, whereas in other cases the crude requires so much refining as to be tantamount to over-refining, as the result of which acidity develops.

Acidity has some very curious effects in a transformer. First of all, I

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have never seen a job that has been spoiled below the oil level by acidity in the oil; I have not seen yet any great deterioration of dielectric strength due to acidity. But above the surface of the oil I have seen what appear to be small mushrooms on the low-tension copper; I have seen a $\frac{1}{16}$ -inch tank lid corroded right through. It appears to me that the acid content is given off in the form of a vapour which is slightly more volatile than the main body of the oil, and the vapour attacks the ironwork above the surface. That is pretty well confirmed, I think, by the fact that you can, by ventilating above the oil level, so dilute the acid or acid gas that it does not attack the ironwork. In transformers which have been very prone to acidity, when the lid has been renewed it has been lifted by 1-inch blocks off the top of the tank, and then has continued to work without any further signs of corrosion.

There is another point arising out of acidity. In one of the papers it is stated that an expansion vessel or, to give it its modern name, a conservator, does not corrode. I can point to two cases, however, where the $\frac{1}{4}$ -inch-thick end plate of the expansion vessel was corroded away. That is very difficult to explain; but there it is.

A previous speaker has said that you can put two transformers to work, both doing the same job, and that they will give totally different results. I can recall a very definite case of that sort. We had two transformers put into service in parallel in the same substation, sharing the load; they were not overloaded at any time, and the temperature was of the order of 65° C. At the end of two years the lid on one of them was corroded, while the other was untouched. The oil had an acid content slightly above that stated in the B.S.I. specification.

Those are just experiences from the purely practical side. I feel that the engineer is in the position that he knows roughly what he wants; he looks to the oil technologists to give it to him, and he will not be particularly happy until he gets it.

THE CHAIRMAN : I take it that you are familiar with breathers. Are you familiar with those which are charged with calcium chloride ?

MR WEAVING : Yes.

THE CHAIRMAN : Do you think they are good or bad things ?

MR WEAVING : Calcium chloride breathers are all right if they are kept in order. Otherwise they are a danger rather than a safety device.

THE CHAIRMAN : Is there a danger of increased corrosion in the presence of calcium chloride ?

MR WEAVING: I cannot say from actual experience, but I should most certainly suggest that there is that danger, for they are taking in air through a soggy mass of saturated calcium chloride.

MR D. V. ONSLOW (The British Electrical and Allied Industries Research Association): The researches described in the papers by Mr Gossling and Mr Pollitt were carried out under the direction of the E.R.A. Committee dealing with insulating oils over a considerable number of years. The work was always carried out by several investigators as a check on the results. These papers deal with the sludge and acidity tests, but the E.R.A. has also carried out a great deal of work on all the tests specified in B.S. Specification, especially on the electric strength test. In the sludge test considerable investigations have been made on the effect of the rate of air-flow, the method of cleaning the copper used as a catalyst, the effect of very small temperature changes during the test, the type of glass used for the flask. All these factors had an effect on the test, and it was necessary to specify them exactly in order to get good reproducibility and repeatability.

Research has also been carried out on the thermal conductivity of transformer oils and on the effect of various metallic and other catalysers on the oxidation of oils.

It is generally admitted that any oxidation test must be an accelerated test, and therefore cannot exactly imitate what happens in practice.

Although the Michie test is criticized in some quarters, no one appears yet to have been able to devise a better test. The Americans have been experimenting for about twenty-five years, and have not come nearer to the Michie test after having originally rejected it. For many years they would not use a catalyst, but have had to acknowledge that its use is necessary, and are only now making experiments on the condition of the copper to be used, which is an important factor.

In Mr Barton's paper he states that the I.E.C. has recommended a test of 100° C using oxygen. I cannot trace any such recommendation for such an international test. Any recommendation which was made was only for investigation purposes by the national committees.

If a temperature of 100° C were employed, as suggested by Mr Barton, the time taken to carry out a routine test would be excessively long. The use of oxygen instead of air would accelerate the test, but pure oxygen is not present in a transformer in practice, and the same objection therefore can be made to its use as to the use of a higher temperature for acceleration purposes. The E.R.A. carried out tests many years ago on the use of oxygen, and they found that a gummy type of sludge was produced, and not comparable to what is found in practice. It is used in the German tar test, and, as has been stated in Mr Pollitt's paper, this test has revealed lack of consistency of results, and is ill-suited to investigational purposes. It is also doubtful whether the use of oxygen would afford greater reproducibility. Since the rate of air-flow has a considerable effect on results, the rate of oxygen flow would have to be still more accurately controlled, since the effect would be greater.

Where time is not important, the E.R.A. has recommended that for rescarch purposes a temperature of 120° C should be employed.

As mentioned in the paper by Gossling and Michie, the E.R.A. are commending to the B.S.I. an amendment to limit the acidity developed in the sludge test. With the limit suggested the present Class "A" oil will not pass the test, and will automatically be eliminated.

In many of the cases of breakdown in transformers which have been brought to the notice of the E.R.A. it has been found that the oil has been in service for ten to fifteen years without having once been cleaned. Instead of blaming the oil it should rather be a matter of surprise that the oil has stood up so long.

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It would also appear that if conservator tanks were used on all transformers there would be practically no trouble, even if the oil were not cleaned, and the small extra cost of a conservator would be amply repaid by the decrease in maintenance costs.

DR ALAN WOLF (Patent Office): The British Michie sludge test has been criticized on the score that it lacks reproducibility. I suggest that it can also be criticized because such high temperatures are employed, the test becomes unreliable in its application to what I think will very likely be the transformer oils of the future-i.e., transformer oils inhibited against oxidation. I will identify myself 100 per cent with the chairman when he says that in our armour of defence against transformer-oil deterioration we should certainly include some of the many modern oxidation inhibitors which have been developed. I would like, however, to issue a warning that, if experience of turbine-oil oxidation, both in the laboratory and in practice, is to be regarded as a guide, accelerated oxidation tests must be carried out at a lower temperature, and preferably at a temperature not exceeding 100° C. Indeed, I would prefer to reduce it to about 95° C, which is now a common American practice in the examination of the stability of steam-turbine oils. These, incidentally, of all the oils produced by the petroleum industry, are probably most closely allied to transformer oils both in their properties and with regard to the conditions to which they are subjected in service. In steam turbines, of course, the oil usually becomes more or less contaminated with water, but I suggest that a comparable amount of contamination with moisture occurs also in the transformer, partly moisture introduced by condensation from the air breathed into the transformer, partly residual moisture which may be still present in the cotton windings of the installation, and partly even formed chemically during the later stages of oxidation and polymerization of the oil.

Incidentally, the differences in the moisture content of the transformer windings immediately before filling up with oil, and to which previous speakers have referred, may account for the remarkable differences sometimes noted in the rate of deterioration of the oil in two sister transformers which apparently are identical in design loading and general operating conditions. To anyone who has been closely associated with turbine lubrication, this experience is very familiar, two or more sister turbines, apparently identical in design, output and general operating conditions behaving in a markedly different way in respect of the rate of deterioration of the oil, and consequent incidence of lubrication troubles. In turbines such differences are attributed to local hot spots and other variables, such as the degree of aeration of the oil and of leakage of high-temperature steam from the glands into the oil.

While lowering the test temperature has the advantage of not discriminating against inhibited oils in which the additive is either volatilized or otherwise rendered ineffective at high temperatures, when you reduce, a fresh difficulty arises owing to the length of time required for the test. Thus in the case of turbine oils, a modern efficiently inhibited oil may require testing for as long as over 6000 hours before it suffers a measurable degree of deterioration. The only way I can suggest at the moment of attempting to minimize this difficulty is to add a definite proportion of some standard oxidation accelerator to the oil, a practice which is quite common in America for the laboratory evaluation of motor oils. Lead, iron, or copper naphthenate in very small quantities can materially reduce the time of oxidation. Such a test might also be useful for the purpose of indicating the capacity of the oil for resisting the tendency for catalytic oxidation, as the manganese or lead dries into the oil from imperfectly baked insulating varnishes.

I would issue a warning, however, with regard to the use of artificial oxidation accelerators. It may be found advisable not to put in too much, otherwise the test becomes rather a test of tolerance of the oil to oxidation in the presence of an abnormal amount of oxidation catalyst, giving what is sometimes called a copper, lead or iron tolerance figure, rather than a true test of the resistance of the oil to oxidation under normal operating conditions.

One other point I should like to make. A good many speakers have been puzzled by the fact that in some cases a very high acidity, perhaps even up to 10 or 20, can be tolerated without any trouble occurring in practice, whereas in others trouble is experienced even before the acidity reaches 1, and certainly before it reaches 2. Again this is exactly the sort of thing met with in some steam turbines, and what is really of importance in both cases is, not so much the acidity of the oil at any one time, but the rate of increase of acidity-i.e., the shape of the acidity/time curve. If samples of the oil are withdrawn from the transformer at reasonably frequent intervals (preferably monthly) and their acidity determined, it will very often be found that there is a very pronounced tendency for sludging and corrosion to occur at about the time that there is a very marked increase in the steepness of the acidity/time curve-in other words, when the curve becomes exponential in character. When that occurs, it is the danger signal, and undoubtedly the oil should either be changed or drastically reconditioned.

THE CHAIRMAN: You were not suggesting that there are not antioxidants which will operate at temperatures higher than 100° C?

DR WOLF: By no means, inhibition power at high temperatures depends on the type of anti-oxidant. For example, if you take the Air Ministry test, operated at 200° C, a number of the anti-oxidants, particularly those of a phenolic or substituted amine type, either cease to function altogether, or are much less efficient. The efficiency of some of them begins to fall off markedly even at 150°, although they may give excellent results at 95°. Admittedly some other anti-oxidants, particularly disulphides, can operate efficiently at very much higher temperatures, presumably because their action depends on the formation of protective sulphide films on catalytic surfaces, such as copper, rather than on any breaking of a chain of oxidation reactions by suffering alternate oxidation and reduction themselves.

Written Communication.

The corrosion of conservator tanks referred to by some of the speakers is quite understandable, as the condensation of moisture charged with volatile oxidation acids is merely transferred from the main to the conservator tank. Complete immunity from sludging and corrosion might perhaps be gained by having three conservator tanks in series, the second and third functioning purely as a trap or liquid seal, as in the so-called "Double absorption pipette" of the familiar Hempel gas-analysis apparatus.



MR J. S. FORREST (Central Electricity Board): I have been rather impressed during the discussion by the emphasis on chemical tests, and it is surprising that most of the tests for an *electrical* insulating oil are tests of its chemical or physical properties. In B.S.S. 148, for example, there is

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only one electrical test (for electrical strength), and this is not a very satisfactory test, particularly in the case of used oil.

I would like to discuss the possibility of developing other electrical tests—from the point of view of the transformer oil user, and in particular from the point of view of one interested in determining by test whether or not a sample of used oil is fit for further service.



Now, a power-factor measurement provides a measure of the quality of any dielectric, and gives useful results in the case of oil. The power-factor test, however, is not suitable for use on site by relatively unskilled operators. Fortunately, a D.C. resistance test, which is much easier to make, gives substantially the same information—resistance being approximately inversely proportional to power factor.

I would like to describe briefly some of the resistance measurements we have made.

The oil-cell is shown in Fig. 2; it requires nearly 1 litre of oil, but this is not a disadvantage from our point of view, and it minimizes the possibility of the sample being contaminated. The resistance measurement is made at 5000 volts using an electronic test set.

Some typical results obtained with Class "B" oil are shown in Fig. 3. The resistance given in megohms (multiply by 2000 to get resistivity in megohm-cm) is shown as a function of temperature, and the power factor (at 20° C) and acidity are also given. Considering first temperatures of about 20° C, we see that for new oil (Curve A) the resistance is about 50,000 megohms. For oil which has been used, but is in good condition, the resistance drops to 5000 megohms (Curve B); the power factor has now increased to 0.0011, and the acidity is appreciable, but still well within the B.S.S. limit for new oil. Finally, Curve C shows that for a used oil in bad condition, with a power factor of 0.042 and an acidity of 0.76 mg/g, the resistance is only 200 megohms. In this case we consider that the oil is unfit for further service. I think that these results show that the resistance test is valuable to the user, and that it gives at least as reliable a guide to the quality of an oil as any other single test. In this connection we have adopted the following tentative limits : if the resistance is over 10,000 megohms the oil is good, if under 1000 it should be reconditioned or scrapped. If the resistance is between these limits, other confirmatory tests should be made.

Turning now to the effect of temperature on resistance, it is seen that there is a very significant difference in the characteristics of the new and the used oil. Further work seems to be required on this question, and I have not been able to explain the maximum which occurs at 50° C in the case of the new oil. It is likely, however, that the shape of the resistance-temperature curve might provide useful information on the purity of the oil. Measurements of dielectric absorption also offer a fruitful field for investigation.

THE CHAIRMAN : I notice that you show an acidity of 0.76, and I understood you to say that you would scrap the oil at that figure. Is that correct?

MR FORREST: Yes, we would scrap or re-treat it; we should not leave it in service. Our tentative limit for acidity is 0.5 mg/g. Some 99 per cent of our oil will still pass the B.S.S. test for new oil. If we had more acid oil we might have to adopt a higher limit.

MR R. M. CHARLEY (English Electric Co., Ltd.): I am able to speak on the subject only as a manufacturer of transformers. I understand that the view has been expressed that the troubles experienced in recent years in connection with transformers, which troubles have been attributed largely to oils, are really due to varnish. I protest against that suggestion. I do not think there is any connexion, assuming, of course, that a transformer is well designed, that a suitable varnish is used, and that the treatment of the windings with that varnish is appropriate.

I was struck by Dr Rayner's remark that the unfortunate scientists who were charged with the preparation of a specification for oil many years ago were completely led up the wrong street. I think they were. I do not see that there was any justification to have produced a Class "A" oil, and I think the evidence from many years of experience has proved that. 1 would go so far as to say that, if a modern transformer were used with the oils that were available thirty years ago, there might not have been the troubles that brought about the revision of the oil specification. Transformer designs have been greatly improved, particularly in respect of the arrangement of windings which was responsible for hot spots; it was the hot spot temperature, not the average temperature of the windings, which was largely responsible for the sludging of the oil. Such designs have disappeared in these days from the transformers of all manufacturers—or nearly all.

I have been interested in the transformer industry of Great Britain for about thirty years, and I have always advised transformer users against the use of Class "A" oil. I claim no credit for that, but I do think to-day that that policy has been justified, and I hope we shall not go back to the equivalent of the Class "A" oil that has been used in the past. I suggest, as most people have done, that there should be a specification for a single class of oil only, suitable for both switchgear and transformers. It has been suggested that it might be a better oil than Class "B": by all means let us have a better oil than Class "B," but not if the object is to attain a lower sludge value which may run us into some risk of the other troubles, such as acidity, which has been very serious. Class "B" oil has proved itself as being suitable for transformers, particularly if they are equipped with oil conservators. If there were any justification for the application of oil conservators to transformers, it was brought out during the discussion this afternoon. I will venture the suggestion to those who will be charged with the preparation of the new specification for the oil, that while they should use every effort to produce the best possible oil for use in transformers, they might very justifiably suggest that any precaution that can be taken in the transformer itself should be taken. They might make the recommendation that transformers should be provided with oil conservators.

During the whole of this meeting there has been no suggestion, I believe, concerning the elimination of oil altogether. Quite naturally so; this is the Institute of Petroleum ! (laughter). But oil is being eliminated from switchgear, and some people have asked why not eliminate it from transformers? But, of course, the problem is so different. We might say that in transformers we must have a fluid, not necessarily oil : if it is possible to produce a non-inflammable fluid, by all means let us have it if it is suitable in other respects; but I hold no brief for the so-called—and I say "socalled " advisedly—non-inflammable fluids that have been on the market for some years and which have been used in America, but only to a very small extent in Great Britain. I do not believe in the policy at all; neither do I think that, in the experience of the use of transformers in Great Britain from the point of view of fire risk, there is any need to go to great lengths to eliminate oil from transformers. I think that will be borne out by most users of transformers.

I hope it will be possible for the oil industry to produce a better oil than we have at present, that there will be only a single oil which will be suitable for use in transformers and in switchgear; and I strongly recommend that all transformers should be equipped with oil conservators.

THE CHAIRMAN: You say you would like to see a better oil. I take it that you have not experienced sludge really?

MR CHARLEY : No.

THE CHAIRMAN : Nor serious acidity with Class " B " oil ?

MR CHARLEY : No.

THE CHAIRMAN : I suggest we have been inclined at this meeting rather to talk about the white oil being over-refined. I think Mr Wood-Mallock would agree that is rather a misnomer. It is refined by sulphuric acid, is it not?

MR WOOD-MALLOCK: I think the answer is that oil is refined to meet the specification. If in so doing you have to carry it to a degree of refinement where you destroy its natural properties, it is over-refined; but if you can use a refining process which reduces the sludge of a Class "A" oil and leaves the acidity characteristic of a Class "B" oil, it is not over-refined, but is very well refined.

THE CHAIRMAN: Is it not difficult to use the term "over-refined"? Would you not say "incorrectly refined"?

MR WOOD-MALLOCK: It is not one that I should use at all. You can say "incorrectly refined " if you like.

THE CHAIRMAN : It seems, Mr Charley, that we have used a wrong term.

MR R. A. LOCKE (Gresham Transformers, Ltd.): Recently I was called upon to carry out some investigations because we wanted to decide on a new varnish for our transformers. For this purpose we tried some twelve different varnishes, and only two of them were considered to be worth while using. I can say that the varnish has a lot of effect on both the sludge and the acid values.

I was rather interested in Mr Pollitt's suggestion concerning a method of testing transformer oils while in use. I was considering beforehand that maybe the power factor method, in which you put the transformer oil between the plates of a condenser and measure the loss during the heating up of the oil, would be a very valuable method, possibly in the original specification, because if you could take the power factor during the period when the oil was being heated up or during an ageing test, possibly you would have a means of readily determining the value of the oil. The method of ageing has been used a lot in cable testing, in the stability testing of cables, in which case we have a power factor curve which falls as a straight line and then, at a definite voltage, begins to rise.

THE CHAIRMAN : I think, Mr Locke, that Riley and Scott made the same suggestion in the J.I.E.E. in 1928.

MR LOCKE : I do not know off-hand.

MR E. TOBIN (Hackbridge Electric Construction Co., Ltd.): Most of the papers and most of the comments in the discussion have been concerned with acidity; but we want to consider all the factors, not acidity only. All the C.E.B. transformers have been behaving satisfactorily, and we have to be very careful that we do not put something into the oil or change its composition just to satisfy these modern acidity requirements, and as a result obtain a poorer oil for our really important transformers.

A number of speakers have suggested that we should have one grade of oil, and the point I have made is rather in favour of having two grades, although I would like to see just one grade which is suitable for all transformers.

All the transformers which have given acid troubles have been without conservators; they are all small indoor types. The outdoor transformers, and certainly the big ones, all with conservators, have not given acid trouble. I think that a lot of the trouble has been due to insufficient ventilation of the substations. There is something which remains in the air and which possibly enables the chemical changes to take place in the oil. Generally when there is a transformer which has developed acidity, particularly when there is corrosion, you can smell it immediately you open the door, and that is likely to give air conditions which will accelerate the chemical changes.

Although I have seen quite a number of transformers with corroded tank lids, I have known only one or two cases of actual breakdown due to acidity, and in those cases pieces of metal which have not been acted on by the acid have fallen in with it, so that actually there was metal in contact.

I have seen some transformers that were more than twenty years old, with acid values as high as 24 mg/KOH, and they seemed to be working quite well. There was no corrosion; but there was fairly free ventilation in them. The oil was rather sticky and messy.

I was very interested in Mr Forrest's measurement of insulation resistance. The insurance people always have an insulation resistance test on a transformer before renewing a premium, and in the case of some acid transformers in the past the insulation resistance has fallen to 0.5 megohm, although the normal value was 100. So that the insulation resistance has been reduced to a very low value.

MR F. MEYER (The Sterling Varnish Co., Ltd.): I feel somewhat diffident in speaking at this gathering, in view of the remarks which have been made about insulating varnish; but as I am primarily concerned with the manufacture of insulating varnish, I cannot allow the opportunity to slip by without saying a few words at least in its defence.

We have carried out a considerable amount of research work in the laboratory on the acidity development in transformer oils, and our conclusion is that the transformer can be made or marred by the way in which the insulating varnish is used. In other words, insulating varnish can be a very good inhibitor or a very good accelerator, depending on how it is used when the transformer is impregnated with it.

In a recent series of tests we impregnated two coils with one varnish which we normally sell to quite a number of transformer manufacturers. One of the coils we impregnated in a manner which to our minds was perfect, and we impregnated the other in the worst possible manner so as to leave the varnish inside the coil un-oxidized and even to leave solvent in it. Then we had a third coil in oil, without any varnish treatment at all.

We continued the test for something like six months, taking the acidity value each month. At the end of six months, the worst case was the coil

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which had had no varnish treatment at all; the second worst was the coil in which the varnish had been very badly applied; and we obtained very good results indeed with the correctly varnished coil. The message I give you, therefore, is to use insulating varnish, but be sure to process it properly.

MR E. L. HOYLE (The General Electric Co., Ltd.): I should like to amplify the remarks of Mr Meyer. I have carried out tests on coils and varnish in oil, and I went even further than Mr Meyer, for I used a bare copper coil, an unvarnished cotton-covered coil, an unvarnished papercovered coil, and cotton-covered coil treated with twelve different varnishes. The bare copper coil showed the highest rate of acid development, the unvarnished cotton-covered coil was next, then the unvarnished papercovered coil and then the varnished coils.

Among all the reasons given for acid development in transformers, no one has emphasized the effect of the copper. I think it is the catalytic effect of the copper in the transformer which is responsible for the high rate of acid development. Protect the copper against the effect of the oil and the rate of acid development will be reduced.

Varnish provides one means of doing that. It is perhaps not a permanent method, or is not as permanent as some methods can be; but I feel that it is a line of approach which has not received sufficient attention—the prevention of the catalytic effect of copper on the oil.

MR W. H. WELLS (Hackney Electricity Works): I have experienced the occurrence of acidity, not only in indoor transformers, but also in outdoor transformers fitted with breathers. In many cases I have seen the top cover plate badly corroded away, and therefore went into the question as to whether I could recondition the oil. I was rather surprised to hear to-day that the method of passing it through alumina was very expensive and not a commercial proposition. For my experiment I procured an old 40-gallon oil drum and an old transformer tank, and put 1 cwt of alumina into the drum.

Using a small motor pump of approximately $\frac{1}{4}$ hp, I first passed through the alumina 250 gallons of oil. The acidity value of that oil was 1.44 mg/KOH at the start; the final acidity value after the oil had passed through the alumina for a considerable number of hours was 0.097 mg/KOH. This I considered satisfactory and tried another 250 gallons of an acidity value not quite so high—*i.e.*, 0.62. The final acidity value after 100 hours was 0.042.

Another 300 gallons is in course of being reconditioned, its acidity value being 2.42. This was some of the worst oil I had, and after 84 hours the acidity value is down to 1.38 mg/KOH.

These tests occupied more time than they need have done, as only 1 cwt of alumina was purchased, and in between times has had to be re-activated to enable the reconditioning of the oil to be completed. The tests were carried out with the oil unheated.

I think by the results obtained it is not quite right to say that this method is not a commercial proposition. 320 gallons of the reconditioned oil have been put into a transformer, the transformer put on load and during the next six months periodic tests will be taken to see the effect on the transformer, and the effect of service on the oil itself. DR ALAN ROBERTSON: I should like to reply to several of the points raised in the discussion.

First, it cannot be stressed too strongly that the catalytic action of metals is due mainly to the effect of the metals in solution. Copper stearate is a more effective catalyst for oxidation than is metallic copper itself. This may give a clue as to what happens when the temperature is varied in the sludge test; the concentration of volatile acids in the air circulating around will obviously be greater with a higher temperature, so that more copper will be dissolved, and therefore, more atoms will be formed.

It is also of interest that reference has been made to the acidity increasing very markedly just as corrosion occurred in the tank top. Presumably, then, the concentration of the metal in the oil would have been very much increased through the solution, and so the degree of acidity would also have increased; the concentration of metal catalyst would have become very high, and the acidity would have become much greater at that point.

Some points were raised by Dr Saloman in connection with the induction period. With the hydrocarbons with which we carried out most of the experiments—in particular tetralin—there was no induction period, but we have found it with some other pure hydrocarbons, especially those with a secondary carbon atom such as decalin. I think that recent work by Dr Gee and Dr Bolland at the Rubber Research Institute gives us some answer to the problem of the induction period. It is that there is a very low oxidation rate at the start, then the peroxide decomposes to form free radicles. These free radicles act as an auto-catalyst, and the reaction will be speeded up.

Then Dr Mardles made the point of the investigation of the long chain paraffins. We have studied them and some results are given in Table II of our paper. We did not use them for detailed work because the peroxide which was formed was very unstable and could not be isolated. Also the rate of oxidation was very small, being 0.4 c.c. per hour, compared with 12 c.c. per hour with tetralin at 110° C.

With regard to adding a catalyst to increase the rate in the sludge test, I would give a word of warning. Table II will also show that different metallic catalysts in solution may completely alter the relative order of the different oils.

DR PHILIP GEORGE (written communication): The induction period noted in the oxidation of an oil can arise in two ways. Firstly it may be due to the slow removal of natural inhibitors present in the oil, such as sulphurand nitrogen-containing compounds. Secondly it may be due to the existence of an extremely slow thermal oxidation yielding hydroperoxides, which then break down, giving free radicals which initiate a second more rapid chain oxidation as Dr Robertson has indicated. I should like to explain this more fully.

Hydroperoxides of the general formula R_1R_2 CHOOH can decompose in at least two ways : unimolecularly to give a ketone R_1R_2 CO and water without necessarily forming free radicals as intermediates, and by a second mechanism yielding free radicals. These hydroperoxides are derived from the hydrocarbon R_1R_2 CH₂, and in the oxidation of some of these hydrocarbons—*i.e.*, tetralin—no induction period in the usual sense can be observed; it has become just a slight autocatalytic increase in the rate. This is because the first decomposition mechanism is predominant. Dr Robertson and I studied this autocatalysis in the case of tetralin, and we showed that it follows kinetically the strict mathematical expression predicted from our suggested mechanism. In terms of chain reactions it is the process of degenerate chain branching which we referred to at the end of our paper on the Mechanism of the Oxidation of Liquid Hydrocarbons. The experiments of Gee and Bolland, referred to by Dr Robertson above, confirm our proposed mechanism. They studied the oxidation of ethyl linoleate, and showed that ethyl linoleate hydroperoxide is an extremely good "catalyst" for the oxidation of its parent hydrocarbon.

Hydroperoxides of the general formula R₁R₂R₂COOH-*i.e.*, tertiary hydroperoxides derived from the hydrocarbon R1R2R3CH-cannot decompose unimolecularly to give a ketone because of the absence of the necessary hydrogen atom on the α -carbon atom to the -OOH group. The free radical decomposition mechanism predominates in this case (see George and Walsh, Trans. Faraday Soc., 1946, 42, 94). It is not surprising, therefore, that it is with these hydrocarbons that induction periods of very pronounced autocatalysis is observed. To sum up : oxidation with a marked induction period represents an extreme case where the thermal oxidation is very slow, the hydroperoxides formed break down, yielding free radicals which initiate a second more rapid chain oxidation; oxidation with marked autocatalysis is due to a fairly rapid thermal oxidation producing hydroperoxides, the free radical initiated reaction proceeding at a rate comparable to the thermal rate; oxidation with slight autocatalysis or with none represents the other extreme case; here the thermal oxidation is rapid, and more or less completely masks the slower radical initiated reaction.

MR J. C. WOOD-MALLOCK : So many points have been raised, and with such authority, that it is quite impossible to reply at length to more than one or two. I was particularly interested in the question of variable results with two transformers on the same service, using the same oil, and would suggest that the variable results are due to pro-oxidants present in the transformer cases, either because the transformer has been used before, or because catalysts have been left in the transformer case during the course of manufacture. We have found that the amount of certain catalysts required to accelerate oxidation reactions is so minute that the only method we have found suitable for measurement is spectrographic analysis. Very few parts per million of calcium sulphonate or calcium naphthanate are required to increase the sludge figure by 100 per cent, and such a quantity could not be released by ordinary chemical analysis. The same theory would apply to varnish trouble. Where driers are being used and the degree of cooking of these varnishes is variable, the possibility of a very minute amount of the soap used as a drier going into solution in the oil is ever present and this I believe would certainly lead to trouble.

As to measuring the insulating resistance of the transformer oil, we constantly use this method of test, although a lot of our electrical friends have rather doubted its value. I have shown in the paper that, by suitably blending transformer oils or bases for transformer oils, a very much higher degree of insulation stability can be obtained. Dr Salomon referred to oxidation being initiated by a dehydrogenation stage. That is particularly interesting to us, in that the aromatic oils which we propose to add do absorb hydrogen during their life in the oil, particularly under electrical stress; if they absorb nascent hydrogen they may very well interrupt the oxidation chain.

In conclusion I would like to repeat that I deprecate very strongly the use of the term "over-refining." An oil is refined to specification; if it is refined to the point at which it meets that specification, it is not overrefined.

It is up to the user to lay down a specification which ensures that all oils conforming to it are suitable for his purpose, and it is up to the refiner to produce such oils. It has been my intention to show that whatever new requirements are made of transformer oil in the future the producer will be in a position to deliver the goods.

MR. P. W. L. GOSSLING: There has been a fair amount of discussion on varnish, and we feel from the results in transformers that it can mean something. But I must make it clear that it is not a point that can be dealt with in the oil specification. There has been a tendency to refer to varnish as though it were a material like a piece of copper, which could be subjected to close chemical specification. As things are, that is not the case; it is for the transformer makers to attend to the matter and perhaps to arrange for some research which possibly they could refer to another appropriate panel of the E.R.A. In that way it may ultimately be possible to cater for it; but it is not a matter for the oil panel to deal with in their specification.

There has been quite a lot of discussion also on the temperature at which tests are carried out. It has been pre-supposed that a lower test temperature would result in improved reproducibility; but I have not seen any work which supports that. On the contrary, a certain amount of cooperative work carried out by the oil companies on testing at a lower temperature has shown that the reproducibility obtained at, say, 110° or 120°, is no better than the 15 per cent variation from the mean which the Institute of Petroleum has at present in the test. As to the kind of reproducibility obtained in the E.R.A. work, really there was nothing in it either way between the 150° and the 120° C tests. The average reproducibility for all pairs at 150° C for 45 hours was 10.3 variation from the mean, while at 120° C for 96 and 120 hours it was 11.3 and 9.4 per cent variation respectively. That is for sludge formation. In the acidity measurements the average reproducibility was 8.2 per cent at 150° C, against 10.7 and 10.3 per cent respectively for 96 and 72 hours at 120° C. That is slightly in favour of the higher temperature.

Another point in connection with the high temperature; Mr. Onslow stressed that it is an acceptance test which we require and which we must have, and the length of time for the test is important. Another speaker has referred to a test at 95° C taking 2,000 hours. That cannot be considered as an acceptance test, of course. The point is that the E.R.A. work, and work by other contributory laboratories, shows that there is correlation between the results of tests at 150° C and tests at, say, 120° or 100° C, as shown in Fig. 4. Here we show acidity vertically and temperature horizontally. The 2.5 mg limit which is proposed by the E.R.A. for incorporation in the transformer oil specification is shown. We took a number of oils, some of them selected because we knew they were from different sources, and some



we refined ourselves from our crudes. You will see from the results that it is fairly reasonable to conclude that we get a separation of oils into two types by the proposed acidity limit of 2.5 mg in a test carried out at 150° C.

Votes of Thanks.

MR J. S. PARKER: I should like on your behalf to thank the chairman and the authors of the various papers. Anyone who knows anything about arranging for papers will appreciate that the chairman must have put in a great amount of work, and I think he has gathered together an excellent team, who have covered the whole scope of transformer oil testing.

I invite you to accord a very hearty vote of thanks to our chairman, and to the authors of the several papers, who have so ably supported him.

(The vote of thanks was carried with acclamation.)

THE CHAIRMAN, responding: It has been a great pleasure for me to have been able to gather together these eight papers. I have been fortunate, not only in securing the papers, but also in that so many electrical engineers have attended to give us their point of view. I am sure we have all learned a great deal from the very frank discussion.

Lastly, it is only proper that, from the Chair of the Institute of Petroleum, we should offer our thanks to the Institution of Electrical Engineers for the use of their magnificent hall.

(The vote of thanks was carried and the conference closed.)

Written Discussion.

MR V. BISKE: Firstly I would like to endorse the general conclusions come to by Mr Barton. Experience with the sludge test, over several years, shows that anomalous results do occasionally occur, without there being an obvious cause, and despite the test being under constant observation for the whole of the 45-hour period. I particularly agree with Mr Barton that fairly wide variations in the characteristics of the petroleum spirit, used for precipitating the sludge, do not appear to affect the results.

As regards the extremely intriguing figures put forward by Gossling and Romney with respect to condenser water temperature and its effect on the sludging value, I would like to suggest that it would have been of interest to carry this work somewhat further. At one period, due to water supply difficulties, condenser water temperatures of the order of 140° F were experienced fairly frequently, for a considerable proportion of the duration of the test. The sludging values obtained in these cases did not appear to be anomalous, and were in line with the expected figures, although the results are not now available. If the suggested increase of 2 per cent per ° F above 63° F were strictly applicable figures of the order of 2 per cent sludge would have to be expected. Is it perhaps the case that, although an increase in condenser water temperature within the limits examined in Mr Gossling's paper cause a rise in sludge values, a really high condenser water temperature, perhaps above 100° F or thereabouts, causes the value to fall again, so that the results obtained, whilst not strictly accurate, are not markedly out? The cause of the effect of condenser water temperature is not clear, but perhaps the following, purely speculative, suggestion may be tentatively put forward. With a slight rise in condenser-water temperature a small proportion of the more volatile oxidation products is not returned to the reaction flask. If we assume that the formation of these reaction products is a part of the same reaction that causes the formation of sludge, then, if the volatile products are removed from solution, this will be the mass-action effect, tend to displace the reaction more in the direction of the further formation of the escaping products, accompanied by the formation of more sludge.

If, however, the condenser temperature is pushed to a really high figure, then, possibly, the loss of volatile oxidation products is greater than their rate of formation, and any effect such as that mentioned above is counterbalanced by the smaller amount of copper catalyst that is brought into solution, by the lesser quantity of active low-molecular-weight acids that is present.
GENERAL DISCUSSION ON TRANSFORMER OILS.

In connection with the question of the acidity of the oil after oxidation, it would be advisable to define the technique employed for determining this. A method that appears suitable is to precipitate the sludge and allow to stand overnight; the sludge is then filtered off and the acidity determined on an aliquot part of the filtrate, calculating back to the amount of oil that this contains, and assuming a nil acidity for the petroleum spirit present. This, of course, is the procedure described by Gossling and Romney, but it is not clear whether it has been adopted by all workers.

Finally, as regards Mr Ellis' plea for oils of a cold test below -30° C. There is, of course, no difficulty in meeting this requirement—in fact, it is safe to say that the vast majority of B.30 oils are not dewaxed, but are made from wax-free distillates, and thus have pour points depending purely on viscosity characteristics, and which are usually in the region of -50° C.

MR H. DUNKLEY (Hull Corporation Electricity Department): The following figures may be of interest, showing the acid conditions found among 533 transformers on a normal distribution system when a quick survey was taken as a result of two cases of bad acid and sludging.

	Acidity. mg.KOH/gm.							No. of Transformers.
8.0-9.0								2
6-0-8-0			1					1
4-0-6-0								1
3-0-4-0		-						3
2.0-3.0								4
.0-2.0								23
0.9 - 1.0			2.27	-				9
0.6-0.9			-	100	-			21
-4-0-6	-							27
$) \cdot 2 - 0 \cdot 7$	- 1.							141
$0 - 0 - 0 \cdot 2$		1.4						301
								533

Mr Sayers' valuable contribution showed 170 out of 10,000 transformers as giving trouble due to acid, but he did not define the meaning of trouble. This would be of interest.

The worst trouble noted in the Hull undertaking is that of the baking of sludge on the windings, choking oil-ways. This has been found on a transformer with acidity as low as 1.73, and though usually associated with high acidity, has been absent with a figure as high as 8.46, where the tank above oil level was perforated by corrosion.

It is, of course, a fairly simple matter to weld in new plates, but the removal of hard deposits on cores is difficult in the extreme.

Experience with the above transformer agreed with the I.M.E.A. results. Routine attention to acid formation should be practicable now that the staff position is improving, so that unexpected trouble in future should be even less than recently reported.

PROFESSOR H. WEISS and DR T. SALOMON: (1) Mr A. A. Pollitt in his paper on "Oxidation Tests for Transformer Oils" pointed out, in criticizing the Swiss test, that "the inclusion of cotton threads is novel, but since the acid development is a fairly direct index of the tendering of the cotton, the inclusion of cotton is of doubtful value."

The cotton test is not a measure of acidity development in the oil; Dr Staeger observed with certain highly-refined oils a rapid deterioration in the transformer, and he introduced the cotton test in order to exclude them from use in a transformer. There are many over-refined oils (Class "A") which do not diminish the mechanical strength of the thread after artificial ageing, and there are also oils not over-refined (Class "B") which will be excluded by this test.

Several years before the war we had occasion to study some of those oils, and we found that their rapid deterioration was due to the presence of small quantities of organic sulphates formed during the refining of the oils by strong sulphuric acid; those organic sulphates, very stable at ordinary temperature, may be decomposed suddenly after long-time heating and liberate SO_3 which will resinify oil and attack thread.

(2) Many contributions in the discussion attributed the rusting of transformers to the action of free volatile acids. This is not always true. We have often observed rusting on the lid of a transformer without a conservator filled with Class "B" oil after a short time of service. The rusting was due to the action of moisture dissolved in the oil, and accumulated on the lid of the closed-type transformer. The phenomenon disappeared when a one-way valve was installed on the lid to let the moisture out.

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