

GENERAL DISCUSSION

MR. G. H. VON FUCHS.¹—Mr. E. R. Thomas, who presented the Liander and Ericson paper, gave us a rather complete description of the Swedish paper, but he left out one very important point made in the paper, at least a point that I consider very important. I would like to read it to you: "It is evident from Fig. 18 that after the induction period the inhibited oils are oxidized in a way that is particularly reminiscent of the behavior of the same oils when uninhibited. In view of the above mentioned results, it is pertinent to inquire whether an oil should be refined to the highest sensitivity or whether it should be refined only to an extent which gives, after the induction period, a normal oil with an acceptable resistance to oxidation."

MR. F. S. OLIVER.²—It is interesting to note the difference in viewpoints expressed by the French and Swedish authors. Mr. Salomon indicates in his paper and in his fifth conclusion that, by means of his test, he can make a prognosis as to (1) when a new or used nonsludged oil will start sludging, (2) when, in the case of a used or sludged oil, sludging started, (3) whether a negligible or important quantity of sludge is in the transformer, and (4) when a new "sludge" shower will happen and its relative importance. Messrs. Liander and Ericson, on the other hand, state in their

conclusions what appears to be a diametrically opposite view: "The requirement to foretell in detail the behavior of an oil during the several decades it may be in service, by means of accelerated tests lasting only a few hours and carried out under circumstances greatly differing from those in practice, must be regarded by and large as an insoluble problem."

Although we have not attempted to use the modified sludge accumulation test in the manner described by the various authors, our data do indicate that for tests of the "TOOT" type there is a definite relationship between the laboratory test results and the service performance of various oils; the best oils have both the longest laboratory life and the longest sludge-free service life.

It is gratifying to note that all the authors instead of merely measuring sludge at a few fixed intervals plot both acidity and sludge *versus* time of test. Our experience with oxidation tests of a different type such as the "TOOT" indicates that curves of acidity and interfacial tension plotted *versus* time for the period before the first appearance of sludge are extremely valuable in rating an oil.

Mr. Salomon's paper appears to present interesting and plausible theories, but it is very difficult to agree or disagree with many of his points since there are several sections which seem ambiguous

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and require clarification. For example, in discussing Fig. 3, he indicates that oil H and oil L are behaving differently when preheated for four and six weeks.

This difference is not apparent from the curves, possibly because the meaning of cross hatching, a vertical rise, and apparent extrapolation of parts of oil L curves are not explained. A more thorough explanation of many of the various graphs would be helpful.

MR. T. A. McCONNELL.³—I wondered if you noticed the similarity between our round-robin test results that have been reported upon to date and the sludge-shower theory developed in Mr. Salomon's paper. I am referring to the results of the sludge accumulation test and to a lesser extent, I believe, to the pressure oxidation test in which we experienced a series of hills and valleys with the trend always upward.

At the time our separate papers were presented, we attempted to explain those phenomena by stating that it could well be that we were building up soluble sludge in the oil that, at certain points shown in the laboratory tests, had precipitated out. We reasoned that, when certain test results were lower than those exhibited by previous samples, indications were that we were having this shower of sludge within that period. I just wondered if you had noticed the similarity.

MR. F. M. CLARK.⁴—I do not think there is any doubt of the fact of the showers of sludge, but the thing I neglected to say (in presenting Mr. Salomon's paper) is that because of this you cannot make a prognosis in the future on any one sample. You must know the history of the oil. I think basically we agree on that.

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MR. E. R. THOMAS.⁵—I would like to ask Mr. Bravey if he would give a very short description of the actual mechanism with which he is recording oxygen absorption.

I know the reference was given to the paper where it has been described, but it might be enlightening to us if we can have just a brief description.

MR. D. W. BRAVEY (*author*).—First I shall give the full reference to the paper concerned: *Journal of Scientific Instruments*, Vol. 30, p. 307 (1953). Briefly oxygen or atmospheric pressure is static above a thin layer of oil under test. When oxygen is absorbed by the oil, the subsequent drop in pressure causes an electrical circuit to be made. The current passes through an electrolytic cell, generating more oxygen which is fed into the apparatus. As soon as atmospheric pressure is reached again inside the apparatus, the electrical contact is broken. The duration of the electrical current is of course proportional to the amount of oxygen absorbed by the oil, but instead of recording current, we have found it more practical and simple to incorporate in the electrical circuit a second electrolytic cell in series with the first, and to record continuously the total gas pressure in the second cell.

MR. M. ZWELLING.⁶—May I start the discussion on the point that I am opposed to the use of soluble catalysts for aging tests of transformer oil.

I would like to point out some curves in the paper by Liander and Ericson to support my contention.

In the first place, let us examine two sets of curves, Figs. 5 and 6. Figure 6 shows how the amount of copper dissolved into oil can vary widely with different oils. Then Fig. 5 shows one oil, A, with a solid copper catalyst in which,

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as the heating period proceeds with time, there is (1) a rise of copper dissolution, (2) a rise of acidity, and (3) a rise of sludge.

It seems to me that, when one starts an aging test with all transformer oils (whatever their source or refinement) exposed to a certain amount of dissolved copper, one completely disregards the evidence shown in Fig. 5 that oxidation proceeds in a certain order. Instead, we place all the oils on an equal basis of the same quantity of dissolved copper, a situation that does not occur in actual service. The amount of dissolved copper normally proposed for aging tests of this kind far exceeds the level shown in Fig. 5, even at a time when the amount of acidity and sludge has become appreciable.

To put it in a different way, when we add soluble copper at the beginning of an aging oxidation test, we make an assumption that never exists in actual service: we assume that all oils have had at the start of oxidation the same amount of dissolved copper in them. Figure 6 shows that this assumption is not true.

I would also like to mention that I oppose all tests of the type that proceed so quickly with time, because as in Liander's paper, the shape of many of the curves shown, which appear to be important to the authors, actually express what may occur in service a long time after the period in which everyone who uses transformers is interested.

MR. CLARK.—Beyond the induction period?

MR. ZWELLING.—Yes, in fact, way beyond the induction period. Let us take Fig. 14 of Liander's paper as an example.

Here is shown a comparison between experimental and normal transformer oils, the results of which indicate to the authors that the test method is valid for testing the aging characteristic of transformer oils. In this case, we have a bracketed shadow section to show the

area where curves resulting from the testing of commercial oils will lie. Experimental oils whose curves fall outside this bracketed section are, therefore, considered to be unworthy. I wonder if this is so, since the period of time of test causing a rise in acidity in which we are interested (less than 1 and often less than 0.5 mg KOH per g) is such that all the curves, experimental and normal oils, fall within the bracketed section. For the same oxidation time, this is also true of the sludge curves.

Where the curves of the authors exhibit large differences in various transformer oils, the period of oxidation time is far beyond that in which we are interested, that is, what oils will do in service. On the other hand, if we examine the curves during that period of time in which the rise of acid and sludge is meaningful, the difference between various oils is so small that reasonable conclusions are not possible.

MR. E. L. RAAB.⁷—To pursue Mr. Zwelling's remarks further with reference to the Liander and Ericson paper, it appears to me that considerable evidence given throughout the paper can be interpreted in opposition to the use of soluble catalysts in evaluating transformer oils. For a given series of oils refined to different degrees and derived from different crude types, the molecular constitution will vary. These variations can be such that marked differences will result in the amount and rate of copper dissolution in the oils. By the use of either soluble copper or soluble iron catalysts or both in laboratory oxidation tests, it would appear that a marked disservice can be done to those oils which are more resistant to taking copper into oil solution.

Figure 6 indicates that oil S 5 is by far the most resistant oil to taking copper into solution, whereas oil S 4 ap-

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parently attacks copper to a considerably greater degree. Figures 2 and 4, where a solid copper catalyst is used, indicate that oil S 5 is considerably superior to oil S 4 in its resistance to both acid and sludge formation. However, Fig. 14 where soluble catalysts are used, although indicating S 4 to be considerably inferior to S 5 in acid formation, shows it to be equivalent in sludge formation to S 5. Again when oils S 5 and S 1 are compared, the use of a solid catalyst (Figs. 2 and 4) indicates S 5 to be superior. Figure 12, however, indicates S 1 to be at least equivalent for low concentrations of soluble copper, and for high concentrations it is superior to S 5.

It therefore appears to be unrealistic to divorce the metallic dissolution effect from the oxidation effect—which is done to a great degree when soluble catalysts are used—in view of the fact that the first stage can and does markedly affect the second. To quote a phrase from the concluding remarks in this paper, “The chain of events during oxidation with a metallic catalyst appears to be that the metal is dissolved in the oil at an early stage and when dissolved acts as a catalyst in the oxidation occurring in the liquid phase.” Earlier in this paper the statement was also made that “the quantity of copper dissolved by the oil depends on the character of the oil.”

MR. VON FUCHS.—I am referring to both the Liander paper and the Bravey paper now. They present viewpoints which make one think. It would help us in this process of thinking if we were told about the type and degree of refining the oils received. Neither of the papers tell us that. No specific dispersion or aniline point values are given. This information could probably be added before the papers are published. There was a statement made in the Salomon paper that the base oil is good, that it is just the impurities which cause the oils to be unstable. I think this is an excellent

thought. I am sorry, though, that Mr. Salomon did not elaborate on this point, but I am fully in agreement with him as far as he went.

The presence of corrosive impurities can be determined by such tests as the Frigidaire copper corrosion or Dithizone test by means of which one can tell when an oil starts dissolving copper at an early stage. If this happens, this will not be a good oil in the long run.

If one inhibits such an improperly refined oil and measures the formation of peroxides during the modified turbine oil oxidation test (Method D 943),⁸ one will find that peroxides form at an early stage. Thus, the corrosivity of an oil toward copper is an important criterion of oil quality and should have been included in the papers.

MR. CLARK.—If I understand Liander's paper correctly, he substantially says that the oils will differ in the ability to dissolve copper, but the amount of copper dissolved has nothing to do with the rating of the oil in its oxidation stability. Part of the copper goes in solution and is important in the corrosive characteristics of the oil, to which we pay no attention in our oxidation tests.

MR. THOMAS.—I think he pointed out that the actual copper that remains in the oil as analyzed afterwards is in the order of hundredths of a part per million, in other words, over 99 per cent of the copper in there has acted as a catalyst and the remainder has gone into solution in the oil.

MR. CLARK.—I do not find that. Is that true? Mr. Liander says, “The conclusion may be drawn from these and other tests not reported here that in the case of oxidation in the presence of metallic copper catalysts one must distinguish between two separate events

⁸ Method of Test for Oxidation Characteristics of Inhibited Steam-Turbine Oils (D 943 - 54), 1955 Book of ASTM Standards, Part 3, p. 425.

which overlap. One is dissolution of copper in the oil and the other is the ability of the dissolved products to influence catalytically the oxidation of oil. Corrosion is thus regulated by one set of factors whereas oxidation is governed by others."

MR. RAAB.—Mr. Clark has just stated that "oils will differ in the ability to dissolve copper, but the amount of copper dissolved has nothing to do with the rating of the oil in its oxidation stability." I certainly did not obtain that impression from the synopsis of the Liander and Ericson paper. To quote the synopsis, "When solid copper is used as a catalyst, two things take place. One is a dissolution of copper in the oil; the other consists of oxidation of the oil, catalytically influenced by the dissolved copper. The dissolution of the metal takes place mainly at the beginning of the oxidation, the extent of this 'corrosion' depending partly on the properties of the solid metal and its area and partly on the type of oil. The oxidation is governed by the type and concentration of the catalyst and is, furthermore, dependent on the type of oil."

Now I interpret this statement to mean that if one oil attacks copper more rapidly than another and takes more copper into oil solution, then the amount of soluble catalyst present is definitely one of the factors influencing the rate of oxidation.

MR. BRAVEY.—Regarding the amount of copper dissolved by an oil, I think Mr. Clark answered the question by pointing out that the amount of copper dissolved by different oils does not necessarily correlate with the susceptibility to oxidation of those oils. However, in defense of the use of soluble catalysts, I should like to make a further point. All laboratory tests, whether with solid or soluble catalysts, are carried out in small, clean glassware, often with air or oxygen pumped artificially through the

oil which is at a higher temperature than is met with in service. In practice, however, there is a far larger bulk of oil in intimate contact with dirt, varnish, cellulosic materials, and the metals of the transformer. To say that any solid copper catalyzed laboratory test is nearer to practical conditions than a soluble copper test is, I think, an assumption. The aim should be to devise a reasonably rapid laboratory test that will evaluate oils in the same order as they will perform in service, or at least will differentiate between those of satisfactory performance and those of inadequate performance. Obviously service conditions must be departed from in order to accelerate oxidation in the laboratory, and to obtain a repeatable test.

There is one other point brought out by Mr. von Fuchs, the degree of refining of the oils mentioned in the Irving and Bravey paper. Four of these oils are commercial oils, and it would be improper to disclose full details concerning them; the other three are experimental oils selected solely because of their varied response to the inhibitor concerned. It must be emphasized that the aim of this paper is to describe a test method for inhibited oils which is possibly worth further investigation, and I should hesitate at this stage of development of the test to compare the absolute merits of the various oils arbitrarily chosen to illustrate the method.

MR. VON FUCHS.—This will leave the paper incomplete.

MR. CLARK.—I think Mr. Salomon has been misquoted. He said you cannot, from a short test, prognosticate the future, and so does Mr. Liander; but Mr. Salomon goes on to say that by a series of tests you can establish the degradation of the oil and from that series of tests predict future behavior.

MR. BRAVEY.—It has been asked if we have measured how much copper

actually remains in solution in different oils after the tests have run for some time, compared with the initial concentration of dissolved copper. We have not carried out any consistent measurements on the amount of soluble copper present in different oils during the test, but we do know that in a very short time in all cases the bulk of the copper is precipitated out, that is, it is not in a soluble form for the greater part of the test period.

MR. W. G. WALKER.⁹—The published data giving the results of oxidation tests on petroleum oils using both solid and soluble catalysts indicate that for a given oil under given conditions the total sludge formed is proportional to the area of solid catalyst exposed or to the volume of soluble catalyst used.

A deduction which can be drawn from the above results is that the rate of formation and ultimate volume of sludge is dependent not primarily upon whether the catalyst is solid or soluble but upon the intimacy of the contact between the sample and the catalytic elements or upon the diffusion of the catalytic elements in the sample.

Since it is obvious that a liquid catalyst provides much more rapid initial diffusion than that provided by a solid catalyst, it is expected that the sludge formation using a liquid catalyst will be at a much higher rate than that using a solid catalyst. All published data support this conclusion.

If the only objective of an oxidation test is to obtain relative indications of sludge in a minimum time, a soluble catalyst will provide a means for obtaining this objective.

No direct correlation between the use of a solid and the use of a soluble catalyst can be obtained until the effective areas of both catalysts exposed to the sample are reduced to a common unit. In the

meantime, those oils in which it is desired to study the induction period for producing sludge by oxidation will have to be tested with a solid catalyst. Where relative total sludge is the only objective of the oxidation test, the use of a soluble catalyst will shorten the time of the test appreciably.

MR. CLARK.—It seems to me we have an agreement that the increased area of solid copper promotes oxidation. We also have evidence that some oils will take into solution a larger amount of copper than other oils. We also have evidence from Mr. Liander that when he adds soluble copper it precipitates out almost immediately to such an extent that you cannot even measure what is left in the oil.

Now, following up Mr. Walker's comments, may I suggest that the soluble copper on precipitating from the oil gives a solid copper surface of large value and that the catalytic action is a surface reaction. Therefore, with solid copper and soluble copper, you are getting the same thing and you could duplicate the soluble copper by a solid if you could use a sufficiently finely divided copper metal.

MR. VON FUCHS.—On the contrary, I am opposed to the use of soluble copper. During a recent meeting of Section B of Subcommittee IV of Committee D-9, round-robin tests on five samples of insulating oil of known service performance were reported utilizing modified IEC methods. In all cases where either copper naphthenate or copper and iron naphthenates were used as catalysts, the rating of the oils was reversed. The oil which had the best performance in the ASTM cooperative transformer field test records collected during the past 10 yr rated only second best when the soluble catalysts were used.

When you are using soluble copper as a catalyst, you may have some of it precipitate out as early as 2 hr after start of

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the oxidation test. Thus, your soluble catalysts will cause the oil to form sludge or at least something which will look like sludge. How will you then tell when the oil really starts to sludge? There is no need today to have sludge in transformer oil. The refiners know how to make oil and how to inhibit it so it will not form sludge in service.

MR. CLARK.—The discussion refers to tentative results so far accumulated on the oils. It remains to be seen whether we are really trying to differentiate between the quality of two good oils, splitting hairs so to speak, or whether we are trying to differentiate between an acceptable oil and one that is not acceptable. Furthermore, the repeatability of tests such as these may well be questioned if too fine a distinction between two acceptable oils is attempted.

MR. E. S. ROSS.¹⁰—Has any relation been established (a) between copper solubility and the rate of acid formation and (b) closely associated to that, any correlation between the nature of acids, or their corrosibility, and the rate of copper solution? And to tie in those two questions with a third subject which bears on the whole picture, the nature and quantity of acids formed under deteriorating conditions definitely are related to the degree and nature of the treatment given the oil. I think this involves a number of the questions asked, regarding the exact natures of those oils used, and might give us an answer as to why differences are exhibited. For instance, that might indicate why you get much higher copper solubility in one case and why in another case perceptibly less solubility and more of something else. That, to me, is a sign that the copper salts formed have different natures, and the reason for the different natures is due to the different types of acids that may be formed.

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MR. VON FUCHS.—It could be.

MR. CLARK (*by letter*).—The problem of diagnosing the properties of transformer oil at any selected time during its commercial use and predicting its behavior in the future is indeed a difficult one, and Mr. Salomon is to be congratulated on his approach to its solution. The problem of oil maintenance in use and a prognosis concerning its future freedom from service trouble are greatly dependent on the requirements specified. If an oil in service is specified to be free from sludge, it is clear that a series of studies concerning the change in the "period" of the oil during its first cycle might be conceived as a basis for predicting the future condition of the oil under continued use of the same type and degree of severity. Yet, experience in the United States, using the Snyder Life Test, has shown that the "first trace of sludge" criterion is indeed an unreliable gage. Change in the oil, normally associated with the shipping or the use of the oil during the first few weeks or months of its service, may frequently cause traces of sludge to precipitate in laboratory tests substantially at time zero.

I would appreciate Mr. Salomon's comments. Does he believe that, if the transformer maintenance specification called for complete freedom from sludge, the shape of the time-sludge curve could be safely used to diagnose and prognosticate concerning the oil in commercial use? If so, would this same solution be of reliable application in gaging the changes occurring in an inhibited oil in commercial use?

There has been some evidence adduced that moisture contamination and voltage application are not without effect on the sludging reaction. Have these effects been noticed by Mr. Salomon and, if so,

do the sludge-time relations described by him show any change that would prevent their use as a gage for oil maintenance in service?

Soluble copper catalysts have been described in the companion papers presented at this Symposium. If the soluble copper catalysts of these papers be substituted for the solid copper used by Mr. Salomon, does experience indicate that the relations and conclusions of this paper would be in any way altered? If so, does Mr. Salomon have any explanation?

And finally, if one were to specify that an oil in service must be maintained free from sludge, does Mr. Salomon have any indication that the more complicated testing procedures which he suggests have any more merit than the use of the interfacial tension test which has shown considerable value as a service control test of maintenance?

Messrs. Liander and Ericson have made an important contribution to the study of sludge formation in mineral transformer oils. The catalytic effect of solid copper and the increased effect of increased copper area have long been recognized. The advantage associated with the use of a soluble copper compound in its greatly increased catalytic action, thereby shortening the time necessary to obtain significant sludge formation for proper oil evaluation, warrants renewed consideration. There have been many claims made that to add a soluble copper compound to different transformer oils places an oil at a disadvantage when it is characterized by but little tendency to corrode and dissolve solid copper as compared to the other oils. This appears to be a fallacious objection since the authors have shown that the amount of copper taken into oil solution from a solid copper surface is not related to the ability of the oil to resist sludge precipitation. It necessarily follows that a given amount of soluble

copper compound added to a series of oils will affect the sludge formation to a variable degree in each oil, depending on conditions not clearly demonstrated. This agrees with observations already accepted for the similar variation in the effect of solid copper on the sludging of different transformer oils.

One of the important observations which has been recognized by practical engineers is that the amount of copper in oil solution during transformer operation is extremely small. The authors recognize this in their findings. In fact, although 10 or 20 ppm of soluble copper may be added to an oil, the amount remaining in oil solution after a few hours of oxidation is too small to be accurately measured. Yet the sludging reaction shows no effect of this precipitation of the copper from oil solution.

I can agree with the authors that the problem of copper corrosion may well be distinct from the problem of copper catalysis of oil oxidation. It is difficult, however, to accept the surmise suggested by the authors that "not all of the dissolved copper is catalytically active." Have the authors any evidence that an oil-soluble copper compound can be added to an oil without an acceleration of the oxidation reaction? The observation made by the authors is to the effect that only the concentration of the metal is involved and that the acid constituent of the metal soap is without influence.

Since copper is taken into oil "solution" from the base metal without reference to the oxidation stability and the degree of oxidation of the oil, the authors' observations relating to the similarity in the oil reactions, whether in the presence of soluble or solid copper, lead me to ask the following question. Is solid surface catalysis satisfactorily excluded and is the greater catalytic effect of the so-called soluble catalyst not traceable to

the greater surface effect of its oil "suspended" soap and later the greater surface area of the flocculated metal compound?

The authors discourage the hope that an accelerated laboratory oxidation test can be used to foretell the behavior of an oil in years of transformer use. Of course, a test of this type cannot be used to predict with safety the usability and "life" of an unknown oil in years of normal transformer service subject to all types of unexpected and accidental effects. Studies of this type are useless, however, if there is to be no implication that the behavior observed and the conclusions drawn in the laboratory are of practical significance. In accordance with the ideas of Salomon, it is to be expected that knowledge obtained by a study of oil samples taken from the transformer over the period of its commercial use can be used as a gage of the oil behavior for at least some extension into the future.

The paper by Messrs. Irving and Bravey is another in the growing group of papers relating the advantages accruing from the use of a soluble metal catalyst in the laboratory examination of mineral transformer oils to determine their resistance to sludge formation. The companion paper on this subject by Messrs. Liander and Ericson must be considered along with the data presented by Mr. Salomon who, on the other hand, utilizes metallic copper as the catalyst of oxidation.

The authors refer to the work of the International Electrotechnical Commission and one draws the conclusion that the authors present their data in support of an international testing method. This I think is unfortunate for the problems inherent in the establishment of a sludge test on a local and limited basis are multiplied, the broader one considers the field of its application. In this connec-

tion, Mr. Salomon's caution must be remembered, that the suitability of a laboratory test is largely conditioned on the specific application envisaged.

Information concerning the sludge forming characteristics of the noninhibited oils in accordance with the present ASTM tests (D 1313¹¹ and D 1314¹²) would be appreciated as a point of departure in considering the validity of the test suggested, since specific details concerning the degree of refining of the oils and other pertinent data are lacking.

The rate of oxygen absorption and the study of the induction period in the oxidation of mineral oils for transformer use give valuable information in helping an engineer to select a properly refined oil for transformer use. From a practical standpoint, however, the transformer engineer is not primarily interested in the rate of oxygen absorption. He is interested only in the type and quantity of those products such as sludge and acidity which react adversely to the proper functioning of his apparatus. Most generally the practical value of the induction period is conditioned by the same interest. The burden of demonstrating the practical relationship of these factors lies with the proponent of such testing procedures.

It is obvious, also, that to suggest a test for even a local application demands supporting data with regard to its reproducibility and repeatability. The problem in establishing a sludge testing procedure in the ASTM has never been the lack of ideas for new types of tests but has invariably been the difficulty of

¹¹ Method of Test for Sludge Formation in Mineral Transformer Oil by High-Pressure Oxidation Bomb (D 1313 - 54), 1955 Book of ASTM Standards, Part 5, p. 721.

¹² Tentative Method of Test for Sludge Formation in Mineral Transformer Oil by Sludge Accumulation (D 1314 - 54 T), 1955 Book of ASTM Standards, Part 5, p. 727.

establishing a reproducible and repeatable test of practical significance to the transformer manufacturer and operator.

MR. C. A. DUKE.¹³—It is well for us to examine our test methods periodically and compare them with those of other countries. The Symposium offered an excellent opportunity for a comparison of theory and methods.

We need an accelerated "life" test and are quite interested in any move toward providing such a test. The paper presented by Mr. Bravey gives hope that with continued work eventually some form of soluble catalyst will be found that will give the desired correlation between test results and performance.

MR. L. B. SCHOFIELD.¹⁴—On behalf of Section Z and Subcommittee IV of Committee D-9, I wish to thank the authors of the three excellent papers for the very comprehensive reports on their studies of sludge formation in insulating oils. What they have presented to us will be of great value in the developmental work now being done on sludge testing procedures, and in the efforts toward standardization.

Mr. Salomon's methods of following the degradation of oils and the prognosis of future performance are so ingenious and elaborate that they are very difficult to interpret. The one feature of his work that is most interesting is the inevitable question that it poses—are such elaborate and intricate procedures practicable and prudent for controlling the serviceability of oil in all the transformers on a large utility system? Although such procedures may be applicable in developmental work by the oil producers, do we not have much simpler tests and observations that are sufficiently reliable

and more economical for keeping a vigilant watch on transformer oil performance?

The very important Liander and Ericson work and the Irving and Bravey paper demonstrate the application of soluble catalysts in making accelerated aging tests on oils. This introduces new techniques to us which may have possible advantages for comparatively fast evaluation of oil sludging propensities. The methods may or may not be compatible with current American practices. Certainly these papers present a challenge to all of us to do much more research to establish just which methods will show more dependable correlation with service performance of oils in a transformer.

MR. HALVARD LIANDER (*author's closure*).—We regret that our report is too compact and concentrated to be easily readable. Within the space given we have been able to relate only a fraction of our experimental data. Therefore, some of our views and conclusions may appear as somewhat obscure or loosely founded.

It seems that the main point of argument is whether an accelerated test method for the oxidation resistance of transformer oil should copy service conditions as closely as possible or whether it can be devised on a more theoretical basis. To the best of our knowledge the Swedish standard test procedure SEN 14.06 approaches service conditions more closely than any other short-time method of testing (21). After some 30 years' experience with this and other methods, we are convinced that there is hardly any other alternative than to base the test method on fundamental facts about the oxidation of mineral oils, if a better method is wanted.

To begin with the matter of catalysis, we all seem to agree that the oxidation of transformer oils in service is influenced

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¹⁴ Chairman of Section Z, Subcommittee IV, Committee D-9.

by metal catalysts. In opposition to Mr. Clark, who in the discussion suggested that it is only when precipitated that the soluble copper exerts its catalytic influence, we maintain that the catalytic action is exercised by metals in solution in the oil.¹⁵ As we have pointed out, therefore, "one must distinguish between two separate events which overlap. One is dissolution of copper in the oil and the other is the ability of the dissolved products to influence catalytically the oxidation of oil. Corrosion is thus regulated by one set of factors whereas

soluble catalysts thus is logical, if the object is to isolate the problem of oxidation.

It remains, however, to show that by such a simplification we have not neglected any essential practical factor. Consequently we have also studied the rate of dissolution of copper in various oils (Figs. 5 and 6). It is probable that Mr. Raab has the results of this investigation in mind when it appears to him "that considerable evidence given throughout the paper can be interpreted in opposition to the use of soluble cata-

TABLE III.—COMPARISON OF OXIDATION PRODUCTS.

		A	B	S 1	S 2	3	S 4	S 5
Solid copper	Corrosivity, mg per sq dm	0.2	1.0	1.0	0.2	1.2	0.2	0.1
	Acidity, mg KOH per g and sq dm Cu	1.1	2.0	3.2	1.3	67.0	4.2	0.6
	Sludge, per cent per sq dm Cu	0.5	1.1	1.3	0.4	36.0	0.6	0.2
Soluble copper	Acidity, mg KOH per g and mg Cu	1.3	2.3	2.9	2.1	60.0	4.3	1.9
	Sludge, per cent per mg Cu	0.5	0.5	1.0	0.7	39.0	0.6	0.6

oxidation is governed by others." This was also stressed by Mr. Clark.

Copying service conditions the normal way would be to use solid metal catalysts, and preferably, as in the Swedish standard method, both copper and iron. Now, the rate of dissolution of the metals in the oil is of course dependent on the characteristics of the oil, but furthermore on the proportions of metal surfaces exposed to the oil, surface conditions, thickness of insulation or varnish, and many other features having no bearing whatsoever on the course of the true oxidation reaction. Even Mr. Zwelling will agree, we believe, that the use of

lysts in evaluating transformer oils." But let us have a closer look at the evidence. In the accompanying Table III we have compiled some illuminating data for two commercial transformer oils, A and B, and the complete series of experimental oils, S 1 to S 5. The table contains the total amount of copper dissolved after 164 hr with 1 liter per hr of oxygen bubbling through 25 g of oil at 100 C, calculated per unit area (100 sq cm per 25 g of oil) as an average of the experimental data cited in Fig. 6. The corresponding mean values of acidity and sludge have been deduced from Fig. 4 and may be compared with acid number and sludge value for the same oils oxidized with 10 ppm of a soluble copper catalyst (naphthenate) instead of solid copper but otherwise in identical manner

¹⁵ It seems probable that the metals act in passing from the monovalent to the divalent condition in the case of copper, and with iron from the divalent to the trivalent condition (E. A. Evans, *Journal, Inst. Petroleum*, Vol. 32, No. 271, July, 1946, p. 394).

(data from Fig. 12 completed with results not published in the report).

It is true that the rate of dissolution of copper varies appreciably for different oils. But although the over-refined oil S 3 and the under-refined oils S 1 and B dissolve copper more readily than the normally refined oils (A, S 2, S 4, and S 5), the rate of dissolution for these latter oils is practically the same.

As would be expected, the relation between the amounts of oxidation products for these oils is about the same with solid and soluble copper catalysts. But curiously enough this is also the case with the other oils tested, the over-refined oil S 3 as well as the under-refined oils S 1 and B. For reasons not further investigated, numerical ratios of the oxidation products are almost exactly the same in both series for the same oil.

We have, therefore, arrived at the conclusion that in using soluble catalysts we have not placed any oil at a disadvantage. If it is suspected that an oil is abnormal, we have recommended a special study. As an example of such a study, we have cited an oil with deactivator and shown that even in this case soluble catalysts can be used with advantage.

Mr. von Fuchs, who is opposed to the use of soluble catalysts, refers to the results of some round-robin tests. Having no knowledge of these test results, we cannot meet his criticism. We might mention, though, that in testing normal transformer oils using solid and soluble catalysts we obtain results placing the oils in the same order, and we have carried out a large number of such tests.

With soluble catalysts there is, as Mr. von Fuchs says, a deposition of a catalyst complex in the beginning of the test. This deposit is, however, quite negligible and does not obscure the real point of sludge precipitation.

One point regarding catalysts remains

to be cleared. Mr. Clark objects to our statement that "not all the dissolved copper is catalytically active." The statement of course applies only to the experiments with water added. In this case, apparently, the copper has been only partly dissolved in the oil, the remainder staying catalytically ineffective in the water phase.

Pursuing the idea that an accelerated oxidation test should simulate service conditions, Mr. Zwelling is not only opposed to soluble catalysts but also to the extension of the oxidation curves beyond the data at which an oil in service would usually be discarded. In reply we might say that we started this work with the idea of continuing oxidation only to an acid number of 1 mg KOH per g (21). In the course of the investigation it was, however, found more advantageous to go further than that in order to get a clear distinction between the various types of oil. Oxidation conditions being so different there is no reason to believe, moreover, that an acid number of, say, 0.5 mg KOH per g in the laboratory test would correspond to exactly the same figure in service.

In answer to Mr. Ross we regret not being able to give any information about the nature of the acids formed. But we do not believe that they have much influence on the corrosion of the copper. From Fig. 5 it is evident that the attack of the metal starts even before any measurable amounts of acid have been formed.

We agree with Mr. von Fuchs that it would have been valuable to have all the data about the experimental oils, but unfortunately we are not in the position to say more about them than what appears in our report. For the understanding of this investigation, we think, however, that the published data are quite adequate.

MR. T. SALOMON (*author's closure*).—

Oil oxidation, as a chain reaction, needs a starter or initiator, which may be produced by the oil components, in the case of the noncatalyzed oxidation and the oxidation catalyzed by a metal, or by products added to the oil, when the oxidation is realized with a soluble catalyst, like peroxides, metallic soaps, etc.

The mechanism of the oxidation and the nature and rate of the different steps of the chain reaction depend upon the initiator used. We use different means and different ways to oxidize mineral oils, but the final products of the reaction seem to be very similar. The important point in the conception of an artificial aging test for mineral oils is to rate their oxidation stability in the same way as their oxidation *in vivo* in the transformer during normal operation. It is not yet proved that this condition is fulfilled by tests using soluble catalysts. It is admitted by some authors that oil-soluble catalysts have a great importance for the oxidation of an oil in operation. Our experience has not brought proof for this thesis. We have never found significant amounts of dissolved metals in normally used oils, but in certain heavily sludged oils. This thesis asserts that the dissolution of metal takes place at the beginning of the oxidation, and that this dissolved metal acts as a catalyst of the oil oxidation. We have found, in the course of our studies, that the action of metallic catalysts is limited to the inhibition period of the oil. The oxidation proceeds in the same way and with the same speed if we take out the metal after the inhibition period or if we let the oil remain in contact with the metal up to the end of the oxidation test. If traces of metal are dissolved in the oil before the oxidation starts, these traces are not measurable with the test techniques now available. We have found also that oils of low stability do not need the presence

of a metallic catalyst, since their sludge curve remains the same when the oxidation is carried out with or without copper.

The problem of the corrosivity of the oils is different from that of the oxidation. It happens often that an oil corrosive toward copper has also a lower oxidation stability, but it happens also that an oil contains compounds corrosive toward copper, which, when oxidized, exert an inhibiting effect on the oil and even stop its oxidation. We had recently the opportunity to examine those particular cases.

In usual cases, oils become corrosive toward copper, when they contain sulfonation compounds, by acid treatment, or some natural sulfur compounds. In our experience, "green" oils, by oxidation with copper, are produced only when some sulfonation compounds are present. Staining or discoloration of the copper wire during the oil oxidation may also be produced by some reactive types of natural sulfur compounds. The special case mentioned above deals with oils containing some unknown types of natural sulfur compounds. More fundamental studies on the types of the sulfur compounds existing in the oils are needed to define their constitution and their effect on the performance of the oils.

The corrosive effect to copper is one of the aspects of the problem of impurities in the oils, the importance of which has also been underlined by Mr. von Fuchs. There are other impurities, natural and artificial, produced by the refining treatment applied. We cannot discuss here in detail this problem. We wish only to emphasize that these impurities, even as traces, are often responsible for the disturbing effects in oxidation tests, and that our knowledge on the composition of these impurities is still limited.

Impurities introduced into the oil during its operation may also produce a

very limited effect. This happened, for example, when we tried to establish the effect of transformer sludge on the performance of a new oil. We contaminated new oils, before putting them in operation in different small transformers, by adding about 125 ppm of transformer sludge, taken from old and heavily sludged transformers. No adverse effect on the oil stability was observed after a 13-yr period of operation.

An important disturbing effect on the performance of the oil may be observed when the oil is contaminated by varnish incompletely polymerized. In these cases, insoluble "sludge material" may be found at zero time with oils taken out after a very short time of operation. These varnish products may act as an initiator and modify the course of the oil oxidation.

Mr. Clark asks if the shape of the time-sludge curve could be safely used to diagnose and prognosticate the complete freedom from sludge in the transformer. The answer is "yes," provided the oils do not contain any impurities which may produce insoluble "sludge-like" material. (See the case of an oil contaminated by varnish products mentioned above.) We can indicate to those who are interested in this field how to differentiate this insoluble material from the sludge produced by oil oxidation.

The sludge formation at time zero, observed by Mr. Clark on laboratory tests with new oils, after shipping or after a very short operation time in transformers, appears to be a very special case. We have never observed such a rapid sludging under those conditions described with refined oils of the normal type. We may ask if there was not an effect of impurities, as described above.

We have no experience with the Snyder Life Test and cannot explain why the "first trace of sludge" criterion used there is an unreliable gage; perhaps, be-

cause these traces are detected visually, which is not always very easy. In our test technique, the value of the first sludge traces is measured by weight and controlled by the figures found after several "periods," up to five or six; the experimental figures have to agree with the "calculated" values within the experimental error established.

Mr. Clark asks also if the shape of the sludge-time curve could be safely used to gage the changes occurring in an inhibited oil in commercial use. This is possible. When measuring the decrease in the inhibition period of the oil after a given time of operation, you can evaluate how long the inhibiting effect will act under the given working conditions. When the inhibitor is exhausted, you can prognosticate in the usual way the behavior of the remaining base oil. It would be more convenient to take as reference oil the oil sample taken from the transformer, before putting it into operation, and not the new oil, as received from the supplier, in order not to be disturbed by the drying effect.

There is one particular point which needs to be verified in the field. Some commercial inhibitors produce in the laboratory test a small quantity of insoluble "sludge-like" material. Is this material also formed by the oil oxidation in the transformer?

Mr. Clark questions the effect of moisture and that of voltage application on the sludging reaction. The effect of moisture cannot be stated by our test, working in open air. Such an effect, attributed normally to the moisture present in the oil, has been noted during our field tests in some tightly closed transformers by a limited increase in the oxidation characteristics of the oil. This effect is more likely produced by the retention of volatile oxidation compounds, since it is known from the results found with a laboratory test working in a

closed vessel fitted with a reflux condenser. These volatile oxidation compounds are more or less soluble in water; we may then ask if the increase of the oxidation rate in the presence of water, noted by some authors, cannot be explained by the fact that these volatile compounds are retained in the oil to a greater extent when water is present in the oil. At any rate, since the performance of an oil in operation is dependent on the working conditions applied, the presence of moisture in the transformer has to be considered as one of these parameters.

We made, about 17 yr ago, comparative aging tests in our apparatus with and without voltage application. No effect on the speed of aging of the oils has been observed when working under a gradient as high as 10,000 v per cm.

Mr. Clark asks also if our conclusions can be applied to tests using soluble catalysts. The answer is "no," because the results found with soluble catalysts are not similar to those obtained with solid catalysts. Soluble catalysts cannot be used for testing used and sludged oils, because these metallic soaps added to the oil act like detergents and retain in solution a part of the sludge present in the oil and otherwise precipitated.

The interfacial tension test is only a control test to define the state of an oil. Experience has shown that oils which are about to start sludging in the transformer, or those which have already produced the first sludge "shower," may reach different interfacial tension values, depending on the type of the oil. If it is proved by field test that the first sludge "shower" of a given oil will occur when the oil reaches the same interfacial tension value as that found for the new oil at the end of its first "period" in the artificial aging test, then the interfacial tension test would be a useful tool to control the state of the oil in operation.

The interfacial tension value characteristic for the production of the first sludge "shower" in the transformer could be easily established during the aging test of the new oil. It would then be sufficient to follow the decrease of the interfacial tension of the oil during its operation up to this critical value. This value would be valid only for the oil tested, provided that the oil was not contaminated during its operation by impurities having an effect on the interfacial tension. Such a test technique would be a better means only for the diagnosis, not for the prognosis of the evolution of the oil in operation. There is a broad field open for new research work and new progress.

Mr. McConnell mentions the formation of hills and valleys when drawing the curve of the sludge figures, found according to the ASTM sludge accumulation test, *versus* time of operation. Such a variation in the sludge figures, more or less important, may be observed after a make-up with new oil, as it is described in our paper. A large diminution of the sludge value will be always found, even without any make-up, when the oil passes from the state "about to start sludging" to that of the first sludge "shower," that is, when we obtain the first straight-line relation curve. As the autocatalytic increase in sludge formation has ceased with the formation of the first sludge "shower," sludge figures found for the same oil after the same heating time will be lower than before. This difference may reach about 50 per cent.

Mr. Oliver asks for more details about the particular shape of sludge curve *L* in Fig. 3. Sludge produced by the aging of the oils is of two different types: that which is insoluble in the hot and in the cold oil, and that which is soluble in the hot oil but insoluble in the cold oil. In

all aging tests, the two types of sludge are tested together, since they are always produced simultaneously but in various proportions according to the type of the oil. This does not happen with *new over-refined oils* which behave in a different manner. At the end of the first "period," the starting point of the sludge curve, there is only sludge of the first type produced. The second sludge type appears only during the second "period," and then the two sludge types increase

in the usual way. This explains the big increase of the sludge figure during the second "period," as indicated by the cross hatching of this part of the sludge curve. This difference in the sludging characteristics is not observed with the used over-refined oils. We do not know why! The facts described above are all experimental. To follow the evolution in the sludging characteristics of oil L (Fig. 3), we have to compare curve L' , L'^{-4} , and L^{-6} .