D1 Material and emerging test techniques

New Laboratory Methodologies for Investigating of Insulating Liquids - Further Developments in Key Functional Properties

New Laboratory Methodologies for Investigating of Insulating Liquids. Further Developments in Key Functional Properties

WG D1.70

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Executive summary

The scenery of insulating liquids is continuously changeing, requiring questioning existing standards and seeking answers for reproducing of phenomena in service in the lab, as well as methods for determining of the life span of liquids.

All those properties can be considered as functional requirements for liquids.

The aim of the brochure has been to look on some of them and propose solutions, e.g. for the fault free gassing of some liquids in service, for the use of oxidation inhibitor as an ageing marker in mineral oils, evaluation of methods able to distinguisch between individual hazardeous compounds like polycyclic aromatics (PAC) and polycyclic aromatic hydrocarbons (PAH) as well as the measurement uncertainty for thermal characteristics of insulating liquids. For this purpose several experimental investigations including Round Robin tests have been carried, including:

- development of a method for stray gassing behaviour of insulating liquids independent of their constitution with examples from service manifistating the correlation of observed service behaviour and laboratory tests

- laboratory procedures and their measuring uncertainty for identifying of environmentally hazardeous compounds in insulating liquids like polycyclic aromatics and polycyclic aromatic hydrocarbons. For the identification of individual EPA restricted PAH marker compounds methods like EN 16143 are necessary.

- The implementation of natural and synthetic esters as insulating liquids requires their maintenance and correspondingly the monitoring of the inhibitor content. A Round Robin test with liquid-liquid extraction and a subsequent high performance liquid chromatography (HPLC) with natural and synthetic esters for the quantitative determination of the inhibitor content has been carried out with first results and identification for further work.

- Another interlaboratory study on the determination of thermal characteristics of insulating liquids has been performed. The highest spread of results has been identified with the determination of thermal conductivity at higher temperatures due to convection.

- The determination of oxidation stability in service oils is not covered by the international standardisation. Measuring the inhibitor in insulating oils with time allows a correlation to further ageing parameters, as well as a prediction of life span of the insulating liquid.

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1. Thermo-oxidative gas evolvement of insulating liquids (Stray gassing) and laboratory method for its evaluation

1.1 Introduction

The evolution of gases in liquid insulated equipment has always been a topic of concern and is usually related to a fault in the electrical equipment. There have been an increasingly greater number of reports in the last 10 – 15 years reporting on the so called stray gassing of insulating liquids in transformers, which exhibited no deficiencies based on electrical tests.

Such behaviour was found in both new and aged transformers. In most cases, these were free breathing transformers, generally filled with an uninhibited type of mineral oil. The effect is characterized by a relatively quick increase in concentrations of hydrogen and/or saturated hydrocarbon concentrations at the rates that slow down to near zero with time. The classic interpretation of dissolved gas analysis (DGA) data indicates thepresence of a hot spot below 150 °C (fault description T1), despite the transformer operating far below its nominal rating. The lower than expected oxygen content in the oil suggested an on-going oxidation.

Test methods developed by Cigre and ASTM attempt to provoke stray gassing by oil treatment at elevated temperature of 120 °C and even higher. However, they do not completely reproduce this effect, as the tests at such temperatures, which are far from typical service conditions, strongly contradict real results.

Copper, among other transformer materials, plays a decisive role in the gassing behaviour of some mineral and ester insulating liquids under moderate temperatures. These are the main new findings:

- A laboratory method for the evaluating the tendency to stray gassing in insulating liquids has been developed. Stray gassing is a phenomenon not only limited to mineral oil, but relating to insulating liquids of different origin and is strongly catalyzed by copper. It can evolve at low operating temperatures. Non-inhibited mineral oils show a stronger tendency to stray gassing than inhibited ones. Stray gassing is strongly accelerated by air.

- It was observed that similar gassing patterns of the same oil types exist when stray gassing tests and cases of transformers DGA are compared, therefore oils of transformers with suspected stray gassing should be subjected to stray gassing test to get more reliable evaluations.

- As stray gassing has been not only found in new oils but also in aged oils, there is a need to further evaluate whether the existing fault description (T1) in the evaluation scheme of IEC 60599 standard is really connected with a fault or with the stray gassing.

1.2 Gassing tendency, stray gassing and fault gases. Clarifying the difference (1)

Due primarily to similarities in terminology, gassing tendency and stray gassing are often confused. Furthermore, there appears to be somewhat of a disputed belief held by some that the (electrical) "gassing tendency" of a liquid may significantly affect the production/retention of fault gases or even absorb fault gases – a view which has not been directly studied and thus is unsubstantiated in actual equipment. Herein a short overview of gassing tendency, stray gassing and fault gases will be provided in an attempt to clarify the differences between these properties and tests.

1.2.1 Gassing Tendency – under electrical stress and ionization

Gassing tendency is the common name given to a test formally called "Gassing of insulating liquids under electrical stress and ionisation" (tested to IEC 60628 (2) or ASTM D2300 (3) see Table 1. IEC 60628 Method A (see Figure 1) and ASTM D2300 (modified Pirelli method) are the most common. In IEC 60628 method A the test is done on hydrogen saturated oil at 80 °C. The applied voltage is 10kV AC using cylindrical electrodes near the oil / hydrogen interface. The test period is relatively short at between 100-120 minutes. IEC 60628 method B has a different, smaller volume test cell, longer

duration (15-18 hours) and other differences, including being run with nitrogen (rather than hydrogen), but is done much less commonly.

In these gassing tendency tests, if the volume of gas in the gas phase (measured by burette) of the test cell increases (after a fixed period) the oil is said to be "gas evolving", and if the gas quantity decreases "gas absorbing". The gassing tendency, and indeed the specific conditions of IEC 60628 method A have been generally considered to be most relevant to discharge events in capacitors and cables (4).

Figure 1: Example of the test cell and burette assembly used in IEC 60628 Method A – "Gassing Tendency". This test is not related to stray gassing

Due to the fact that the test method is very specific the "gassing tendency" should rather be viewed as a result of a test rather than a material property. Moreover, in IEC 60628 (2) it is explicitly stated that:

"At present, however, though it is generally agreed that gas absorbency of the impregnant has a positive effect in minimizing ionization problems in impregnated insulation systems used at high electrical stress, correlation of gassing-cell test results with equipment performance is limited. Engineering judgement is necessary in interpreting the test results in relation to any intended application."

Nonetheless the gassing tendency of insulating liquids have been shown to be dependent on aromatic and polyaromatic content (4) – that being, generally, the higher the aromatic content the lower the gassing tendency (the more "gas absorbing"). See Table 1 for a general illustration of the relationship - and some values. Notice how the values for Method A and Method B can differ substantially – which is expected as they are rather different test conditions. The actual chemical nature of the aromatic molecule(s) can also impact the gassing tendency (4) (5).

Table 1: Extract of gassing tendency data from Table 4.14 from (4) for illustrative purposes – there is a general indirect relationship between higher aromatic content and lower gassing tendency

Approximate Aromatic Content of mineral oil [Ca%]	Gassing Tendency IEC 60628 Method A [mm³/min]	Gassing Tendency IEC 60628 Method B [cm³]
5,8	+22,1	+7
13,4	+9,3	+7
16	+24,6	-3
17,2	-7,9	-0,3
18	-6,8	-1,4

It must however be noted that several studies into breakdown and pre-breakdown phenomena (where the electrodes and thus the discharge(s) occur entirely in the liquid phase) have also shown dependencies to aromatic content and aromatic type (as well as other aspects of a liquid and/or its additives chemistry). Large gap point-plane streamer studies, under step-impulse applied voltage, have clearly shown a streamer's branching (mainly studied in hydrocarbons) are impacted by aromatics (among others) (6) (7) (8) (9). In short, aromatics have been shown to impact the speed of propagation of a streamer. There have also been studies done with AC applied voltage in point-plane and point-sphere configurations – so called "PD studies" which have shown dependencies to (again among others) aromatic content (and nature) and PD intensity/pulse repetition (10) (11) (12) (13) (14). Moreover, there do appear to be relationships between PD intensity/duration and (mainly hydrogen) gas production (10) (13) (14). Therefore, it is most likely the relationship between aromaticity and gas production under electrical stress (in practical high voltage insulation systems) is **indirect.** The causal link is probably between the intensity of the discharge/breakdown event/streamer and the "remaining gas" that is then dissolved in the oil after the event. However, the relationship between aromaticity, gassing tendency and pre-breakdown & breakdown phenomena is far from fully understood. For further reading on the above topics, consult (15) the companion to this one which deals with dielectric properties of insulating oils in much deeper detail.

See Table 2 for clarity which methods are applicable to "gassing tendency" and which for "stray gassing".

Table 2: Methods for Gassing tendency and Stray gassing

Test	IEC Standard	ASTM Standard	Cigre
Gassing tendency (under electrical stress and ionisation)	60628, Method A (2) 60628, Method B (2) 2nd edition 1985	ASTM D2300 (3)	-
Stray gassing	New proposed IEC method, already implemented in IEC 60296:2020 (16)	ASTM D7150 (17)	TB 296:2006 (18)

1.2.2 Stray gassing

Generally, the term "stray gassing" is used rather broadly to refer to gases present in equipment (when doing DGA) that are not believed to be due to an electrical or thermal fault. It has been defined previously as being the production of fault gases (such as hydrogen and ethane) at temperatures below what is considered a fault temperature (i.e. < 200 °C) (18) (19).

In practical equipment such as a power transformer, two main types of "stray gassing" or "unusual gassing" are believed to occur:

- Gas production due to thermo-oxidative stress on the insulating oil.
- Gas production due to reactions or out-gassing of incompatible materials.

Combinations of the above can also occur (catalytic metals) and passivator additives have been known to contribute to hydrogen production in the absence of an electrical fault (20). What also complicates matters is that the above conditions could also be interpreted as a "fault" – but it is probably necessary to keep in mind the types of faults generally associated with DGA diagnosis are those that pose an impending risk to the safe operation of the transformer in the short to midterm.

A common type of laboratory test intended to characterise the gases produced under thermo-oxidative stress are also generally referred to "stray gassing" tests. An example of such a test is ASTM D7150 – and in this brochure a new method is developed, which has been already included in IEC 60296 (16). These tests characterise the oil in laboratory conditions and provide an indication of which gases are produced under certain simulated conditions.

1.3   Definition of stray gassing (21)

The definition of stray gassing was firstly described in a Cigre Brochure, namely TB 296/2006 (18). This TB, titled "RECENT DEVELOPMENTS IN DGA INTREPRETATION", reported the experience of a joint Task Force (D1.01/A2.11) about the first studies on the phenomenon later called "stray gassing", defined as "*the formation of gases from insulating mineral oils heated at relatively low temperatures (90-200 °C)*".

This definition gives to stray gassing a purely "thermal" meaning, evoking the idea that temperature is the only affecting parameter. In the widespread opinion of the community of transformer users, however, the stray gassing phenomenon if often assumed as every kind of gas formation which origin does not deal with a fault. In other words, when abnormal gas pattern is observed in a transformer in absence of one of the commonly identified faults (thermal or electrical).

The results of experiments done by TF11 team showed that many of the oils available in the market of the early 2000s were prone, at 120 °C, to develop mainly hydrogen, then methane and ethane in minor amounts. Experiments performed at 200 °C showed a different gas pattern, where ethane and methane were formed in larger quantity.

After more than 10 years, this phenomenon seems to be quite far from being fully elucidated, and several experts reported that it still creates confusion in the users, when a gas development in a transformer requires a correct interpretation. In the daily experience, in fact, stray gassing is often invoked when the gassing pattern of a transformer is not clearly attributable to a fault, or when misleading DGA results are provided.

This WG gathered some of the experience of insulating oils stray gassing behaviour among its membership. It appeared quite evident that the phenomenon of stray gassing has no clearly defined borders, and strongly depends on the procedure used to evaluate it.

The following clauses describe the knowledge collected by this WG in this domain, the reasons that lead to the definition of a new procedure to estimate stray gassing, and the detailed procedure itself.

1.4   Experience collected on stray gassing

Among the available methods to measure stray gassing, mostly two are used:

Method called "TF11"—It comes from the Cigre TB 296/2006, where it is described in § 3.1. This method is usually performed at 120 °C (even if the Brochure reports also a procedure at 200 °C), and implies the aging of the nitrogen- or air-saturated oil in a gas-tight glass syringe. The aging has durations of 16 and 164 hours, which results are then compared. The oil aged 164h is then re-saturated with nitrogen or air and submitted to a second 16h aging. DGA is performed after each aging step.

ASTM D7150 Method—This method derives some principles from the TF11 one. The investigated oil is saturated both with nitrogen and air (in two different aliquots, each in a glass syringe), then aged at 120 °C for 164h. DGA is performed after aging.

Even if these two methods are the most common, a variety of deviations were used to understand the effects of other variables, such as presence of paper, effect of copper or other metals, temperature, etc.

The application of these test protocols at different temperature showed that a certain gas formation may appear also at very low temperatures (down to 40-45 °C), if a sufficient testing duration is achieved.

The oxygen availability in the reaction makes the difference in the gas development. This was quite evident when ASTM D7150 method is applied: the air-saturated oil makes more gases than the nitrogen-saturated oil in the majority of cases.

The introduction of copper in the ambient reaction has put in evidence that metals can catalyze the gas formation, thus accelerating the phenomenon even at low temperatures. A similar experience done with core steel indicated a similar, but weaker effect.

In addition, the use of Kraft paper immersed in the tested oil can alter the gas formation, leading to major carbon oxides formation instead of a strong hydrocarbon development.

About the use of stray gassing as a qualification measure, of an assessment tool for transformers maintenance, there are currently some rules for oils Type A in IEC 60296:2020 which are based on the stidies in this brochure. When abnormal gas formation are observed in transformers during the service, however, there is no criteria to compare this gassing to the eventual stray gassing of the oil. Some utilities reported that they include in their purchase requirements a limit for stray gassing, but this is left to the agreement between buyer and supplier.

1.5 New evidences of stray gassing—the recent experience

Different experts converged in reporting a common experience: some unexpected stray gassing patterns were observed in the last years, in transformers in service (22) (23) (24) (25) (26) (27) (28) This "new" stray gassing:

- can take place even at low temperatures
- shows sometimes a pattern where hydrogen is not the major gas
- possibly related to oxidation stability

To better understand this phenomenon, and with the aim of having a more complete assessment tool for stray gassing evaluation, this WG decided to set up a new test protocol.

As the outcome of a survey within the WG members, some assumptions were made:

- If "stray gassing" is a phenomenon that can take place in absence of faults, it must be evaluated at temperatures that the transformer can reach during its ordinary service. This temperature should not be over 105 °C, because this is the maximum oil temperature admitted by the IEC loading guide (IEC 60076-7 (29))
- To achieve an appreciable gas formation in a reasonably short time at such a low temperature, it can be useful to speed up the gassing reaction using copper a catalyst. This appears to be also consistent with the real life, where oil is usually in contact with copper. Nevertheless, copper can also quench the gas formation in some cases.
- The presence of air in the reaction also accelerate the gas formation. This assumes stray gassing to be a thermo-oxidative process rather than a merely thermal one. In this sense, the definition given by TF11 should be extended. Actually, TF11 performed its experiments in air-saturated oils, to increase the gas formation rate (§ 3-2); this indicates that magnifying oxygen effects on stray gassing were considered since the origins.
- It is useful to run the stray gassing test also in absence of oxygen. This is in line with the existing ASTM D7150 method, and also can give information on the occurrence of this phenomenon in sealed transformers (with membrane, or nitrogen blanket).
- The presence of paper during the thermal aging produces a large amount of carbon oxides, and this may hinder the formation of other gases generated by oil's decomposition.
- Mechanisms of gas formation provoked or catalyzed by external factors are manifold (material incompatibility, paints, polymers, electroplated metal surfaces, etc.), but they are not strictly related to the type of oil used, and should not be considered in the definition of stray gassing.

On the base of these considerations, a new method set up was established. It is described in the following clauses.

1.6 Stray gassing method

1.6.1 Required materials

Performing this test procedure requires the following materials and/or chemical reagents:

- Ventilated oven, able to maintain 105 ± 2 °C

- 100 ml syringes, suitable for DGA (see specific requirements in IEC 60475)

NOTE   The syringes should be of good quality and have a good gas tightness, to avoid the leak of gases during the incubation time and later.

- 3-way metal stopcock (chrome plated brass, stainless steel, or equivalent)
- Measuring cylinder 100 ml (class B)
- Copper foil, 0,25 mm thickness, purity 99,89% or higher
- High vacuum silicone grease.
- Dry air, free of hydrocarbons

NOTE   Synthetic air (purity > 99,999 %) for Gas Chromatography is suitable

- Dry nitrogen, free of oxygen and hydrocarbons

NOTE   Nitrogen (purity > 99,999 %) for Gas Chromatography is suitable

1.6.2   Pretreatment of syringes

Syringes must be clean and dried prior to this pre-treatment.

Treat the upper part of the piston (close to the handle) with high vacuum silicone grease, dispersing a thin, uniform layer of silicone around the entire circumference of the piston.

Immerse the lower part of the piston in the tested liquid, avoiding the contact between the oil sample and the grease.

1.6.3   Oil treatment and Incubation

According to this procedure, a representative sample of mineral oil is subjected to following incubation procedures:

- A first portion of sample oil saturated with air (as described in Procedure A), a second portion of sample oil saturated with nitrogen (as described in Procedure B).
- The two portions are stored at 105 °C, for 48 hours, in glass syringes, with and without copper in contact with the oil.
- Finally, DGA according to IEC 60567 (30) is performed on each incubated sample.

1.6.3.1   Procedure A: Stray gassing under oxidative condition

Place a suitable volume of the sample oil in a beaker, and purge it for 15 min with air. The prepared oil shall be sufficient to fill two syringes with 50-60 ml of oil, one with copper foils inside, the second without copper (oil only).

Prepare two syringes as above described. In one of the two, place two copper foils, cut and folded in a shape that allows their introduction in the syringe without occluding the ingress of the oil from the tip (Figure 2). The total surface of copper must be 9.6 to 10 cm^2. Copper must be prepared prior using as described in the standard for oxidation stability IEC 61125 (31).

Fill both syringes with 50 to 60 ml with oil.

Firmly close each syringe with the metal 3-way stopcock.

Figure 2: Syringes with and without copper strips

Place the syringes in the ventilated oven, in vertical (or semi-vertical) position, with piston up and laying on the stopcock.

NOTE   The vertical positioning limits the gas leakages from the tip of the syringe.

Keep the syringes at 105 °C, for a duration of 48 ± 0,5 h.

After cooling down the syringes to room temperature, run Dissolved Gas Analysis (DGA, according to IEC 60567 (30)) on the tested oils.

1.6.3.2 Procedure B: Stray gassing under inert condition

Perform all steps from described for procedure A, after having purged the oil with nitrogen instead of air.

1.6.4   Precision data of the method

Precision data were evaluated with a Round Robin Test.

In a limited set of experiments, the standard deviation of three replications performed in the same laboratory, by the same operator, and on the same sample, was estimated in the range 8% < Std. Dev. < 25%, for final gas concentrations over 25 µl/l of hydrogen, methane or ethane.

NOTE   The repeatability estimated for this test method includes the repeatability of the DGA measurement performed after incubation. For information about the repeatability of DGA, see IEC 60567 (30).

The standard deviation of the Round Robin Test, where the same sample was tested by different laboratories (n = 18), was estimated in the range 30% < Std. Dev. < 80% for final gas concentrations over 25 µl/l of hydrogen, methane or ethane.

NOTE   The reproducibility estimated for this test method includes the reproducibility of the DGA measurement performed after incubation. For information about the reproducibility of DGA, see IEC 60567 (30) .

Despite the high spread of individual results (for different gases, under different incubation conditions), the results of the RRT in terms of estimation of an oil as "stray gassing" or "non-stray gassing" were the following:

- Occurrence of false negatives (laboratories casting an oil as "non-stray gassing" when the majority of the results cast the oil as "stray gassing"): 1 or 2 cases on 18 laboratories.
- Occurrence of false positives (laboratories casting an oil as "stray gassing" when the majority of the results cast the oil as "non-stray gassing"): None.

1.7 Study of stray gassing behaviour of different insulating liquids

A RRT was performed on a set of insulating liquids, including mineral oils of different type and provenience, and non-mineral liquids, such as esters and silicones. The list of insulating liquids submitted to stray gassing testing in the RRT is presented in Table 3.

Table 3: List of the insulating liquids submitted for the RRT on stray gassing

Sample #	Insulating liquid type	Relevant Standard
1	Mineral oil, unused, uninhibited	(16)
2	Mineral oil, unused, inhibited, passivated	(16)
3	Mineral oil, recycled, inhibited	(16)
4	Mineral oil, unused, inhibited	(16)
5	Mineral oil, unused, inhibited	(16)
6	Mineral oil, recycled, uninhibited *	(16)
7	Mineral oil, recycled, inhibited	(16)
8	Synthetic ester	(32)
9	Natural ester on soya bean bases	(33)
10	Silicone	(34)

Note * : the actual content of inhibitors of sample # 6 was not the object of a complete agreement. Some laboratories found complete absence of DBPC and DBP, some others found some small traces of DBPC (up to 0,06%). Therefore, there is a doubt if it was an uninhibited or a trace inhibited one.

The number of laboratories participating to the RRT varied from 18 to 19. Laboratories giving a contribution to the study were: *GE Grid Solutions, Labelec, Wiener Netze GMBH, EEI Nikola Tesla, EGAT, Shell Global Solutions, Alliander, Nynas, Savita Oil Tech. Ltd, EFACEC Energia, JXTG Nippon Oil & Energy Corp., APAR India, Ergon Refining Inc., ABB Norway, VUM Verfahren Umwelt Management GMBH, TERNA, Sea Marconi, Siemens.*

All the laboratories applied the test protocol as describe in the former chapter, and the collection of the results gave the following outcomes:

1.7.1 General evidences

A first evidence emerged from the gathered data is that gases formed in appreciable quantity in at least one condition are: hydrogen, methane, ethane, carbon monoxide, carbon dioxide.

Acetylene was never observed, and ethylene was present in amounts very close to the detection limit (1 to 2 µl/l). For this reason, they are neglected in the following evaluation.

Carbon dioxide was formed to some extent in almost all conditions, so it did not give any differentiation between different liquids. It was also neglected in the following evaluation.

Oxygen and Nitrogen are not gases formed during the oxidation or thermal degradation of the oil, so they are not very important in stray gassing assessment, nevertheless they are good indicators of the correct application of the method; if a high oxygen content is found in the oils saturated with Nitrogen, this is an indication of leakages in the syringe.

For the above mentioned reasons, the following clauses will deal with hydrogen, methane, ethane, and carbon monoxide content in the insulating liquids after the stray gassing test procedure. This does not mean that, in the future for some kind of oils, other gases (here neglected) would not become important in the gassing pattern.

1.7.2 Robustness of the method

As stated before, the repeatability r and Reproducibility R (expressed as relative standard deviation) were:

$$8\% < r < 25\% \qquad 30\% < R < 80\%$$

These values are valid in case of appreciable gas content (over 25 µl/l). For very low gas formation repeatability and Reproducibility can be much higher (in percentage), due to the closeness to the detection limit; in these cases the precision data should be neglected.

During the data evaluation, outliers were identified with Grubbs G1 test and Huber test.

As it can be perceived, some samples showed a larger occurrence of outliers, especially oil 1, 6 and 10. It is noteworthy that oils 1 and 6 are the only uninhibited ones among the minerals, and their stray gassing is quite relevant if compared to other oils (see 1.7.3.3 for details). Therefore, for oils more prone to form stray gassing the spread of the test results is higher and the occurrence of outliers is more frequent. This may also be due to the fact that syringe's tightness is more important when larger amount of gases is formed (and can thus be lost).

1.7.3 Stray gassing patterns for mineral oils

After having removed the outliers, and as the average of the remaining results, the following clauses report the stray gassing patterns identified during the RRT.

(Y-axis—concentration is expressed in µl/l)

1.7.3.1 Stray gassing pattern 1 for mineral oil

The pattern shown in Figure 3 is illustrative of an uninhibited unused mineral oil – Oil 1.
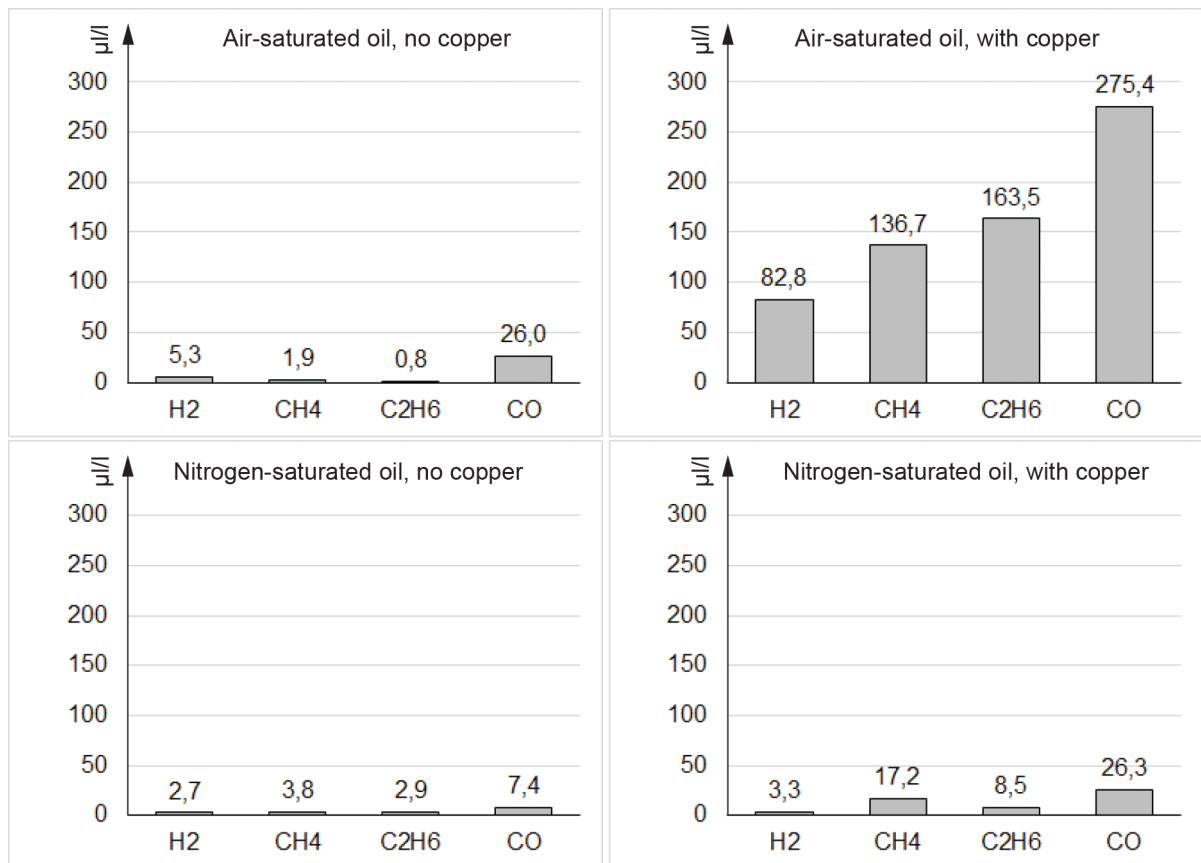
Figure 3: Stray gassing pattern 1

1.7.3.2 Stray gassing pattern 2 for mineral oil

The pattern shown in Figure 4 is illustrative of an inhibited unused mineral oil, additivated with a triazolic passivator additive – Oil 2
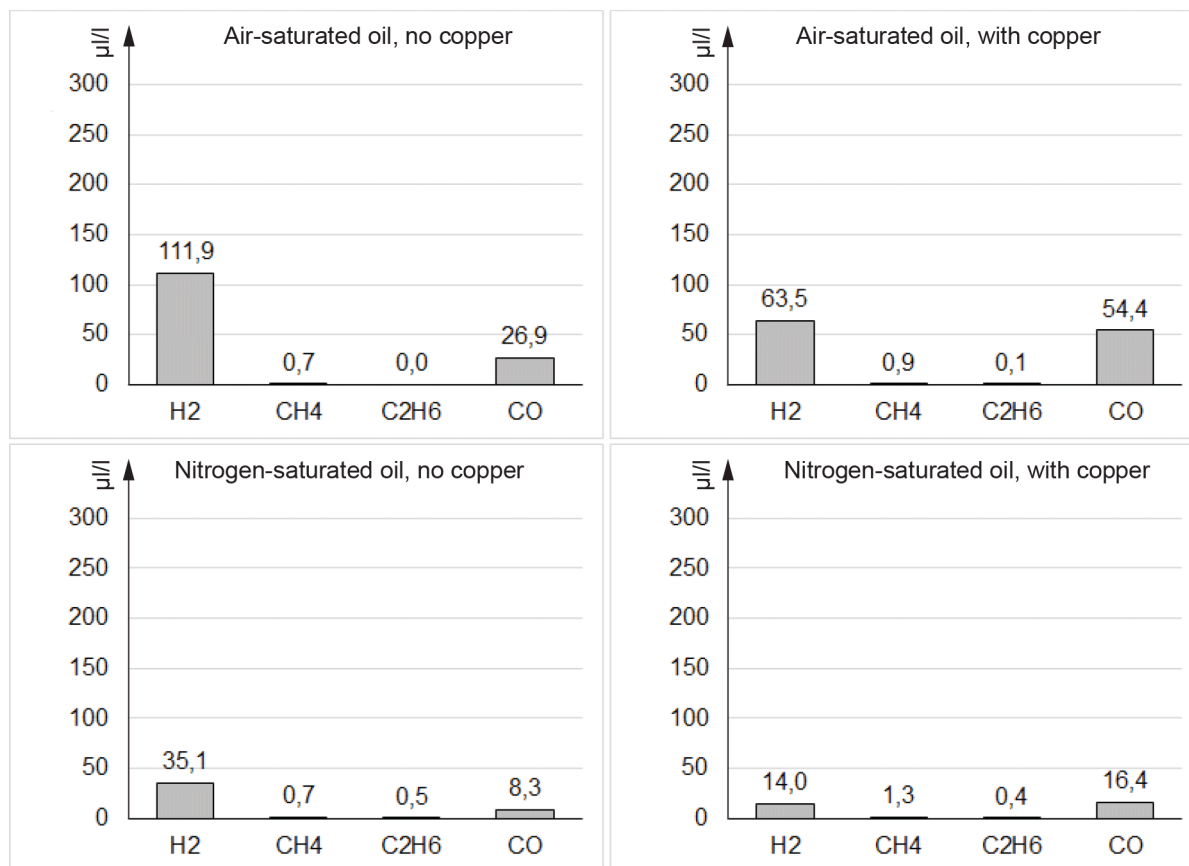
Figure 4: Stray gassing pattern 2

1.7.3.3 Stray gassing pattern 3 for mineral oil

The pattern shown in Figure 5 is illustrative of inhibited mineral oils, both unused and recycled – oils 3,4,5,7. The graphs show typical values, considering the very low deviation between the tested oils.
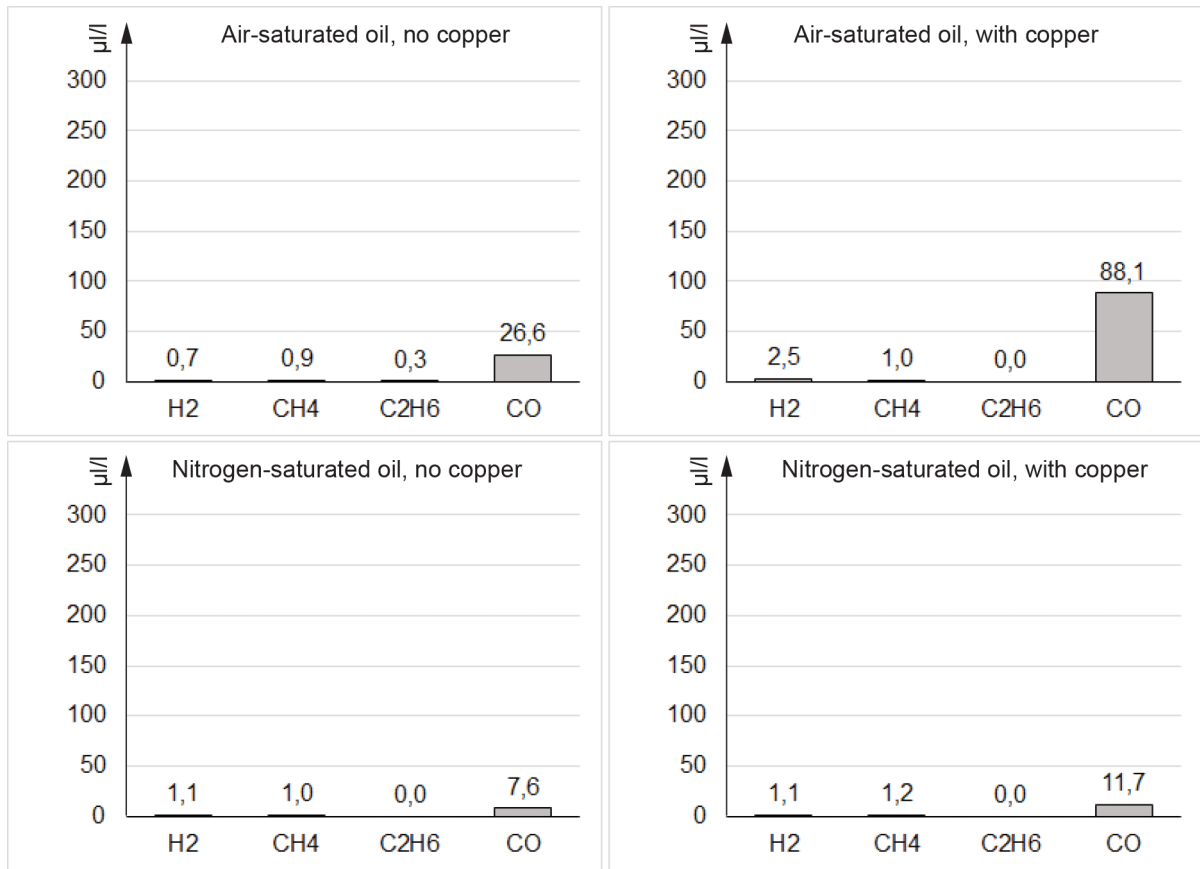
Figure 5: Stray gassing pattern 3

1.7.3.4 Stray gassing pattern 4 for mineral oil

The pattern shown in Figure 6 is illustrative of an uninhibited recycled mineral oil – Oil 6
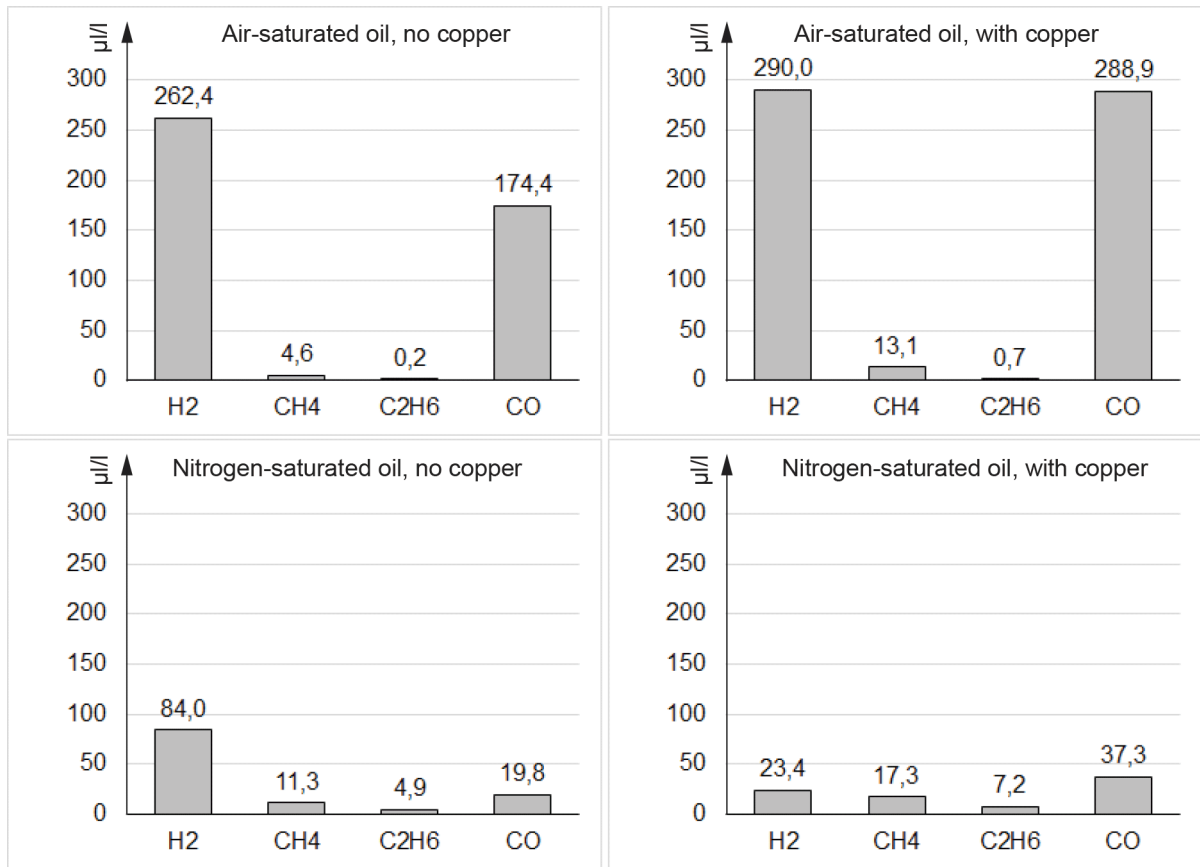
Figure 6: Stray gassing pattern 4

1.7.4   Stray gassing for synthetic and natural ester

The stray gassing behaviour of the tested synthetic (oil 9) and natural ester (oil 10) are represented on Figure 7 and Figure 8.
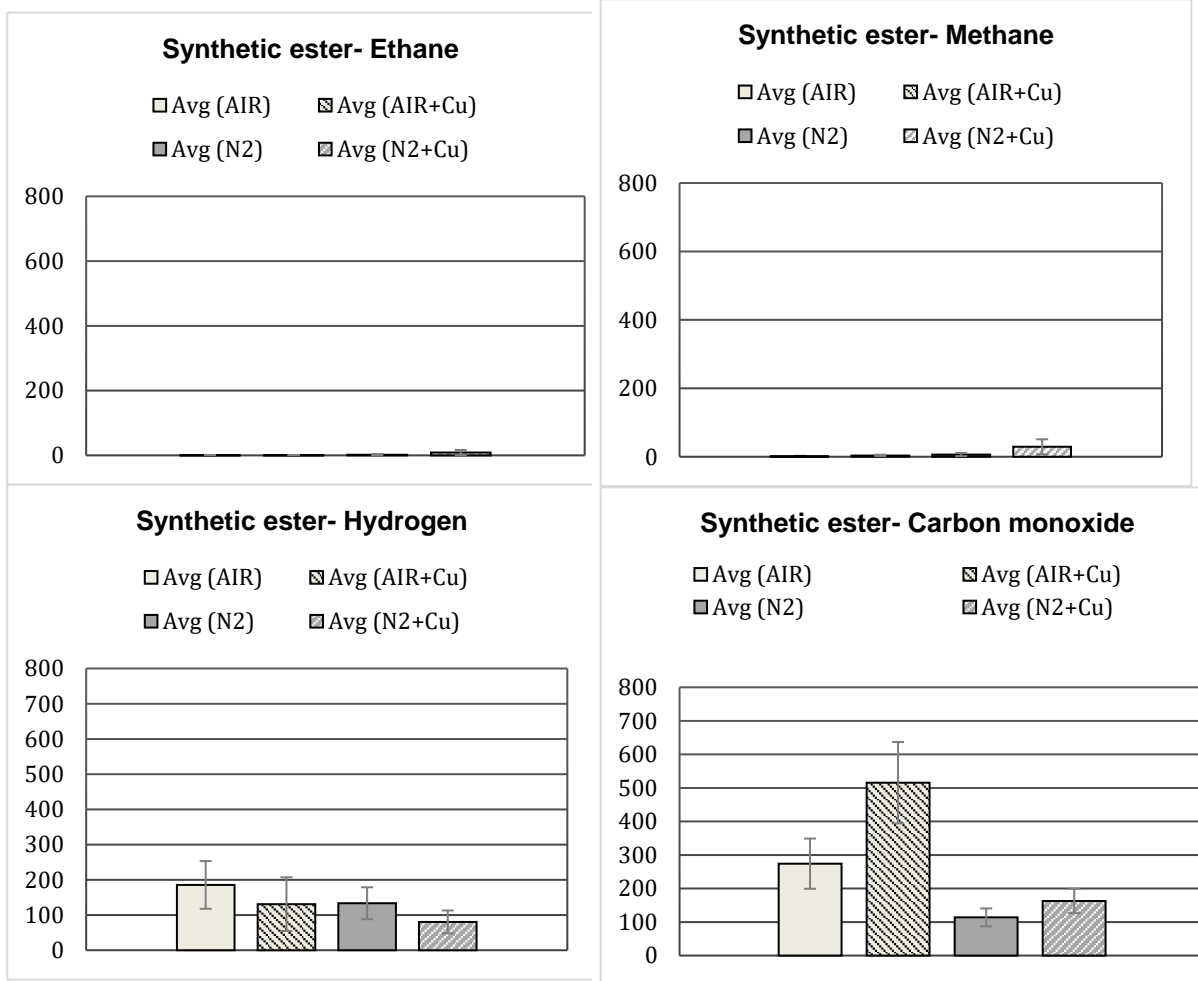
Figure 7: Stray gassing of synthetic ester (Oil 8) at 105 °C for 48h under different conditions: air – air saturated; air+Cu – air saturated in the presence of copper; N2 – nitrogen saturated; N2+Cu – nitrogen saturated in the presence of copper
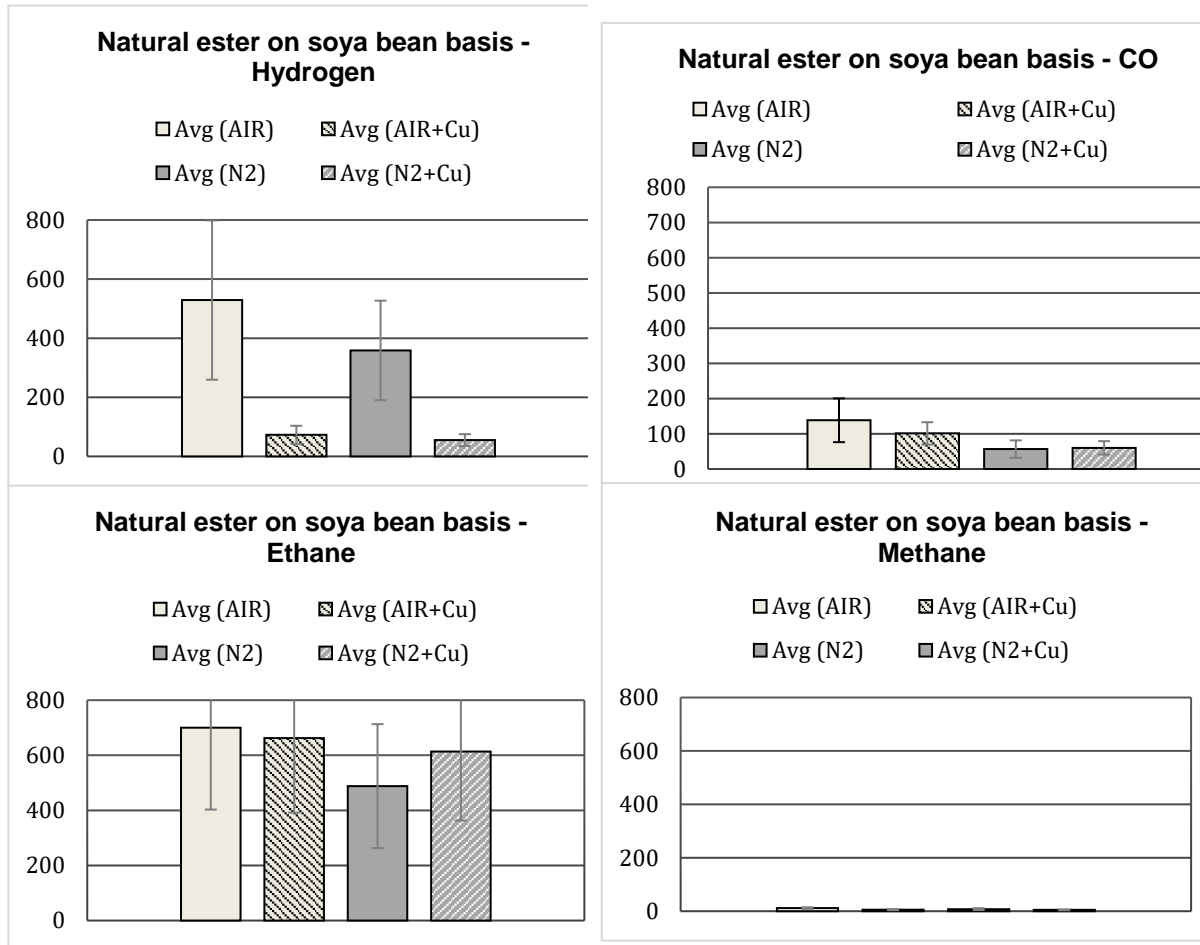
Figure 8: Stray gassing of natural ester (Oil 9) on soya bean bases at 105 °C for 48h under different conditions; air – air saturated; air+Cu – air saturated in the presence of copper; N2 – nitrogen graph for it is shown.saturated; N2+Cu – nitrogen saturated in the presence of copper

The tested insulating liquid on silicone bases (oil 10) did not show stray gassing in the tested conditions, therefore no graph for it is shown.
The results of the RRT have shown that the new procedure can put in evidence the tendency of an insulating liquid to form gases under thermo-oxidative stress, even at normal operating temperatures (105 °C). Another advantage of the described procedure is the relatively short duration (48 h).

From the stray gassing patterns resulting from the RRT it seems possible to make some "grouping". Some liquids show a very low tendency to stray gassing. These are oils 3, 4, 5 and 7; these are inhibited oils, both virgin and recycled. A common characteristic of these fluids seems to be the chemical stability, given by the high grade of refining and the presence of the inhibitors. In addition, oil 10 also belongs to this group, being a silicone (very high chemical stability).

Among mineral oils, a different pattern is shown by uninhibited oils: sample 1 and 6, in fact, are much more prone to stray gassing, even if the gas ratios are not the same. Sample 1 shows a gas pattern more similar to a T1 faulty condition (ethane is the major hydrocarbon gas); this condition is often observed in service. Sample 6 is more similar to sample 2, that is a passivated oil. stray gassing due to passivation was already observed and documented in literature (35), and seems to be adequately simulated by the method here proposed.

Esters showed a stronger stray gassing than inhibited mineral oils, especially sample #8 (natural ester), where the ethane formation is very strong. This phenomenon is usually observed in service and shall be considered when evaluating gas-in-oil behaviour of those insulating liquids.

As a final note, but very important, it must be considered that this RRT explored quite a wide range of insulating liquid types, but not all of them. Other stray gassing patterns (not described here) could be found in other types of insulating liquids. It would be, therefore, very important to consider the use of

the stray gassing as a parameter for new insulating liquid assessment, in order to be able to compare, in future, the gassing pattern of liquids in service to the one observed during the evaluation or acceptance steps.

2 Service cases of stray gassing. Possibilities for identification and mitigation

In this chapter service cases of stray gassing are presented. In some cases the method described in Chapter 1 has been used for identification of the gas production as stray gassing, in other cases mitigation procedures, e.g. oil reclamation have been performed and the gasing behaviour prior and after has been evaluated.

In the present criteria for evaluation of gas-in-oil analysis according to IEC 60599 (36) , stray gassing is considered for a T1 fault, e.g. a thermal fault at a temperature < 300 °C. Since stray gassing can take place at normal operating transformer temperatures and mainly in uninhibited oils (which were prevalent during the development of those criteria) it will make sense to have a critical review of those criteria (Table 4) at the next revision of IEC 60599.

Table 4: Dissolved gas analysis interpretation table (Table 1 in IEC 60599 (36))

Case	Characteristic fault	$\dfrac{C_2H_2}{C_2H_4}$	$\dfrac{CH_4}{H_2}$	$\dfrac{C_2H_4}{C_2H_6}$
PD	Partial discharges (see Notes 3 and 4)	NS [a]	< 0,1	< 0,2
D1	Discharges of low energy	> 1	0,1 to 0,5	> 1
D2	Discharges of high energy	0,6 to 2,5	0,1 to 1	> 2
T1	Thermal fault t < 300 °C	NS [a]	> 1 but NS [a]	< 1
T2	Thermal fault 300 °C < t < 700 °C	< 0,1	> 1	1 to 4
T3	Thermal fault t > 700 °C	< 0,2 [b]	> 1	> 4

NOTE 1   In some countries, the ratio C_2H_2/C_2H_6 is used, rather than the ratio CH_4/H_2. Also in some countries, slightly different ratio limits are used.

NOTE 2   Conditions for calculating gas ratios are indicated in 6.1 c).

NOTE 3 CH_4/H_2 < 0,2 for partial discharges in instrument transformers. CH_4/H_2 < 0,07 for partial discharges in bushings.

NOTE 4   Gas decomposition patterns similar to partial discharges have been reported as a result of stray gassing of oil (see 4.3).

[a]   NS = Non-significant whatever the value.

[b]   An increasing value of the amount of C_2H_2 ~~may~~ can indicate that the hot spot temperature is higher than 1 000 °C.

The data in (37), Table 5 and Table 6 show that the amount of ethane and methane increases quicker with the depletion of oxygen in comparison to the cases where this depletion is not so pronounced. Ethylen was not so markedly influenced by the O_2/N_2 ratio which is also indication that ethane and methane can be a consequence of oxidation processes.

Table 5: 90th percentile gas concentrations as a function of O2/N2 ratio and age in µL/L (ppm), Table 1 in (37)

Gas	O_2/N_2 Ratio ≤ 0.2				O_2/N_2 Ratio > 0.2			
	Transformer Age in Years				Transformer Age in Years			
	Unknown	1 – 9	10 – 30	>30	Unknown	1 – 9	10 – 30	>30
Hydrogen (H_2)	80	75	75	100	40	40	40	40
Methane (CH_4)	90	45	90	110	20	20	20	20
Ethane (C_2H_6)	90	30	90	150	15	15	15	15
Ethylene (C_2H_4)	50	20	50	90	50	25	60	60
Acetylene (C_2H_2)	1	1	1	1	2	2	2	2
Carbon monoxide (CO)	900	900	900	900	500	500	500	500
Carbon dioxide (CO_2)	9000	5000	10000	10000	5000	3500	5500	5500

Table 6: 95th percentile gas concentrations as a function of O2/N2 ratio and age in µL/L (ppm), Table 2 in (37)

Gas	O_2/N_2 Ratio ≤ 0.2				O_2/N_2 Ratio > 0.2			
	Transformer Age in Years				Transformer Age in Years			
	Unknown	1 – 9	10 – 30	>30	Unknown	1 – 9	10 – 30	>30
Hydrogen (H_2)	200	200	200	200	90	90	90	90
Methane (CH_4)	150	100	150	200	50	60	60	30
Ethane (C_2H_6)	175	70	175	250	40	30	40	40
Ethylene (C_2H_4)	100	40	95	175	100	80	125	125
Acetylene (C_2H_2)	2	2	2	4	7	7	7	7
Carbon monoxide (CO)	1100	1100	1100	1100	600	600	600	600
Carbon dioxide (CO_2)	12500	7000	14000	14000	7000	5000	8000	8000

In the next sections some examples of stray gassing in service are presented.

2.1 Industrial, free breathing transformer, 65 MVA, 20 kV, manufacturing year 2007, uninhibited oil

In this case the predominating gases in the DGA of this free breathing transformer were ethane and methane. Electrical tests on-site did not reveral any problems. The development of ethane decreased after degassing, but increased again afterwards (Figure 9), (38).
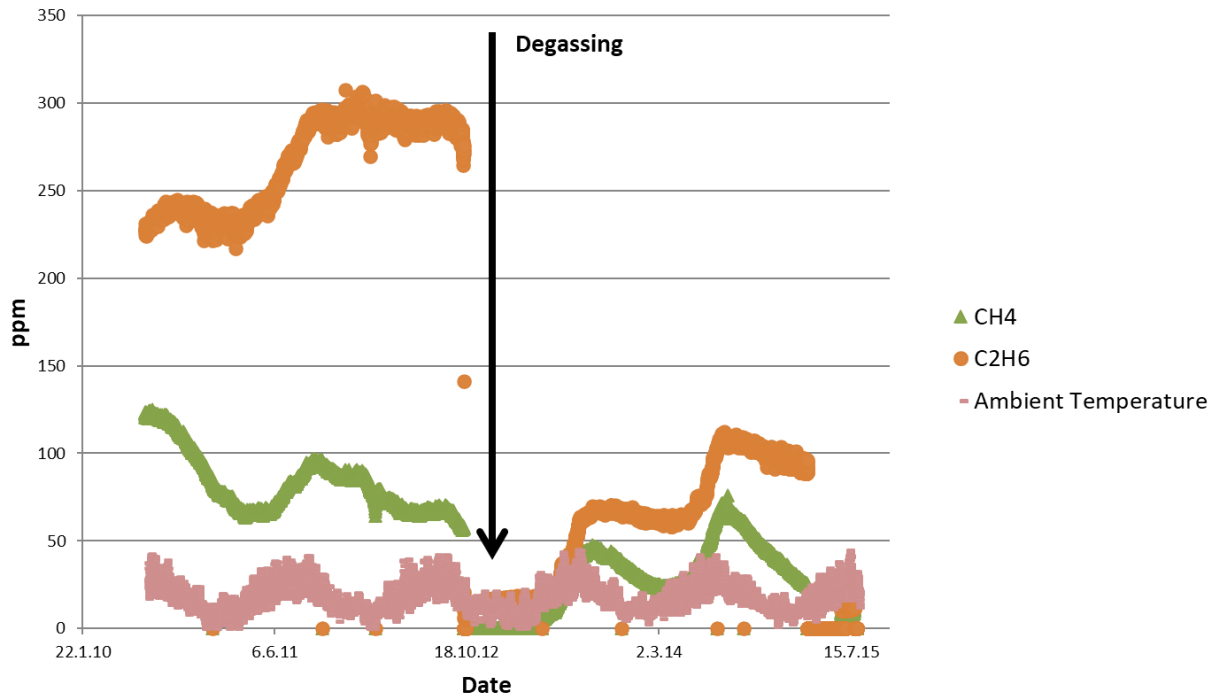
Figure 9: Development of ethane and methane with time (38)

2.2 Generator transformer, 675 MVA, 400 kV, manufacturing year 2001, uninhibited oil, passivator added 2010

Since corrosive sulphur has been detected in this transformer, passivator has been added. This led to a continuous increase of hydrogen, which may interfere with the evaluation of the gas-in-oil analysis (Figure 10) (38).
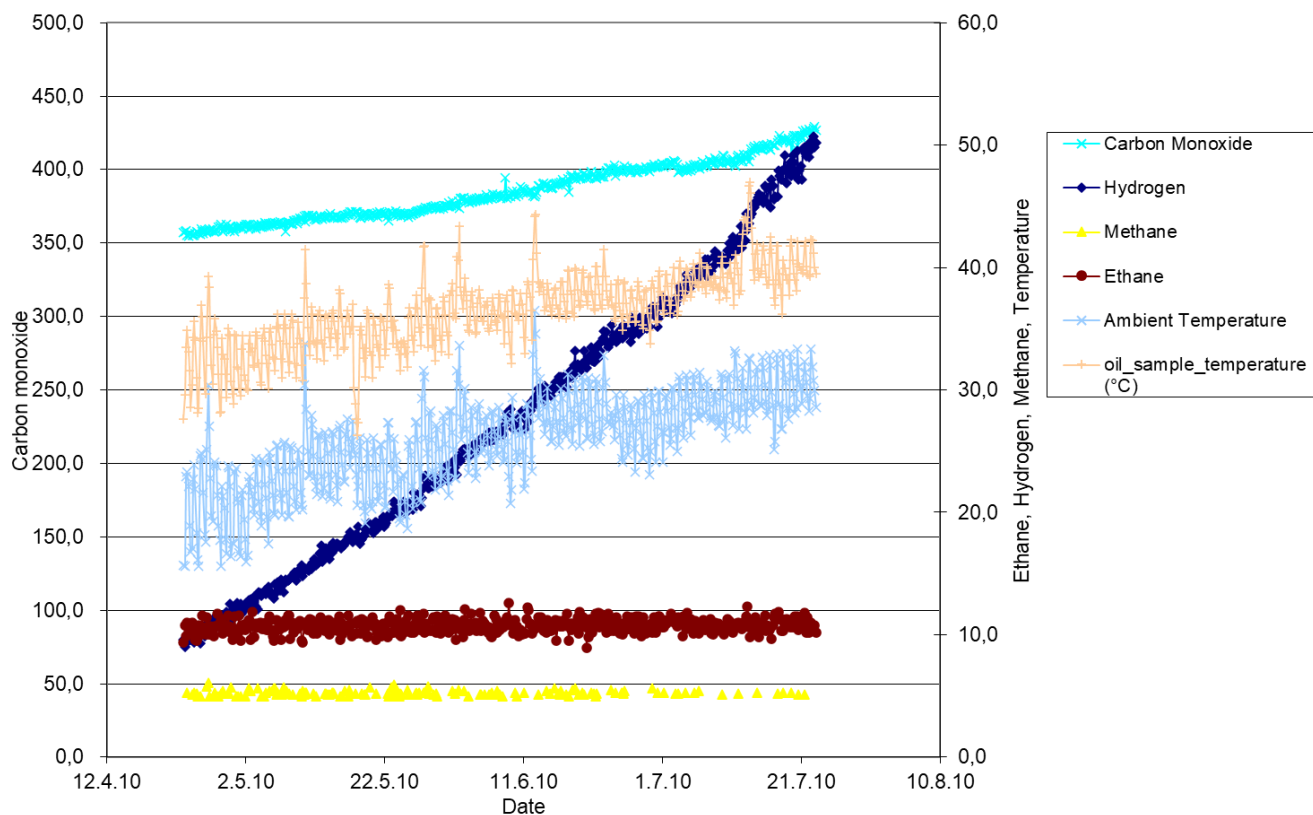
Figure 10:Development of hydrogen after oil passivaton (38)

2.3 Network Transformer with rubber bag, 48 MVA, 110 kV, manufactured 2008, natural ester on soya bean bases

This network transformer, filled with natural ester based on soya bean bases showed continuous development of ethane, reaching a steady state after several years (Figure 11). The hydrogen content decreased in the same time. The transformer is in service and operating normally.
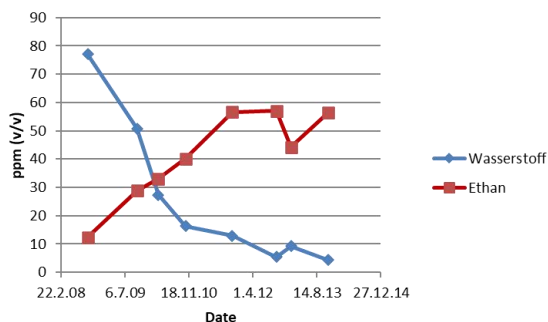
Figure 11: Development of hydrogen (blue line) and ethane (red line) in a network transformer filled with natural ester on soya bean bases.

2.4 Transformer from distribution system, 8 MVA, 35 kV, 13 years in service, uninhibited mineral oil (39)

The operation history of the transformer showed following:

- Since the beginning, from 2005. to 2016. a constant increase of hydrogen, ethane and methane was observed (Figure 12)
- Cyclic consumption of oxygen was observed
- The increase of hydrogen was followed by lower concentration of oxygen, which can be a sign of progressive oxidation of the oil
- Uninhibited oil and higher aromatic content indicated a lower degree of oil refining

Figure 12 Development of the gas concentrations in the oil during the service

In order to verify the origin of the gases stray gassing tests according to Cigre TB 296 (18) at 120 °C have been carried out and are represented in Table 7.

Table 7 Gas concentrations dissolved in the oil after the stray gassing tests in µl/l (ppm)

Stray gassing tests at 120 °C (CIGRE TB 296 (18))								
	H_2	CH_4	C_2H_2	C_2H_4	C_2H_6	CO	CO_2	O_2
Intial	0	0	0	0	0	5	101	29311
16 h	844	293	0	9	113	826	1213	258
164 h	814	316	0	17	123	969	1999	517
(164+16) h	130	38	0	6	22	988	1140	272

Additionally the stray gassing test has been carried out according to the procedure of Cigre D1.70 Part 1.6 (this brochure) in the presence of air and air and copper. The results are presented in Table 8.

Table 8 Gas concentrations dissolved in the oil after the stray gassing tests in µl/l (ppm)

Test for stray gassing at 105 °C, with air (CIGRE WG D1.70)								
	H_2	CH_4	C_2H_2	C_2H_4	C_2H_6	CO	CO_2	O_2
Initial	0	1	0	0	3	9	210	30229
48 h	899	223	0	9	100	855	1241	513
additional 164 h	932	234	0	13	108	903	1721	435
Test for stray gassing at 105 °C with air and copper (CIGRE WG D1.70)								
	H_2	CH_4	C_2H_2	C_2H_4	C_2H_6	CO	CO_2	O_2
Initial	0	1	0	0	3	9	210	30229
48 h	527	267	0	14	194	851	1348	638
additional 164 h	612	258	0	15	175	899	1780	203

Conclusions:

- All stray gassing tests showed the similar results, hydrogen, methane and ethane were produced in similar ratios as in the transformer.
- The test acc. to CIGRE WG D1.70 (Table 8) with presence of copper, showed a lower amount of hydrogen and higher amount of methane and ethane, due to the catalytic effect fo copper.
- CIGRE D1.70 test showed that no increase of methane and ethane was observed after prolonged time (164 h), while rise of hydrogen was modest and not affected by the copper (Table 8) .
- It can be concluded that 48 h of the test is long enough to adequatelly reproduce stray gassing of the oil.

2.5 Network transformer, 25 MVA, 20 kV, manufacturing year 2020, uninhibited oil

Shortly after commissioning the oil showed a gassing behaviour (sampling 2021). In order to identify whether the gases are produced out of the oil (stray gassing), the sample has been degassed and the stray gassing test with and without copper has been performed (Table 9). In both cases hydrogen methane and ethane have been built in high concentrations and the higher concentrations occurred in the presence of copper.

Table 9: Gas values in original state, after degassing and after stray gassing tests according to 1.6. All values are in µl/l (ppm).

Gas		Sampling 2021	Sample degassed and air saturated	Procedure only with air (48h 105 °C)	Procedure with air and copper (48h 105 °C)
H_2	Hydrogen	166	1	990	1381
CH_4	Methane	22	2	162	303
C_2H_6	Ethane	132	1	145	268
C_2H_4	Ethylene	10	< 1	9,6	13
C_2H_2	Acetylene	< 1	< 1	< 1	< 1
C_3H_8	Propane	121	3	126	212
C_3H_6	Propylene	27	< 1	14	19
CO	Carbon monoxide	225	2	513	910
CO_2	Carbon dioxide	3250	398	603	1088
O_2	Oxygen	3561	29778	362	374
N_2	Nitrogen	53148	56892	53334	50727

The results demonstrate the strong Stray Gassing tendency of the oil and shows the higher gas development in the combination of air and copper.

2.6 Family of 53 free breathing transformers 20 – 31,5 MVA, 60 kV, manufacturing year 2003 - 2014, uninhibited oil

All these transformers, filled with the same uninhibited oil showed the same pattern of continuous development of ethane and methane with time, reduced oxygen content and no signs of solid insulation degradation (no furanic compounds) (40). A representative curve showing the time development of ethane, methane, hydrogen and ethylene is shown on Figure 13.
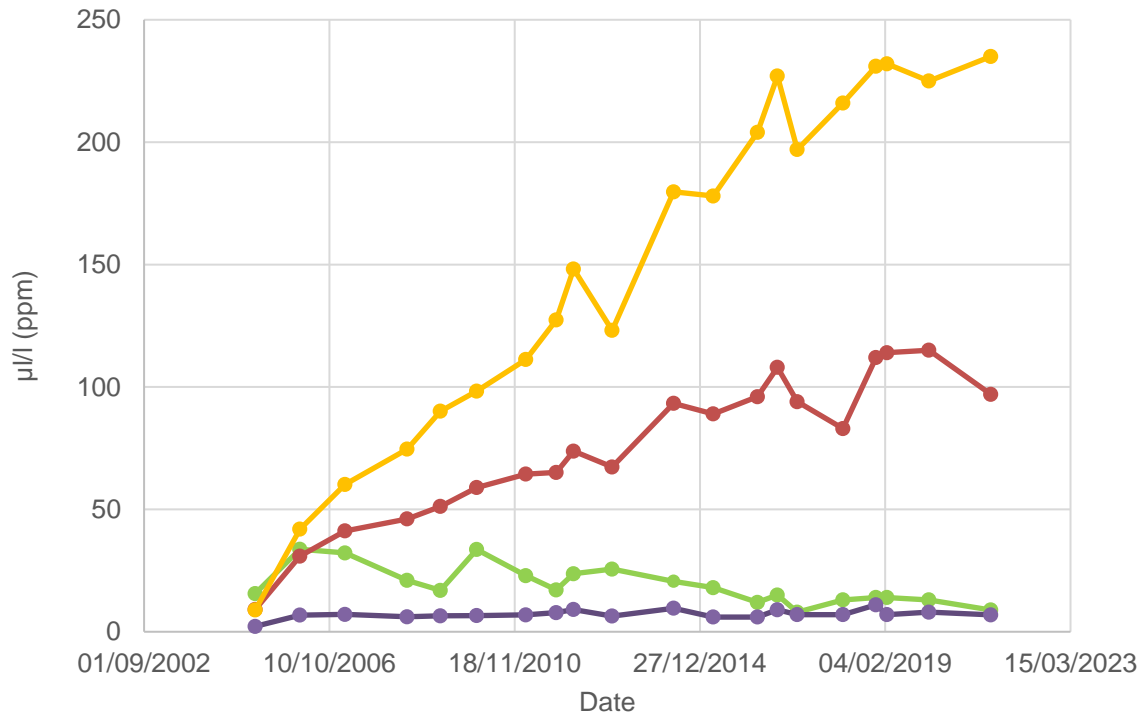
Figure 13: Exemplary development of gases due to stray gassing with time (yellow line – ethane, brown line – methane, green line – hydrogen, violet line – ethylene)

2.7 Step up free breathing transformer, 780 MVA, 420 kV, manufacturing year 1985, uninhibited oil. Removing of stray gassing behaviour after reclaiming.

Very often stray gassing behaviour is accompanied with oxygen depression like in this case prior regeneration. Regeneration with fuller's earth with consequent inhibiting removes the source of gassing. It is plausible that also the ageing products in oil which consume oxygen have been depleted and so the oxidation reaction producing stray gassing (ethane and methane) has been stopped (Table 10).

Table 10: Development of ethane and methane after regeneration of the insulating oil

Gas	2009, prior reclaiming (ppm)	2 years after reclaiming (ppm)
Hydrogen	45	32
Methane	96	8
Ethane	205	20
Ethylene	30	5
Carbon monoxide	579	332
Carbon dioxide	5986	4412
Oxygen	6150	24850
Nitrogen	55493	68080

3 Tests for PCA/PAH compounds in oil and their meaningfulness

3.1 Background

Abbreviations & Definitions:

PAH: Polycyclic Aromatic Hydrocarbons– containing two or more fused aromatic rings with carbon and hydrogen only in the structure

PCA: Poly Cyclic Aromatics – containing two or more fused aromatic rings, but the carbons can be substituted with other heteroatoms (e. g. N,O,S).

Traditional mineral insulating oils, are hydro-treated crude oil distillates. Older technologies of refinement included acid clay treatment whilst modern refining technologies are mainly severe hydrotreatment and some solvent refinement. Crude oil distillates can contain varying amounts of polycyclic aromatics (PCA) which are naturally occurring in the crude oil – and these can be reduced in the final product by the severity of the refining treatment. Hydrotreatment converts the polycyclic aromatic compounds into less hazardous partially saturated compounds (Figure 14).
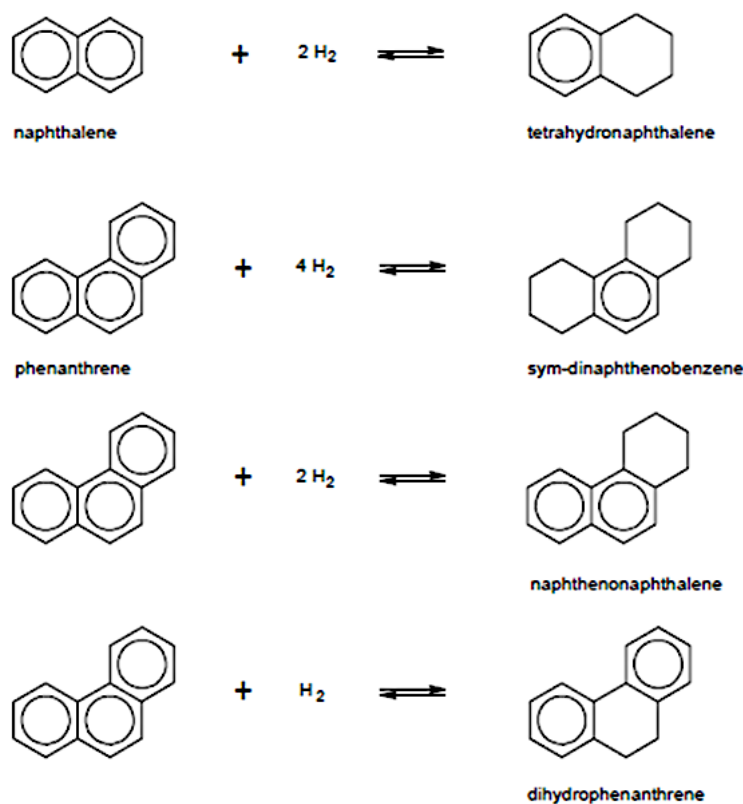
Figure 14: Saturation of naphthalene and phenanthrene

From the perspective of health & safety – PCA are of concern as some are associated with carcinogenic and mutagenic potential. PCA with more than 3-7 fused rings are considered higher cancer potential. In the context of insulating liquids – dermal carcinogenicity is the most relevant. Hundreds of animal studies have been performed in the last years to understand the hazard profile of different grades of petroleum products. Skin tumors and prostate cancer is the critical effect due to content of PCAs (Figure 15).

From a toxicological perspective, carcinogenicity and mutagenicity are complex events and depends on many factors such as the role of co-carcinogens, initiators, and promotors. The consequence of this is that the best picture of carcinogenic potential of a substance is achieved by testing the actual substance in mouse skin painting studies.

Figure 15: Chimney sweeps in the 19th century were particularly vulnerable due to the formation of PCAs during incomplete combution of organic matter, e.g., fire logs

3.1.1 IP 346

Historically, much work has been done finding a screening method, preferably a chemical analytical method, that would correlate to the results from actual mouse skin painting studies. Numerous methods were assessed but the test called IP 346: Determination of Polycyclic Aromatics in Unused Lubricating Base Oils and Asphaltene Free Petroleum Fractions – Dimethyl Sulphoxide Extraction Refractive Index Method (41; 42) was found to correlate with carcinogenic potential as found when tested in animals . The gravimetric method relies on the fact that the principal carcinogens of virgin oils are 3-7 ring PCA which are readily extractable into dimethyl sulfoxide (DMSO). It is rapid and easy to use, but has chemical limitations in its applicability :

The IP 346 method defines the chemical scope of applicability, based on the specific types of samples for which the inter-laboratory validation study was conducted, as lubricating base oils with at least 95% of components boiling above 300 °C. Correlation of 133 base oils that have mouse skin painting studies and DMSO extract data of the same oil has been found with high (over 90%) sensitivity, specificity and accuracy. Therefore, the IP 346 method specifically applies to "unused, additive-free lubricating base oils having an atmospheric boiling point of 300 °C minimum at 5% recovered sample". According to the method, if the sample does not meet the distillation requirement, it should be distilled under vacuum. Many mineral insulating liquids may need to be distilled to meet the distillation requirement. . The method may apply to samples outside of this range, but the method precision has not been determined for such materials.

In 1994, IP346 was introduced in the regulation and since it has been used to define a cancer hazard classification threshold for virgin petroleum substances. First the "Note L" was included in the former Dangerous Substance Directive No 67/548 EC and later re-established in the Classification, Labelling and Packaging (CLP) Regulation (EC) No 1272/2008 of 16 December 2008. This means that the applicability of IP346 for classification purposes is limited to a limited number of CAS numbers including lubricant base oils. For other petroleum substances (including white oils, distillate aromatic extracts, acid treated and untreated oils as well as non-virgin oils the IP346 method may only be used for informational purposes, because of a general lack of carcinogenicity data to correlate to (43).

Note L: The classification as a carcinogen need not apply if it can be shown that the substance contains less than 3% DMSO extract as measured by IP 346 'Determination of polycyclic aromatics in unused lubricating base oils and asphaltene free petroleum fractions — Dimethyl sulphoxide extraction refractive index method', Institute of Petroleum, London. This note applies only to certain complex oil-derived substances,".

Mixtures like formulated transformer oils are considered non-carcinogenic if all the components are proven non-carcinogenic according to current regulations of classification and labelling.

More recently, a critical review of the method was performed and it was concluded that IP 346 is still relevant and applicable to current day unused mineral oils. The results are reported in the Concawe report 6/16 Critical review of the relationship between IP 346 and dermal carcinogenic activity (44): "The underlying strength of the use of IP 346 as a predictor of carcinogenic activity is that it is based on a comparison of results (% w/w) with the findings of skin cancer in mouse skin painting studies". This comparison showed a strong correlation between skin cancer incidence and DMSO extractable content (specifically ≥3% w/w), where the extractable portion has been shown to correlate with the polycyclic aromatic content (PCA) of the substance. Based on this relationship, the IP 346 has been applied by the petroleum industry to differentiate those mineral hydrocarbon base stocks that are likely to be dermal carcinogens from those that are unlikely to be so."

3.1.2 Modified Ames Test

Another screening method for understanding the genotoxic carcinogenic potential of chemicals is an in vitro method using bacterial cells: Ames Test. It was early recognised by the petroleum industry that this assay gave false negative results for virgin petroleum substances: clearly carcinogenic (in vivo) substance showed no mutagenic potential in vitro. Based on this knowledge, Mobil developed Modified Ames test where more than 100 virgin oils samples have been correlated in skin painting and and in vitro assay. The new, modified assay is more sensitive and correctly screens for carcinogenic potential in virgin oils. In 1995, the method was adopted by ASTM as E1687 "Standard Test Method for Determining Carcinogenic Potential of Virgin Base Oils in Metalworking Fluids" (45). As oils are not soluble in water as required in in vitro tests, DMSO extract (as for IP 346) was used which can be dissolved in aqueous cell media. Additionally, to induced metabolic activation which is required for petroleum substances, hamster liver is used instead of less sensitive rat livers.

3.1.3 Marker substances

Benzo(a)pyrene (BaP) was the first isolated and identified occupational carcinogen. It belongs to a sub-set of PCA, namely polycyclic aromatic hydrocarbons (PAH) and has served as a model compound in understanding molecular mechanisms and DNA binding behind carcinogenicity . The planar chemical structure of BaP (Figure 16) and subsequently its major metabolite benzo(a)pyrene 7,8-diol 9,10-epoxide (Figure 17) allows for binding to the DNA in the bay region which potentially could initiate cancer development.
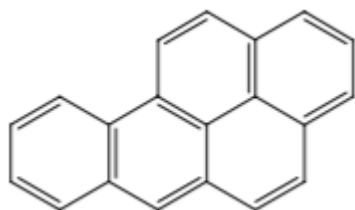
Figure 16: Chemical structure of benzo(a)pyrene (BaP)
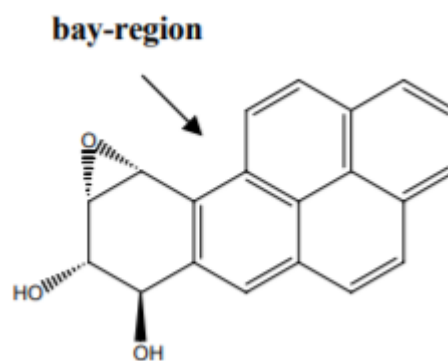
Figure 17: Chemical structure of benzo(a)pyrene 7,8-diol 9,10-epoxide

In the EU, eight PAH are classified hazardous for human health and if a mixture contains more than 0.01% or 0.1% (depending on the PAH and depending on the application) of the PAH, the product needs to be classified accordingly (at least carcinogenic, but in some instances also mutagen and reprotoxic) (42), (46). Transformer oils are not routinely measured for PAHs as modern-day refining processes typically convert the PAHs into saturated hydrocarbons and only ppb levels (if any) will remain in the final product. As discussed above, IP 346 is still seen as a sufficiently robust method for carcinogenic potential in the base oils use for transformer oil. It is clear that more than the presence of eight PAH contribute to the health hazard of petroleum substances. Data rather shows the opposite,

that the combination of PCA/PAH (as analysed in IP 346) is required for indicating carcinogenic potential and only looking at a few select PAH would underestimate the health hazard.

Figure 18 describes the eight PAHs of concern in Reach – Echa (42).
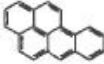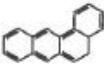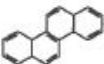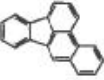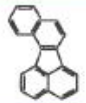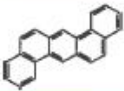
PAH	CAS-no	Boiling point (°C)	Molecular structure
Benzo(a)pyrene	50-32-8	495	
Benzo(e)pyrene	192-97-2	492	
Benzo(a)anthracene	56-55-3	437	
Chrysen	218-01-9	448	
Benzo(b)fluoranthene	205-99-2	357	
Benzo(j)fluoranthene	205-82-3	n.d.	
Benzo(k)fluoranthene	207-08-9	480	
Dibenzo(a, h)anthracene	53-70-03	525	

Figure 18: 8 PAHs compounds restricted under Reach- Echa (42)

3.2 Testing methods investigated in the Round Robin Test

The purpose of the RRT was to evaluate the presence of PAH in mineral oils by different laboratories. Depending on the analytical capabilities of the laboratories following testing methods have been applied: IP 346, EN 16143, ASTM D6591 (Table 11). Since the number of obtained analytical data was not high enough, the results shall be considered only as an indication and cannot be statistically evaluated.

Table 11: Used methods for determination of PAHs in the Round Robin Test

Method	Principle	Compounds determined	Participating laboratories
IP 346:2004 (41)	PCA -DMSO Extract	Polycyclic aromatic content soluble in DMSO extract	Savita Oil Technologies Limited, India, Apar India, JXTG Nippon Oil & Energy Corporation Japan Shell Global Solutions Germany Ergon refining, USA Terna Italy
EN 16143:2013 (47) and Grimmer method (48)	PAH "8 Markers" In Extender Oils, LC Cleaning and GCMS	8 Reach individual PAHs and Grimmer list (22 PAH)	Shell Global Solutions Germany Efacec Portugal (modified method) Siemens Germany (modified cleaning procedure)
ASTM D6591:2019 (49)	Standard Test Method For Determination Of Aromatic Hydrocarbon Types In Middle Distillates— high Performance Liquid Chromatography Method With Refractive Index Detection	% Mono, Di, Tri, Poly	Labelec Belgium Ergon refining USA Siemens Germany

3.3 Mineral oils investigated in the Round Robin Test

Following mineral insulating oils – unused and recycled have been investigated, additionally oil 4 has been spiked with 34,8 mg/kg BAP and declared as oil 11 – see Table 12 .

Table 12: Insulating mineral oils used in the Round Robin Test

Oil 1	Mineral oil, unused, uninhibited
Oil 2	Mineral oil, unused, inhibited, passivated
Oil 3	Mineral oil, recycled, inhibited
Oil 4	Mineral oil, unused, inhibited
Oil 5	Mineral oil, unused, inhibited
Oil 6	Mineral oil, recycled, uninhibited *
Oil 7	Mineral oil, recycled, inhibited
Oil 11	Oil 4 + 34,83 mg/kg BAP

3.4 Results and conclusions out of the Round Robin Test

The results of the Round Robin Test according to the used methods 3.2 are presented in detail in Annex A. As already mentioned, due to the low number of participating laboratories, as well as partially modified testing procedures no statistical evaluation could be done.

General conclusions (method dependent) are the following:

3.4.1 IP 346 results

IP 346 method can not recognize between individual EPA restricted PAH compounds. The % standard deviation between the participating laboratories is 30 – 60 (see A.1).

3.4.2 ASTM D6591 results

The sum of mono + di + tri + poly PAH portions was comparable between the 3 participating labs, however it does not have a direct correlation to the carcenogenicity of the insulating liquid (see A.2).

3.4.3 EN 16143:2013 and Grimmer method results

The laboratories working with the EN 16143 (2 labs) and modified method (1 lab) and determining individual PAH compounds were able to determine BAP which was artificially spiked in oil 11 (see A.3).

4 Test methods for additives in insulating liquids

4.1 Introduction

Additives are used in transformers to enhance the functional properties of the insulating liquid and extend the life of a transformer. Additives are used to enhance oxidation stability, minimize corrosion, and lower the pour point of the liquid. These additives are discussing in IEC 60296 (16). It is important that the additives are identified and their concentrations are known so that the concentration level can be monitored over the life of the transformer. If the additive concentration is depleted below certain threshold values, the operator has the option of adding additional additive or topping-off. The maintenance of the transformers is discussed in the maintenance guides, IEC 60422 (50) for mineral oils, IEC 61203 (51) for synthetic esters and IEC 62975 (52) for natural esters.

4.2 Additive types

There are three basic additives which are often used in insulating liquids. These are antioxidants, of which inhibitors are a sub-class, metal passivators or deactivators which also function as antioxidants, and pour point depressants. There are analytical laboratory tests for some but not all of the possible additives which are described for mineral oils in IEC 60666 (53). This section will describe the different types of additives and the different analytical methods.

4.2.1 Antioxidants

Antioxidants are the most commonly used additives and the function of antioxidants is to improve the oxidation stability of the liquid. Oxidation is a complex free radical chain process which involves three steps in the mechanism (1) initiation, (2) propagation, and (3) termination. The termination of the initiation step or stopping the propagation step will prevent the chain process from progressing and stop the oxidation associated with that chain. The inhibitors described in IEC 60296 (16) are phenolic types. Hindered phenols and amines are primary antioxidants which react with the peroxy radicals to form stable molecules and stable free radicals and this terminates the chain reaction. Other antioxidant additives, such as sulphur and phosphorus containing compounds, are so-called secondary antioxidants which decompose the hydroperoxides to prevent further reaction. There are standardized test methods currently available to detect and measure 2,6-di-tert-butyl-para-cresol (DBPC), also known as butylated hydroxytolulene (BHT), and 2,6-dit-tert-butylphenol (DBP) (Figure 19) . In ester liquids also Irganox® 109 and Irganox® 1010 are often applied (Figure 19). There are no standard test methods for the amine type, sulphur-containing, or phosphorus-containing antioxidants.

DBPC (=2,6-Di-tert-butyl-para-cresol)	DBP (=2,6-Di-tert-butyl-phenol)
Irganox® 109	Irganox® 1010
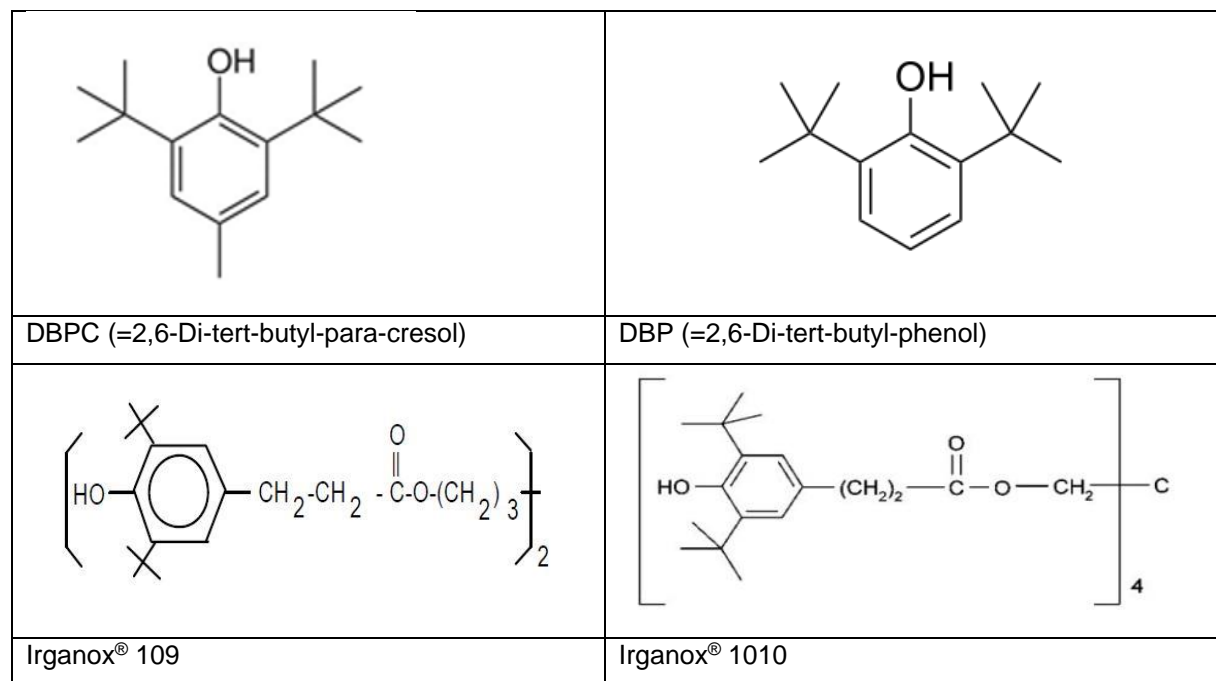
Figure 19: Most commonly used inhibitors in insulating liquids

The inhibitor content will decrease over the life of the transformer. The rate of decrease will depend on many factors such as the temperature, oxygen content, the presence of metallic catalysts, and the inherent stability of the insulating liquid (54). An adequate level of inhibitor is required to minimize oxidation of the insulation liquid, Figure 20 (55). The guides recommend that the inhibitor concentration be maintained at greater than 40% of the original value.
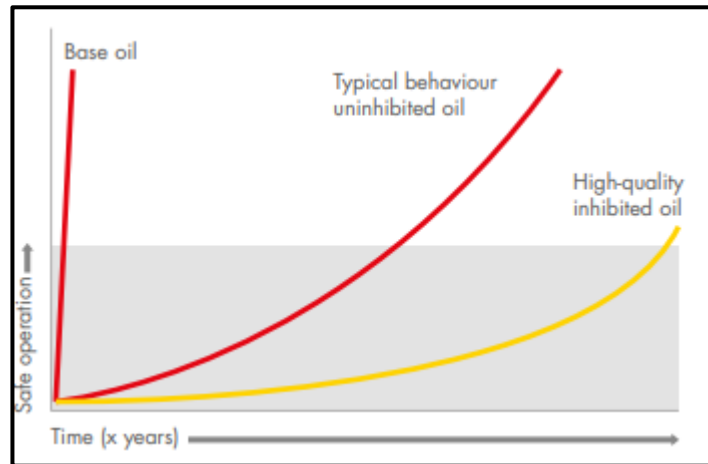
Figure 20: Oxidation rates of transformer oil (55)

Precautions should be made in the selection of all additives, especially antioxidants, since additives are designed to chemically react within the system to prevent or stop unwanted reactions. Reaction products can be generated and these can result in further issues. For example, it has been demonstrated that while dibenzyl disulphide (DBDS) is an excellent antioxidant in industrial applications where there are no soft metals such as copper present, it can generate corrosive sulphur which is detrimental to the copper in transformers.

Any references to inhibitors are to the synthetic inhibitors, synthetically produced compounds. Mineral oils can contain naturally occurring compounds which can function as natural inhibitors. These compounds are thought to be aromatic hindered sulphur compounds. Transformer oils which contain only natural inhibitors are defined as uninhibited transformer oil. There are no standardized methods for the detection and measurement of natural inhibitors.

4.2.2 Metal passivators

Metal passivators are also referred to as metal deactivators and they can also be used to reduce the buildup of electrostatic charges. These compounds will either form a thin protective film on the copper surface to prevent the reaction with corrosive sulphur compounds and the deposition of copper sulphide in the paper or they will complex with copper in the liquid to prevent the catalytic oxidation effect of copper. Benzotriazole derivatives are typical metal passivator additives. These include N-bis(2-ethylhexyl)-aminomethyl-tolutriazole (TTAA, Irgamet[®] 39), benzotriazole (BTA) and 5-methyl-1H-benzotriazole (TTA). Those can be determined in mineral oils by means of HPLC according to IEC 60666. There are standardized test methods currently available for the detection and measurement of these additives. There are several other compounds can be used as metal passivator additives, such as N,N-bis(2-ethylhexyl)-1H-1,2,4-triazole-1-methanamine (TAA), diamino-diphenyldisulphide, nicotinic acid, hydroquinoline and other sulphur-based compounds. There are no standard test methods for these compounds.

Knowledge of the concentration of passivators is important for two reasons. First, research has shown (56) that passivators will decompose under laboratory conditions to generate stray gasses, especially hydrogen. The generation of stray gasses due to the passivators needs to be considered during the interpretation of the dissolved gas analysis (DGA). Secondly, if the transformer contains corrosive or potentially corrosive sulphur, the guides recommend that the passivator content be above 50 µg/kg (ppm) to remain effective.

4.2.3 Pour point depressants

Pour point depressants are used to decrease the pour points of insulating liquids and improve their low temperature properties. Pour point depressants are high molecular weight polymers such as polymethacrylates and polynaphthalenes. There are standardized test methods currently available for the detection and measurement of the pour point depressants. Pour point depressants are generally as inert as the insulating liquid but may be subject to oxidation. Pour point depressant concentrations generally do not decline with time and should not be removed during reclamation/reconditioning. It is not necessary to detect and measure the pour point depressants since the measured pour point of the liquid can be used to determine the suitability of the liquid. However, the mixing of different liquids could reduce the concentration of the depressants and render them ineffective.

In case of mineral oil all additives shall be declared (IEC 60296) and the inhibitor is DBPC or DBP. For natural and synthetic esters, the compulsory declaration has historically been absent due to confidentiality concerns. However, the new standard ASTM D8240 (published in 2022) contains language requiring "If additives are used, the chemical family and function of all additives and maximum concentration of each family shall be declared in product data sheets and certificates of compliance." The exact language is in the revision of IEC 62770 (at FDIS stage at this writing) and it is expected to be included in the upcoming revisions of ASTM D6871 and IEC 61099. New test methods for the identication and determination of inhibitors used in natural and synthetic esters are under development. IEC 60666 is currently under revision and a new ASTM test method is being developed.

4.3 Analytical methods for additive detection

The basic analytic techniques used to detect and measure additives are Fourier transform infrared spectroscopy (FT-IR), gas chromatography (GC) with various detection methods, high-performance liquid chromatography (HPLC), gel permeation chromatography (GPC), and thin layer chromatography (TLC). Unless noted otherwise, these are all described in IEC 60666.

FT-IR is used for the detection and measurement of the phenolic inhibitors DBPC and DBP. The infrared absorption at the (O-H) stretching frequency of the hindered phenols (3650 cm-1) is used for the detection and measurement. ASTM D2668 (57) uses the frequencies of 860 cm-1 to detect and measure DBPC and 745 cm-1 to detect and measure DBP.

GC/FID (Flame ionization detector) is used to detect and measure the phenolic antioxidants per ASTM D4768 (58).

GC/MS (mass spectrometry) is used for the detection of the phenolic inhibitors and DBDS (IEC 62697). Other detectors can be used for DBDS, including electron capture detector (ECD), atomic emission detector (AED), sulphur chemiluminescence detector (SCD), flame photometric detector (FPD), or MS/MS.

HPLC with an ultraviolet (UV) detector is used for the detection and measurement of the phenolic inhibitors and the metal passivators.

GPC is used for the detection and measurement of the pour point depressants. A refractive index (RI) detector is used for the polymethacrylates and a UV detector for the polynaphthalenes.

TLC is used for the detection and semi-quantitative measurement of the phenolic antioxidants.

HPLC is the more versatile method for the detection and measurement of additives. A recent paper (59), describes the simultaneous detection and measurement of several inhibitors and passivators. A modified version of this procedure was used in the round robin study.

4.3.1 Testing methods investigated in the Round Robin Test

Inhibitor content detection in mineral oils is well described in IEC 60666, since also the inhibitor type is well defined in IEC 60296. This information is, however, missing in the present standards for unused natural and synthetic esters and requires analytic evaluation.

For this purpose following HPLC with photoarray detector method has been proposed:

4.3.2 Sample preparation

Liquid-liquid extraction: 1 ml oil in 10 ml volumetric flask in acetonitrile, 10 min. stirring, wait until the upper phase is clear and transfer in sample vial for HPLC.

Injection volume: 1 μl

Mineral oil and natural ester separate into two phases with acetonitrile. Synthetic ester and acetonitrile are completely miscible.

4.3.3 Chromatographic conditions

Column: Hypersil BDS-C18, 125 mm x 3 mm (columns of different sizes are possible, provided that a suitable separation of the compounds is achieved).

Calibration should be verified to be linear in the range 1 – 500 mg/kg insulating liquid

Eluents: A – water, B – acetonitrile, Flow: 0,3 ml/min. Example for a gradient flow is shown on Table 13 and an example for the retention times on Table 14.

Table 13: Example for a HPLC gradient flow

Time (min)	A	B
0	40	60
2	40	60
4	20	80
8	2	98
20	2	98
22	20	80
24	40	60

Table 14: Example for retention time of the components

Substance	Detection Wavelength (nm)	Retention time (min)
Irgamet 39	263	2,08
DBP	273	10,38
DBPC	280	11,04
Irganox®109	280	14,76
Irganox®1010	280	21,23

There is information (60) that the method can be adopted to determine also t-butyl hydroquinone (TBHQ), however this has not been investigated in the RRT.

4.3.4 Mineral oils investigated in the Round Robin Test

The insulating liquids evaluated by this method have been the same as in Table 3, Section 1.7, page 16. Following laboratories took part in the Round Robin Test:

Labelec-Portugal, EEI Nikola Tesla-Serbia, EGAT-Thailand, Savita Oil Tech. Ltd-India, EFACEC-Portugal, Sea Marconi-Italy, Siemens-Germany, ABB-Norway.

A typical chromatogram of the compounds (100 µg/kg) dissolved in white oil (paraffinic oil with CAS Nr 8012-95-1) and then processed as described is shown in Figure 21.
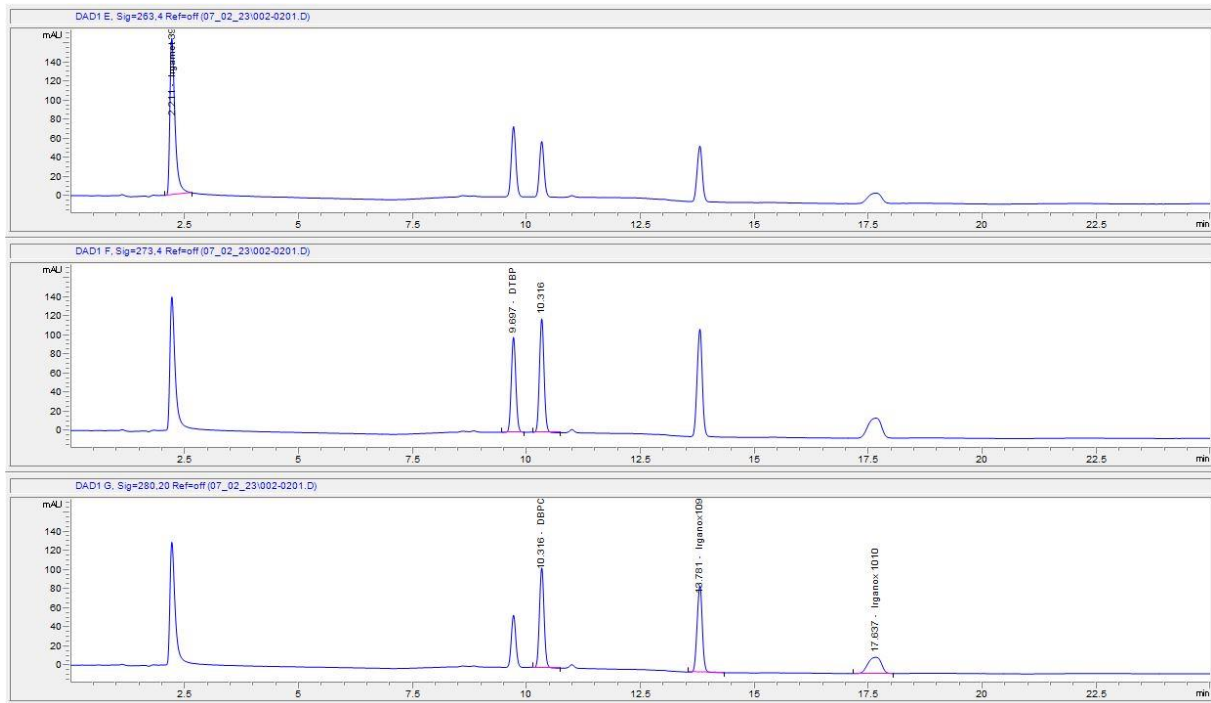
Figure 21: Typical chromatogram of the determined compounds dissolved in white oil and processed as described in 4.3.2 and 4.3.3

4.3.5 Disturbances in the measurement

A lot of UV-absorbing aromatic compounds can be present in the insulating liquids. These substances may interfere with the heavier additives (especially Irganox-type). Typically, inhibited oils (low aromatics) show few interferences. Some interferences with the uninhibited oil 1 and the reclaimed uninhibited oil 6 are shown below Figure 22 and Figure 23. Ultra high performance liquid chromatography (UPLC) diminishes the interferences (61), but cannot completely resolve them.

Interferences / OIL1 at 273nm
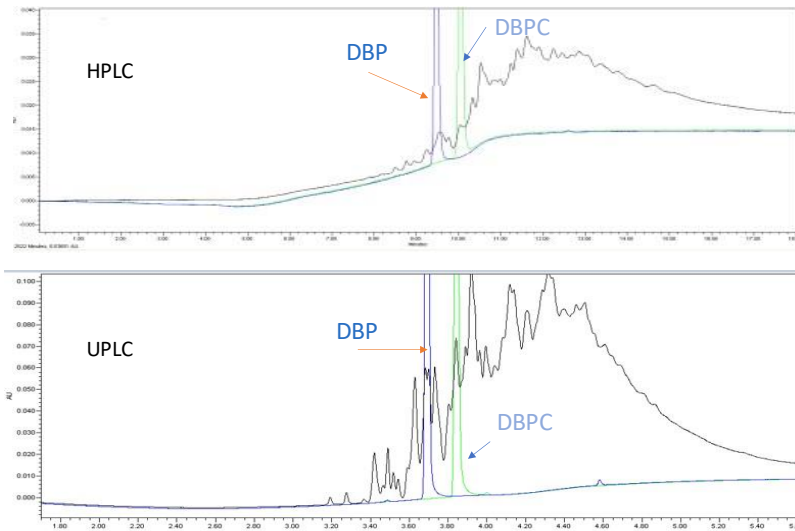
Figure 22: Interferences, detected with oil constituents at 273 nm at the example of oil 1

Interferences / OIL6 at 280nm
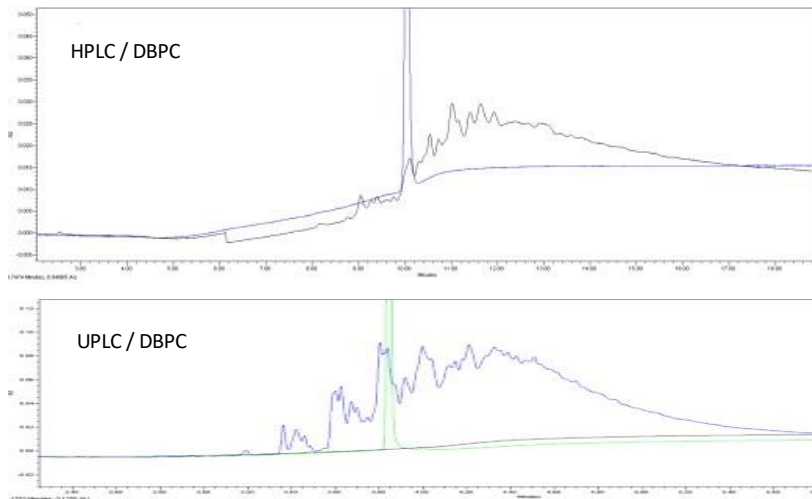
Figure 23: Interferences, detected with oil constituents at 280 nm at the example of oil 6

A well known method for the detemination of DBPC is by means of gas chromatography or GC-MS according to IEC 60666 (53). A typical GC sprectrum is shown on Figure 24.

GC METHOD
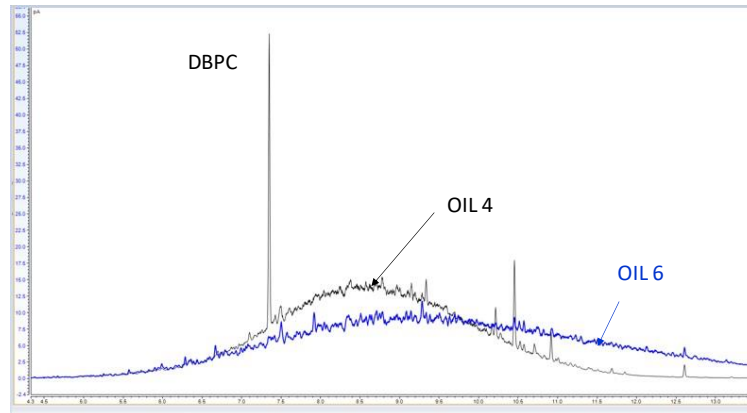
Figure 24: A typical spectrum of DBPC by means of gas chromatography

4.4   Results of the Round Robin Test for additives

At this stage, few laboratories have participated in the RRT and the divergency in results is high. The available results are shown in detail in Annex B (see Annex B. Results for Round Round Robin test for additives). This method will be further developed to deliver more reproducible results.

5 Ageing monitoring in insulating liquids via inhibitor consumption

5.1 Introduction

The role of primary antioxidants in insulating oil is to slow down oil oxidation and act as radical destroyers in the oil. For inhibited insulating oil this antioxidant (usually synthetic) is added to the oil prior to oil delivery (see 4.2.1, page 38).

The ageing behaviour of inhibited mineral insulating oils is that as they undergo oxidation in an oil-filled electrical equipment firstly the inhibitor (primary anti-oxidant) is gradually depleted. The progression of oxidation (and therefore production of significant acids) is nearly completely stopped until the inhibitor reaches the "minimum sufficient concentration" for that particular oil. IEC 60422 gives guidance around the management of inhibitor. Experience shows that topping up the inhibitor before the inhibitor concentration has reached 40% of its original value (but preferably between 40-60%) is best engineering practice. This sufficiently ensures that the top-up occurs before reaching the minimum sufficient concentration for a wide range of inhibited insulating oils in use. Measurement of inhibitor (primary phenolic type – which is the most widely used) is very mature for mineral oils and methods are well described in IEC 60666.

The consumption of the inhibitor in service can be monitored following the procedure for oxidation stability according to IEC 61125. Existing experience on monitoring inhibitor depletion and volatile acids would enable better prediction of oil behaviour in service and allow an improved maintenance of paper/oil insulation. The inhibitor testing can be done with alternative methods, e.g. HPLC, since this would allow very low amount of oil to be used. A similar approach can also be used in the maintenance of natural and synthetic esters since they all contain primary antioxidants.

In the following the experience with following up the inhibitor of unused and reclaimed mineral oils in service is presented.

5.2 Assessing of oxidation stability by inhibitor consumption in unused and reclaimed inhibited mineral oils – laboratory investigation

For the test setup the oxidation procedure of IEC 61125 (31) with some modifications (increased number of tubes for repeated measurements) has been utilized. During the oxidation stability test (during the 500 hours) measurements of volatile acidity (VA) and inhibitor content (DBPC) were performed (62).

The experiment was performed in order to investigate the suitable way of performing DBPC measurement during 500 h in five time intervals, in order to create inhibitor consumption curve. This was done by taking 1 ml of oil from the same ageing tube five times and once at each time interval from five ageing tubes, in order to compare results and see whether decreased amount of the oil after multiple measurements had an impact on the result in comparsion to the higher amount of the oil in tubes which were sampled once.

At the end of 500 h, measurements of DDF (dielectric dissipation factor), TA (total acidity) and sludge were performed.

Seven inhibited oils were tested (3 unused and 4 recycled), as shown in Table 15.

Table 15: Types of oil tested (modified IEC 61125 method)

	Oil	Description
Unused oils	Unused oil 1	High grade unused oil
Unused oils	Unused oil 2	High grade unused oil
Unused oils	Unused oil 3	Standard grade unused oil
Recycled oils	Oil 1	Re-refined using desulphurization and dechlorination technology on-site
Recycled oils	Oil 2	Re-refined using desulphurization and dechlorination technology on-site
Recycled oils	Oil 3	Reclaimed with fuller earth + reagent - originally inhibited with 0,25 % DBPC, additionally re-inhibited up to 0,34 % DBPC
Recycled oils	Oil 4	Reclaimed with fuller earth + reagent – uninhibited, additionally re-inhibited up to 0,34 % DBPC

The properties of recycled oils prior and after the reclamation/re-refining process are shown in Table 16.

Table 16: Properties of recycled oils before and after the reclamation/re-refining process

Oil property	Oil 1		Oil 2		Oil 3		Oil 4	
	before	after	before	after	before	after	before	after
DDF, 90 ºC	0,0147	0,004	0,0031	0,0014	0,00714	0,00470	0,1358	0,0310
Acidity, mg KOH/g	0,01	<0,01	0,02	<0,01	<0,01	<0,01	0,543	<0,01
IFT, mN/m	35	47	39	44	/	/	/	/
DBPC, %m	0,30	0,34*	0,30	0,42*	<0,01	0,32*	<0,01	0,34*
DBDS, µg/kg	78,4	n.d.	39,7	1,47	127	2	< 1	< 1
PCB, µg/kg	8	2	62	11	< 2	< 2	/	/
Irgamet® 39, µg/kg	n.d.	n.d.	/	/	97	< 5	97	< 5

n.d. – not detectable,

* - additional inhibitor added after the process

The results of the inhibitor depletion in unused and reclaimed oils is shown on Figure 25 and Figure 26 and the results for total acidity (TA), DDF at 90 °C and sludge after 500 h ageing procedure at 120 °C acc. IEC 61125 on Figure 27 and Figure 28 respectively.

5.2.1 Results and discussion on the inhibitor depletion in unused Oils

There was a marked difference in inhibitor consumption between high grade unused oils and standard grade oil (Figure 25). Based on the results of DBPC measurement during the ageing the unused oils, it can be seen than DBPC was not completely consumed after 500 hours of ageing of unused oils 1 and 2, which are "high grade" oils, in comparison with „standard grade Unused oil 3", where DBPC was not detected, after 500 hours of ageing. Both high grade oils had similar consumption rate and Total acidity, suldge and DDF results after 500 h of ageing.

5.2.2 Results and discussion on the inhibitor depletion in reclaimed oils

Recycled oils had lower resistance to ageing in comparison to high grade unused oils. However, recycled oils 1 and 2 had the same inhibitor consumption like new standard grade oil 3 (Figure 25 and Figure 26), DBPC was consumed after 500 h. Other two recycled oils were much less resistant to oxidation ansd inhibitor was consumed after shorter period (Figure 26).
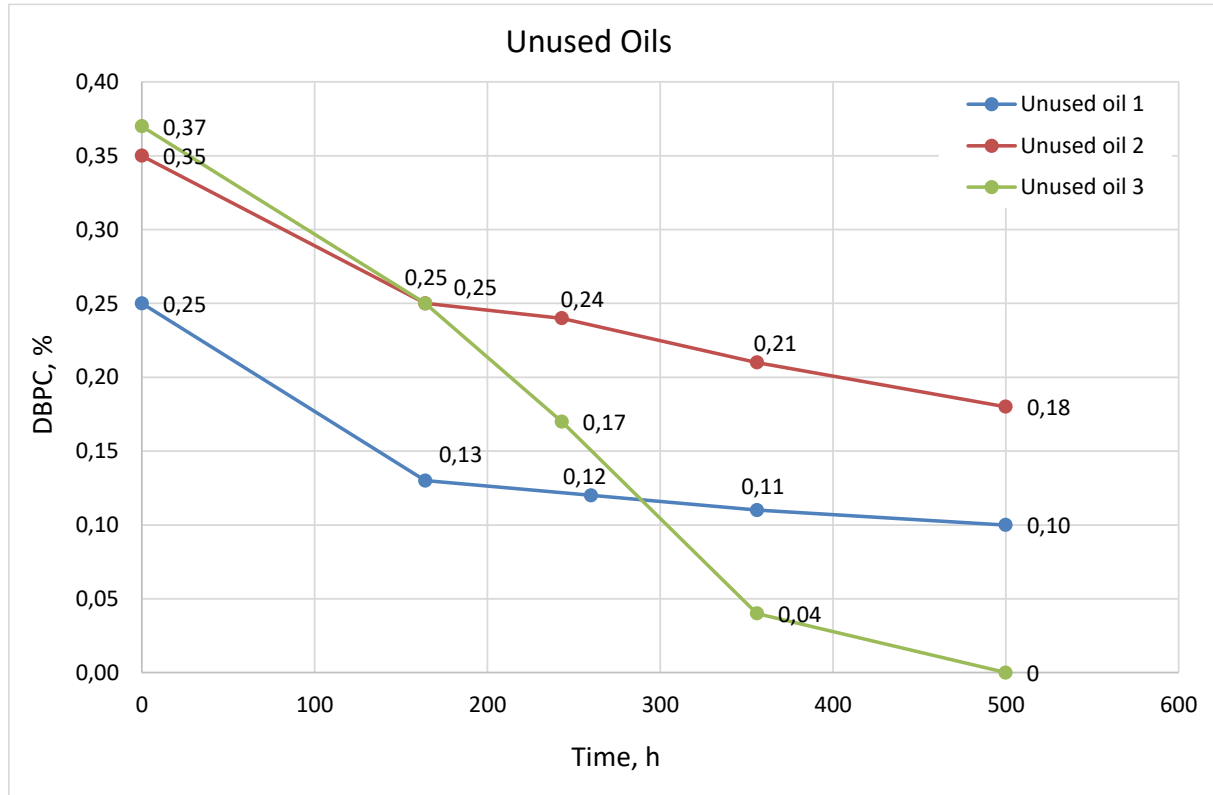
Figure 25: Consumption of DBPC during the ageing of unused oils
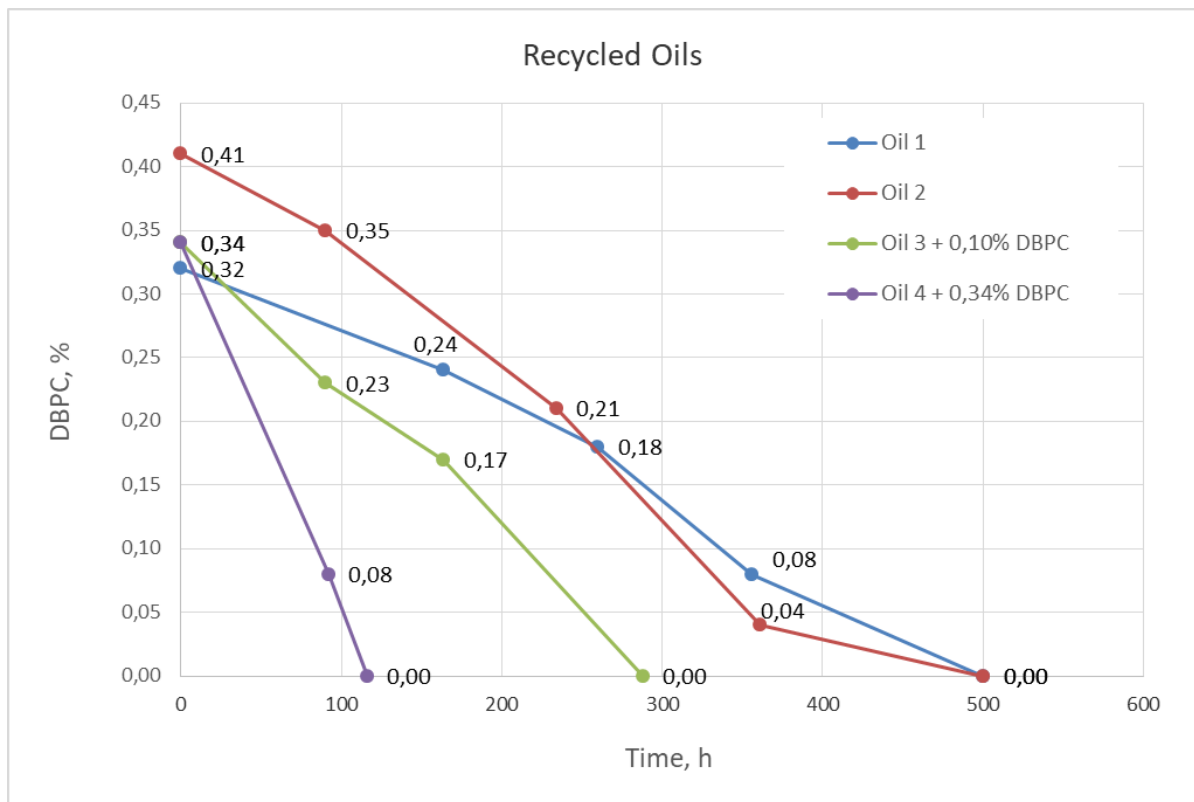
Figure 26: Consumption of DBPC during the ageing of recycled oils
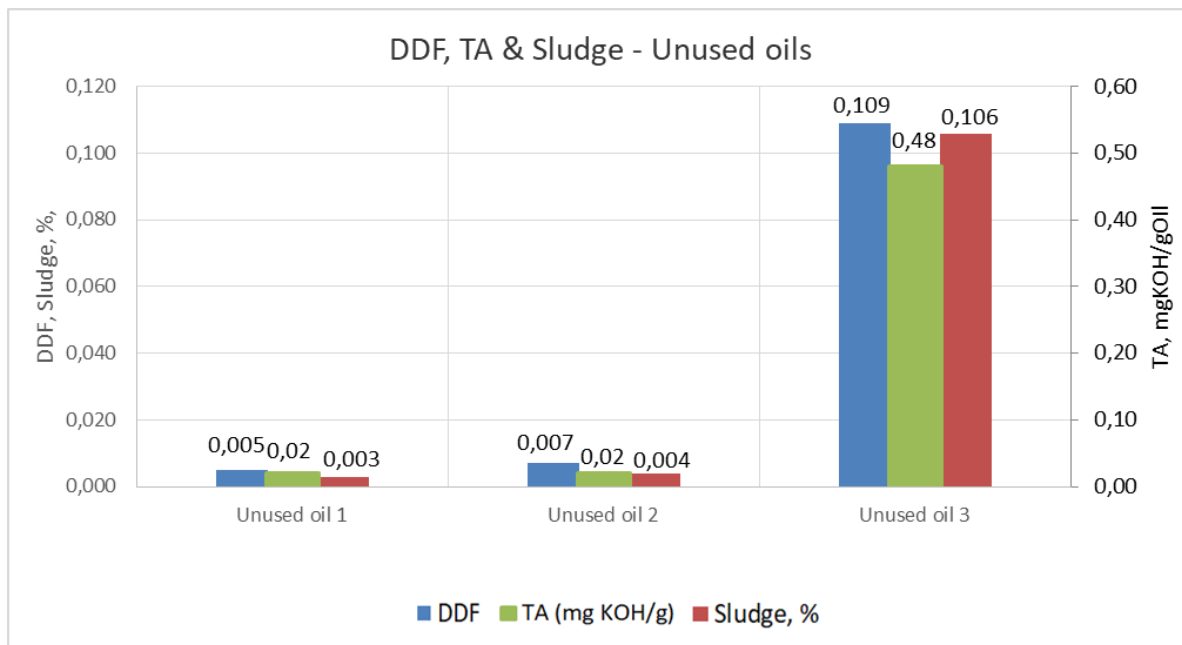
Figure 27: Results of DDF, TA and sludge after 500 hours of ageing of unused oils

48
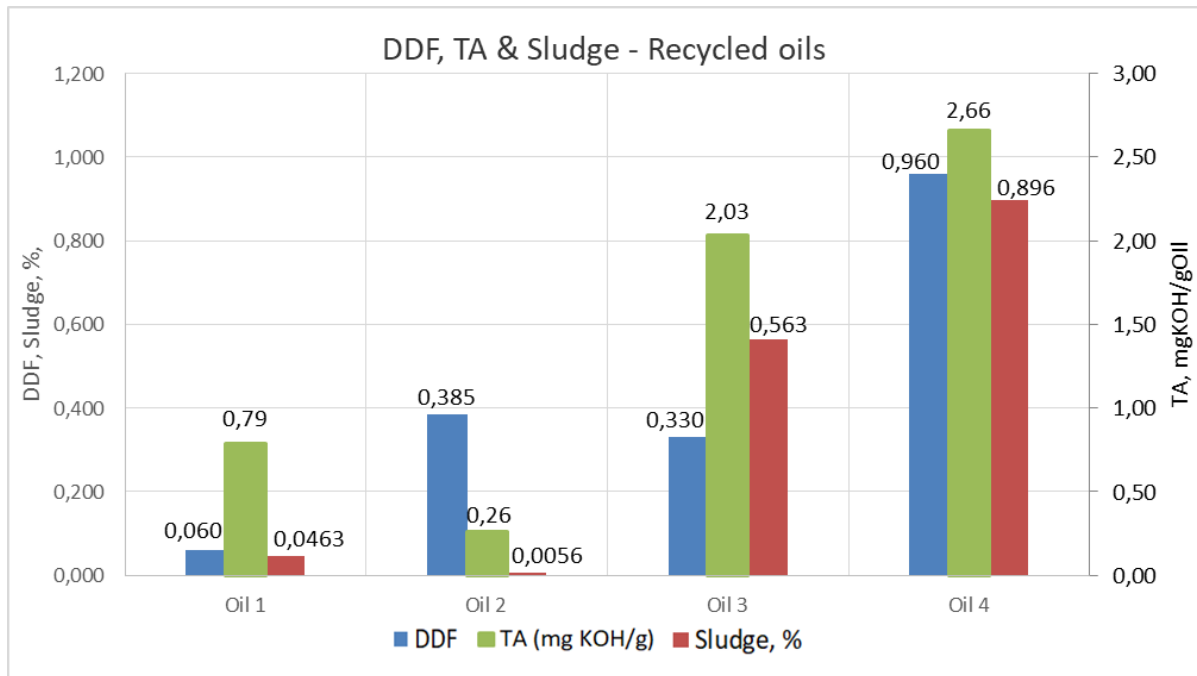
Figure 28: Results of DDF, TA and sludge after 500 hours of ageing of recycled oils

Recycled oils under investigation were of different degree of refining. Oils 1 and 2 were more refined. This was obtained using dechlorination and desulphurization tehconology, while oils 3 and 4 were reclaimed oils using fuller's earth and reagent to remove DBDS and acidity. Marked difference in degree of oils refining was observed comparing different initial oil properties and this had significant impact on different oxidation stability of these oils (Figure 26 and Figure 28).

After 500 hours of ageing higher values of DDF, total acidity and sludge were observed for recycled oils 3 and 4, in comparison with oils 1 and 2, which is in correlation to higher DBPC consumption during ageing of recycled oils 3 and 4 (DBPC was completely consumed after 288 h (oil 3) and 116 h (oil 4).

Recycled oils 1 and 2 will have slower ageing rate during its further service in electrical equipment in same or similar working conditions in comparison to oil 3 and 4. Oil 4 was reclaimed too late, when oil reached advanced degradation stage. These examples show the importance of reclaiming or re-refining of service aged oils in due time, before advanced stages of oxidation are reached, in order to obtain longer extended life of the oil after treatment.

No significant difference in consumption of DBPC was observed when oil was taken at each time interval from different 5 tubes and from the same tube five times. This observation will enable future application of this measurement with only one additional tube per each oil, in total 5 tubes.

5.2.3 Comparison between DBPC consumption and development of volatile acidity (VA) for unused and reclaimed mineral oils

Comparison of DBPC consumption in different tubes and VA are shown on the following Figure 29 - Figure 35, for Unused and Recycled oils.

It was obvious that high rate of production of volatile acids occurred after the inhibitor was consumed in standard grade new oil 3 and in reclaimed oils 1 and 2, while the rate of volatile acids production in high grade oils was similar through the whole ageing period (Figure 29 - Figure 31). Increase of the VA production was observed at DBPC levels between 0.05 - 0.10 %.

These results are showing the importance of monitoring the inhibitor consumption during service, since after it is being consumed high amount of volatile acids can be generated. Volatile acids are of lower molecular weight and may be aggressive towards paper degradation. During the ageing of new and recycled oils VA were generated in approx. 50% of total acids (TA). This ratio of VA to soluble acidity can be different and it would be good practice to have these data available for further monitoring of oils in service.
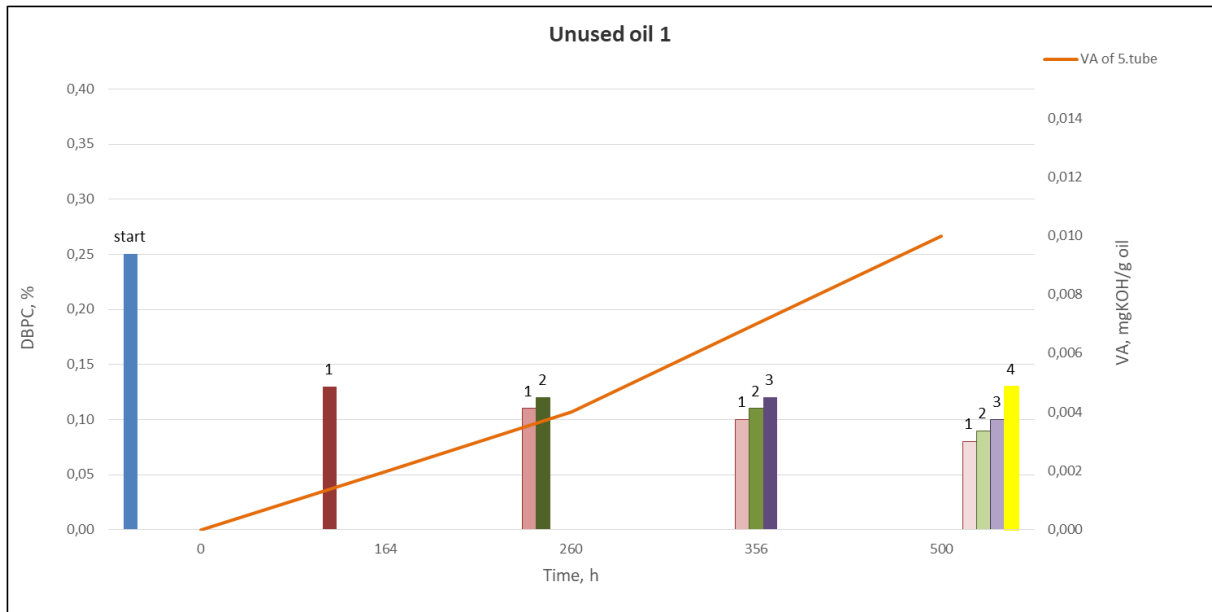
Figure 29: Consumption of DBPC and VA during the ageing of unused oil 1
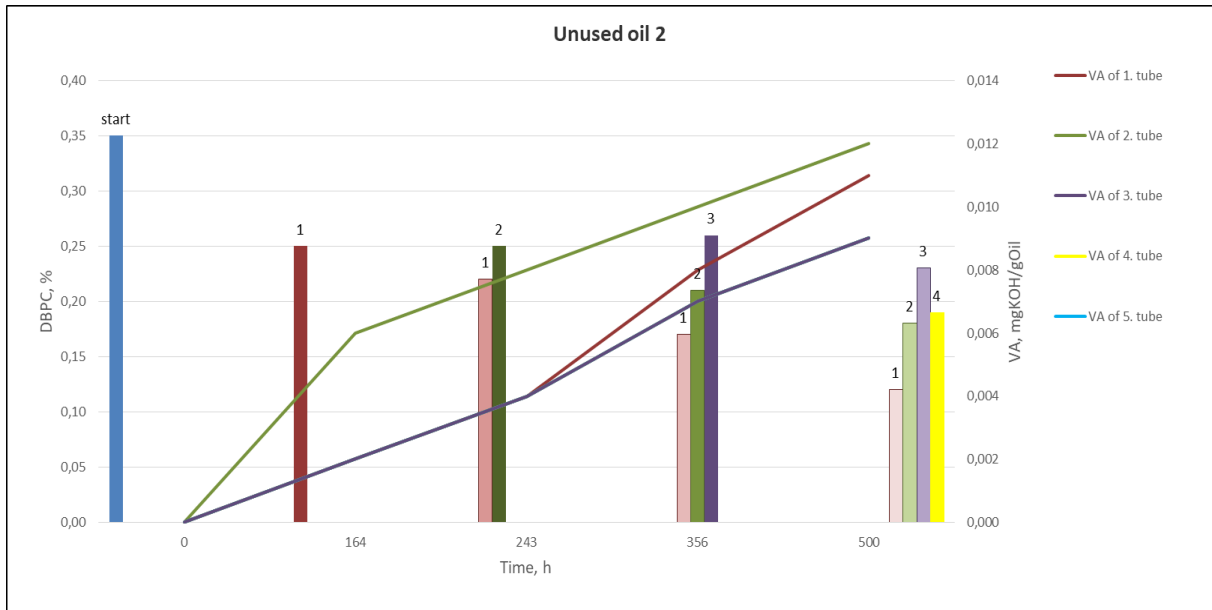
Figure 30: Consumption of DBPC and VA during the ageing of unused oil 2
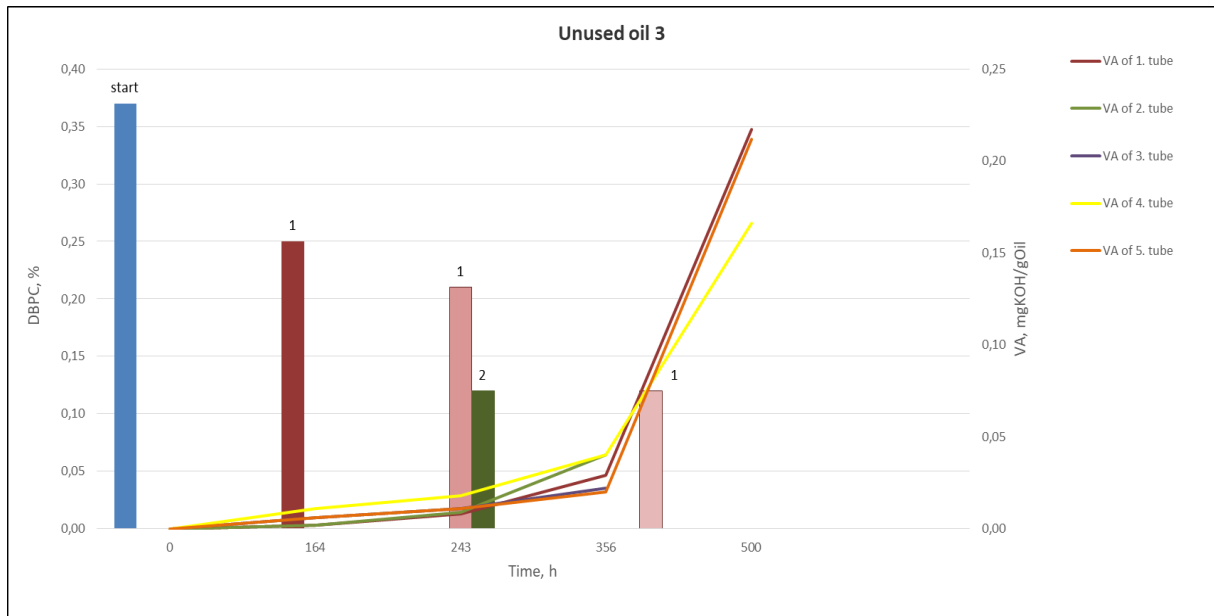
Figure 31: Consumption of DBPC and VA production during the ageing of unused oil 3
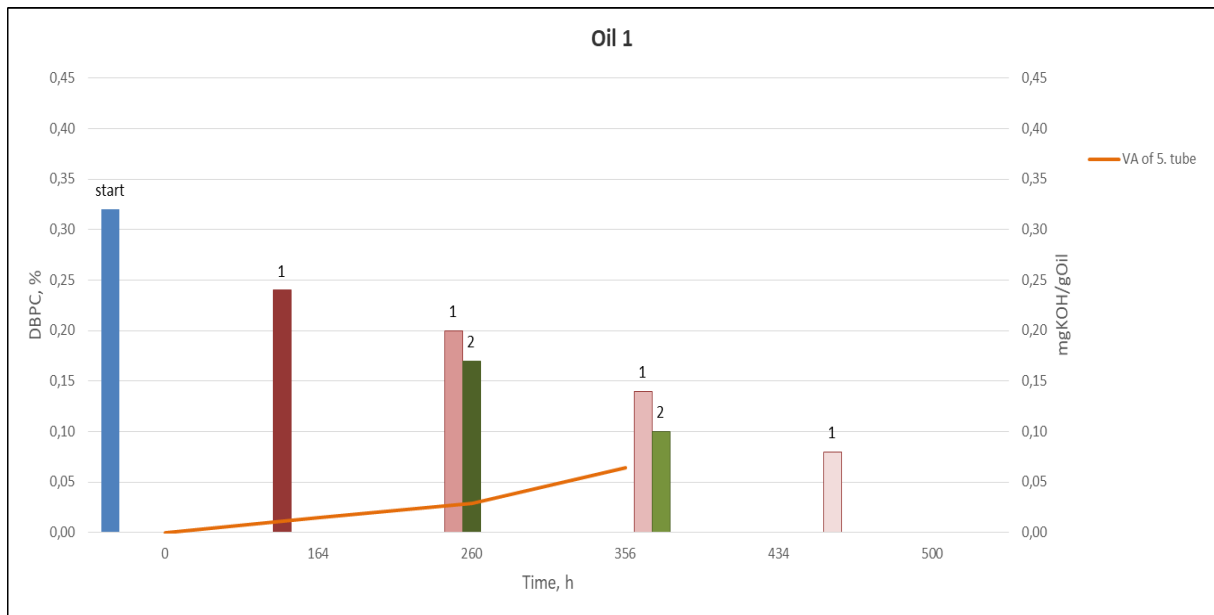
Figure 32: Consumption of DBPC and VA production during the ageing of recycled oil 1
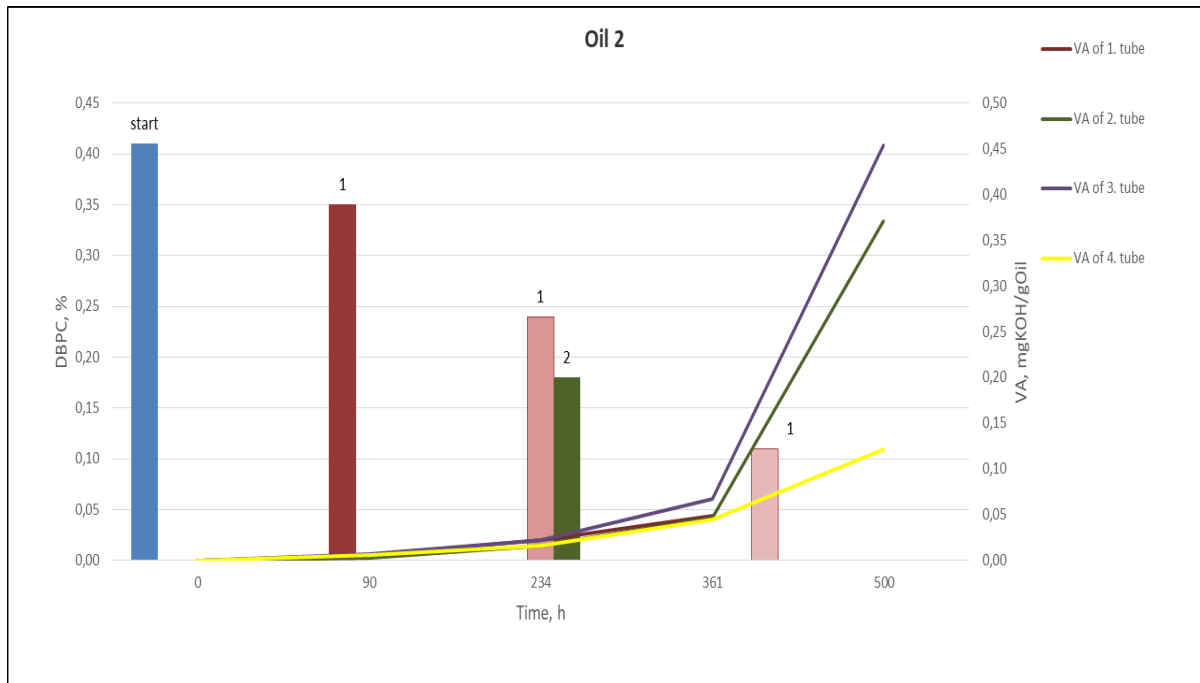
Figure 33: Consumption of DBPC and VA production during the ageing of recycled oil 2
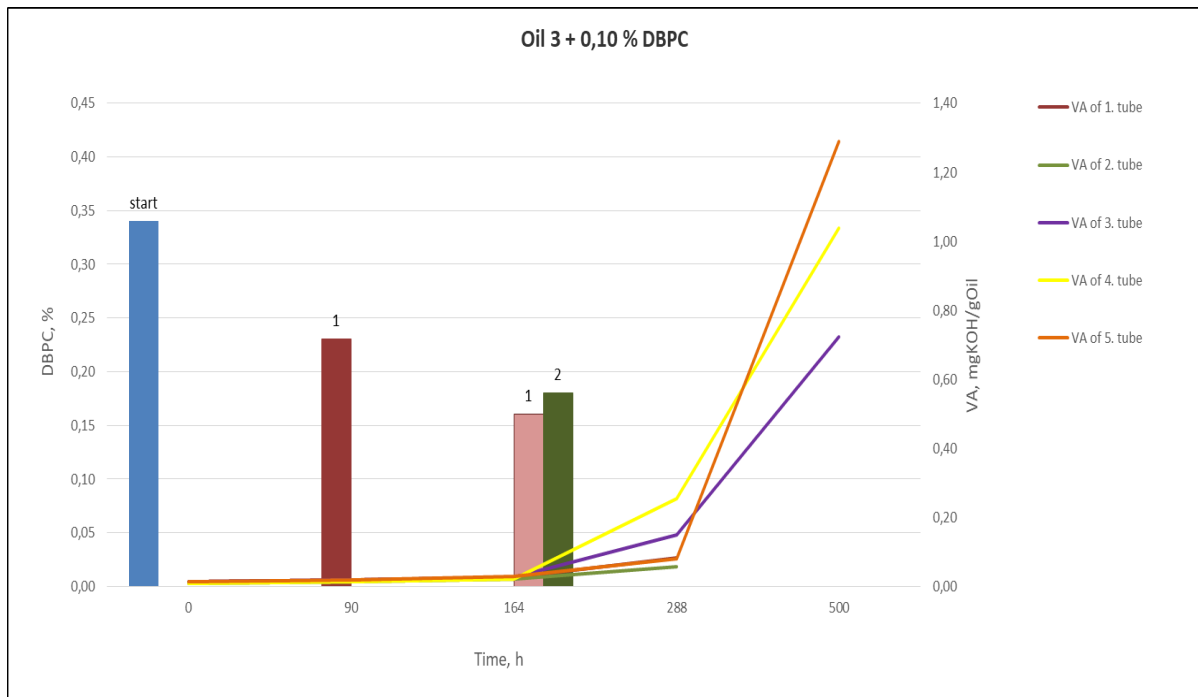
Figure 34: Consumption of DBPC and VA production during the ageing of recycled oil 3
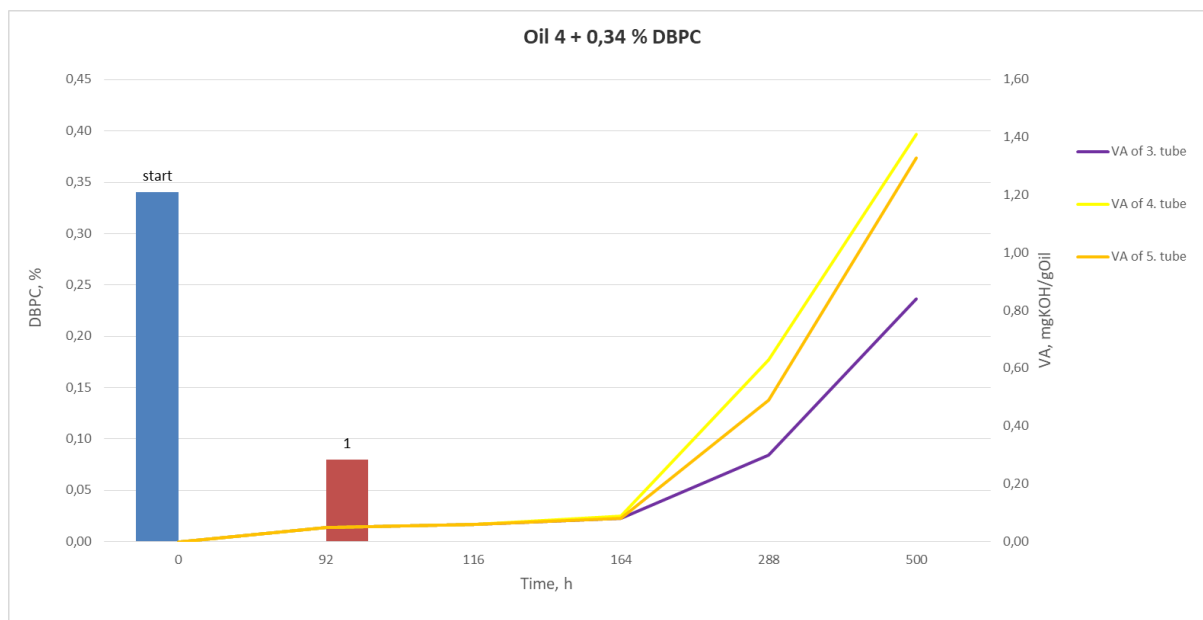
Figure 35: Consumption of DBPC and VA during the ageing of recycled oil 4

5.2.4 Conclusion

These results are showing the importance of monitoring the inhibitor consumption during service, since after it is being consumed high amount of volatile acids can be generated. Volatile acids (VA) are of lower molecular weight and may be aggressive towards paper degradation. During the ageing of new and recycled oils VA were generated in approx. 50% of total acids (TA). This ratio of VA to soluble acidity can be different and it would be good practice to have these data available for further monitoring of oils in service.

For other insulating fluids, such as natural esters, monitoring of the inhibitor content is of at most importance, to obtain DBPC, or other inhibitors, consumption curve and maintaining oxidation stability. After ageing, besides volatile and soluble acids measurements, instead of DDF measurement, viscosity measurement would be more beneficial in terms of the evaluation of the functional properties of the insulating liquid.

5.3 Consumption of inhibitor and related changes in oil properties – examples from mineral insulating oils in service (experience in Serbia)

Monitoring of the condition of the oil during service and its ageing rate are important. Inhibitor consumption can predict the decay of oil properties and result in timely reclamation and/or oil replacement. The response of the oil to the inhibitor can vary, depending on the degree of refining of the base oil (63). This difference in response can be manifested as differences in the amount of oil ageing for certain DBPC content. This can be seen in practice, oils of higher quality may retain low acidity for a long period even when the DBPC content is mostly consumed (Figure 36, Figure 37), while some oils have higher acidity for higher DBPC content (Figure 38).

5.3.1 Example 1: GSU in hydro power plant, 220/15,65 kV, 100 MVA, oil in service since 1966
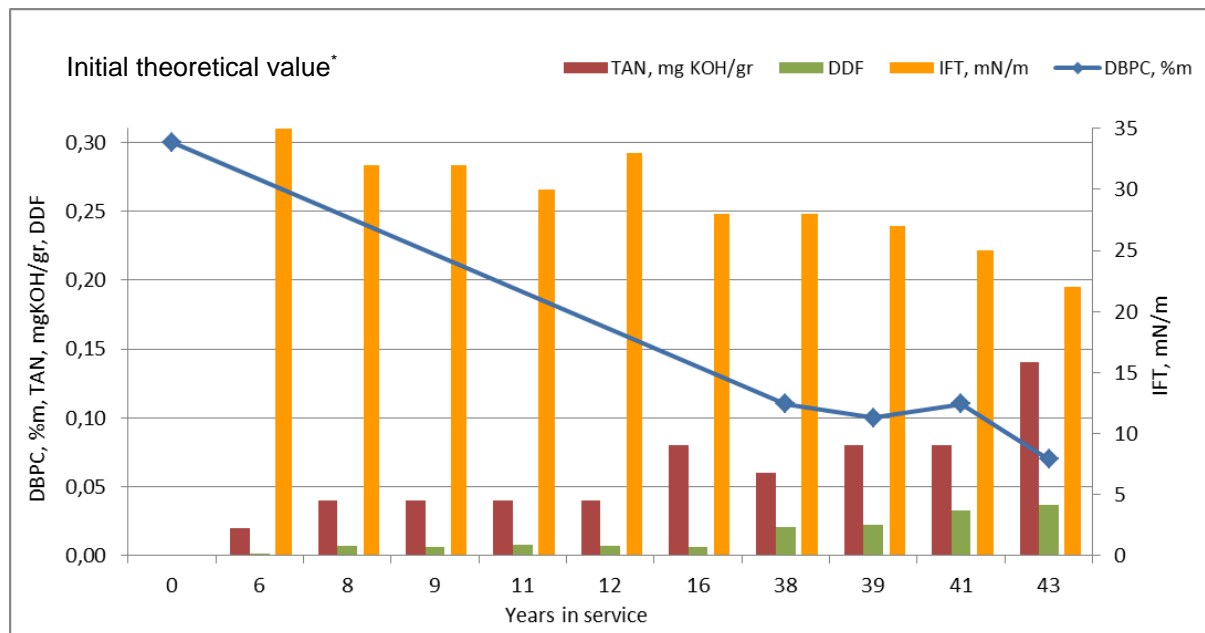
Figure 36: DBPC consumption and change of Acidity (TAN), IFT and DDF of oil from transformer in a hydro power plant

5.3.2 Example 2: GSU in a thermal power plant, 10,5/121 kV, 120 MVA, oil in service since 1982
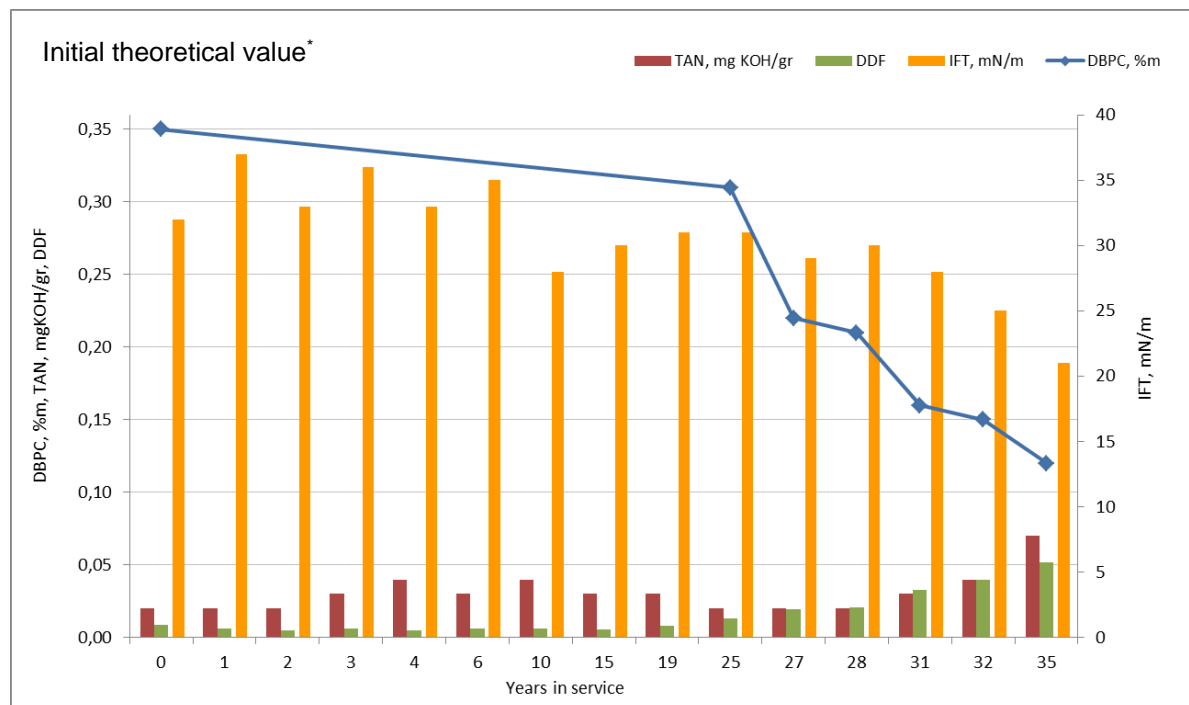
Figure 37: DBPC consumption and change of Acidity (TAN), IFT and DDF of oil from transformer in thermal power plant

5.3.3   Example 3: Transformer from distribution system, 110/35 kV, 31,5 MVA, oil in service since 1974
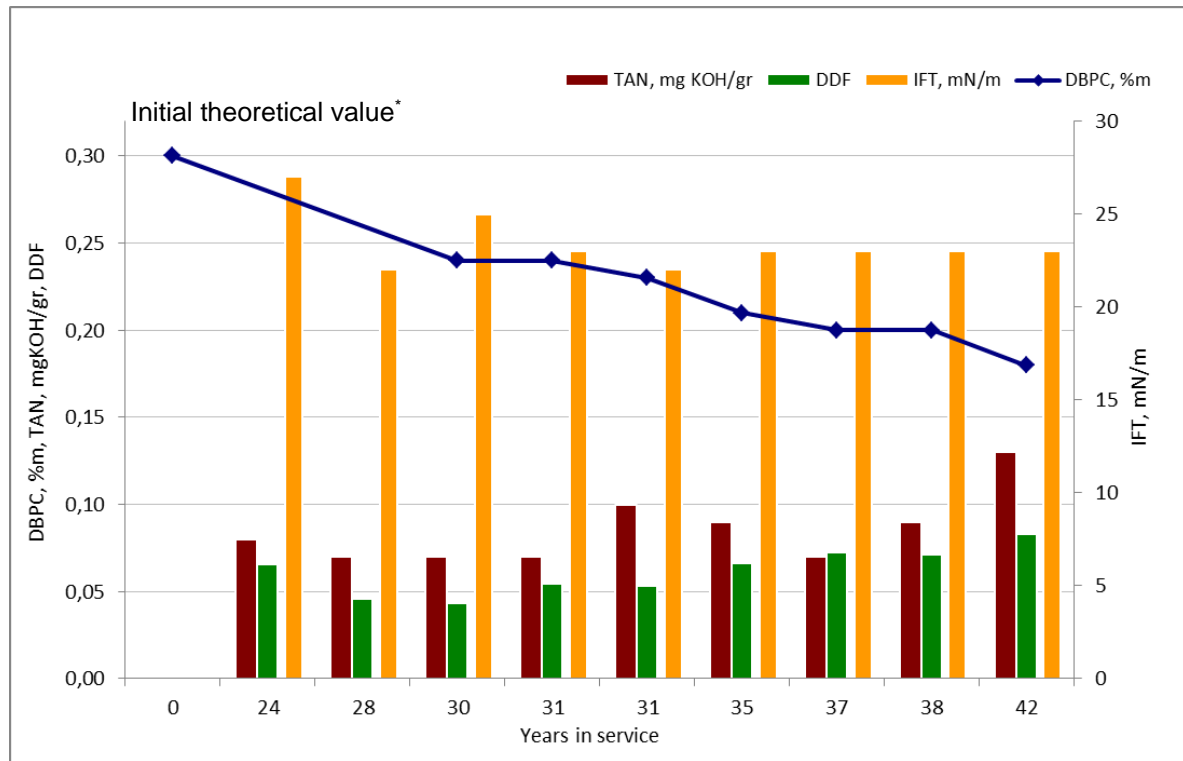
Figure 38: DBPC consumption and change of Acidity (TAN), IFT and DDF of oil from transformer in distribution system, 110 kV

A relatively slow consumption of DBPC of oils in service in transformers of differnt application (HPP, TPP, Distribution) was observed (Figure 36 - Figure 38). After the inhibitor was consumed below 0,10-0,15 % ageing rates became faster (Figure 36 - Figure 38). Most significant increase of acidity was observed in the oil of transformer with lowest DBPC content (Figure 36). Differences amoung oils were observed, due to difference in base oil quality. Apart from oil quality, transformers design, preservation system (presence of oxygen), and in particular working conditions of transformer (load, stresses) can have a significant impact on oil ageing.

Comparison of inhibitor content of high grade new oils after 500 h oxidation stability test show that this value (0,10%-0,15 %) corresponds to oils in service after approximatelly 40 years.

5.4   Alternative methods for the determination of oxidation stability of mineral oils

5.4.1   Introduction

Long testing times (500 h) for the testing of oxidation stability according IEC 61125 are not oil manufacturers and customer friendly and lead to big deviations and inadequate repeatability and reproducibility. There is a need for shorter and more efficient testing method for inhibited oils.

5.4.2   RPVOT method

The RPVOT stands for 'Rotating Pressure Vessel Oxidation Test' (previously called RBOT, Rotation Bomb Oxidation Test).

The ASTM D2112 (RPVOT) method can be used to screen the oxidation stability of unused mineral insulating oils but is applicable only for fully-inhibited type mineral oils (64). ASTM D3487 (2016), which is an internationally used Standard Specification for Mineral Insulating Oil Used in Electrical Apparatus, gives a specific property requirement for RPVOT of minimum 195 minutes for type II oils (meaning insulating oils where greater oxidation resistance is required and where this is usually achieved by the addition of a suitable oxidation inhibitor) (65) .

Figure 39 below shows the basic set-up of the RPVOT analysis method and a typical analysis result graph.
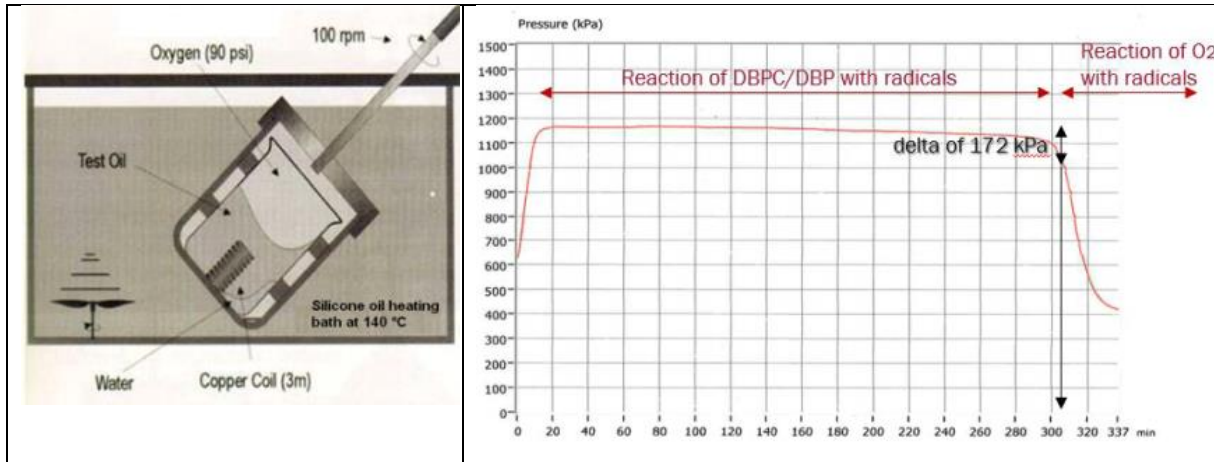
Figure 39: basic set-up of the RPVOT analysis method and a typical analysis result graph

This accelerated ageing test determines how long the mineral insulating oil with its amount of added synthetic phenolic antioxidant (mostly DBPC) can resist degradation before the formed radicals start to react with oxygen. The longer it takes before a specific pressure drop of oxygen is detected (an indication of significant oxygen consumption), the better the combination of base oil and phenolic antioxidant to resist degradation/oxidation.

Figure 40 shows the relationship between the RPVOT result according ASTM D2112 and oxidation stability result according IEC 61125 (500h incubation). In this figure results are given for 25 different unused mineral oil samples fully-inhibited type which were produced during 2014-2019 period.

The data of Figure 40 indicate that an analysis result of 300 minutes or higher when performing a RPVOT test according ASTM D2112 should give an analysis result of total acidity lower than 0,3 mg KOH/g oil when IEC 61125 500h test would be performed (66).
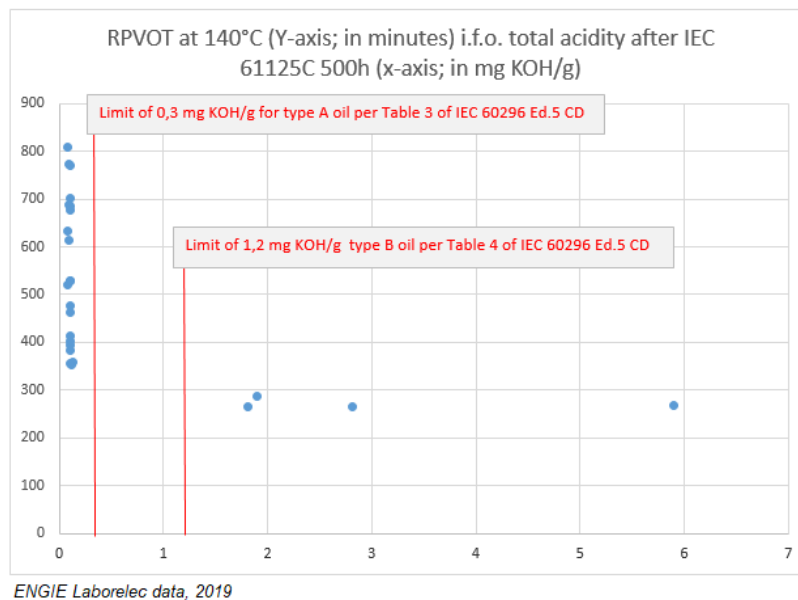
Figure 40: Relationship between the RPVOT-result according ASTM D2112 and oxidation stability result according IEC 61125 (500h incubation)

5.4.3   Conclusion

This method has some advantages, e.g. it gives a quick and reproducible result, but it also has some disadvantages, it is applicable for fully inhibited oils with DBPC as only inhibitor. Some earlier tests show that the implementation of further inhibitors may lead to misinterpretation of the oil performance (67).

5.5   Alternative methods for the determination of oxidation stability for natural esters

5.5.1   Principle of the method

In Brasil the method for oxidation induction period is widely used for the comparison of the oxidation stability between different natural esters (68).

The principle of the method consists in the monitoring of an ageing parameter with time. The change of the initial slope of ageing is an indication of the depletion of oxidation inhibitors to an extent which strongly accelerates the ageing behaviour(Figure 41). The comparison of this oxidation time between different natural esters allows a comparison between their oxidation stability. The method is based on EN 14112 (69) and carried out without the presence of copper. The recommendation is to use Hogh air flow (10 l/h) and 130°C in order to shorten the test time. The method allows a continuous monitoring of conductivity in the water trap, which is correlated to volatile and total acidity.
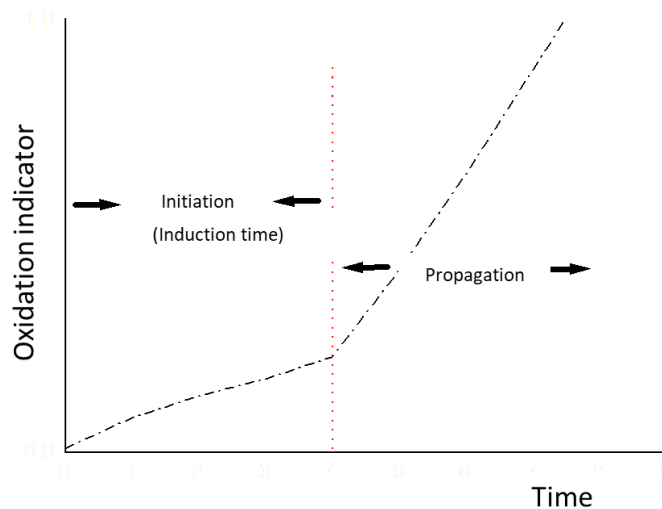
Figure 41: General presentation of the oxidation procedure according EN 14112 (69)

5.5.2 Results

Four different natural esters have been evaluated according to EN 14112 at 130 °C
and air flux of 10 l/h with the determination of induction period (IP) in hours. The results are
presented on Table 17. Natural esters 1 and 2 have the same amount of fatty acids, however,
different unknown additives.

**Table 17:Induction period (IP) in hours of 4 different natural esters tested at 130 °C and air flux of 10 l/h
according to EN 14112**

Natural esters type	Stearic acid (saturated fatty acid) %	Oleic acid (monoinsaturated fatty acid) %	Linoleic and linolenic acids (poly(unsaturated acids))	IP (h)
Natural ester 1 (polyinsaturated)	15.85	25.35	58.80	3
Natural ester 2 (polyinsaturated)	15.85	25.35	58.80	13
Natural ester 3 (polyinsaturated)	18.36	35.28	46.36	15
Natural ester 4 (polyinsaturated)	13.90	87.74	28.36	40

5.5.3 Conclusion

The method has some advantages and disadvantages. Advantage of the method is that it can well
differentiate by the induction period (IP) between different natural esters, which has not been possible
in the described case using ASTM D2440 and IEC 61125 methods. A disadvantage is the high air flux
used (10 l/h) of EN 14112 which does not represent the service conditions when using natural esters,
since those are operated in transformers with air exclusion.

6 Measurement of thermal characteristics for insulating liquids

6.1 Introduction

The thermal performance of an oil-filled electrical equipment requires knowledge of the oil thermal characteristics like thermal conductivity, specific heat capacity, thermal expansion coefficient. They are, however, not to be considered as acceptance, but as design parameters. WGs and users dealing with transformer thermal modelling need numerous values concerning liquid and solid insulation at different temperatures. One aim of Cigre D1.70 was to determine the most used methods for the determination of :

- Density
- Viscosity
- Thermal conductivity
- Specific heat capacity

in insulating liquids at different temperatures and the measurement uncertainties of those.

6.2 Analytical methods

The measurement of density and viscosity in insulating liquids is well known.

Density ρ (g/cm^3) is measured according to ASTM D1298 / ISO 3675 / ASTM D7042
Kinemaitic viscosity V (mm^2/s) is measured according ISO 3104 / ASTM D 445 / ASTM D7042
Thermal conductivity λ(T) (W/(m•K)), describes thermal transport and

$$\lambda(T) = \rho(T). C_p(T). \alpha(T)$$

Equation 1

Where:
ρ(T) Density, (g/cm^3), material characteristics
C_p(T) Specific heat capacity, (J/gK) describes ratio of the heat added to (or removed from) an object to the resulting temperature change
α(T) Thermal diffusivity, (cm^2/s), material characteristics

can be theoretically calculated if density, specific heat capacity and thermal diffusivity are well known. Thermal diffusivity in liquids can be measured only at room temperature due to convection.

The methods for measurement of those characteristics in insulating liquids are the following:

Thermal conductivity can be measured acc. ASTM D 7896 (Standard Test Method for Thermal Conductivity, Thermal Diffusivity and Volumetric Heat Capacity of Engine Coolants and Related Fluids by Transient Hot Wire Liquid Thermal Conductivity Method), 2014 (70).

Specific heat capacity can be measured acc. to DSC method (ASTM E1269-11) (71).

Thermal diffusivity for liquids can be measured only at 20 °C because of convection phenomena) (70) .

Heat of combustion - ASTM D240:2019 (Standard test method for heat of combustion of liquid hydrocarbon fuels by bomb calorimeter (72) oder ISO 1716:2018 (Reaction of fire tests for products – Determination of the gross heat of combustion (calorific value)) (73).

Thermal expansion coefficient is determined according to (ASTM D1903:2008) and is actually based on calculation of densities at different temperatures (74).

6.3 Scope of the small Round Robin Test carried out on thermal properties of insulating liquids

Following labs took part at the restricted RRT conducted (not all labs could determine all properties at all insulating liquids and at all temperatures): Shell Global solutions, Siemens, Ergon Refining, Nynas, Austrian Institute of Technology, M&I.

Temperature region: -30 °C – + 140 °C (however not all temperatures could be measured by all laboratories)

Following insulating liquids have been investigated:

10   Inhibited naphthenic (a blend of two different naphthenic sources, different crude sources and different suppliers) acc. ASTM D3487

20   Inhibited isoparaffin acc. ASTM D3487

30   Uninhibited naphthenic acc. IEC 60296

40   Inhibited naphthenic (one of the components (~2/3) in 10) acc. ASTM D3487

4   Inhibited naphthenic, high grade acc. IEC 60296

8   Synthetic ester acc. 60199

Key measured properties of the restricted Round Robin Test were:

- Density (ISO 12185, ISO 3675, ASTM D7042)

- Kinematic Viscosity (ISO 3104 / ASTM D445 / ASTM D7042)

- Thermal Conductivity (hot wire method, ASTM D7896:19)

- Specific Heat Capacity (ASTM E1269, DSC)

Some results are graphically shown in order to illustrate the comparibility of results between different labs.
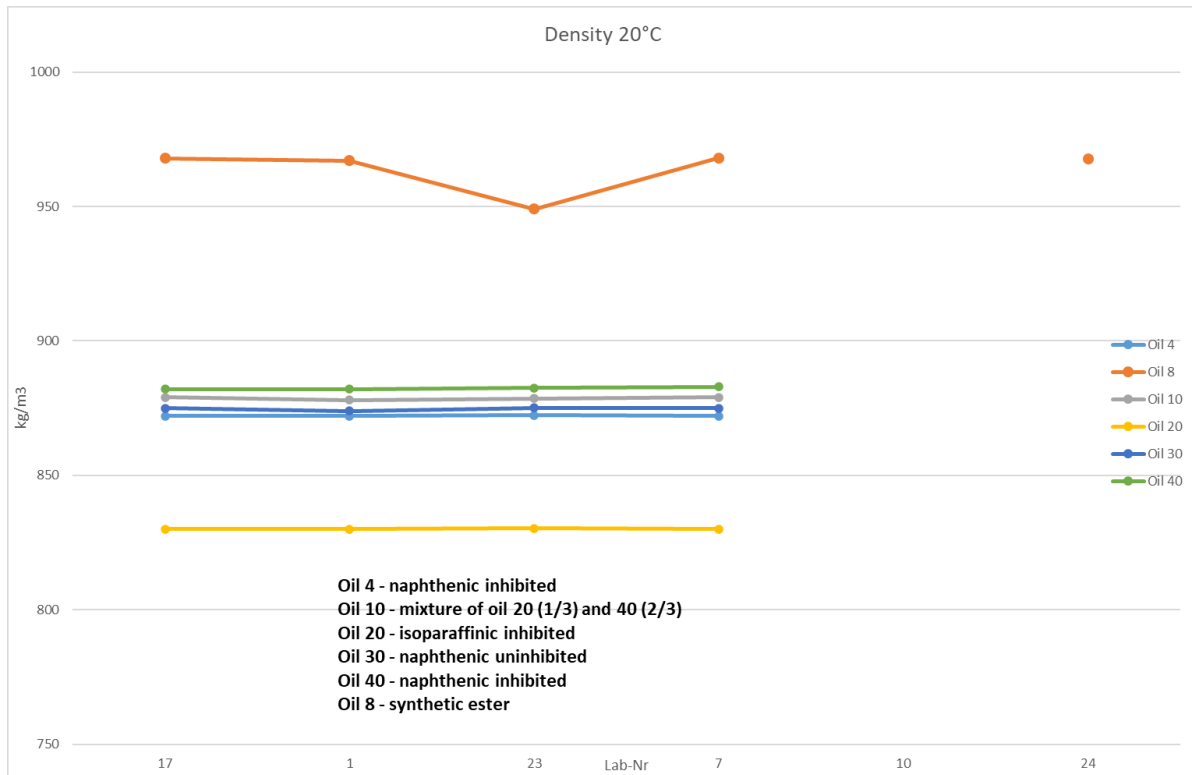
Figure 42: Density measurement at 20 °C
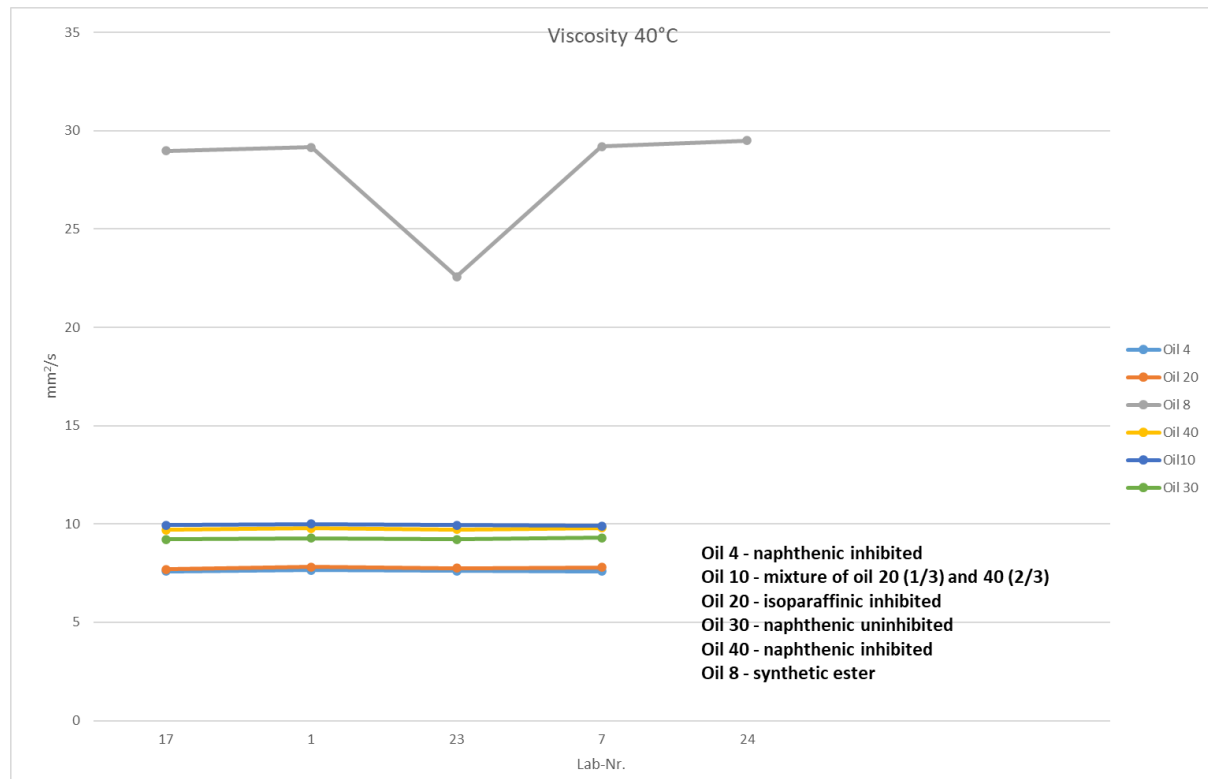
Figure 43: Viscosity measurement at 40 °C
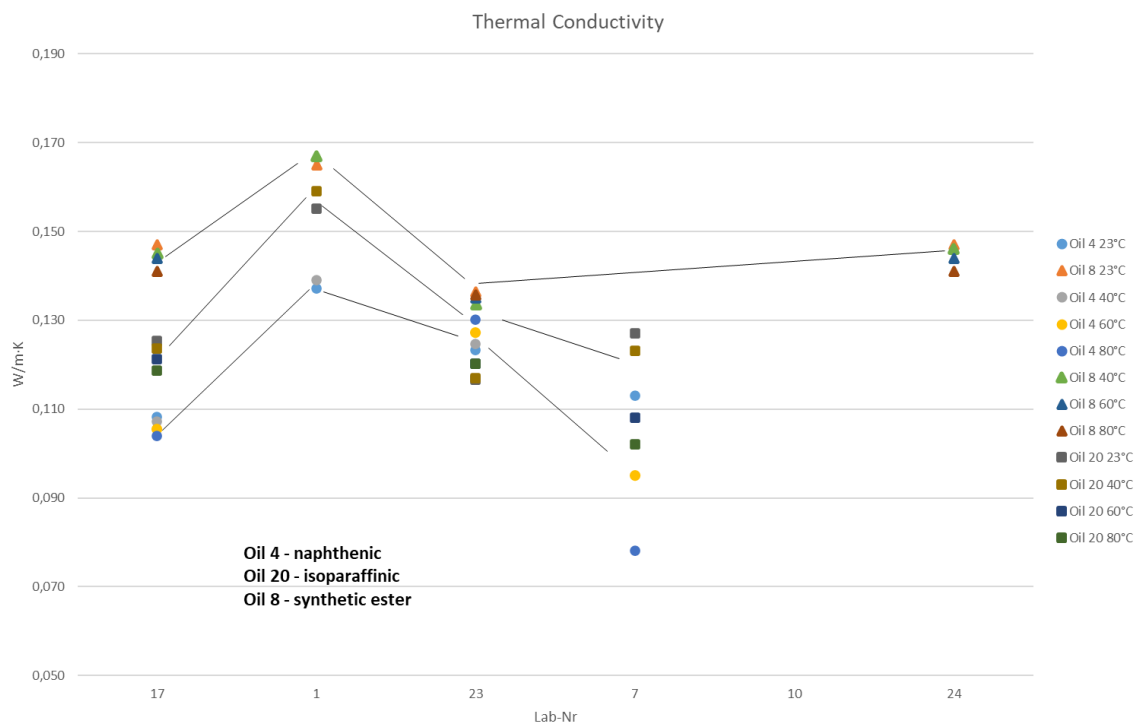
Figure 44: Thermal conductivity measurement at different temperatures
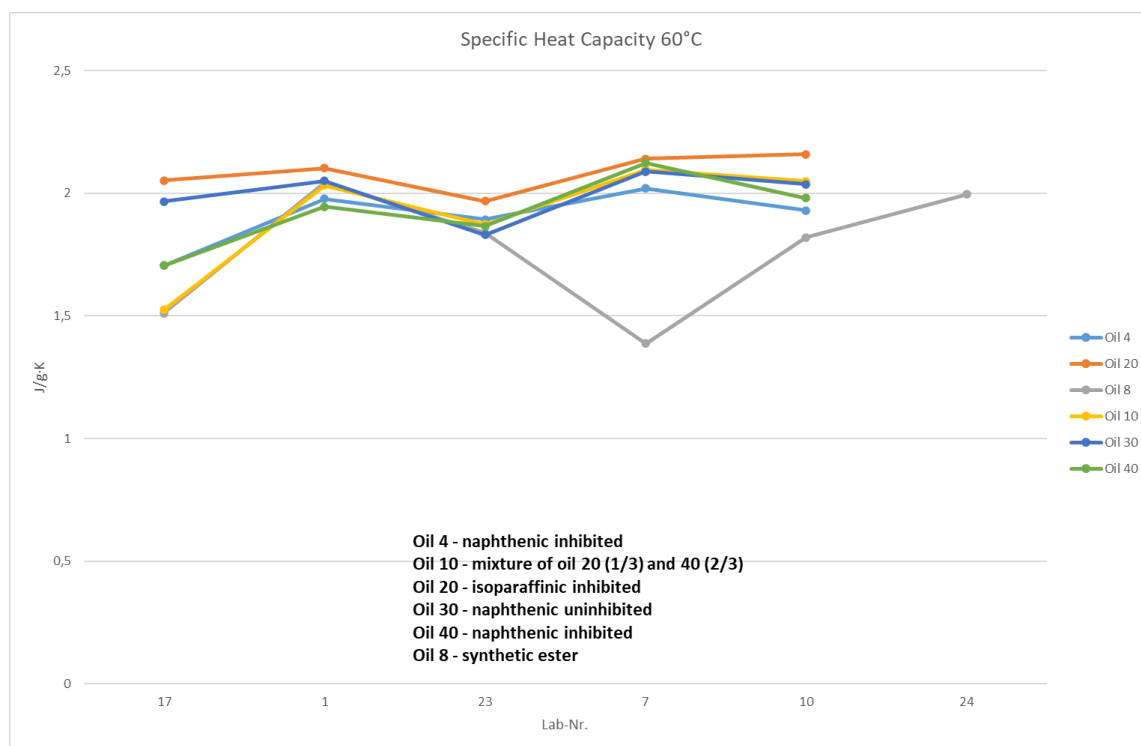
Figure 45: Specific heat capacity measurement at 60 °C

6.4 Conclusions

6.4.1 Density

- Most liquid manufacturers provide fairly accurate density data

- Liquid batch to batch variations are fairly minor

6.4.2 Kinematic viscosity

- Most liquid manufacturers provide fairly accurate viscosity data in the range 0 – 100 °C

- At sub-zero temperatures -30 to 0 °C measurement and batch variability becomes much more significant

- Among different mineral oils the viscosity/temperature relationship (viscosity index) can differ substantially

- Extrapolations of viscosity to cold temperatures can have very large errors

6.4.3 Thermal conductivity – a big spread of results

- Same value can be assumed for a rather wide range

- Differences between liquids are small but due to measurement inaccuracy wrong values can easily be given

6.4.4 Specific heat capacity

- Often overestimated if not measured

- Best to have at least one data set for each liquid type, but overall differences are small

7 Conclusions

Functional properties of insulating liquids are important for the design of electrical equipment. Although numerous standards, describing different functional properties in unused state and in service exist, there is always a need of update, especially when other insulating liquids like ester liquids are entering the market.

- A laboratory method describing the thermo-oxidative stray gassing of mineral oil, as well as synthetic and natural ester liquids has been developed.

This method is able to differentiate between fault gas development, due to the constitution of the insulating liquid and due to failure in the electrical equipment. In the present criteria for evaluation of gas-in-oil analysis according to IEC 60599, stray gassing is considered for a T1 fault, e.g. a thermal fault at a temperature < 300 °C. Since stray gassing can take place at normal operating transformer temperatures and mainly in uninhibited oils (which were prevalent during the development of those criteria) it will make sense to have a critical review of those criteria.In service examples manifistating stray gassing at normal operating temperatures, as well as possibilities for its mitigation are reported.

- In order to prevent oxidation ester insulating liquids shall be additivated. Tests for the qualitative and quantitative determination of those additives in mineral oils, natural, synthetic ester liquids, as well in silicone liquids have been carried out among several laboratories. The measurement uncertainties show that those methods shall be further developed and updated in international standardisation.
- The gravimetric method IP 342 for carcinogenic PCA adopted in international standards relies on the fact that the principal carcinogens of virgin oils are 3-7 ring PCA which are readily extractable into dimethyl sulfoxide (DMSO). It is rapid and easy to use, but has chemical limitations in its applicability: Round Robin tests have shown that methods like EN 16143 are necessary for the identification of individual EPA restricted PAH marker.
- The determination of thermal characteristics of insulating liquids is connected with different measurement uncertainty for different parameters. The highest spread of results has been identified with the determination of thermal conductivity at higher temperatures due to convection. Du to this fact it is worth considering of measuring of thermal conductivity at ambient temperature.
- On the basis of experimental data and service evidence can be concluded that the depletion of oxidation inhibitor in inhibited mineral oils is a good indication for prediction of the life span in service.There are some values implemented in international standards concerning mineral oil. This approach can in future be extended to ester insulating liquids as well.

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Annex A. Round Robin Test results for PCA/PAH

A.1. Results for IP 346

Six laboratories took part at the RRT for PCA/PAH on 7 insulating liquids (Table 18). One additional insulating liquid (11) which was in fact oil 4 has been spiked with 34,83 mg/kg BaP and 3 laboratories analyzed it, however, no differientiation to the original liquid (oil 4) could be done (see 3.4.1).

Table A1: Result of the RRT according IP 346 (unit in %)

LabNr/Oil	1	2	3	4	5	6	7	11 (Oil 4 + 34,83 mg/kg BaP)
16	0,86	0,71	0,80	0,79	0,82	1,13	0,88	0,13
11	1,2	0,8	1,35	1	1	1,14	1,56	1,05
14	2,4	1,7	2,1	1,4	2,1	2,4	2,3	1,4
17	2,4	1,6	1,7	0,89	2	2,27	2,04	
7	1,7	1,15	1,66	0,65	1,26	1,9	1,43	
13	2,28	1,45	2,64	2,12	2,75			
MV	**1,81**	**1,23**	**1,71**	**1,14**	**1,65**	**1,77**	**1,64**	**0,86**
Median	1,99	1,30	1,68	0,95	1,63	1,90	1,56	1,05
StD	0,61	0,38	0,57	0,50	0,68	0,54	0,49	0,54
StD%	33,63	30,91	33,60	43,48	41,35	30,67	30,13	62,66

A.2. Results for ASTM D6591

Three laboratories (Labelec Belgium, Ergon refining USA, Siemens Germany) took part in a small RRT determining the portion of monoaromatic %, diaromatic % and tri aromatic hydrocarbons (%) in 7 insulating liquids and of one additional (11) insulating liquid consisting of liquid 4, spiked with 34,82 mg/kg BaP (Table 19). The method can not differiate between single PAH compounds (see 3.4.2).

Table A2: Results for RRT according to ASTM D6591

LabNr/Oil	1	2	3	4	5	6	7	11 (Oil 4 + 34,83 mg/kg BaP)
8								
%MAH	21,4	12,5	17,495	7,415	16,245	19,8	19,9	7,615
%DAH	0,365	0,115	0,07	0,155	0,195	0,32	0,185	0,13
%T+AH	0,545	0,33	0,725	0,21	0,605	0,68	0,705	0,27
Sum Poly+AH	**0,91**	**0,445**	**0,795**	**0,365**	**0,8**	**1**	**0,89**	**0,4**
Sum all	**22,31**	**12,945**	**18,29**	**7,78**	**17,045**	**20,8**	**20,79**	**8,015**
1								
%MAH	23,97	12,6	17,76	9,31	18,68	21,14	21,74	8,83
%DAH	0,37	0,34	0,1	0,1	0,57	1,64	0,56	0,09
%T+AH	0,32	0,06	0,48	0,2	0,19	0,38	0,22	0,21
Sum Poly+AH	**0,69**	**0,4**	**0,58**	**0,3**	**0,76**	**2,02**	**0,78**	**0,3**
Sum all	**24,66**	**13**	**18,34**	**9,61**	**19,44**	**23,16**	**22,52**	**9,13**
7								
%MAH	15,65	9,08	11,51	6,71	13,54	16,76	15,47	6,09
%DAH	1,04	0,26	2,28	0,48	0,45	0,45	0,43	0,05
%T+AH	0	0	0	0	0	0	0	0
Sum Poly+AH	**1,04**	**0,26**	**2,28**	**0,48**	**0,45**	**0,45**	**0,43**	**0,05**
Sum all	**16,69**	**9,34**	**13,79**	**7,19**	**13,99**	**17,21**	**15,9**	**6,14**

A.3. Results for individual PAHs according EN 16143

The RRT carried out on the determination of individual PAH markers according to EN 16143 and according to a modified method with a fluorescent detector could identify the spiked amounts of BaP in oil 11 (Table 20), see 3.4.3.

Table A3:Results of the RRT according EN 16143 for undividual PAH markers

Compound/Oil	Lab 1 - EN 16143						mg/kg	
	1	2	3	4	5	6	7	11 (Oil 4 + 34,83 mg/kg BaP)
Benz[a]anthracene	3,73				2,26	1,44		
Chrysene			8,8			8,1		
Benzo[b]fluoranthene								
Benzo[k]fluoranthene								
Benzo[j]fluoranthene								
Benzo[e]pyrene								
Benzo[a]pyrene								37,4
Dibenzo[a,h]anthra-cene								
Sum of 8	**3,73**	**0,00**	**8,80**	**0,00**	**2,26**	**9,54**	**0,00**	**37,40**

	Lab 7 - EN 16143						mg/kg	
	1	2	3	4	5	6	7	11 (Oil 4 + 34,83 mg/kg BaP)
Benz[a]anthracene	0,02		0,061			0,161		
Chrysene	0,07		0,019			0,046		
Benzo[b]fluoranthene			0,019			0,046		
Benzo[k]fluoranthene								
Benzo[j]fluoranthene								
Benzo[e]pyrene	0,022		0,026	0,028		0,047	0,023	
Benzo[a]pyrene								25,4
Dibenzo[a,h]anthra-cene								0,067
Sum of 8	**0,11**	**0,00**	**0,13**	**0,03**	**0,00**	**0,30**	**0,02**	**25,47**

Lab 12 - HPLC with fluorescent detector					mg/kg			
Compound/oil	1	2	3	4	5	6	7	11 (Oil 4 + 34,83 mg/kg BaP)
Benz[a]anthracene						1,44		
Chrysene			9,7			9,65		
Benzo[b]fluoranthene								
Benzo[k]fluoranthene								
Benzo[j]fluoranthene								
Benzo[e]pyrene								
Benzo[a]pyrene								29,92
Dibenzo[a,h]anthra-cene								
Sum of 8	**0,00**	**0,00**	**9,70**	**0,00**	**0,00**	**11,09**	**0,00**	**29,92**

Annex B. Results for Round Round Robin test for additives

B.1. Results for DBPC

The RRT for DBPC delivered results varying between 9% – 18% coefficient of vaiation, which is an indication that the method shall be improved (Table 21), see 4.4.

Table B1: Results of the RRT for DBPC for different oils (outlieres are marked yellow)

	LabNr	Oil 1	Oil 2	Oil 3	Oil 4	Oil 5	Oil 6	Oil 7	Oil 8	Oil 9	Oil 10
	1	0	2815	3360	2930	2790	0	2580	520	140	0
	6	70	3200	3545	3225	3104	7	3410	558	1110	4130
	8	299	2200	2530	2100	2310	650	2700	20	120	0
	11	210	3219	3440	2111	2923	365	3415	2432	160	0
	12	0	2030	4050	2350	2710	0	3570	2400	150	0
	15	0	3100	3100	2900	2900	0	3200	2500	< 50	0
	21	0	3460	3810	3360	4030	0	5250	3335	205	0
AVG		83	2861	3405	2711	2790	146	3146	1681	155	0
STD DEV		114	505	457	483	247	241	375	1187	28	
Coef of variation (%)		137	18	13	18	9	165	12	71	18	

B.2. Results for DBP

The RRT for DBP could not be evaluated, since no DBP could be reliably identified (Table 22), see 4.4.

Table B2: Results of the RRT for DBP for different oils (outlieres are marked yellow)

	LabNr	Oil 1	Oil 2	Oil 3	Oil 4	Oil 5	Oil 6	Oil 7	Oil 8	Oil 9	Oil 10
	1	0	0	0	0	0	0	0	0	0	0
	8	0	0	0	0	0	0	0	0	0	0
	11	810	416	322	0	487	360	772	161	0	0
	15	0	0	0	0	0	0	0	0	0	0
	21	0	0	0	0	0	0	0	0	0	0
AVG											
STD DEV											
Coef. Of variation (%)											

B.3. Results for Irgamet[®] 39

The RRT for Irgamet[®] 39 could not be evaluated reliably for oil 2 with a coefficient of variation 8%, (Table 23), see 4.4.

Table B3: Results of the RRT for Irgamet[®] 39 for different oils (outlieres are marked yellow)

	LabNr	Oil 1	Oil 2	Oil 3	Oil 4	Oil 5	Oil 6	Oil 7	Oil 8	Oil 9	Oil 10
	1	0	45	0	0	0	0	0	26	0	0
	6	0	39	0	0	0	23	0	13,5	0	0
	8	0	45	0	0	0	0	0	31	0	0
	11	0	44	0	0	0	0	0	0	0	3
	12	0	0	0	0	0	0	0	0	0	0
	15	0	41	0	0	0	0	0	0	0	0
	18	9	49	7	7	9	10	9			
	21	0	38	0	0	0	0	0	0	0	0
AVG			43				1		10		
STD DEV			4				3		13		
Coef. Of variation (%)			8				350		125		

B.4. Results for Irganox® 109

The RRT for Irganox® 109 could not be evaluated, since no Irganox® 109 could be reliably identified (Table 24), see 4.4.

Table B4: Results of the RRT for Irganox® 109 for different oils

	LabNr	Oil 1	Oil 2	Oil 3	Oil 4	Oil 5	Oil 6	Oil 7	Oil 8	Oil 9	Oil 10
	1	0	0	0	0	0	0	0	0	0	0
	9	0	0	0	0	0	0	0	0	70	0
	12	0	0	0	0	0	0	0	12	0	0
	15	0	0	0	0	0	0	0	200	< 200	0
	21	0	0	0	0	0	0	0	240	92	0
AVG									90	41	
STD DEV									107	41	
Coef. Of variation (%)									118	102	

B.5. Results for Irganox® 1010

The RRT for Irganox® 1010 delivered high coefficient of variation, which is an indication that the method shall be further improved (Table 25), see 4.4.

Table B5: Results of the RRT for Irganox® 1010 for different oils (outlieres are marked yellow)

	LabNr	Oil 1	Oil 2	Oil 3	Oil 4	Oil 5	Oil 6	Oil 7	Oil 8	Oil 9	Oil 10
	1	0	0	0	0	0	0	0	2275	3628	0
	8	0	0	0	0	0	0	0	1600	3100	0
	11	0	0	0	0	0	0	0	418	3642	0
	12	0	0	0	0	0	0	0	32	393	0
	15	0	0	0	0	0	0	0	< 500	3700	0
	21	0	0	0	0	0	0	0	540	4400	0
AVG									973	3694	
STD DEV									833	414	
Coef. Of variation (%)									86	11	

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