

## Testing Challenges with Ester Insulating Liquids

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### SUMMARY

Ester insulating liquids have advantages to other insulating liquids in terms of biodegradability and fire safety. Ester filled transformers are often used in urban buildings and traction transformers because of their high fire point and in offshore parks and susceptible environmental regions because of their biodegradability. Ester filled transformers are already available in the highest ratings.

Although these insulating liquids have already been used for decades, there are still a lot of open questions concerning testing methodologies, as well as applied diagnostic procedures.

In this article some important, but still missing in the standards procedures for testing are discussed, e.g. calibration and interpretation of gas-in-oil analysis, monitoring of inhibitors, compatibility between different ester insulating liquids, detection of mineral oil contamination.

### KEYWORDS

Ester insulating liquids, Gas-in-oil analysis, calibration, diagnosis, determination of additives, compatibility, fire point, detection of contamination

## GAS-IN-OIL ANALYSIS OF SYNTHETIC ESTER LIQUIDS

The procedure of dissolved gas analysis is a mature procedure for identification of faults in liquid insulated electrical equipment. Until today, however, available standards contain only measuring and evaluating procedures for mineral oils. Although mineral oils can be of different nature and ageing status, users work with common accepted solubility coefficients equal for all. The same testing and evaluation procedures as for mineral oil have been used since years also for the measurement of silicone and natural and synthetic insulating liquids filled in equipment like transformers, reactors, bushings and even cable sealing ends.

### *Calibration standards for gas-in-oil analysis*

Calibration standards with insulating liquids can be prepared, using a defined amount of gases in a defined amount of oil [1,2]. Calibration standards in mineral oil are commercially available.

Today a lot of analysis of different insulating liquids next to mineral oil are performed. A big portion are conducted by means of headspace technique because of speed, automatization and efficiency. It is not feasible to prepare calibration standards for every type of insulation liquids, therefore in this report a general procedure for a comparative calibration of a headspace apparatus with further insulating liquids based on mineral oil calibration is presented. The principle of this calibration is based on experimental determination of slopes of curves prepared with gas mixtures with different concentrations and different insulating liquids following the same procedure. This allows a cost effective and experimentally feasible calibration of all lab gas chromatographs with insulating liquids other than mineral oil. This method shall be used under following prerequisites:

- The calibration curves shall be linear and shall have zero as origin. For this purpose, blank values at zero concentration shall be reliably determined and considered.
- The ratio volume oil/volume gas in the headspace vial shall be the same.
- The temperature of conditioning and extraction of gases in the headspace extractor shall be the same.
- The atmospheric gases have been separately determined according to the procedure described in [1, Annex C] and [3].

In Table 1 the insulating liquids and in Table 2 the gas mixtures used in this study are presented.

*Table 1. Insulating liquids used in the study*

Mineral oil acc. to [4]			Synthetic ester acc. to [5]	Natural ester acc. to [6]	Silicone liquid acc. to [7]
Inhibited isoparaffinic oil	Inhibited naphthenic oil	Uninhibited oil			

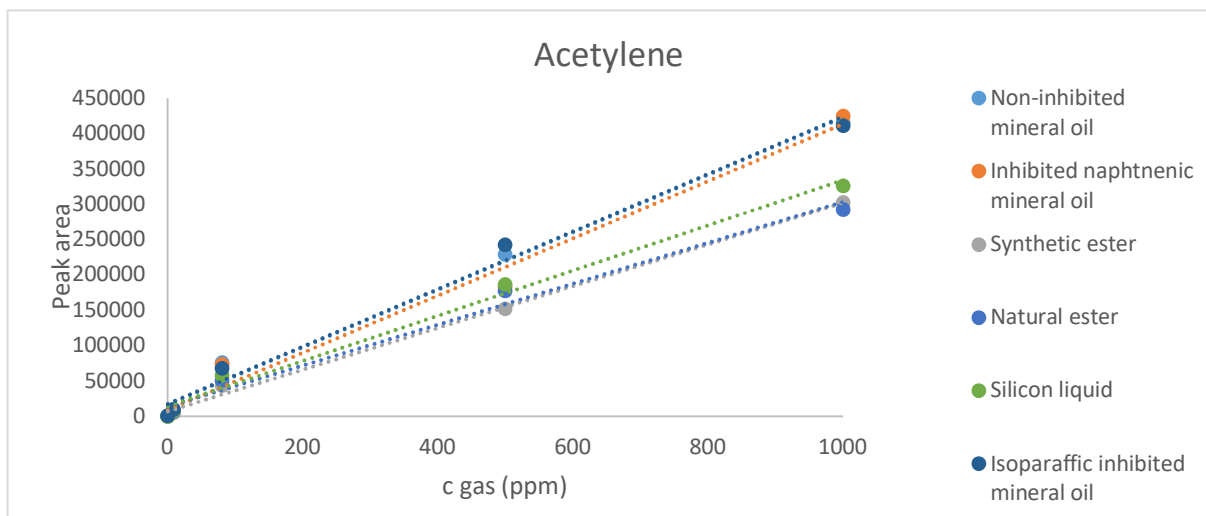
*Table 2. Gas mixtures used in the study*

	Helium (99,999%)	Mix 1	Mix 2	Mix 3	Mix 4
<b>Ethane (99%)</b>	0	4	40	100	1000
<b>Propane (99,5%)</b>	0	2	20	100	1000
<b>Propene (99,3%)</b>	0	3	30	100	1000
<b>Methane (99,5%)</b>	0	23	230	500	1000
<b>Acetylene (99,6%)</b>	0	8	80	500	1000

<b>Carbon monoxide (99%)</b>	0	83	830	1000	1000
<b>Carbon dioxide (99,9%)</b>	0	9	90	2200	10000
<b>Hydrogen (99,999%)</b>	0	200	2000	700	1000
<b>Ethylene (99,5%)</b>	0	6	60	500	1000

*Procedure [8]*

The method makes use of the equilibrium between the gas and liquid phase established in a headspace vial. This is used for DGA determination when a glove box or a rotating table are flooded with helium and a defined volume of the insulating liquid is introduced in the vial. Exactly in the same manner the method can be used if the glove box or rotating table are flooded with the specific gas mixture and fault gas free oil is filled to a defined ratio in the vial. The slopes of the linear curves for each gas have been determined out of the plot of GC peak areas versus individual gas concentrations for each tested insulating liquid. These slopes are set in relation to the slope of the isoparaffinic mineral insulating oil tested under the same conditions. Example for the calibration curves with different insulating liquids from Table 1 with the different gas mixtures from Table 2 for acetylene is shown on Fig. 1 and for ethylene – on Fig. 2.



*Figure 1. Calibration curves for acetylene with different insulating liquids and gas concentrations*

The curve dispersion for acetylene is much higher than for ethylene. This represents the more significant differences in the gas solubility of the tested insulating liquids for the gas acetylene than for the gas ethylene and is expressed in the value of F.

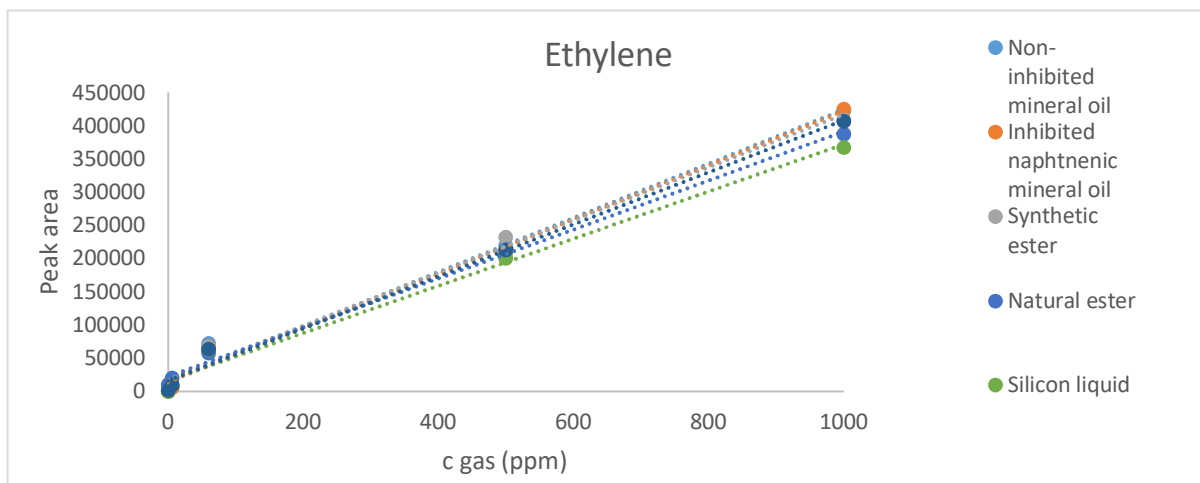


Figure 2. Calibration curves for ethylene with different insulating liquids and gas concentrations

In Table 3 the factors F for all tested gases and insulating liquids are shown.

Table 3. Experimentally determined factors for all tested gases and insulating liquids

	F Isoparaffic inhibited mineral oil	F Non-inhibited mineral oil	F Inhibited naphthenic mineral oil	F Synthetic ester	F Soya natural ester	F Silicon liquid
Mean F CO <sub>2</sub>	1,00	1,02	1,04	0,86	0,70	0,80
Mean F C <sub>2</sub> H <sub>4</sub>	1,00	1,11	1,10	1,03	0,98	0,91
Mean F C <sub>2</sub> H <sub>2</sub>	1,00	1,10	1,09	0,69	0,76	0,81
Mean F C <sub>2</sub> H <sub>6</sub>	1,00	1,11	1,08	1,13	0,93	0,98
Mean F C <sub>3</sub> H <sub>6</sub>	1,00	1,09	1,10	1,10	0,99	1,05
Mean F C <sub>3</sub> H <sub>8</sub>	1,00	1,11	1,11	1,17	1,10	1,09
Mean F H <sub>2</sub>	1,00	1,11	1,11	1,17	1,10	1,09
Mean F CH <sub>4</sub>	1,00	0,98	0,95	0,98	0,98	0,84
Mean F CO	1,00	0,97	0,97	0,93	1,00	0,90

The determined factors for mineral oils are very similar, independent of the mineral oil constitution.

Factor value below 1 for a certain gas in an insulating liquid means that it is better soluble in this liquid than in mineral oil – this is the case with acetylene in the tested natural and synthetic ester, as well as in silicone liquid; carbon dioxide in the case of natural ester and silicone insulating liquid. In order to create a calibration curve with another insulating liquid following steps shall be performed:

- Linear calibration curve with mineral oil (gas in oil in ppm/GC area)
- Multiplying the gas concentrations in oil with the value 1/F. Examples for 1/F multiplication factors for the investigated insulating liquids are presented in Table 4.

Table 4. Examples for 1/F multiplication factors for the investigated insulating liquids

	1/F Synthetic ester	1/F Soya based natural ester	1/F Silicone insulating liquid
CO <sub>2</sub>	1,16	1,42	1,25
C <sub>2</sub> H <sub>4</sub>	0,97	1,02	1,10
C <sub>2</sub> H <sub>2</sub>	1,46	1,31	1,24
C <sub>2</sub> H <sub>6</sub>	0,88	1,08	1,02
C <sub>3</sub> H <sub>6</sub>	0,91	1,01	0,96
C <sub>3</sub> H <sub>8</sub>	0,85	0,91	0,92
H <sub>2</sub>	0,85	0,91	0,92
CH <sub>4</sub>	1,02	1,02	1,19
CO	1,07	1,00	1,11

*Evaluation of gas-in-oil analysis of synthetic esters*

As synthetic ester in transformers of offshore wind farms or traction applications usually operate at high temperatures, one has to consider not only the generally known rules for gas formation under electrical and thermal faults [9] but also the thermo-oxidative gassing (known as „stray gassing“) of the liquid itself in conjunction with presence of copper [10]. The literature is rich of data on laboratory tests of ester liquids under different conditions and their comparison to mineral oil. There are however controversial opinions whether the gassing is similar or not to that of mineral oil under fault formation [11 – 15]. It is also important to know that the rate of hydrogen development in case of partial discharge activity for synthetic and natural esters is much higher than that of mineral oils [16].

The following main types of faults are known from the evaluation of mineral oils:

- PD – partial discharge faults,
- D – arc discharge faults,
- T – thermal faults, which can be described as T1, T2 or T3 type depending on the temperature range at which it appears.

Real faults seldom fall into only one classification. For example, a D fault develops a moderate or high amount of thermal gases, which overlap with a T fault. Despite that Halstead principle postulates a high production of hydrogen in case of thermal faults, in practice, hydrogen concentrations remain significantly below those of ethylene. Different experimental schemes are being used to calculate the values and ratios at thermal and dielectric faults, however, they remain of limited validity for real cases because of different energy intensity and thermal distributions involved. Thus, in practical evaluation, a combination of concentration threshold and ratio values seems the most pragmatical and reasonable way. The threshold values of the typical key gases cannot be postulated identical for different transformer fleets, since the transformer operation, design, cooling system, etc. must be also be considered and it therefore makes sense to evaluate the 95% and 99% limits for the transformer fleet of interest.

Keeping in mind common physical dependencies as well as practical experience we recommend the following criteria for the evaluation of faults in a homogeneous fleet of offshore turbine transformers (912 transformers with aramide insulation in age 3 – 9 years (22-36 kV, up to 6,8 MVA), 1818 analyses) and traction transformers (130 transformers with aramide insulation in age 3 – 12 years (15-25 kV, up to 6,3 MVA), 323 analyses).

A summary of the above presented information is enclosed in Table 5, while the development of the severity of all the fault types can reliably be assessed by following change of the ratios between methane/hydrogen, acetylene/ethylene and ethylene/ethane with time.

Table 5. Proposed criteria for PD, D and T faults in synthetic esters

Criteria for PD fault		Criteria for D fault		Criteria for T fault	
Key Gas values and Ratios		Key Gas values and Ratios		Key Gas values and Ratios	
$H_2 \geq 100$ ppm	$CH_4/H_2 \leq 0,2$ $C_2H_2/C_2H_4 \leq 0,1$	$H_2 \geq 50$ ppm and $C_2H_4 \geq 10$ ppm	$CH_4/H_2 \leq 1$ $C_2H_2/C_2H_4 \geq 1$ $C_2H_4/C_2H_6 \geq 2$	$C_2H_4 \geq 50$ ppm	$CH_4/H_2 \geq 0,3$ $C_2H_2/C_2H_4 \leq 0,1$ $C_2H_4/C_2H_6 \geq 1$

*Comparison of the interpretation schemes between mineral oil and synthetic ester*

Direct comparison between the used evaluation schemes for mineral oil and synthetic ester do not show significant differences for the major types of faults (Table 6).

Table 6. Comparison between the criteria for mineral oil [9] and for synthetic esters for PD, D and T faults

Case		$C_2H_2/C_2H_4$		$CH_4/H_2$		$C_2H_4/C_2H_6$		
		Mineral oil	Synthetic ester, Ratios	Mineral oil	Synthetic ester, Ratios	Mineral oil	Synthetic ester Ratios	Synthetic ester, Threshold values
PD	Partial discharge	NS	$\leq 0,1$	$< 0,1$	$\leq 0,2$	$< 0,2$	NS	$H_2 \geq 100$ ppm
D1	Discharge low energy	$> 1$	$\geq 1$	0,1 to 0,5	$\leq 1$	$> 1$	$\geq 2$	$H_2 \geq 50$ ppm $C_2H_4 \geq 10$ ppm
D2	Discharge high energy	0,6 to 2,5		0,1 to 1		$> 2$		
T1	Thermal fault $< 300^\circ C$	NS	$\leq 0,1$	$> 1$	$\geq 0,3$	$< 1$	$\geq 1$	$C_2H_4 \geq 50$ ppm
T2	Thermal fault $> 300^\circ C$ but $< 700^\circ C$	$< 0,1$		$> 1$		1 to 4		
T3	Thermal fault $> 700^\circ C$	$< 0,2$		$> 1$		$> 4$		

## ADDITIVES IN ESTER INSULATING LIQUIDS AND THEIR MONITORING

Additives are artificial substances that are added to insulating liquids to slow down the ageing process of the liquids. Various influences (e.g. operating temperatures, moisture and operating mode) result in a deterioration of the properties of insulating media, which in turn has a strong influence on the service life of the electrical equipment. Additives can be used to influence such processes. They improve specific properties of the insulating liquids so that they can withstand increased stresses during operation. Oxidation inhibitors and metal passivators are typical additives for this purpose.

Most of the used inhibitors in ester liquids are phenol-based and have a high flash point, which makes them particularly suitable for high-temperature applications. Typical examples of such inhibitors are 2,6-di-tert-butyl-phenol (DTBP), 2,6-dir-tert-butyl-para-cresol (DPBC), Irganox L109 and Irganox 1010 (Fig. 3).

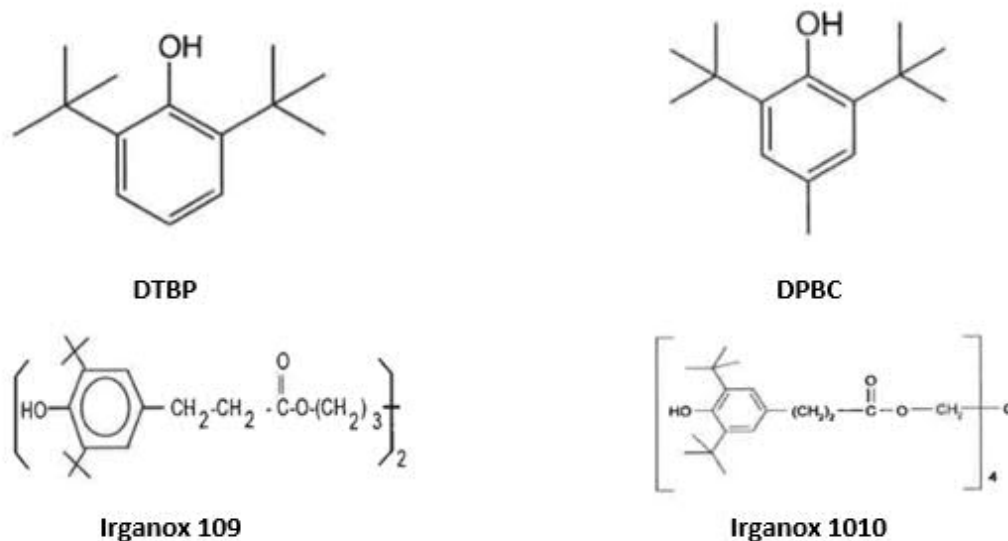


Figure 3. Examples of inhibitors used in ester liquids

Metal passivators protect the copper parts installed in a transformer. These additives adhere to the copper surfaces and protect them from corrosion. They also inhibit the catalytic effects of the copper on the insulating medium, which would accelerate its ageing. Common metal passivators are Irgamet 39<sup>®</sup> and Benzotriazole (BTA) (Fig. 4).

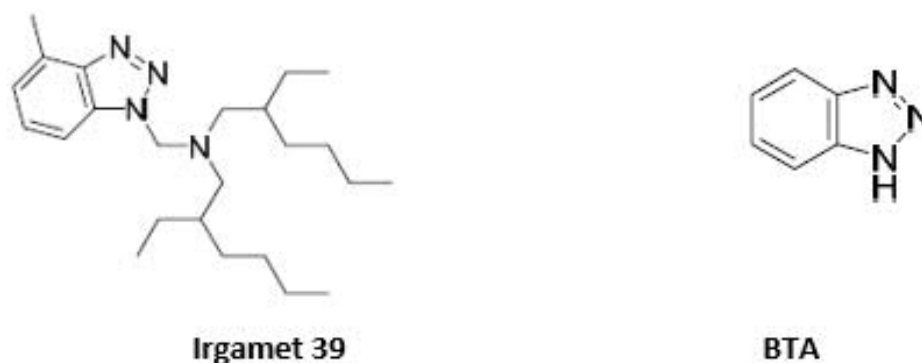


Figure 4. Examples of passivators used in ester liquids

Up to now no recognized procedure for the quantification of additives in ester liquids exists, which is a handicap for a maintenance standard. Different ester insulating liquids on the market have been investigated and the type of inhibitors has been determined. A high pressure liquid chromatography (HPLC) method specially for ester insulating liquids has been developed, which allows a quick and reliable determination of different types of phenolic inhibitors and thus their maintaining in service. The determination of additives in ester liquids is carried out in two steps. In the first step, the additives are extracted using acetonitrile and in the second step, the extract is analysed using HPLC.

An optimisation possibility for HPLC is the adjustment of the gradients of the mobile phase. For the determination of inhibitors and passivators in ester liquids, the gradient of acetonitrile and water (1:1) to 100% acetonitrile over a certain period of time was chosen (Fig. 5).

The preferred wavelength for the evaluation of the individual components was determined at 273nm. A typical chromatogram is shown in the figure below.

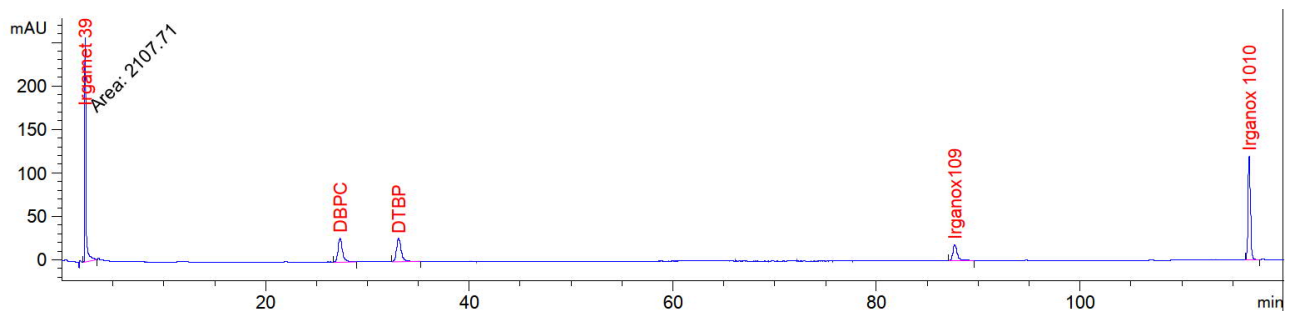


Figure 5. Typical chromatogram of additives in ester liquids

## COMPATIBILITY OF ESTER INSULATING LIQUIDS

The compatibility assessment of ester insulating liquids requires knowledge on used inhibitors and general liquid composition. The miscibility and compatibility between the commercial synthetic esters on the market is usually provided. In case of natural esters a special emphasis shall be placed on susceptibility to oxidation.

## DETECTION OF MINERAL OIL CONTAMINATION

Mineral oil contamination may reduce the biodegradability of the ester insulating liquid, but it can also reduce considerably the fire point, which is responsible for the fire safety. Instead of complicated testing a simple on-site test like refraction index is proposed.

Examples of refractive indices of some insulating liquids are shown in Table 7. A quick test (applicable even on site) can give useful information, whether contamination by another insulating liquid has taken place.

Table 7. Examples for refractive indices

$n_D^{20}$	Mineral oil (naphthenic type)	Synthetic ester	Silicon insulating liquid
	1,4710	1,4522	1,4028



## CONCLUSIONS

- A method for the relative calibration of any insulating liquid on the basis of known mineral oil calibration has been developed. The comparison is done on the basis of gas mixtures with different concentrations and comparison of the curve slopes (going through origin) with the curve slope of the mineral oil. Using a known mineral oil calibration curve a creation of a calibration curve for any other insulating liquid based on the determined relative slope factors  $F$  is possible. With exception of acetylene and carbon dioxide all other experimentally determined factors are very similar to those of mineral oil, which would suggest that the evaluation schemes for those liquids would be also similar to those already known for mineral oil.
- A gas-in-oil evaluation scheme for synthetic ester filled transformers for offshore turbines and traction application is proposed. It is based on a combination of absolute values and ratios of key gas contents, which reliably recognizes partial discharge, high energy discharge and thermal type faults.
- A method for the quantification of additives in ester insulating liquids by means of high pressure liquid chromatography has been developed.
- Some further preliminary studies on ester type compatibility and detection of mineral oil contamination are presented.

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