Fact or fiction – benefits of inhibited versus uninhibited hydrocarbon oils for transformers

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SUMMARY
Most of the industry involved in the transmission/distribution of electricity is in agreement that the latest inhibited oils are the best option available. They can offer a consistent and well defined base oil composition and quality, and excellent antioxidant response. This results in exceptional performance, and helps ensure trouble free transformer operation. They also offer the possibility of achieving very low intrinsic sulphur levels, minimizing the potential risks of oil related corrosive sulphur issues developing in service. Such oils are readily capable of achieving the highest levels of oxidative and thermal stability and do not require copper passivators. However, many customers/utility companies, with long experience using uninhibited oils appear resistant to change to inhibited products. This paper seeks to explore the reasons behind the customer’s perceived reserve, and to explore ways forward to enable the industry as a whole to benefit from the advantages of modern transformer oil technology. Customer concerns identified include questions over the compatibility and resultant performance of systems with mixed oil inhibition types.

Contents:
• Uninhibited and inhibited (naphthenic and iso-paraffinic) hydrocarbon transformer oils. Typical product features/benefits, and how these can be tested, assessed and improved, using examples from the latest generation of Shell products.
• Transformer manufacturers and utility companies – perceptions and findings from the field.
• Laboratory performance evaluation of the two product types, primarily in terms of oxidative stability. For mixed and pure uninhibited and inhibited oils.
• Shell recommendations on how to obtain maximum oil performance benefits.
• Conclusions - review of the relative merits of the two product types and confirmation of the benefits of inhibited versus uninhibited products.

KEYWORDS
Oxidation, uninhibited/ inhibited insulating oils, miscibility, compatibility, sulphur, iso-paraffinic

1. Typical product features & benefits of unused uninhibited & inhibited hydrocarbon insulating oils

Table 1 lists some of the more important typical physical/chemical, and performance characteristics of uninhibited versus inhibited hydrocarbon insulating oils. The primary insulating oil performance requirements of insulation, cooling and preventing corrosion, depend on a number of factors including, the base oil used to make the fluid, how it’s been processed, and also the type and level of additivation. Crude oils used to make insulating oil can contain a wide variety of aromatic, naphthenic and paraffinic hydrocarbons, and also sulphur, nitrogen or other hetero-cyclic species. Typically unsaturated and aromatic hydrocarbons and hetero-cyclic species if left in the oil, can be prone to more rapid oxidative degradation, resulting ultimately in the formation of oil insoluble oxidation products (giving deposits such as sludge’s), and oil soluble organic acids and polymeric species (giving thickened, potentially corrosive oil), which will both shorten the life of the oil and the service interval of the transformer, and which can give rise to costly and time consuming unplanned maintenance. All insulating oils will degrade in service with time, but it is the rate at which this occurs that can be controlled, by the lubricant developer’s knowledge of base oil and additive chemistry.

Sulphur compounds found in crude and finished insulating oils, depending on their type and quantity (total sulphur in crudes can be up to 2 % by weight or more), can function as natural antioxidants and/or sources of potentially corrosive sulphur [1]. Refining of the crude by distillation,
hydrotreatment and/or solvent extraction can convert or remove the most unstable components [2].

<table>
<thead>
<tr>
<th></th>
<th>Limits IEC 60296</th>
<th>Uninhibited</th>
<th>IEC 60296 – sect 7.1</th>
<th>Inhibited (0.3% BHT)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Shell Dimna 92 ZU-I</td>
<td>Higher oxid stab &amp; low sulphur</td>
<td>Shell Dimna 93 ZK-I</td>
</tr>
<tr>
<td>Double point</td>
<td>max 90°C</td>
<td>0.002</td>
<td></td>
<td>0.001</td>
</tr>
<tr>
<td>Breakdown voltage</td>
<td>min 30 kV</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Neutralisation number</td>
<td>max 0.01 mg KOH/g</td>
<td>&lt;0.01</td>
<td></td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Sulphur Content ppm</td>
<td>No general requirement</td>
<td>&lt;500</td>
<td>1,500 max</td>
<td>&lt;40</td>
</tr>
<tr>
<td>Corrosive sulphur</td>
<td>Not in current standard</td>
<td>Not corrosive</td>
<td>Not Corrosive</td>
<td></td>
</tr>
<tr>
<td>Oxidation Stability</td>
<td>IEC 61125 C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total acidity</td>
<td>164/382/500 hours</td>
<td>164 hours</td>
<td>600 hours</td>
<td>500 hours</td>
</tr>
<tr>
<td>acidity</td>
<td>max 1.2 mg KOH/g</td>
<td>0.9</td>
<td>max 0.3</td>
<td>0.02</td>
</tr>
<tr>
<td>max 0.8 %</td>
<td>0.3</td>
<td></td>
<td>max 0.05</td>
<td>0.01</td>
</tr>
<tr>
<td>Oxidised dissipation factor (ODF) at 90°C</td>
<td>max 0.5</td>
<td>0.100</td>
<td>max 0.05</td>
<td>0.005</td>
</tr>
</tbody>
</table>

Table 1 uninhibited versus inhibited insulating oils – typical properties

Amongst the most critical parameters for predicting the field performance of insulating oils are oxidative stability using IEC 61125C, and the test for potentially corrosive sulphur (IEC 62535).

Knowledge of the type and level of sulphur species can be informative as to whether an oil could become potentially corrosive, although given the complex range of different sulphur compounds present and how they may interact in a transformer, a detailed chemical understanding and explanation is still far from clear and is the subject of active study [3].

Inhibited oils are typically more refined than uninhibited oils, and therefore have the lowest levels of unstable molecules remaining, they also respond in a strong synergistic manner to synthetic antioxidants such as the commonly used phenolic antioxidant, butylated hydroxy toluene (BHT). This is shown in the oxidation testing results in Table 1, which demonstrates how they can readily exceed the highest levels of oxidative stability as defined in section 7.1 of IEC 60296. Uninhibited oils by their very nature contain a wider range and variety of less stable components, which are more
susceptible to degradation, and therefore cannot provide such high levels of oxidative stability.

In terms of minimizing the potential risk of corrosive sulphur issues developing in an insulating oil in service, then typically the lower the total sulphur content in the fresh oil the better. Such a trend favors the more highly refined inhibited products which have the lowest sulphur contents, often less than 40 ppm. New synthetic iso-paraffins provide the possibility of achieving oils with zero detectable sulphur levels. Removing or avoiding certain specific sulphur compounds such as mercaptans or disulphides which have been shown to cause corrosive sulphur problems [1] also helps reduce the risk of such issues developing.

Figure 1 2D Chromatogram of sulphur species in a representative uninhibited insulating oil

Figure 1 shows a 2D chromatogram of the naturally occurring sulphur species in a market
representative uninhibited insulating oil (total sulphur content ~300 ppm) meeting IEC 60296, which is not corrosive according to IEC 62535. The sulphur species are required to provide the low level natural oxidative stability characteristics required of uninhibited oils. It was generated using two coupled gas chromatographs with a SCD (sulphur chemiluminescence detector); one separates the oils components in terms of their volatility or boiling point, the other on the basis of their polarity. The data is presented as a contour plot, with each of the peaks representing either different sulphur containing molecules or their isomers. As can be seen the number of sulphur containing components is large, making individual identification of each species complex. Before commercialization such oils are thoroughly tested to ensure they meet all the latest and most stringent tests for corrosive sulphur, such as the IEC 62535 test. However given the extremely long typical service life and variable operating conditions such oils will meet in service, it is difficult to predict with certainty what chemical species could ultimately be formed given the broad range of sulphur species typically present in the commercial product, and more importantly their reactivity towards copper. Typically therefore the latest generation of uninhibited oils from Shell have significantly lower levels of total sulphur than earlier products, for example from >500 ppm to <300 ppm, i.e. ~40% lower, to minimize such longer term risks.

2. Transformer manufacturers and utility companies – perceptions and findings from the field

Almost all of the industry involved in the transmission and distribution of electricity is in agreement that the latest inhibited oils – for use as an electrical insulating and cooling medium – are the best option available. They can offer a consistent and well defined base oil composition and quality, and excellent antioxidant response. This results in exceptional performance, such as predictable and long oil life and helps ensure trouble free transformer operation. Increasingly transformer manufacturers are recognizing the technical benefits of inhibited versus uninhibited oils and have a preference for these oils especially in most demanding applications. Such oils are readily capable of achieving the highest
levels of oxidative and thermal stability and do not require the presence of copper passivators, thereby avoid the complicating requirement of regular passivator content testing and re-additivation. However, many customers/utility companies, with long experience using uninhibited oils appear resistant to change to inhibited products. Customer perceptions, comments and concerns, identified regarding the global market trend moving from uninhibited to inhibited insulating oils include:

- No concerns expected/experienced, regard inhibited products as providing highest level of technical performance in service, actively promoting/using, recognize market trend moving to these products
- Question over the miscibility & compatibility of uninhibited versus inhibited oil types in topping up
- Concern about topping up severely aged in-service oil with fresh oils (of either type) in terms of impact on solvency and possible deposit formation
- Question over the resultant insulating oil performance of a mixed oil inhibition system after topping up or re-use following reconditioning
- Concern over loss of service history of system/oil condition monitoring – resetting clock to zero

This paper seeks to investigate some of these performance related questions.

3. Laboratory evaluation of mixed inhibitor oil types

To evaluate and clarify some of the customer concerns raised over the move from uninhibited to inhibited oils. Especially in terms of compatibility and resulting performance if mixed in service, a number of mixed and unmixed test oils, both aged and unaged, and in different ratios and combinations have been tested. Tables 2 to 5 show the various oils (the only additivation being the use of BHT antioxidant), the mixing ratio (weight %), the tests and the results. Testing was primarily using the IEC 61125C oxidation test to simulate and assess expected ageing in service and especially
potential miscibility/compatibility issues.

<table>
<thead>
<tr>
<th>Potential Corrosive Sulfur (IEC 60289)</th>
<th>Limits IEC 60296</th>
<th>100% Uninhibited Shell Diala 82 ZU-I</th>
<th>85.15 wt% S2 ZU-I/S3 ZK-I</th>
<th>15.85 wt% S2 ZU-I/S3 ZK-I</th>
<th>100% Inhibited (0.3% BHT) Shell Diala 82 ZU-I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidation Stability</td>
<td>Non corrosive</td>
<td>Non corrosive</td>
<td>Non corrosive</td>
<td>Non corrosive</td>
<td>Non corrosive</td>
</tr>
<tr>
<td>Total acidity</td>
<td>max 1.2 mgKOH/g</td>
<td>0.81</td>
<td>0.61</td>
<td>&lt;0.01</td>
<td>-</td>
</tr>
<tr>
<td>Sludge</td>
<td>max 0.8 % m</td>
<td>0.27</td>
<td>0.12</td>
<td>0.03</td>
<td>-</td>
</tr>
<tr>
<td>Dielectric Dissipation Factor (DDF) at 90°C</td>
<td>max 0.5</td>
<td>0.070</td>
<td>0.002</td>
<td>0.007</td>
<td>-</td>
</tr>
<tr>
<td>Oxidation Stability</td>
<td>max 1.2 mgKOH/g</td>
<td>-</td>
<td>0.61</td>
<td>0.02</td>
<td>-</td>
</tr>
<tr>
<td>Total acidity</td>
<td>max 0.8 % m</td>
<td>-</td>
<td>-</td>
<td>0.04</td>
<td>0.01</td>
</tr>
<tr>
<td>Sludge</td>
<td>max 0.8 % m</td>
<td>-</td>
<td>-</td>
<td>0.075</td>
<td>0.006</td>
</tr>
</tbody>
</table>

Table 2: Mixed fresh (unused) uninhibited and fresh inhibited, naphthenic based insulating oils

In Tables 3 and 5, the used uninhibited Oil A is a market representative commercial product (in service for more than 5 years). Its performance characteristics are indicative of a lightly aged oils, having an acid value of 0.01 mg KOH/g, and dielectric dissipation factor (DDF) at 90 °C by IEC 60247 of 0.005. No deposit formation was observed on mixing the used and the fresh oils.

Compatibility of insulating oils is dealt with by IEC 60422 “Mineral insulating oils in electrical equipment – supervision and maintenance”. Section 6.12 states that unused oils conforming to IEC 60296, and containing the same or no additives are considered to be compatible with each other and can be mixed in any proportion. It recommends oils of the same type are used for topping up/refilling. Also that problems are not normally found when <5% unused oil is added to used oil (not heavily aged), but that higher levels with heavily aged oils may lead to precipitation. If in doubt to run a compatibility test or consult the oil supplier is the advice given.
As expected, Tables 2 and 3 (all naphthenic based insulating oils) confirm that a mixed inhibition oil system, typically displays resultant performance properties that are an average of the type and quantity of its constituent parts, irrespective of whether the oil is unused or used.

Table 3 Mixed used uninhibited and fresh inhibited, naphthenic based insulating oils

Table 4 Mixed fresh (unused) uninhibited (naphthenic) and fresh inhibited (new synthetic isoparaffinic) insulating oils
Table 5 Mixed used uninhibited (naphthenic) and fresh inhibited (new synthetic iso-paraffinic) insulating oils (no deposit formation was found on mixing)

Tables 4 and 5 show comparable data obtained using a new synthetic iso-paraffinic based inhibited oil with both fresh and used, uninhibited naphthenic based oils. As previously found, the data indicates that a mixed inhibition oil system typically displays resultant performance properties that are an average of the type and quantity of its constituent parts. This is irrespective of whether the oil is unused or used, or as found in these examples, whether the oil types are naphthenic or paraffinic or a mixture of the two. Interestingly, if the oxidative stability characteristics of the mixtures containing the new iso-paraffinic based oil are compared with those for the naphthenic based only mixtures, it can be seen that the inhibited iso-paraffinic based product have significantly improved oxidative stability and resistance to degradation in service compared to the inhibited naphthenic based product (which already meets the highest oxidative stability characteristics of IEC 60296), and hence confers more of these properties into the naphthenic based products it was mixed with. The improvement is to such an extent that in Table 4 a mixture of 15% S2 ZU-I with 85% Oil B still meets the requirements of the highest oxidative stability for IEC 60296. Even though the antioxidant content of the two inhibited
grades was the same type and level, 0.3% BHT. The conclusion from this is that new iso-paraffinic based oil has superior antioxidant response compared to even highly refined state of the art naphthenic oil based products. Also due to its synthetic manufacturing route it is essentially sulphur free and therefore unable to generate corrosive sulphur species.

To further evaluate the oxidative stability (aging characteristics), and compatibility and miscibility of these mixed uninhibited (used and unused naphthenic based) and inhibited products (both naphthenic and iso-paraffinic), additional laboratory testing was also performed. This was derived from IEC 62535, and comprised:

Two glass vials filled with oil to be tested, temperature 100°C (in dark), contain copper wire (with Kraft paper), one crimped with air atmosphere, the other has tube for air ingress (simulates transformer breathing). Third vial contains only oil from the start of the test, crimped with air atmosphere for comparison of color change, and is not oven aged further. The test is run for up to 14 days with regular visual checks (and photographs) for signs of oil degradation (color change, turbidity/deposit formation).

The oils tested were as previously described, and in addition:

Oil C, a high quality commercial uninhibited naphthenic based oil meeting IEC 60296 (with no additives), that has been aged in an oven at 100°C in the dark, with air blown through, until the acid number reached 0.10 mg KOH/g (from a starting value of 0.01). The oil was then filtered before further testing to remove insoluble oil degradation products, its final DDF at this stage was 0.009.

Oil D is a high quality commercial uninhibited napththenic based oil meeting IEC 60296 (with no additives).

Pictures 1 to 3 show the appearance of the oils tested, at the start and after 10 days of the test.
Unused uninhibited, aged uninhibited, and inhibited naphthenic oils at the start and end of 10 days.

Picture 1 shows that after only 5 days, uninhibited Oil D has started to undergo oxidative degradation, and after 10 days this is significant (color change, deposit formation). This is most marked in the vial that is open to the atmosphere with the tube insert. In contrast the inhibited oil shows no significant visible signs of oxidative or other degradation after 10 days (or even after 14 days as the test continued).
Picture 2 100% S3 ZX-I unused inhibited oil, and mixture with either 15 weight % or 85% aged uninhibited naphthenic Oil C at start and end of 10 days

If compared with picture 1 and the behavior of the 100% aged Oil C, it is seen in picture 2 as expected, that with mixtures it is the major component of the mixture which influence the overall bulk degradation of the sample. When the inhibited S3 ZX-I is the main component at 85% with the remainder being Oil C, a significant reduction in degradation is evident with no visible deposit formation, although the oil has darkened slightly. Neither mixture at the start of the test produced a visible deposit when the oils were mixed.
Picture 3 100% unused inhibited (new iso-paraffinic) based Oil B, and a mixture with 15% or 85% aged uninhibited naphthenic Oil C, at the start and end of 10 days

When picture 3 is compared to picture 2, similar degradation and compatibility behavior is seen for the mixtures containing uninhibited aged Oil C and inhibited oil (irrespective of whether it is naphthenic or paraffinic). It can be seen that when Oil B is at 85% then the remaining 15% of the aged Oil C is effectively stabilized in terms of its ability to degrade, and apart from a slight color change no other degradation or interaction with copper is evident. Again no visible deposit was formed on preparing the mixtures of aged uninhibited and unused inhibited paraffinic oils at the start of the test. Demonstrating that the compatibility and miscibility between the iso-paraffinic inhibited and the aged naphthenic Oil C, is comparable and as good as the inhibited naphthenic oil. It also indicates that
differences in solvency between the naphthenic and paraffinic oils are not significant.

4. Shell recommendations on how to obtain the maximum performance benefits by using inhibited oils versus uninhibited oils

The latest inhibited transformer oils have many performance benefits over uninhibited transformer oils. Typically to obtain the maximum benefits from such products they should comprise the bulk of the service fill of the transformer, ideally 100%. As has been seen if mixed with others oils (either fresh or used), then the resulting performance of the mixture is typically an average of the constituents and their amounts.

5. Conclusions - review of the relative merits of the two product types and confirmation of the benefits of inhibited versus uninhibited products

As has been shown, the latest inhibited transformer oils have many advantages over uninhibited transformer oils. They can offer a consistent and well defined base oil composition and quality, and excellent antioxidant response. This results in exceptional performance, such as predictable and long oil life (maximum resistance to degradation in service) which helps ensure trouble free transformer operation, especially for the more demanding applications. Having very low intrinsic sulphur levels, minimises the potential risks of oil related corrosive sulphur issues developing in service. Such oils are readily capable of achieving the highest levels of oxidative and thermal stability and do not require the presence of copper passivators.

No significant compatibility or miscibility issues were observed in the laboratory evaluation of the various mixtures of uninhibited and inhibited oils described in this paper. However given the large variability in composition and therefore performance of commercial transformer oils in the market place, before mixing oils of different types (especially if any are used) consider suitable compatibility testing.
BIBLIOGRAPHY


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