

Properties of Mineral Insulating Oils in Service

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Abstract:

The infrastructure of the electricity grid and super grid system in the hitherto industrialized world was to a large extent built up in the decades following World War II with a peak in investments around 1960-1980. This means that the flotilla of power transformers is now starting to reach projected lifetime of around 40 years. During the last couple of decades there has also been an ongoing deregulation and privatization of electricity generation and distribution. This has led to higher utilization of existing equipment to deliver an ever increasing demand of power. The demand for planned asset management, investments, reliability and availability of power delivery, has also increased. To ensure that aging equipment is working satisfactory and will do so for yet some time, interest in aging behavior of power equipment has increased. Yet there is precious little basic information openly available on how the insulating materials in transformers behave over longer periods of time. Such information is valuable both from the perspective of transformer maintenance/asset management, and as background information to make informed choices on which type of insulating liquid to employ in new equipment.

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1. Introduction

In this study there is a total of 145 separate samples from separate transformers (all samples appeared around the same time for analysis), of which 114 are inhibited and 31 uninhibited. The inhibited oil samples came from transformers in the Nordic region, whereas the uninhibited samples come mainly from the Middle East. The transformers span a range of ages from only a few years up to 45 years.

The samples were analyzed for acidity, interfacial tension, dielectric loss (DDF) and peroxide content. The inhibited samples were also analyzed for inhibitor content.

All of these parameters except peroxide content are standard measurements, but little information exists on how they relate to each other statistically. The peroxide measurements were performed according to a method we have developed. It should tell us more about the oxidation behavior and the efficiency of oxidation inhibitors.

2. Monitoring and Maintenance of Insulating Oils in Service

The insulating oil in a power transformer only account for about 5% of the initial cost of the complete system, but it is a very vital part both for the monitoring of the function of the transformer and the ultimate life time under which the investment cost should be regained with interest. A high quality insulating oil should ideally not contribute to premature ageing of the non-replaceable parts such as winding and solid insulation. Through DGA the oil also serves as an information carrier about what is going on inside the transformer consequently DGA is used for transformer condition monitoring routinely (1).

However, it is vital to ensure that aging of the oil is not excessive and that it performs as it should (2). For this reason there are guides to follow to check the performance of the oil such as IEC 60422 and IEEE C57.106.

3. IEC 60422 Oil Maintenance Guide

IEC 60422 is a guide for the supervision and maintenance of mineral insulating oil in electrical equipment. This standard is used worldwide and is currently under revision. The purpose of the revision of this standard is to bring it in line with current

methodology, best practice and compliance with requirements and regulations affecting safety and environmental issues.

Oxidation of the oil will occur in all equipment where it is in contact with air. In such equipment, oxidation of the oil will occur gradually and naturally over many years.

Oxidation is accelerated as operating temperatures of the oil increase. Oxidation can also be accelerated by the presence of catalysts such as metals or metallic compounds. The cumulative effects of the oil and windings, and the oxidation of the oil increase cumulatively, leading to possible breakdown.

Early warning of the onset of oil oxidation is provided by monitoring of the color and appearance of the oil, regular testing for acidity levels in the oil, monitoring moisture levels in the oil and visual inspection during maintenance for signs of sludgy deposits on internal surfaces of equipment.

The tests for in-service oil are divided into three groups.

- **Group 1** Minimum tests require to monitor the oil and to ensure that it is suitable for continued service.
- **Group 2** These are additional tests which may be used to obtain further specific information about the quality of the oil and may be used to assist in the evaluation of the oil for continued use.
- **Group 3** These tests are used mainly to determine the suitability of the oil for the type of equipment in use and to ensure compliance with environmental and operational considerations.

Individual tests for each group are listed in Table 1. It should be noted if test results for **Group 1** are not exceeding recommended action limits, usually no further tests are considered necessary until the next regular period for inspection.

Although a large number of tests can be applied to mineral insulating oil in electrical equipment, the tests listed in Table 1 are considered sufficient to evaluate the condition of the oil in service and to establish whether the condition of the oil is adequate for continued operation. Corrective actions, based on the results are then suggested.

Table. 1. Tests for Mineral Insulating Oils

Group 1 (Routine tests)	
Colour and appearance	ISO 2049
Breakdown voltage	IEC 60156
Water content	IEC 60814
Acidity (neutralization value)	IEC 62021
Dielectric dissipation factor (DDF) and or resistivity	IEC 60247
Inhibitor content	IEC 60666
Passivator content	IEC 60666, Annex B
Group 2 (Complementary tests)	
Sediment and sludge	IEC 61125 method C
Interfacial tension	ISO 6295
Particles (particle count)	IEC 60970
Group 3 (Special investigative tests)	
Oxidation stability	IEC 61125
Flash point	ISO 2719
Compatibility	IEC 61125
Pour point	ISO 3016
Density	ISO 3675
Viscosity	ISO 3104
Polychlorinated biphenyls (PCBs)	IEC 61619
Potentially corrosive sulfur	IEC 62535
Corrosive sulfur	ASTM D1275B
Corrosive sulfur	DIN 51353
DBDS	IEC 62697

4. Classification of Oils in Service

To assist in the assessment of the condition and subsequent actions, oils in service may be classified as good, fair or poor based on the evaluation of significant properties and their ability to be restored to the characteristics desired.

Good Oil in normal condition, continue normal sampling

Fair Oil deterioration detectable, more frequent sampling recommended

Poor Oil deterioration abnormal, immediate action advisable

5. Aging of Mineral Oils

Even if there are different types of wear and tear on an insulating oil, the main force of aging is of course oxidation. For oxidation to take place there has to be something to oxidize (oil), oxygen, and heat to provide the activation energy.

The details of the oxidation process will not be covered here, which can be found in earlier contribution to TechCon (3), but a brief outline is nevertheless necessary for the continued discussion.

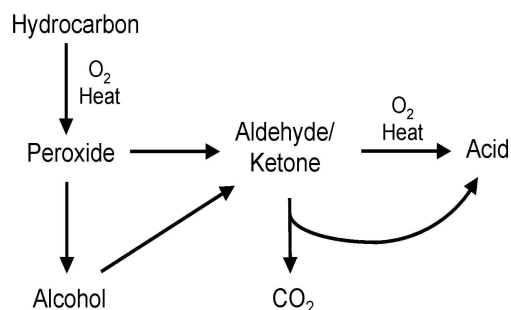


Fig. 1. Principle for Oil Oxidation

When a hydrocarbon molecule (oil molecule) encounters the combination of heat and oxygen (air), it can form a peroxide (Figure 1). Peroxides are inherently unstable and therefore rather reactive. They can easily form alcohols or aldehydes or ketones. These are polar types of molecules that will change the properties of the oil medium in which all this happens. For instance this will affect interfacial tension and thereby the solubility of water in the oil. Water is also a by-product of several of the reactions that underlie these phenomena.

Aldehydes and ketones can react again with oxygen to form acids directly, or be oxidized and loose carbon dioxide to form acids. Carbon dioxide is in fact the most oxidized form of carbon and the absolute end of

the process. However, both aldehydes and acids can react with each other to form complex compounds that are not soluble in oil, i.e. sludge.

This is in essence the oxidative reactions in a mineral oil-based insulating liquid, although in a very simplified form. What is lacking in this simple picture is the positive feedback loop of the reactions of peroxides; peroxides react and form even more peroxides in the same process as other oxidation products are formed. This comes about by chain reactions of radicals of peroxides. Ester-type of liquids follows the same general pattern, but the details differ.

Oxidation inhibitors (natural or synthetic) moderate or stop the reactions of peroxides to give the liquid a protection against the oxidative reactions.

Of these different products one can measure peroxides, the effect of formation of polar compounds on IFT, acidity and also in principle carbon dioxide by DGA.

6. Study of Field Samples

The data for this study was mined from the database of analyses within Nynas IOM, which is our insulating oil management service in Europe with laboratories in Sweden, UK, Norway and Poland. In this case the peroxide content of the oil samples were also analysed using a GCMS-based method developed in Nynas Research department (4).

For maintenance and reinvestment strategies, the development of the different oil parameters over time is perhaps the most interesting insight to be elucidated

from this and similar sets of data. If assets managers know what signs to look for and what development to expect, at least on a statistical level, it should be very helpful to secure power delivery to a minimum cost. Other types of correlations may also be interesting, especially to enable maintenance decisions on less complete data, a situation that is all too common.

Once the values for age, IFT, acidity, peroxide concentration, DFF and inhibitor content had been gathered, the data was divided into two categories depending on whether the oil was inhibited (containing DBPC) or uninhibited.

The data was then analyzed for linear correlations. This does not of course give the whole truth, but even a weak linear correlation between sets of data may indicate that there are other types of interesting correlations. Finally the different data sets were plotted against each other to enable elucidations of such more complex correlations. The results were then compared to the limits set in IEC 60422 (voltage classes above 172 kV).

The weakness of this approach is that it cannot tell you anything about the development over time in the same transformer as it gives only statistical correlations.

7. Inhibited Versus Uninhibited Oils

Before going into details of correlations of the different measurable parameters, a broad comparison of the properties of the set of oil samples should be considered (Table 3).

Table 2. Comparison of Inhibited and Uninhibited Oils (c.d.=complete data)

	Age (years)	IFT (mN/m)	Acidity (mg KOH/g)	Peroxide (mM)
Inhibited				
median	15	39	0.00	0.06
average	16	38	0.02	0.07
extreme	45	24	0.27	0.55
oldest c.d.	37	41	0.03	0.09
Uninhibited				
median	25	27	0.04	0.41
average	21	30	0.07	0.47
extreme	45	14	0.36	2.18
oldest c.d	38	23	0.03	0.32

Even if the data is a bit skewed because of the much higher number of inhibited oils it is clear that most of the numbers are indicating that inhibited oils remain much more pristine during the service life of the transformer. It is very indicative to look at the oldest complete data (oldest c.d.) where the IFT of the uninhibited sample has gone down to alarming levels, whereas the inhibited sample of almost the same age is still in very good shape.

Also take note of the fact that peroxide concentrations in the uninhibited oils are at least an order of magnitude higher than in the inhibited samples. This indicates that destructive oxidation processes are going on to a much larger extent in the uninhibited samples. It also explains why the extreme values are much worse for the uninhibited oils as the processes of oxidation will give these results.

8. Inhibited Oils

In this study there are 113 samples from separate transformers. For 78 of these the age of the transformer (and the oil) was known. A total of 103 transformers are known to be of the free-breathing type with silica drying of the ingoing air. Inhibitor content, acidity and

peroxide content was measured for all samples. 73 samples had been analyzed for IFT (interfacial tension), and 61 for DDF (dielectric dissipation factor, i.e. dielectric loss).

Table 3. Linear Correlations for Inhibited Oils

	Age	IFT	Acidity	Peroxide	DDF	Inhibitor
Age	1.00					
IFT	-0.39	1.00				
Acidity	0.57	-0.57	1.00			
Peroxide	0.33	-0.14	0.57	1.00		
DDF	(0.60)	-0.15	0.18	-0.17	1.00	
Inhibitor	-0.21	0.67	-0.44	-0.39	0.07	1.00

The greatest correlation (Table 3) is found between IFT and inhibitor content. This actually shows that the inhibitor really works. As long as there is enough inhibitor left there will be very little oxidation and therefore very few polar compounds that affect IFT are formed.

Age correlates best to DDF, and second best to acidity. The most likely explanation is that it is chiefly ionisable compounds like acids that affect DDF, but this seemingly high correlation should be taken with a pinch of salt because it is only based on 9 data pairs. In contrast the correlation between age and acidity is based on 78 data pairs and is therefore much more real (see below). Peroxide content has a certain correlation to acidity, which could perhaps be an effect of that during oxidation peroxides first form and then gradually are turned into acids. From a chemical point of view it should also be said that acids can be formed by a route from aldehydes via peroxy-acids which contain a peroxide functionality. The correlation between inhibitor content and peroxide content is weakly negative. The explanation why the correlation is not stronger may be that they are not simultaneous; as long as there is enough inhibitor there will be very little peroxides.

9. Development over Time

It is not meaningful to show all parameters as function of transformer age, because for most parameters there is no trend at all. This includes peroxide and inhibitor content, which are likely to be more dependent on specific loading patterns and the resulting temperature that just time alone.

A certain linear correlation between age and acidity was found (*vide supra*), so this calls for more in-depth analysis. Looking at the data for acidity over time it is clear that no acidity levels at all have in principle developed before about 15 years of service (Figure 2).

Thereafter there is an increasing trend with a few more extreme outliers.

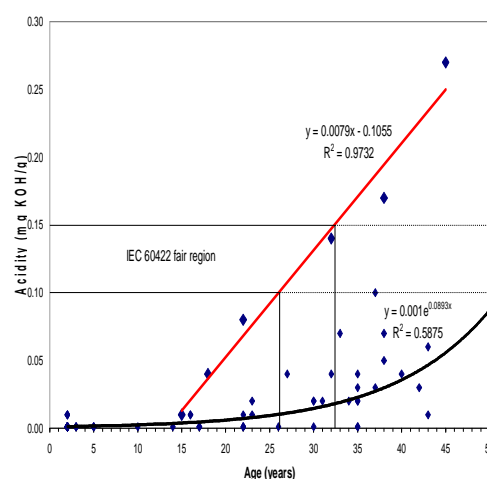


Fig. 2. Development of Acidity of Time for Inhibited Oils

The only type of simple regression analysis that gives a reasonable result for the complete data gives a logarithmic expression (black curve). For this to work all values of zero acidity were substituted by the value 0.001 mg KOH/g, i.e. very close to zero and in practice not measurable. This ensures that also these data points are taken into account in the regression analysis. This would indicate that statistically the acidity would not reach the IEC 60422 fair region (0.10-0.15 mg KOH/g) until after a service life of 50 years, but the regression curve is very sensitive to the weight of the low values at low ages (which are also more uncertain).

If the more extreme outliers are treated separately in an attempt to model a *worst-case scenario*, a linear regression (red line) can be made. This would indicate that oil acidity could reach IEC 60422 fair region after about 27 years, and would in that case pass into the poor region after about 32 years.

9.1. Other Correlations

The greatest linear correlation in the data for inhibited oils was that between inhibitor content and IFT. IEC 60422 recommends that inhibitor levels should be kept above 60% of the original value in order to consider the oil to be in *good* condition. The lower value under which the oil is *poor* is set to 40%, which for an oil that originally contained 0.40% inhibitor would mean a limit of 0.16%. The question then arises if this is enough also to keep IFT at a value that is considered to be fair, i.e. in the range 28-22 mN/m. Figure 3 shows this dependence in our data.

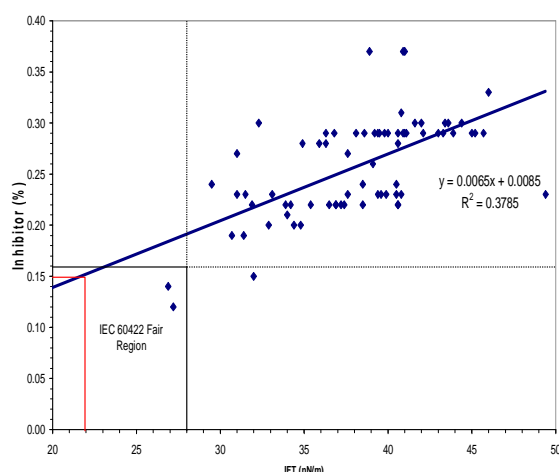


Fig. 3. Correlation Between IFT and Inhibitor Concentration for Inhibited Oils

It is evident that in this data there are only very few samples that contain less than 0.16 % inhibitor, and also very few samples that would not be classified as being in good condition when it comes to IFT. The linear regression does not give a very good curve fit, but the trend is very clear; lower inhibitor content is associated with lower IFT. Presumably the reason is that oxidation, which consumes inhibitor, leads to formation of compounds that lower IFT.

This data analysis clearly shows that an inhibitor content of at least 0.16 % is more than enough to keep the IFT at *fair*, or better, levels.

The regression line would indeed indicate that levels down to about 0.15 % would suffice (red lines). The advice of IEC 60422 is therefore sound and supported by the data analysis.

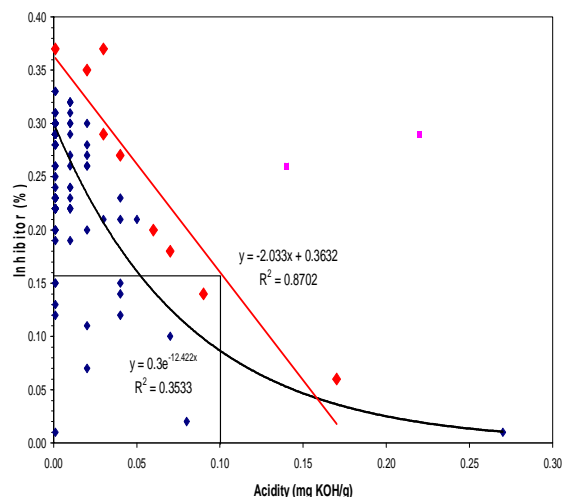


Fig. 4. Acidity vs. Inhibitor Concentration for Inhibited Oils

Another way to corroborate IEC 60422 is to look at the correlation between acidity and inhibitor content (Figure 4). Two outliers are very obvious (pink). Here the acidity is very high despite relatively high inhibitor contents. It is likely that these two transformers have been topped-up with inhibitor in attempts to prolong service-life of already oxidized oils. The rest of the data set appears to have a roughly exponential increase in acidity as inhibitor level drops off. Since the correlation in the regression analysis is relatively weak it is not very useful as a model to predict acidity. However, a worst-case scenario can be constructed by regression analysis of the points giving the highest acidity for a given inhibitor content (orange). This would indicate that to maintain the oil acidity under the limit between good and fair in IEC 60422 (0.10 mg KOH/g), a minimum inhibitor content of 0.16 % is needed. This is in exact agreement with the advice in the standard!

If also the extreme acidity value to the far right is included in the worst-case scenario, the minimum inhibitor content would instead have to be 0.20%, but that grants this one extreme value a very heavy weight in the results.

Yet another way to assess the level at which the inhibitor does its job would be to plot inhibitor content against peroxide concentration (Figure 5). After all, if the inhibitor functions properly there should not be any peroxides which are the first oxidation products to appear.

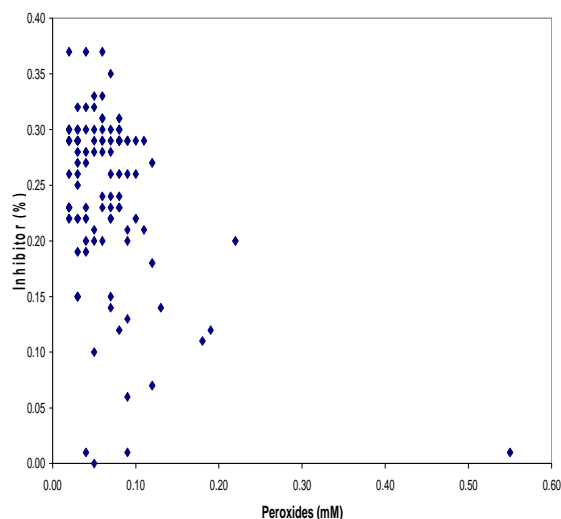


Fig. 5. Peroxide vs. Inhibitor Concentration for Inhibited Oils

Even though higher inhibitor levels seem to have an association with really low peroxide concentrations, the lack of any extreme peroxide concentrations precludes an assessment of at which level the inhibitor is most effective (looking only at these two parameters). The likely reason for this pattern is that the inhibitor actually is very efficient at preventing peroxides to accumulate, also at very low inhibitor levels. Oxidation in the presence of inhibitor only leads to consumption of inhibitor, not to high peroxide concentrations.

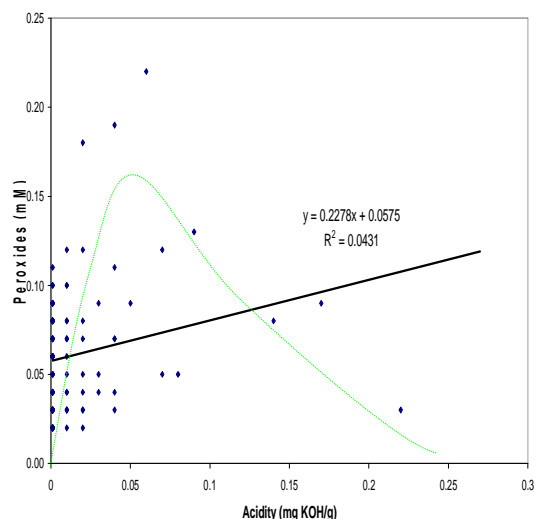


Fig. 6. Acidity vs. Peroxide Concentration for Inhibited Oils

Another correlation that was identified was that between acidity and peroxide concentration. However, if the one extreme high value of peroxide concentration (Figure 6) is lifted out of the data the linear correlation all but disappears. What can instead be seen is that the highest peroxide concentrations are associated with intermediate acidities, and then appears to fall off again. This pattern has in fact been observed during oxidation of base oils containing no inhibitors (2). It can be an effect of the fact that as the polarity of the medium increases, peroxides are stabilized by hydrogen bonds and the chain reaction of oxidation slows down. Hence there will be fewer peroxides in solution at a given time.

9.2. Uninhibited Oils

In this study there are 32 samples from separate transformers. For 27 of these the age of the transformer (and the oil) was known. Acidity and peroxide content was measured for all samples. 20 samples had been analyzed for IFT (interfacial tension), and 19 for DDF (dielectric dissipation factor, i.e. dielectric loss)

Table.4. Linear Correlations for Uninhibited Oils

	Age	IFT	Acidity	Peroxide	DDF
Age	1.00				
IFT	-0.77	1.00			
Acidity	0.59	-0.74	1.00		
Peroxide	0.35	-0.67	0.45	1.00	
DDF	0.83	-0.64	0.52	0.50	1.00

Compared to the inhibited samples above there are many more relatively high linear correlations. Also here the highest correlation against age of the transformer is DDF, but in this case it relies on 50% of

the sample size (compared to only 8 % in the inhibited case), which looks promising. Also IFT and acidity appears to have good linear correlations to age. In this case the peroxide concentration appears to correlate

rather well to IFT, something that was not seen for the inhibited samples.

10. Development over Time

Since the largest linear correlation factor was seen between age and DDF, these parameters were analyzed first (Figure 7).

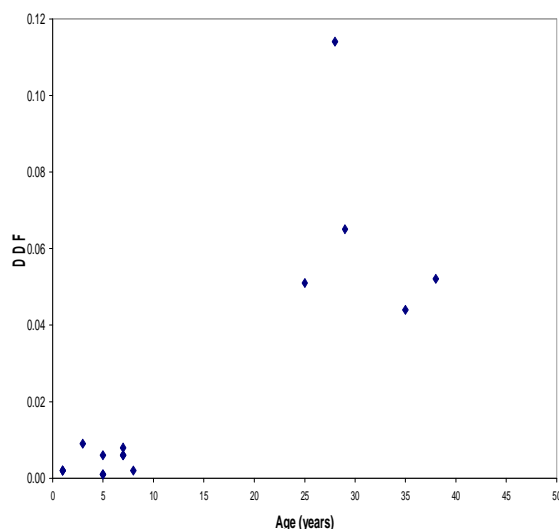


Fig.7. Development of DDF over Time for Uninhibited Oils

Although the linear correlation factor was found to be high (0.83), it is clear that the data points are too scattered for a meaningful regression analysis. The IEC 60422 limit between good and fair condition is very high compared to this data (0.10), so all except one sample would classify as good in this set. The seemingly high correlation to age calls for further study.

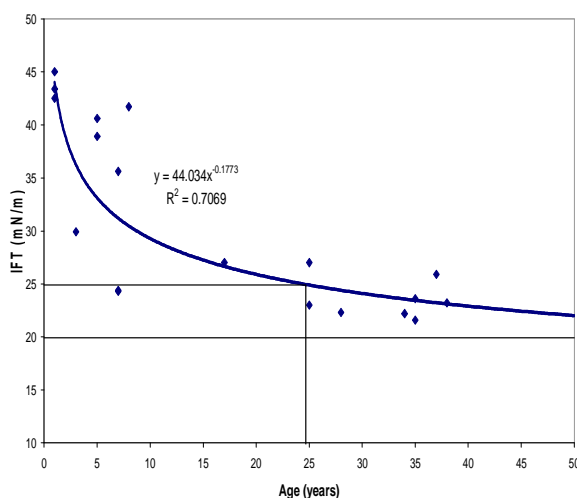


Fig.8. Development of IFT over Time for Uninhibited Oils

The second highest linear correlation was that between age and IFT. An exponential regression analysis (shown in blue in Figure 8) gave a higher correlation factor than a linear one ($R^2=0.60$), and it is in fact well-known that the fall in IFT levels off with time. This gives at hand that IFT in an uninhibited oil would on average stay in the *good* region according to IEC 60422 (above 25 mN/m) for about 24 years. Extrapolation indicates that it would take more than 50 years of service to reach down into the *poor* region (below 20 mN/m).

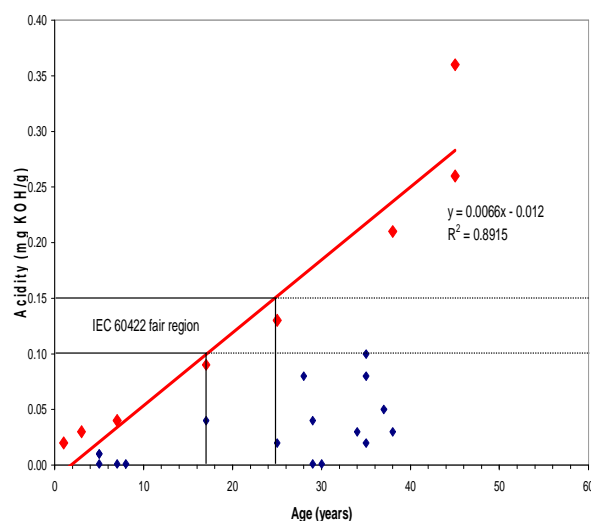


Fig.9. Development of Acidity over Time for Uninhibited Oils

The last identified, somewhat weaker, linear correlation is that between age and acidity. Here no meaningful statistical correlation could be found for the complete data, but as in several of the earlier cases a worst case scenario can be constructed (Figure 9). This indicates a service-life of about 25 years before the acidity reaches the *poor* region where action (new oil or regeneration) is called for.

Other correlations

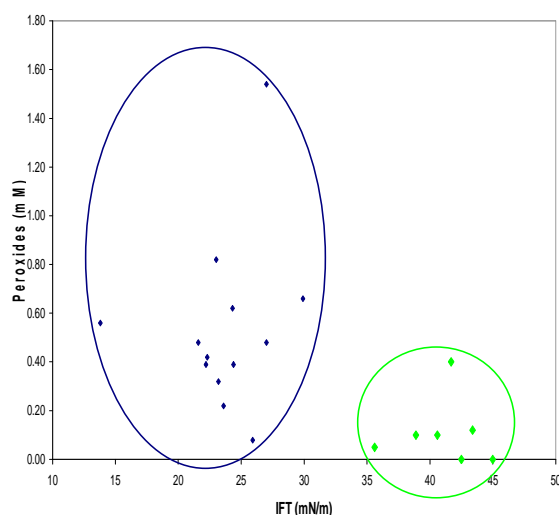


Fig.10. IFT vs. Peroxide Concentration for Uninhibited Oils

When IFT is plotted against peroxide concentration (Figure 10) it is apparent that high IFT is associated with low peroxide concentration and vice versa. In fact the data forms two distinct groups:

Samples with $IFT > 35$ mM/m have an average peroxide concentration of 0.13 mM.

Samples with $IFT < 30$ mM/m have an average peroxide concentration of 0.54 mM.

This result is not trivial to interpret, but higher peroxide concentration in an uninhibited oil could indicate that the natural inhibitors have run out or at least starting to run out. In inhibited oil this is easy to assess by measurement of the inhibitor content, but in uninhibited oils there is no other possibility to judge this.

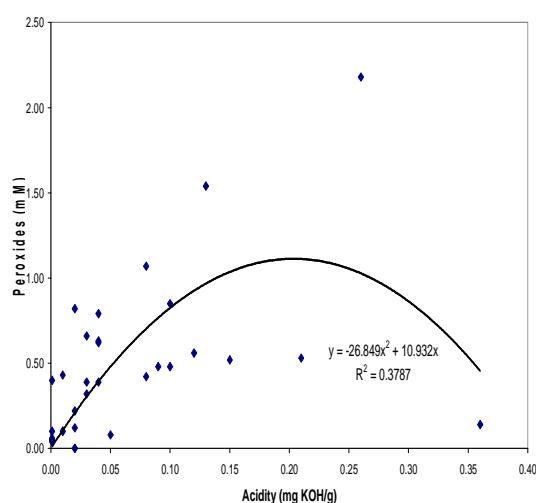


Fig. 11. Acidity vs. Peroxide Concentration for Uninhibited Oils

Lastly acidity was plotted against peroxide concentration (Figure 11). As was the case for the

uninhibited samples, the pattern can be interpreted as an initial rise in peroxide concentration that then falls off. This pattern has also been found in oxidizing base oils (2).

11. Conclusions

The first 15 years of service are totally free of acids for inhibited oil, and in the worst case scenario the acidity goes above the *fair-poor* limit after about 33 years. The average development points to a service-life of more than 50 years for high quality inhibited oils.

This investigation confirms the lower limit of inhibitor content of 0.16% in order to keep the oil virtually free of acids. At these levels of inhibitor there are also no active peroxides to drive formation of polar compounds. This means that for inhibited oils measurement of peroxides adds no information.

In the case of uninhibited oils acids forms from the start (which will contribute to paper degradation), but it nevertheless even in the (statistically) worst case scenario takes 25 years of service before acidity passes above the fair limit if high quality oils are used. Peroxide levels in uninhibited oils were found to have some correlation to other measurable properties such as acidity and interfacial tension, and could perhaps serve a similar purpose as measurement of inhibitor level in inhibited oils indicating when natural inhibitors have been consumed.

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