OXIDATION INHIBITORS FOR INSULATING OILS

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Background:

Mineral oil insulating fluids undergo oxidative degradation in the presence of oxygen to give a number of oxidation products. The final products of oxidation are acidic materials that can affect the characteristics of the insulating fluid as well as cause damage to the components of the electrical unit. Oxygen is a diradical species and the reactions of the oxidative process are complex but they do involve free radical reactions. One way to prevent these types of reaction is to incorporate an oxidation inhibitor that will interrupt and terminate the free radical process of oxidation. Phenolic materials are quite good for this purpose and the two most commonly used inhibitors are 2,6-di-tertiary-butylphenol (DBP) and 2,6-di-tertiary-butyl-4-methylphenol or 2,6-di-tertiary-butyl-para-cresol (DBPC).

Natural Inhibitors

New insulating oil as normally refined contains small amounts of certain chemical compounds that act as oxidation inhibitors. These naturally occurring materials retard oil oxidation until such time as they are expended. The rate at which the inhibitors in the oil are used up is dependent upon the amount of oxygen available, soluble contaminants in the oil, catalytic agents in the oil, and the temperature of the oil. In modern transformers, either sealed to exclude air and moisture or protected by an inert atmosphere, the benefits of the inhibitors can be extended over many years. As the inhibitors are exhausted, the rate of oxidation and the deterioration of the oil increase. Reclaiming processes, such as acid refining or clay treating, can restore the oil so that it has most of its original characteristics, but this has no effect upon restoring the usefulness of the natural inhibitors occurring in the oil. In fact, both Fuller’s earth and activated alumina remove the natural inhibitors and the reclaimed oil has no resistance to oxidation. To overcome this undesirable condition, synthetic oxidation inhibitors should be used to extend the life of the reclaimed oil.

Significance:

The presence of inhibitors in the oil will increase the useful life of the oil with respect to oxidative degradation in the presence of oxygen. As the oil is exposed to this type of oxidative degradation, the oil will be protected as long as there is inhibitor present. However, as the process proceeds the inhibitor will be used up and when it is gone the oil will degrade at a much higher rate. Thus the determination of the amount of inhibitor present can be used to estimate the useful life of the oil. It can also be used to determine whether or not new oil has been properly inhibited prior to its use. As the inhibitor is used up its concentration can be monitored and additional inhibitor added as needed to maintain a proper concentration in the unit. Typical values for fresh oil are in the range of 0.25 to 0.35 % DBP or DBPC by weight.

Inhibitor content is increasingly being performed as a routine test on transformer oil. Due to its Chemical structure, transformer oil oxidizes easily. The oxidation process involves chemical reactions between the oil, oxygen and metallic compounds. The result of these reactions is the formation of oil degradation byproducts, mainly acids, which may affect the dielectric properties of transformer oil. Conservator type or breathing transformers allow oxygen present in ambient air to be absorbed by the oil. This oxygen and high temperatures facilitates the oxidation process within the oil.

The dielectric fluids used in oil-filled electrical equipment contain natural inhibitors. But in order to significantly prolong the useful life of transformer oil, suppliers must add antioxidants to the oil at the manufacturing/refining stage. These antioxidants slow down the oxidation process by trapping oxidation byproducts, called free radicals, and stop the spreading of the oil degradation reaction. During this process, the inhibitor is consumed, to the point where all the remaining inhibitor has trapped free radicals. At this point the reaction will once more continue freely.

Oxidation problems develop when the inhibitor has been completely depleted and oxidation byproducts start significantly affecting the oil properties. Oxidation of the transformer oil is inevitable and there is nothing that can be done to completely stop the process. But there are a few steps that can be taken to slow it down.

First, inhibitor should be present in the oil at all times as the oxidation process continuously consumes it. To check the inhibitor concentration, a representative oil sample is taken from the transformer and sent to a laboratory.

Three analytical methods can be used to determine the amount of inhibitor remaining in the sample:
Infrared spectrophotometry (IR), Gas Chromatography (GC) or High Performance Liquid Chromatography (HPLC).
All three methods are ASTM (American Society for Testing and Materials) accepted procedures and report inhibitor concentration in percent (%) or parts per million (ppm). But detection limits differ for each method. The most commonly used inhibitor is 2,6, ditertary- butyl para-cresol or DBPC.

ASTM classifies new oil in two categories with respect to its inhibitor content. Type I oil should contain 0.08 % of oxidation inhibitor, whereas Type II oil should contain 0.3 % of inhibitor. For units operating in the field, inhibitor content greater than 0.02 % (200 ppm) should be maintained at all times and testing should be performed at least every two years. If the inhibitor content is found to be below 0.02 %, inhibitor should be added to the oil as soon as possible. Moreover, adding inhibitor during oil reclaiming and degassing will bring the oil back to almost new condition.

Specific oil quality tests can be used to determine the stage of oxidation of transformer oil.

Oxidation Stability (acid/sludge) (D 2440) is a method of assessing the oxidation resistance of an oil by determining the amount of acid/sludge products formed when tested under certain prescribed conditions. Oils, which meet or exceed the requirements, tend to preserve insulation system life and ensure acceptable heat transfer.

The test may also be used to check the performance consistency of this characteristic of production oils.

Good oxidation stability is a principal requirement for long service life of transformer oils.

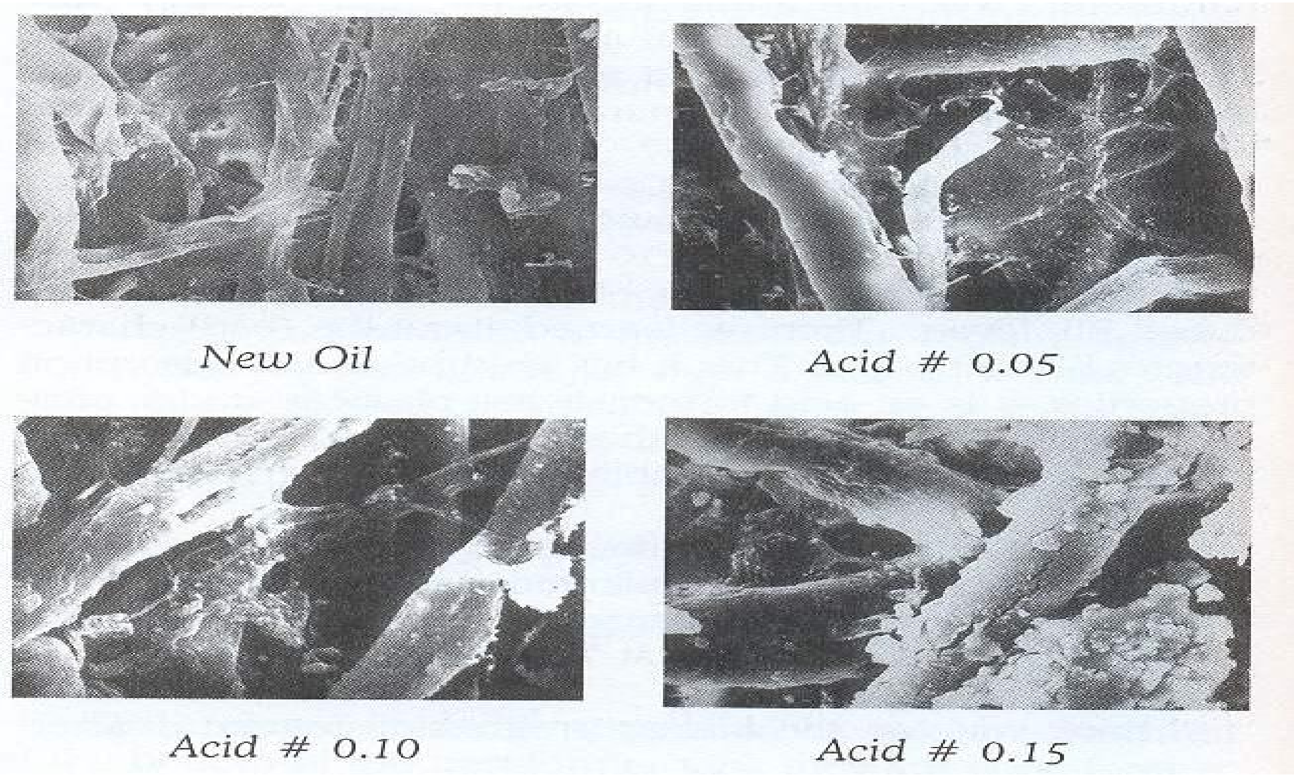
ACIDITY OR NEUTRALISATION NUMBER (NN)

Test Method: ASTM D974

The acidity number reflects the amount of potassium hydroxide (KOH) needed to neutralize 1 gram of oil. Again, measuring the acidity reveals only symptoms of a problem. The acidity alone may not cause a transformer failure, but it can indicate aging of the oil and sludge buildup. High acidity is detrimental to the transformer's insulation system and can lead to rust formation in the presence of water. Sludge will inevitably be formed if high acidity is neglected

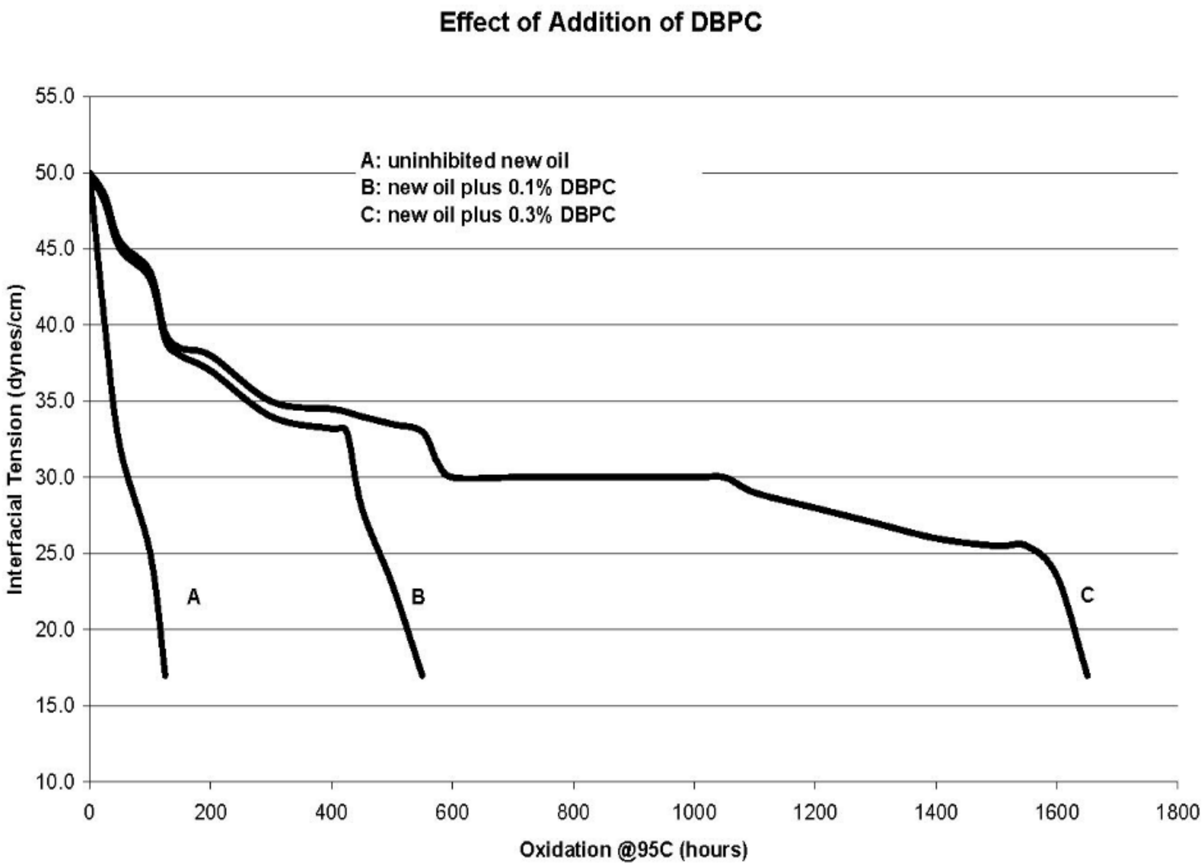
The problem is, oil that reaches an acidity of 0.10 mg KOH/g oil is already causing deterioration of the transformers solid (paper) insulation.

See Scanning Electron Micrograph of Pressboard Spacer at 250X.



INTERFACIAL TENSION(IFT)
Test Method: ASTM D971

Interfacial tension (IFT) is often employed to determine the degree of aging of insulating oil that is in service. During the induction period, i.e. when inhibitor is present and active in the oil, the IFT will remain at a high level, typically, greater than 35 dynes/cm. At the end of the induction period, the IFT will start to decrease due to an increase of hydrophilic compounds in the oil. Decreasing IFT is not in itself an actual problem but is an indication that polar compounds and other oxidation products are forming in the oil.



Comparison of SANS 555 to IEC 296

	Unit	IEC 296(Class11)	SANS 555(2002)
Corrosive Sulfur		Non-corrosive	Non-corrosive
Anit-oxidant additives	% by mass	0.20 – 0.30(inhibited oil only)	No additives
Oxidation stability acidity After 164 h@100 ˚ C	mg KOH/g	No	≤0.15 max
Oxidation stability sludge After 164 h@100 ˚ C	% by mass	No	≤0.03 max
Dielectric Strength	kV/2.5 mm	≥30 min(as delivered) ≥50 min(as treated)	≥30 min
Dissipation Factor @ 90˚C		≤0.005 max	≤0.005 max
Total furfural and furans	mg/Kg		Not detectable
Polyaromatic hydrocarbon	%		≤3.0 max
Gassing tendency	mm^3/min	Not Specified	≤ +5
Polychlorinated biphenyl	mg/Kg	Not detectable	Not detectable

Current situation in South Africa

The SANS code specifies that all new insulating oil should be unhibited despite the allowance in the IEC/ASTM code.

There is a lack of quality control by both the Suppliers of Insulating oil and the transformers manufactures in certain instances (See Case Study at the BHP Billiton Mozal Smelter).

The practice of oil regeneration is generally accepted but the use of synthetic oxidation inhibitors has not found favour with transformers owners despite the obvious benefits.

See Case Study of a Transformer at Durban Electricity where the oil deterioration was significant following regeneration without the addition of oxidation inhibitors.

<u>Conclusion</u>

- Transformer owners can use oil and electrical test results as well as traditional time based maintenance techniques to develop a maintenance program that will provide high reliability at optimum cost.

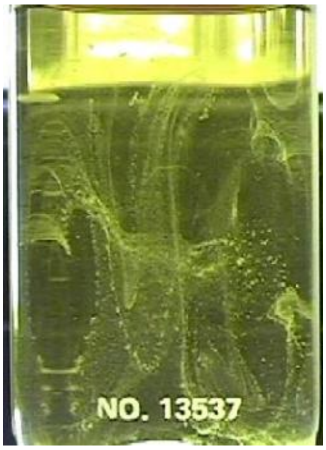
- Properly serviced insulating oil, can give practically unlimited extension of life free from formation of sludge or excessive acidity due to oxidation.

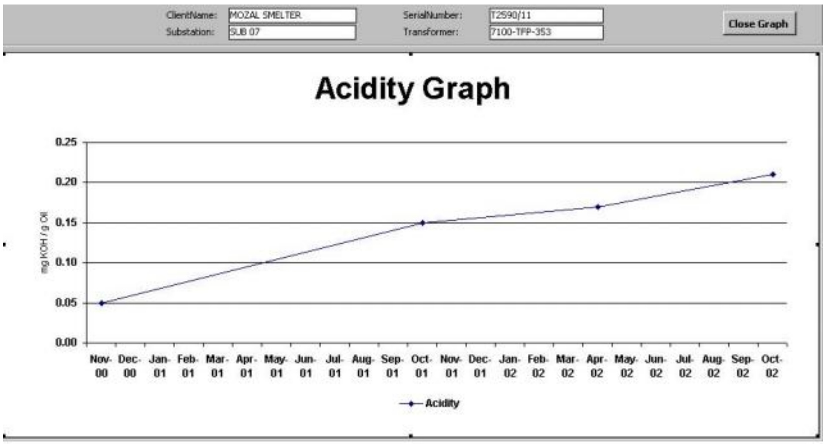
- Reclaimed oil is, in some respects, superior to new oil.

MOZAL SMELTER-TRANSFORMER MAINTENANCE

The acidity in the following transformer reached the stage of Insulation fluid replacement with internal flushing or fluid regeneration after 2 years of service:

Substation	Transformer	Serial Number	Sampling Date	Water	kV	Acidity
SUB 07	7100-TFP-353	T2590/11	17-10-2002	21	48	0.21





The oil colour can be compared to another Transformer oil from Substation 7100-TFP-503 (serial no T2588/1), which has shown no deterioration but is similar in respect to age of service.

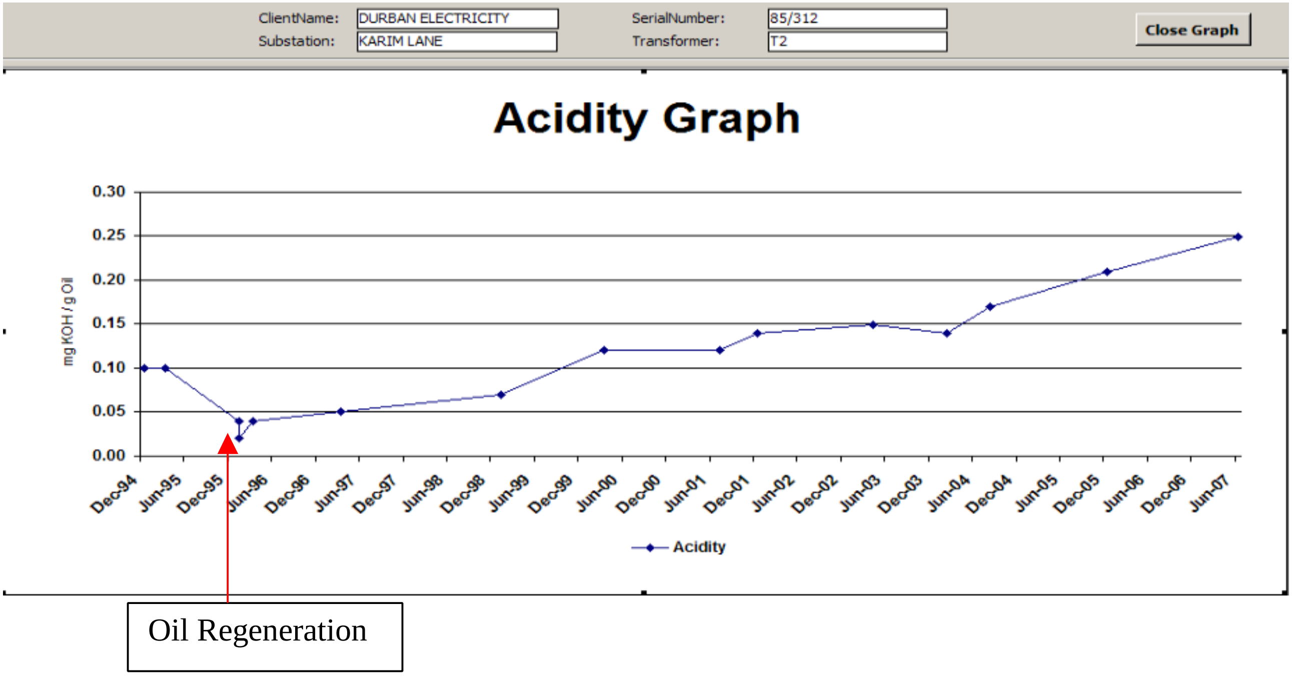
This is an abnormal condition as the insulating oil has reached end of life criteria in a very short time. The transformers were manufactured in 1999.

The cause is the insulating fluid has a poor Oxidation Stability (No conformance to SANS 555
" The oxidation stability, also known as the life test of an oil, will give an indication of the oil's ability to withstand ageing in the form of oxidation and will give an indication of the life expectancy of an oil"

RECOMMEND:
Insulation fluid replacement with internal flushing or Oil regeneration with the addition of synthetic oxidation inhibitors.

Case Study DURBAN ELECTRICITY

Substation: KARIM LANE	Transformer No: T2	Serial No: 85/312
Sample Point: MAIN TANK	Primary Voltage: 33 kV	Secondary Voltage:11 kV
VA Rating: 15 MVA	Vector Group: Dyn11	Impedence:10.1%
Tap Changer: On Load	Make: BONAR LONG	Conservator: Yes
Year Manufactured: 1985	Breather Size: SA5	Oil Volume Litres: 7894



The Transformer insulating oil was regenerated in 1996. The acidity value has more than doubled in 10 years. This indicates oil with a poor Oxidation Stability or the removal of the Natural Inhibitors from the oil regeneration process.

Conditions that have proven satisfactory for processing mineral oil are found in the ASTM Table below. These conditions will not remove the inhibitors as a result of processing.

ASTM Recommended Processing Conditions of Inhibited Oil

Temperature Deg C	Minimum Pressure	
	Pascals	Torr
40	5	0.04
50	10	0.075
60	20	0.15
70	40	0.3
80	100	0.75
90	400	3
100	1000	7.5

ASTM D-3487-00 Note 1
If higher temperatures are used, test the oil for inhibitor content
and add as necessary

REFERENCES

[1] A Guide to Transformer Maintenance (1st, 2nd ,3 rd edition)

[1] IEEE C57,106-1991

[2] ASTM D 4768 – 03 Standard Test Method for Analysis of 2,6-Ditertiary-Butyl Para-Cresol and 2,6-Ditertiary-Butyl Phenol in Insulating Liquids by Gas Chromatography

[3] IEC 60296

[4] ASTM D 3487 – 00 Standard Specification for Mineral Insulating Oil Used in Electrical Apparatus.

[5] Stan Lindgren & Barry Ward, EPRI, "*Management of Aging Power Transformers*" CEA Electricity Conference, 1999

[6] IEEE P C57.XX Draft 10, October 2001, "IEEE Guide for Application of Monitoring to Liquid Immersed Transformers and Components", Donald Chu, Chair

[7] IEEE P C57.140, Draft 8, October 2002, IEEE Guide for the Evaluation and Reconditioning of Liquid Immersed Power Transformers, Rowland James, Chair

[8] SANS 555

[9] NEW TESTS FOR TRANSFORMER OIL by William Morse Morgan Schaffer Corp.