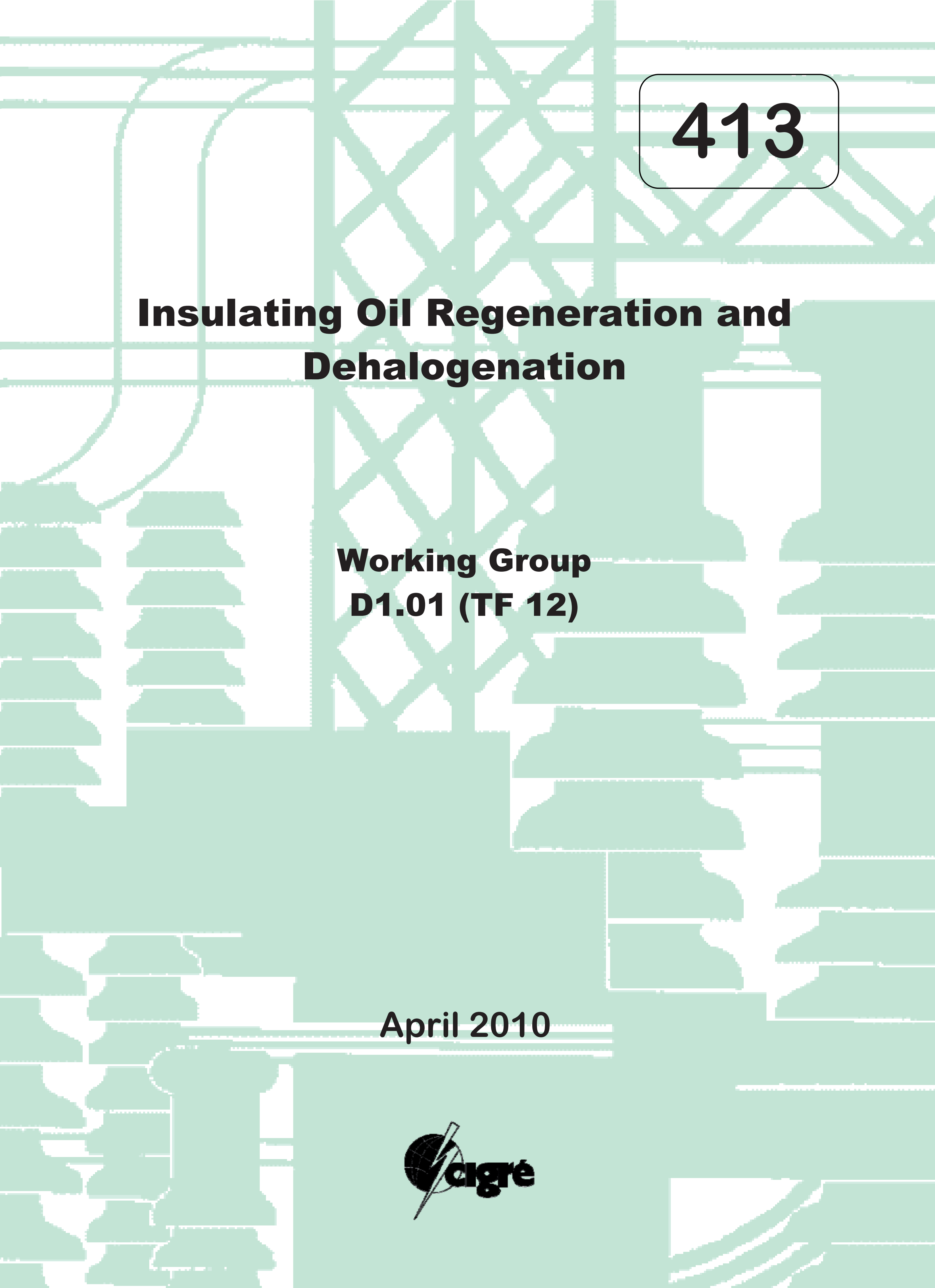

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Insulating Oil Regeneration and Dehalogenation

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Insulating Oil Reclamation and Dechlorination

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1 EXECUTIVE SUMMARY

Mineral insulating oil in service subjected to heat, electrical stress, consequently deteriorates to a point which no longer suitable for further use. The common practices are either change the oil or reclaim the oil. A verity of reclamation technique commercially available, however the reclaimed oil may not pass the requirement of oil oxidation stability test as required by current international oil specification. Consequently such oil should be inhibited using commercially available inhibitors.

Since some mineral oil in service may contaminated by PCB, method of PCB destructions and oil decontamination is described in this report.

2 INTRODUCTION

Management of oil insulated transformers and equipment in electricity Generation, Transmission, Distribution and Use represents, for Utilities and Users, a new technologic challenge of remarkable complexity. This situation may be specially critic in the case of equipment service breakdown with the subsequent direct damages (loss of assets), indirect (loss of production or service interruption) and environmental in the case of leakage of dangerous substances.

Moreover, last years tendency shows a decrease on new transformers commissioning, thus equipment are getting older and approaching the end of original design lives, and organizational changes in large companies focus attention on the need to assess the remaining lives of assets, and the necessity of being accountable to other parties, usually non-experts and often non-technical.

During its operating life, transformer oil deteriorates due, heat (inherent from operation of transformer), external contamination (ingress of water and particles) and internal contamination (by-products of oil, paper and other materials ageing). The first option to recover oil functional properties is the substitution of the aged oil by a new one (refilling). Second option is oil reclamation and studies carried out by CIGRE WG A2.18 [1] show that oil treatment and reconditioning is a very important tool for transformer maintenance and life extension.

The corrosivity of oil may be affected by reclaiming. Some corrosive components may be removed, others may be formed during the treatment. Metal passivators will be at least partly removed. The net effect of reclaiming on corrosive properties of oil may be difficult to predict, at the present level of knowledge. Unless there is already experience from the combination of oil type and reclaiming technique in each particular case, it is strongly suggested that lab scale reclaiming is carried out in order to assess what changes may occur. In some cases oil may need the addition of metal passivator as well as oxidation inhibitor

Finally, the PCB problem has introduced an environmental concern which needs an adequate response.

3 DEFINITIONS

For the purposes of this report, the following definitions apply:

Reclamation/ Reclaiming
The elimination of soluble and insoluble contaminants from an insulating liquid by chemical absorption means, in addition to mechanical means, in order to restore properties as close as possible to the original values.

NOTE – The process may include the use of antioxidants

Reconditioning
A process by which the solid content and the water content of a used insulating liquid is reduced to an acceptable level by mechanical means.

NOTE – Often reconditioning includes degassing as well

Dehalogenation
Decontamination treatment which reduces the PCB and other chlorinated compounds (PCT, PCBT, PCDF, and PCDD) concentration to desired values (i.e. < 2 mg/kg).

4 INSULATING MATERIALS

Oil filled electrical equipment consists of a dielectric system, electromagnetic circuit, current carrying circuit and mechanical components. The insulating materials are composed mainly of organic compounds. As a result they deteriorate rapidly if they are exposed to high temperature. This is particularly true for the solid insulating material types, since those most commonly used are based on cellulose whose ageing characteristic is greatly accelerated above 100ºC, a temperature at which many transformers are currently operated. Accordingly, efficient cooling is considered essential in all electrical equipment, and liquid insulating materials are used for this purpose. The other essential properties of an insulating liquid are high dielectric strength, arc extinguishing capability and as a mechanical lubricant.

Insulating liquids used in oil filled electrical equipment can be divided into two groups - mineral oils and synthetic oils. Mineral oil as an insulating liquid must perform to stringent criteria based upon its physical, chemical and electrical properties, as well as adhering to local and international environmental and health and safety standards. In general flow character and thermal properties of the liquid are the most important factor at the design stage of electrical equipment. The oil's electrical properties are important during equipment operation and its chemical properties for condition monitoring of the oils both before service and in service. Compatibility of the oil with materials used in the construction of the equipment is a very important factor, which manufacturers of the equipment must take in to consideration during design and manufacturing. Health, safety and environmental issues are of the utmost importance to the environment and to those people handling or otherwise in contact with it. Most of the properties of a mineral insulating oil are dependant on the selection of crude oil and the refining technique.

4.1 Mineral Oil

Crude oil is made up of hydrocarbons, a small percentage of which contain oxygen or sulphur. The organic sulphur content can vary from 0.1% to 5%. Crude oil can be divided into three separate types: paraffinic, asphaltic and mixed-base. The paraffinic type crude is high in paraffinic compounds (alkanes) and consists of mostly lighter fractions - gasoline, gas oil and gases. The asphaltic type also contains paraffinic compounds but has a comparatively high concentration of naphthenic compounds (cycloalkanes). Heavy paraffinic crude provides most of the heavier fractions - bitumen and waxes. Mixed-base type crude is a mixture of asphaltic and paraffinic. All types of crude contain aromatic molecules.

Crude oil of all three types has many uses but it has to be refined to separate out the useful fractions. The different fractions are separated according to boiling ranges by distillation in a fractionating column. Insulating oils, including transformer oils, are produced from the fraction with a boiling range between diesel fuel and automotive lubrication oils.

4.2 Transformer Oil

Regardless of the crude from which a transformer oil is refined, it will contain paraffinic and naphthenic hydrocarbons. With the exception of 'white oil', insulating oil will also contain aromatic compounds and various other molecules at varying concentrations. The composition of the finished oil will depend on the choice of crude and on the refining procedure.

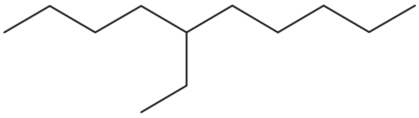
4.2.1 Chemical Composition

The many compounds present in crude oil have different effects on the properties of a refined oil; some will only benefit the oil and some will be harmful, others have both positive and negative effects on the oil, and balancing these compounds is part of the skill in refining an oil. Some of the compounds and their effects are discussed here.

4.2.1.1 Paraffinic Hydrocarbons

There are two types of paraffinic molecule in transformer oil: straight-chain and branched. Straight-chain paraffins or n-alkanes predominate, they are considered to have poor low-temperature properties as they crystallise as the oil temperature cools. Paraffins are poor solvents of water and oxidation products. As a result free water can be present and sludge (water/oil/solid suspension) will precipitate. Paraffins also have lower thermal stability than other hydrocarbons. It is fairly typical for oil refiners to refer to all branched alkanes as "iso-paraffins", rather than applying it to isoalkyl structures only.

Paraffin

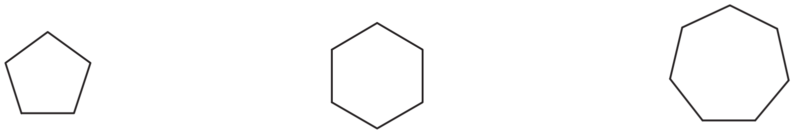


Iso-Paraffin

Figure 1 Typical paraffinic molecules in transformer oil

4.2.1.2 Naphthenic Hydrocarbons

Naphthenic molecules are cyclic alkanes. The ring structure can contain five, six or seven carbon atoms, but six is the most common. In contrast to the paraffins, naphthenes have excellent low temperature properties, which is important for transformers in cooler climates. Naphthenic compounds are also better solvents for oxidation products. However, the naphthenic compounds found in the fraction used for transformer oils are more volatile than the paraffinic compounds. As a result oils with high naphthenic content tend to have lower flash points.

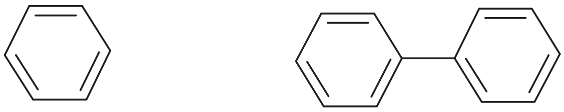


Cyclopentane Cyclohexane Cycloheptane

Figure 2 Typical naphthenic molecular structures

4.2.1.3 Aromatic Hydrocarbons

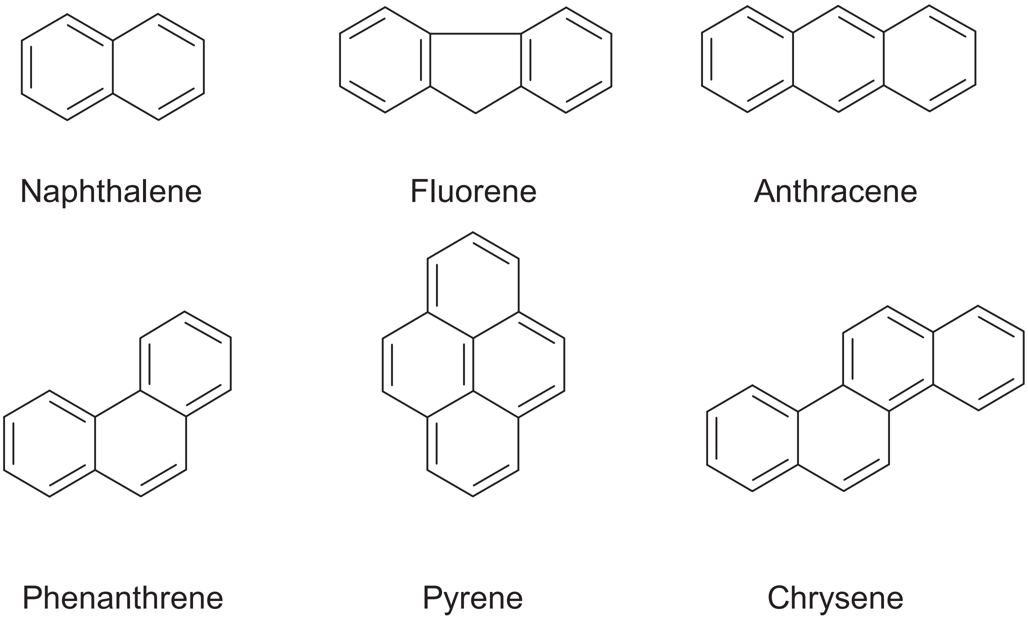
Aromatic hydrocarbons are present in all but the most highly refined transformer oils. Most aromatic compounds in transformer oil contain at least one benzene ring. The chemical and physical properties of aromatic compounds differ greatly from naphthenic compounds, but they have similar dielectric constants. There are many aromatic structures with only one benzene ring, called mono-aromatics, and benzene itself may be present. The aromatic fraction of a transformer oil is important because most of the natural inhibitors to oxidation are aromatic.



Benzene Biphenyl

Figure 3 Typical aromatic molecules

Aromatic compounds, which contain two or more aromatic rings fused together, are called polycyclic aromatics (PCAs) or polyaromatic hydrocarbons (PAHs). Many PCAs are found naturally occurring in crude oil; several of these survive the refining process to form part of a transformer oil. The PCA content is usually higher if the boiling point range of the oil fraction is higher.



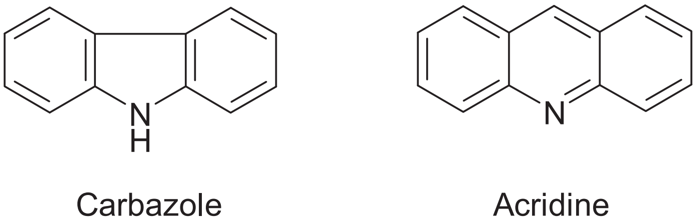
Naphthalene
Fluorene
Anthracene
Phenanthrene
Pyrene
Chrysene

Figure 4 Typical polyaromatic molecules in transformer oil

PCAs are important in many ways and are discussed more fully later in this introduction.

4.2.1.4 Other Molecules

Transformer oil is not wholly composed of pure hydrocarbons. There are also some heteroatoms; typically nitrogen, oxygen and sulphur are present in small quantities. Nitrogen is present in only very small quantities, typically a few ppm, but can be found in two forms: basic (e.g. pyridine, quinoline) and non-basic (e.g. carbazole, pyrrole). Despite the low concentration, nitrogen-containing compounds can have a profound influence on the character of the oil. Some molecules can have unwanted characteristics - they can be charge carrying or oxidation initiators, or they can be extremely useful as oxidation inhibitors or metal passivators (especially of copper).



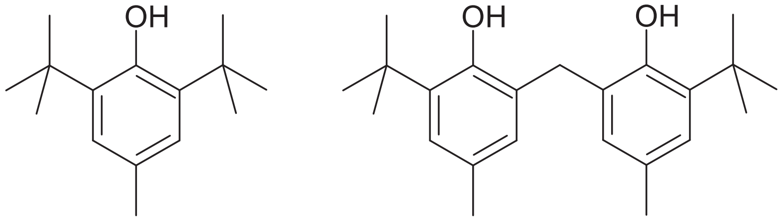
Carbazole
Acridine

Figure 5 Typical nitrogen-containing molecules in transformer oil

An unused transformer oil fresh from the refinery has few oxygen-containing molecules, although some dibenzofuran may be present. Furfuraldehyde (2FAL) is occasionally left as a remnant from the refining process. Phenols can be found in some oils as synthetic additives, for example DBPC. Once an oil has been in service then oxygen-containing compounds are more common. Oxidation of oil, which is discussed in detail later, produces acids, ketones and phenols.

Furan 2-Furaldehyde

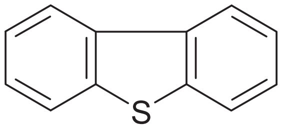
Figure 6 Typical oxygen-containing compounds in transformer oil



Phenol based antioxidants

Figure 7 Typical oxygen-containing compounds in inhibited transformer oil

Although sulphur is more common in oil than nitrogen and oxygen it is still present at low concentrations. The structure of a sulphur-containing molecule greatly influences its effect on the oil. Most organo-sulphur molecules in transformer oil are either corrosive and cause damage to the copper in the transformer or they are antioxidants and destroy the peroxide intermediates; some may be both. For example arenethiols are effective oxidation inhibitors because of the stable arylthiooxy radical (ArS), but they also attack metals such as copper. Mercaptans are usually only present in under refined poor quality oils or they may be generated in service.



$R{-}SH$ $R{-}S{-}CH_3$

Dibenzothiophene Mercaptan (Thiol) Sulphide

Figure 8 Typical sulphur-containing molecules in transformer oil

4.3 Refining Techniques

In its natural state crude oil is of little use and must be refined by distillation or fractionation. The oil is separated into different distillates according to the boiling range. Depending on the crude this is done at normal pressure (paraffinic crudes) or at very low pressure (naphthenic crudes). Lowering the pressure allows separation of heavier molecules by lowering their boiling ranges. Normally fractionation does not take place above 350°C, as the oil will begin to decompose thermally.

Paraffinic crudes are commonly dewaxed (by low-temperature filtration) after distillation to give the oil reasonable low temperature properties. Naphthenic oils do not require dewaxing, as they do not usually contain many n-alkanes.

There are three methods used in refineries which remove unwanted components:

- Solvent Extraction
- Acid-Clay Treatment
- Catalytic Hydrogenation

The solvents used to extract impurities are sulphur dioxide or furfuraldehyde (FFA). Two phases are produced:

- The solvent phase containing the unwanted material
- The raffinate phase, which is a purified oil

It is essential that all traces of the solvent are removed from the oil after extraction as the solvent can cause problems in the finished oil. For instance, transformer oil in service is analysed for FFA, as it is a breakdown product of paper, and any residual FFA from the refining would interfere with this monitoring process.

An increasingly less common technique is acid clay treatment. Depending on temperature and concentration, sulphuric acid can be used for solvent extraction. White oils (free from all aromatics and heteroatoms) can be produced using oleum - sulphuric acid containing free sulphur trioxide.

Acid clay treatment is gradually being phased out due to the environmental impact of its waste products. Activated clay is still occasionally used, however, to remove polar compounds from used oil.

Catalytic hydrogenation is gradually superseding acid clay treatment and solid phase extraction. The unwanted compounds are absorbed onto a catalyst at high temperature and pressure and they react with hydrogen dissolved in the catalyst. It is possible at this stage to increase the naphthenic content of a paraffinic oil at the expense of the aromatic fraction.

4.4 Requirements of Insulating Oil

International standard IEC 60296 [2] describes the specification for unused mineral insulating oils. The three main requirements of insulating oil are:

- To meet the specified insulation criteria the oil must have high dielectric strength and low dielectric dissipation factor to withstand the electric stresses imposed in service.
- To meet the specified heat transfer and cooling criteria the oil must have a viscosity and pour point that are sufficiently low to ensure that oil circulation is not impaired at the most extreme low temperature conditions for the equipment.
- To meet the arc quenching criteria the oil requires a high flash point as well as high dielectric strength and low viscosity, to provide sufficient insulation and cooling thus ensuring that arcing is extinguished.

The more general requirements are in many cases related to, and inter dependent with the three main functional requirements described above, and these are enlarged upon below.

4.4.1 Functional properties

Functional properties are those properties of oil which have impact on its function as an insulating liquid and coolant. The following are critical functional properties:

- The ***viscosity*** of the oil needs to be low enough to ensure that the oil flows well under all (particularly low) temperature conditions thus providing the necessary cooling and, where appropriate, arc quenching properties.
- The ***density*** of the oil has to be low enough to ensure that ice cannot float on the oil surface at very low temperatures and cause internal flashover.
- The ***pour point*** is related to viscosity and needs to be low enough to ensure that the oil flows satisfactorily under low temperature conditions.
- The ***moisture content*** of the oil must be low, otherwise the electrical strength of the oil will be impaired and moisture will be absorbed into any paper insulation, reducing insulation life and increasing the risk of dielectric breakdown.
- The ***breakdown voltage*** needs to be sufficiently high to provide dielectric strength to prevent breakdown of the oil under electrical stress.
- The ***dielectric dissipation factor*** (DDF- the tangent of the loss angle and commonly referred to as tan delta) has to be sufficiently low to ensure that the dielectric losses are small and that the oil thus provides satisfactory insulating properties.

- The oil must have a ***low particle size*** and count and low fibre content as the presence of such contaminants, especially in the presence of moisture, can considerably reduce the electrical strength.

4.4.2 Refining and stability

The following are the properties of the oil that are influenced by the type of refining and the use of additives. They include:

- Well refined oils must have a light yellow colour and a clean appearance. They must be free of suspended material and foreign matter.
- The oil must have a high value of ***interfacial tension*** (IFT) to ensure absence of polar compounds in the oil and suitability of the oil for use as insulating material.
- The oil must have ***low sulphur content*** and contain no corrosive sulphur.
- The oil must have a ***low acidity*** (neutralization value) to eliminate the risks of sludge formation and corrosion.
- The unused oil must have ***low furan content***, otherwise the effectiveness of condition monitoring by trend assessment of furan content is impaired.
- The oil must not contain levels of contamination by ***any individual metal.***

4.4.3 Performance

By ***performance*** it is meant those properties that are related to the long-term behaviour of oil in service and/or its reaction to high electric stress and temperature.

- The oxidation stability of the oil must be high to reduce oxidation processes occurring in service which degrade the oil, whose chemical products include acids and sludge. These compounds can reduce the effectiveness of cooling and cause general internal deterioration leading to eventual failure.
- Anti-oxidant additives (inhibitors) such as 2,6-di-tert-butyl-p-cresol (DBPC) slow down the oxidation of oil. The concentration of antioxidant in oil is decreased during its service life and it is therefore important to monitor this. Oils are grouped into three classes depending on the antioxidant content. These are ***uninhibited***, ***trace inhibited*** and ***inhibited***.

4.4.4 Health, Safety and Environmental (HSE) properties

- The flash point needs to be sufficiently high to eliminate the risks of ignition of vapours above the oil during maintenance or in service. In addition, low flash point may represent an inhalation risk for workers.
- The oil must have undetectable polychlorinated biphenyl (PCB) content to meet the requirements of environmental legislation.
- The oil must have a low polycyclic aromatic (PCA) content to meet the requirements of health & safety legislation.

4.4.5 Specific requirements for special application

Standard IEC60296 gives two categories of insulation:- (i) ***general purpose*** and (ii) ***specific requirement.*** General purpose insulating oil is produced in large volume and suitable for the majority of units manufactured to IEC60076 [3].

For transformers with higher operating temperatures or those designed for extended service life, there may exist further limits for the oil oxidation stability test, using standard method IEC61125C [4] as stated in IEC60296. Mostly, such oil is inhibited as the oil’s response to inhibitor increases in the more highly refined the oil.

For oil forced (OF-) or oil direct (OD-) -cooled power transformers (IEC 60076-2) with a high oil circulation speed (for example HV/DC transformers), the charging tendency of the oil should be taken into consideration as the electrostatic charging tendency of the oil is a function of equipment design, operating temperature, ducting, pump, cooling etc. [5].

For equipment with high electrical field stress or other special design, any gases formed under special stress conditions must be absorbed by the oil. There is, therefore a specific requirement for gassing tendency (see IEC 60628A [6]), and this must be agreed between the oil manufacturer and user of the oil.

Of the various insulating fluid options available to the user, mineral insulating oil has for the vast majority of situations proven to be the most cost effective choice meeting the above functional requirements.

The testing of oxidation stability can form part of the guidelines [4,7] for establishing the suitability of used oil for further use. These guidelines set out several tests which should be performed before any decision is made regarding re-use of the oil. In no circumstance should a decision be made about a particular oil based on one single test or result. Regular interval sampling is important to establish a trend of the oil deterioration as well as the actual condition of the oil. In general, the optimum interval will depend on the type of equipment in operation, power, function and service condition of the equipment (see IEC 60422 [7]).

Insulating oil in service is subjected to high temperature, high oxygen levels, and catalysis, all of which affect its chemical properties. As result, oil performance may change. To avoid damage to the equipment the oil in the unit should be tested regularly and corrective action should be taken. Tests are performed in-service to establish the type of contamination present in a contaminated oil. In general this may be divided into two groups which are discussed in depth later.

4.5 Cellulosic insulating paper

For correct function, each transformer winding needs to be insulated turn from turn. Several solid insulating materials can be used for this purpose. In power transformers, cellulosic insulating paper, also known as Kraft paper, is by far the most widely used material, although nowadays other synthetic insulating materials are used to insulate the areas where the operating temperature is believed to be high (hybrid insulation), or for entire transformers specially designed to operate at high temperatures. These materials, also referred to as aramide papers, should be considered very special cases, and their behaviour will not be considered in this document (for more information on these materials and their applications, see document IEC TS 60076-14).

4.5.1 Manufacturing processes for Kraft paper

Kraft paper is a mat of cellulose fibres extracted from wood and other vegetable sources. Cellulose is never found as a pure compound in nature: cotton fibre is probably the purest natural source of cellulose and even so still contains about 5% of other substances such as lignin and the so called hemicelluloses (pentosanes). Dependent on species, wood contains, on a dry basis, between 40 to 55% cellulose, 15 to 35% lignin and 25 to 40% hemicelluloses.

During paper manufacture, wood is chemically treated to reduce the content of lignin and pentosanes. For electrical insulating papers, the most widely used method is the KRAFT process, in which wood is treated with a mixture of sodium hydroxide (NaOH) and sodium sulphate (Na_2SO_4). An alternative, acidic treatment, consists in treating the wood pulp with a mixture of sulphurous acid (H_2SO_3) and a bisulphite, normally calcium bisulphite ($Ca(HSO_3)_2$). After treatment, the chemical composition of the paper is about 89% cellulose, 7 - 8% pentosanes and 3 - 4% lignin.

4.5.2 Chemical composition

Cellulose is a linear condensation polymer consisting of D-anhydroglucopyranose units joined together by β-1,4-glycosidic bonds, as it is shown in Figure 9. X-ray diffraction studies show that cellulose has both inter- and intra-molecular hydrogen bonds. A number of cellulose chains are held together by the hydrogen bonds, in which the hydroxyl groups are involved, to form a single cellulose fibre.

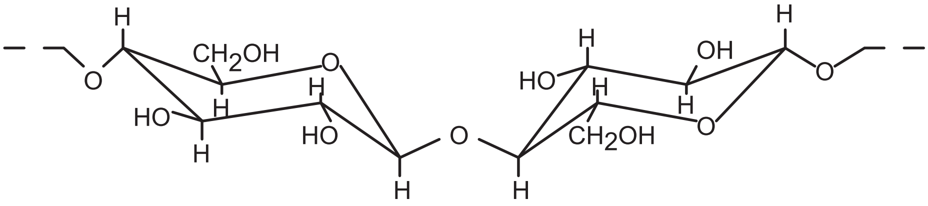


Figure 9 Chemical composition of cellulose

Lignins are complex aromatic polymers, with molecular weight around 11000, formed by three-dimensional polymerisation of cinnamyl alcohol (3-phenyl-2-propene-1-ol). Their detailed structure differs between sources and they do not yet have industrial applications.

Hemicelluloses are not, despite their unfortunate name, cellulose derivatives. On the contrary they constitute a wide group of polysaccharides joined to cellulose fibres through hydrogen bonds.

Cellulosic papers may be thermally upgraded by addition of a thermal stabilising agent such as urea, dicyandiamide or melamine.

It is very important to note that cellulose is constituted by a large number of the very polar C-O and H-O bonds. These bonds may interact with the other polar compounds existing dissolved in the oil, mainly water and acidic compounds, thus making cellulose very sensitive to such compounds (for instance, water in oil is measured in mg/kg but water in paper is measured in % - 1% equals 10.000 mg/kg).

4.6 Mechanism of Kraft paper (cellulose) degradation

Cellulose degradation, like oil degradation, is a very complex process that is accelerated by the combined effect of heat, water, acids and oxygen, all of them available to the cellulose in the environment of the transformer. It depends primarily on the following processes [14, 15]

- ***Hydrolytic degradation:*** The effect of water on cellulose oxygen bonds leads to the formation of C5 and C6 sugars. Then, an acidic-catalysed dehydration occurs and gives furan products.
- ***Oxidative degradation***: Cellulose is highly susceptible to oxidation, the hydroxyl groups being the weak areas where carbonyl and carboxyl groups are formed and can cause secondary reactions giving chain scissions. Low weight products like CO, CO_2, H_2, and H2O are usually observed.
- ***Thermal degradation:*** In temperature range above 130-150°C, the degradation is similar to the normal ageing of cellulose. Oxidative and hydrolytic degradation occurs which severs the cellulose chain, reducing the degree of polymerisation and therefore the tensile strength. The decomposition products are mostly water and carbon oxides.

4.7 Properties of paper

Cellulosic insulating papers must have good electrical properties to withstand electrical stresses as well as good mechanical properties to avoid it became broken whilst in service. However, different mechanical properties may have quite different behaviours during ageing [8].

4.7.1.1 Tensile strength of paper

Another measure of paper effectiveness is given by measurement of its tensile strength [16]. Most of the early transformer work was based on the use of the tensile strength as a measure of paper degradation, taking the reduction of the tensile strength of ***50 % of its original value*** as the end of life criterion. Importantly, it is known that the tensile strength of paper decreases in a linear relationship with the diminution of the degree of polymerisation, and reaches about half of its original value when DP is about 200-250.

4.7.1.2 Degree of polymerisation

A measure of cellulose efficacy is given by the degree of polymerisation (DP) [9]. Paper with an initial value of DP towards 1300 is expected to last the lifetime of the transformer (25-40 years), but a DP of 150-250 is regarded as a end of life criterion for the transformer insulation because at this DP the paper is at risk of mechanical failure. Degradation of the paper can cause the transformer to fail by a number of mechanisms:

a) The brittle paper can break away from the transformer windings and block ducts;

b) Water is a product of degradation and builds up in the paper, reducing its resistivity;

c) Local carbonising of the paper increases the conductivity and may lead to discharges and breakdown

The DP can be determined from the viscosity of dilute polymers solutions according to IEC 60450 [9] or ASTM D4243 [10].

It is noteworthy that insulating papers in transformers in service are inaccessible for sampling, thus direct measurement of the evolution of their properties is impossible. For this reason, there is a general agreement in using the degree of polymerisation of the paper as “marker” property to follow the overall evolution of cellulosic paper condition.

4.7.1.3 Furans and other ageing products

Furan products are measured in oil [11-13], but they originate from cellulose degradation. High Performance Liquid Chromatographic (HPLC) analysis enables the separation and quantitative measurement of furan products. ***2-Furaldehyde*** is the most common product of ageing. But ***2-furfuryl alcohol*** (2FOL), ***2-methyl-furfural*** and ***5-hydroxy-2-methyl-furfural*** (5-HMF) are also detected. Furan products are generally relatively stable at temperatures up to 140°C, though notable exceptions are 2-furfuryl alcohol and 5-HMF. In a newly filled transformer, the concentration in oil of these products increases initially, levels off, then increases exponentially with ageing time to a maximum value.

It is noteworthy that ***water*** and ***carbon dioxide*** are the main by-products of the thermal degradation of cellulose. ***Furans*** and ***carbonyl derivatives*** are the second major degradation products, whereas ***alcohols***, ***acids*** and ***aromatic*** and ***aliphatic hydrocarbons*** are minor products [17]. At the beginning of degradation, mechanical properties are degraded rapidly, thus the paper became brittle with the risk that some portions of paper could peel off the windings blocking the transformer refrigerating ducts. It is very important to bear in mind that cellulosic paper is not a reclaimable material, thus oil reclamation techniques described in this document will never restore the paper properties, although oil reclamation will have a highly beneficial effect by removing the carboxylic acids and sludge that promote and speed up paper degradation. In this way it is possible to indirectly increase the residual lifetime of the paper in the transformer.

5 OIL CONTAMINATION AND DEGRADATION

Contamination in the oil can be divided into two groups - physical contamination and chemical contamination. Physical contamination includes species, such as water or particles, which can be removed by a physical process. Chemical contamination may be described as contamination that must be removed by a chemical process.

5.1 Physical contamination

Physical contamination includes species, such as water or particles, which can be removed by a physical process. Physical contamination of the oil can be established by testing the oil for breakdown voltage and water content. Additional test to establish type of contamination is particle content test. In general there is correlation between break down voltage and water content. There is also correlation between breakdown voltage of the oil and particle content. High moisture and or particle in the oil lead to low breakdown voltage. As moisture and particles can be removed from the oil by a relatively simple filtration, physical contamination is easy to deal with. Filtration of the oil and removal of the moisture, always improve breakdown voltage of the oil.

5.1.1 Water

A source of moisture is from paper degradation, as insulating paper that decomposes under influence of the heat generates carbon monoxide, water and furfural. Moisture also can be generated as result of oil deterioration. Moisture may enter the unit from atmosphere due to leakage, cracked seals and from breather system due to lack of maintenance of moisture absorbent material. High moisture content in paper may increase risk of bubble formation and electrical faults such as partial discharge. The main bulk of the water is stored in the paper insulation (< 99%).

5.1.2 Particles

Mineral oils contain particulate contamination from different sources. In general different type and size of particles may be present in the oil [18]. For example by passing the oil through metal pipe with internal coils for turbulence generation, using pump and storage in containers may impart some contamination to the liquid. In transformers fibres from insulation paper, rust and copper particles may be present in the oil. Such contaminants affect the electrical properties of the liquid and are particularly harmful in capacitors and cables. Oil oxidation products in particular sludge may appear as dark particles in the oil. Degradation and destruction of paper at high temperature may appears as particles in the oil, also presence of carbonaceous material, which may generated from thermal decomposition of oil and paper (carbon) are appear as particles in the oil.

5.2 Chemical contamination

Chemical contaminants are considered to be undesirable materials removable from the oil predominantly by a chemical process. These include acids, ketones, soaps, aldehydes, phenols and sludge. Their undesirable effect will include deterioration of resistivity, DDF and IFT. Their removal from the oil is essential for maintenance of transformer integrity. Methods of removal include clay treatment, solvent extraction and re-refining of the oil. PCBs are a different class of contaminant as they are introduced to the oil by cross contamination with PCB-containing oil.

5.3 Oil degradation

The ageing mechanisms of oil are complicated, but are described in some detail in 4.3.1. In general oxygen reacts with certain hydrocarbons by a free radical process, which is chain reaction mechanism, generating hydroperoxides. Hydroperoxides are unstable and quickly decompose to form ketones and water. Ketones can be oxidised further to form carboxylic acids or cleaved to make aldehydes. The presence of hydroxy groups will result in the production of alcohols and phenols. The final products of insulating oil oxidation are acids, water and sludge. Most oxidation products will have a negative effect on the electrical properties of the oil. The carboxylic acids that are produced will either dissolve in the oil or volatilise into the headspace. Dissolved acids may cause damage to the paper and copper windings, while volatile acids corrode the top of the unit.

Oxidation inhibitors, whether naturally occurring or added after refining, retard the oxidation mechanisms by destroying free radicals and initiators or by reacting with peroxides to form more benign products. Free radical reactions will take place more quickly in the presence of catalysts such as iron, copper and aluminium; the effect of these catalysts can be neutralised by metal passivators. Naturally occurring molecules such as phenanthroline and some organo-sulphur compounds act as radical scavengers as well as deactivating metal catalysts. Some of the phenols, which are produced by oxidation of aromatic compounds, also act as antioxidants. Phenols can donate a hydrogen atom to a peroxy radical to stabilise it and terminating the free-radical reaction. There are certain phenols which are particularly effective as antioxidants and these are usually the synthetic additives in inhibited oil.

The choice of base oil is extremely important in developing inhibited oils. The effectiveness of inhibition is measured by performing an oxidation stability test. The current oxidation stability test [4] takes place in the presence of excess oxygen. This is in contrast to service conditions in electrical equipment where available oxygen is never greater than that given by air saturation in oil. However, the test is designed to accelerate the ageing and therefore, it is conducted at high temperature with excess oxygen and metal catalyst for 164 hours. Several characteristics are measured on oils oxidised in the laboratory. Most of these are only relevant in the context of a better understanding of oil degradation. The measurement of volatile and soluble acids and sludge together with their effect on the electrical properties of the oil are sufficient to control the selection of oils. The acceptable limit for acid and sludge formation is outlined in the standard. This test is for indication only as there is no direct correlation between the results of the test and useful service life of the oil. Recent attempts have been made to develop a rapid test for evaluation of the oil oxidation stability [19].

5.3.1 Chemical Breakdown of a Transformer Oil

The mechanisms by which transformer oil degrades chemically during service have not been well studied, although the effect of degradation on performance has been observed. As in most mineral oils, oxidation is the primary means of degradation in transformer oil [20]. Crude oil and its derivatives are highly complex materials and, as such, create problems in attempts to study breakdown mechanisms. For this reason, experimental studies have been frequently carried out on n-paraffins, which are simpler, yet chemically relevant.

Previous studies have indicated the mechanisms and kinetics involved in the initial stages of oxidation in such model systems. The breakdown of a mineral oil usually takes place by a free radical reaction as described earlier.

5.3.1.1 Formation of oxidation products via a free radical pathway

Initiation
The reaction mechanism starts with the production of a free radical by homolytic fission – bond cleavage with both fragments retaining one electron from the covalent bond. The energy may be provided by ultraviolet radiation, heat, mechanical shear stress or electrical stress. The free radical is a highly reactive molecule (or atom) which has one or more unpaired electrons.

$$\mathrm{R{-}H} \longrightarrow \mathrm{R}\bullet$$

Figure10 Initiation step of a free-radical reaction

The free-radical will react with oxygen to form a peroxy radical, which will lead to the formation of oxidation products.

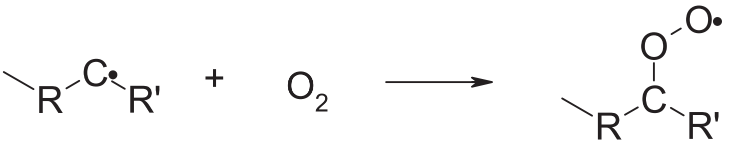


Figure 11 Formation of a peroxy radical.

Propagation

The peroxy radicals continue the reaction by abstracting hydrogen to form oxidation products and new radicals. The hydrogen may come from other hydrocarbons or, if it is long enough, from itself to form bi-functional products.

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Figure 12 Intermolecular hydrogen abstraction

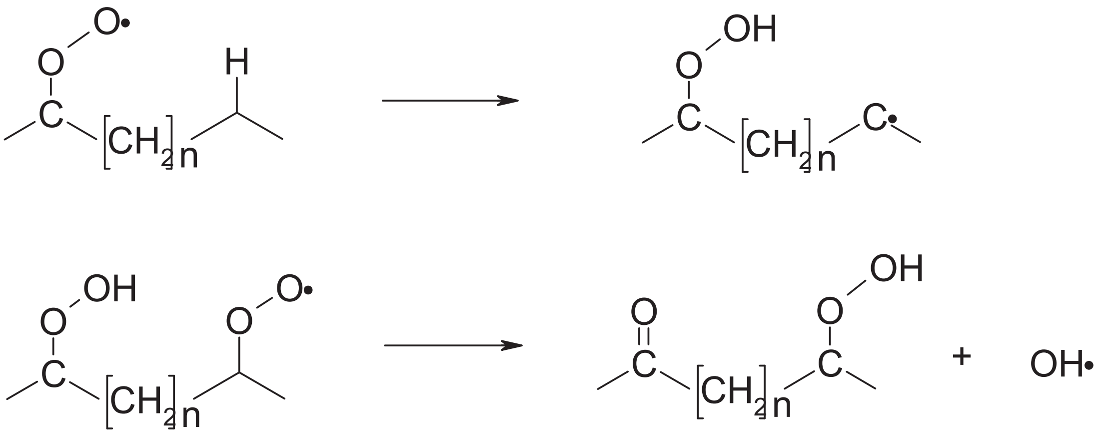

Figure 13 Intramolecular hydrogen abstraction

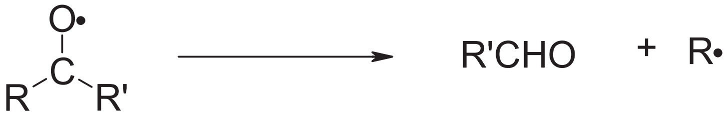

Figure 14 β-Scission of alkoxy radicals

Other propagating reactions are known as branching reactions. The oxidation products may also become radicals, giving different products.

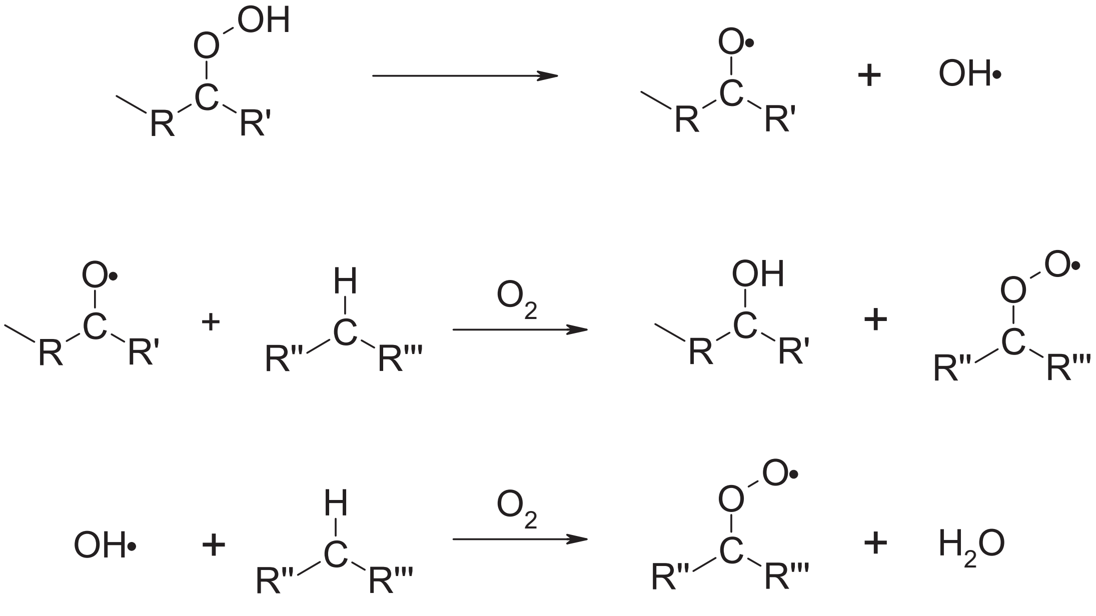

Figure15 Branching in free-radical reactions.

Termination

The free-radical reaction is stopped when radicals react with each other to produce a molecule and no further free radical. Many different products may be formed by the termination step depending on the nature of the radicals which combine. Some examples are shown.

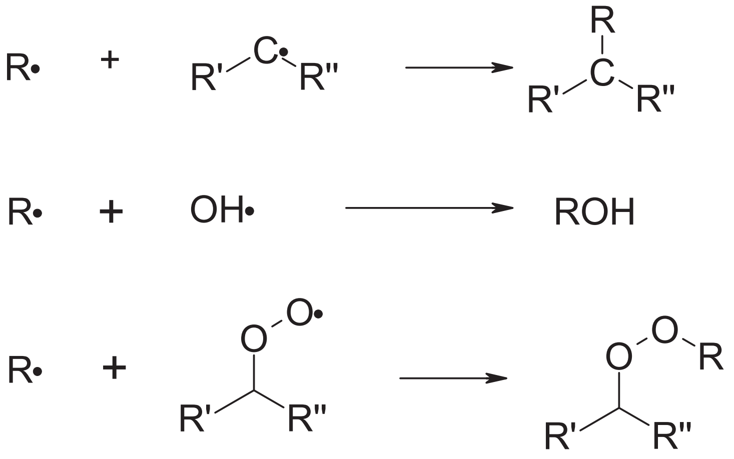

Figure 16 Termination reactions

Solids (sludge) are formed by polymerisation.

Figure 17 Polymerisation

Smaller alkyl radicals can result in unsaturated products.

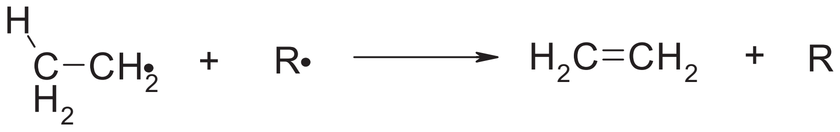

Figure 18 Abstraction of hydrogen (R = methyl, ethyl or propyl)

As previously stated, phenolic compounds are used as antioxidants, they may also be formed during oil breakdown. Phenols donate hydrogen radicals to a peroxy radical and terminate the free-radical process because the phenol is resonance stabilised.

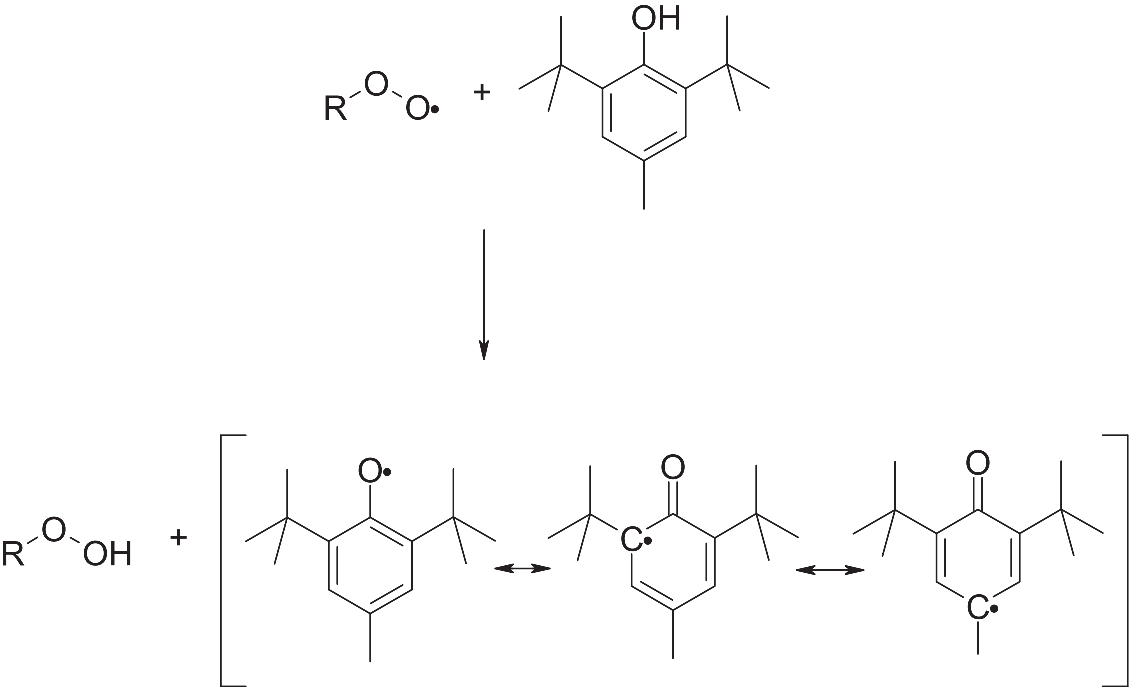

Figure 19 Termination by substituted phenol

Thermolytic fission of hydrocarbons may take place at high temperature hotspots within a transformer; this is a likely source of free radicals. However, it is also possible that a fault resulting in a large amount of discharging may also initiate free-radical reactions because of the electrical energy and the ultraviolet radiation produced. Thus, a fault can accelerate the rate of oil degradation

Under more severe oxidising conditions (e.g. very high temperature hotspots or high energy discharges) however, the picture is more complicated. This is because a larger number of oxidation products are produced and different reaction pathways occur. These new pathways include a reaction by which high molecular weight materials are produced. Such reactions also take place in transformer oil and are the source of sludge which is probably the single-most undesirable type of oil degradation product. The presence of sludge has the overall effect of raising the temperature of the transformer. This occurs in many ways: Sludge deposition impedes the conduction of heat away from the conductors and other parts of the transformer. The build up of sludge in oil ducts reduces the volume of oil passing over heating surfaces. Accumulation in the cooling areas of the transformer has the effect of lagging the cooling surfaces and also reduces the volume of oil passing through the cooling areas.

Analysis of paraffinic systems which have been subjected to severe oxidation conditions indicate that hydroperoxides are always the first degradation products to appear. Alcohols and esters reach a maximum value after a short time, but acids continue to increase with time. Esters are the last oxidation products to appear and are usually very low in concentration.

Formation of **carboxylic acids** increases the corrosiveness of the oil depending upon the nature of the acids, being the most corrosive those having the lowest molecular weight. Corrosiveness is not limited to the transformer metallic parts because it affects as well the mechanical strength of cellulose and other organic insulating materials eventually used on equipment manufacture.

Water is an oil oxidation by-product that accelerates corrosion of metals, destruction of insulating materials and degrades seriously the dielectric properties of the oil and insulating paper due to its high polarity. This degradation is especially serious in the case of presence of particles in the oil.

Formation of **esters and metallic salts of organic acids** seriously negatively affects the dielectric properties of the oil and oil-impregnated insulation, increasing the tendency to form emulsions. The presence of some low solubility metallic salts restricts heat dissipation by blocking refrigeration ducts and coating the heat exchange metallic surfaces inside the transformer.

It is very important to highlight that whereas technical guides for maintenance of oils and transformers in service, for instance IEC 60422, recommend periodic measurements of particles, water, acids and dielectric properties, surprisingly they do not mention the analysis of suspended and dissolved metals. As metals have an enormous deleterious effect on oil quality and degradation, both as oxidation catalysts and by-products, it is strongly encouraged to perform such analysis on a regular basis. Current advances in analytical instrumentation (ICP, AA, X-ray techniques, etc.) provide easy and reliable methods.

5.3.2 Polychlorinated biphenyl (PCB) contamination

PCBs have been used as insulating liquid in electrical equipment. These compounds pose a risk to human health and the environment because of their persistence and ability to bio-accumulate. PCBs are included in the POPs (Persistent Organic Pollutants) listed in the UN/ECE Protocol signed in Stockholm in May 2001.

In order to mitigate the “PCBs risk”, their use has been subject to European legislation since 1976. The last Directive (96/59EC of 16 September of 1996) defines new and stricter regulations relating to the inventory (article 4) and the decontamination and/or disposal of the PCBs and equipment within 2010 (article 3).

5.3.2.1 PCBs in electrical equipment

The use of PCBs as insulating liquid in electrical equipment, particularly transformers and capacitors, in some cases caused contamination of the environment. It is estimated that still large number of such units are in operation world-wide.

A typical scenario for Europe (i.e. France) involving just transformers with insulating liquids for the generation, transmission and distribution of electricity shows the following level of contamination: > 50 ppm of PCBs/PCTs/PCBTs: 545,610 pieces of equipment inventoried at 30/06/2002 and similar situations for the transformers and equipment operated by industries and services (instrument, tap-changers, reactors, rectifiers, furnaces etc.).

During the last 20 years or so, several methods for the decontamination and disposal of PCBs and correlated compounds have been developed and implemented on an industrial scale worldwide. They include incineration, photolysis, radiolysis, dechlorination, bio-chemical transformation and safe landfilling. Among these techniques, closed-loop chemical dehalogenation is of particular interest, since it provides the protection of equipment in operation, thus conserving high valued resources.

The sources of fluid contamination by PCBs are multifold. Some of the main sources are as follows.

- Use of contaminated equipment.
- Regeneration and recycling of used oils contaminated by PCBs.
- Human errors, lack of information or negligence.
- Lack of appropriate equipment for the treatment of contaminated liquids.
- Inappropriate conduct by some manufacturers of new equipment using components recovered from old equipment.

In practice the PCBs risk can be prioritised upon:

1. Large operators of generating, transmission and distribution of electricity with power plants and HV/MV/LV substations.
2. Large users of electricity such as cement factories, steel mills, petrochemical industries, etc.
3. Multi-utilities providing vital services, such as water, gas, waste disposal etc.
4. Infrastructures, such as airports, mass transit, hospitals etc.
5. Waste and machinery de-commissioning handlers.

6 HEALTH AND SAFETY

6.1 Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs and PCA are a group of chemicals occurring naturally in crude oil. There are more than 100 different PAHs which generally occur as complex mixtures (for example, as part of combustion products such as soot), rather than as single compounds. PAHs usually occur naturally, but they can be manufactured as individual compounds for research purposes; however, not as the mixtures found in combustion products. As pure chemicals, PAHs generally exist as colourless, white, or pale yellow-green solids. They can have a faint, pleasant odour.

6.1.1 PAHs, human health and risks

PAHs can be harmful to health under some circumstances.

Several of the PAHs, including benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, chrysene, dibenz[a,h]anthracene, and indeno[1,2,3-c,d]pyrene, have caused tumours in laboratory animals.

The US-Department of Health and Human Services (DHHS) has determined that benz[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, and indeno[1,2,3-c,d]pyrene are known animal carcinogens.

The International Agency for Research on Cancer (IARC) has determined the following: benz[a]anthracene and benzo[a]pyrene are probably carcinogenic to humans; benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, and indeno[1,2,3-c,d]pyrene are possibly carcinogenic to humans; and anthracene, benzo[g,h,i]perylene, benzo[e]pyrene, chrysene, fluoranthene, fluorene, phenanthrene, and pyrene are not classifiable as to their carcinogenicity to humans.

US-EPA has determined that benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenz[a,h]anthracene, and indeno[1,2,3-c,d]pyrene are probable human carcinogens and that acenaphthylene, anthracene, benzo[g,h,i]perylene, fluoranthene, fluorene, phenanthrene, and pyrene are not classifiable as to human carcinogenicity. Acenaphthene has not been classified for carcinogenic effects by the DHHS, IARC, or EPA.[1]

6.1.2 PAHs and insulating mineral oil

PAHs are present in crude mineral oil in nature. After refining, these compounds remain to a large degree in certain fractions (generally the heavier, less volatile fractions). Transformer mineral oil, manufactured through this process, is known to contain small amount of PAH material. The PAHs have some effects on the characteristics of the oil.

The official method for determination of PAH in transformer oil is IP346 [22]. This method is based on the fraction of the oil that is extracted by Dimethyl Sulphoxide (DMSO) and measured gravimetrically.

The more rings and/or hetero-atoms there are, the more polar the molecules become. DMSO dissolves all polyaromatics. A number of simple aromatics and naphthenes are also dissolved by DMSO, especially if they contain hetero-atoms. The result of this is that the IP 346 values end up way over the actual PAHs. This is particularly so of naphthenic oils, since naphthenes are considerably more polar than paraffins.

IP 346 does not claim to measure PAHs. It only claims to measure the content of substances that are soluble in DMSO.

6.1.3 PAHs ,Concentration Limit and Labelling

6.1.3.1 Concentration limit

IP 346 is a standardized test method developed by the Institute of Petroleum which is used to determine which oils must be labelled according to EU regulations. The limit where labelling becomes obligatory is 3% extract of DMSO.

In Directive 88/379/EEC of 7 June 19885 at Article 3.6 (a) it says:

"*No account shall be taken of substances whether or not listed in Annex I to Directive 67/548/EEC, whether existing as impurities or as additives, if their concentration by weight is less than:*

- *0.1% for substances classified as very toxic or toxic;*
- *1% for substances classified as harmful, corrosive or irritant,*

unless lower values have been specified in Annex I to Directive 67/548/EEC"

7 SAFETY AND ENVIRONMENTAL IMPACT OF OIL TREATMENTS

Oil treatment is an industrial activity that is not risk free, thus the treatment of used oil has to be done with proper care. All countermeasures should be taken to minimize any unreasonable risk to workers, public health and the environment. Experienced and qualified personnel well aware of the health and environmental risks associated shall always perform oil treatment, strictly in accordance with local regulations.

A full Risk Assessment shall always be undertaken before commencing any treatment.

Strict control must be undertaken in order to avoid cross contamination by PCB. It is well known that most PCB contaminated oil-filled transformers in service have become contaminated after treatment of the oil with a contaminated machine. Any oil treatment must be done after thorough cleaning of all machine components that have been in contact with oil in the previous treatment (pipes, pumps, heating and vacuum devices, etc.). This is especially important in the case that the previous oil was contaminated or suspected to be contaminated by PCB. On the other hand, should the transformer is to be treated by a third company, transformer the owner must demand a certificate that the PCB contamination in the oil after the treatment will under no circumstances be higher than before the treatment.

Strict control must be undertaken to avoid accidental spills to the environment. Pipes, pumps and hoses must be carefully inspected for tightness. To minimise the risk of accidental spills, it is strongly recommended to fit anti-dropping valves to the hoses connecting the treatment machine to the transformer. To avoid spills through the internal connections of the treatment machine, this must be designed with an oil reservoir of sufficient capacity fitted to level security sensors capable to stop immediately the treatment process.

As oil treatments are usually carried out under vacuum, special attention must be paid to avoid emissions to the atmosphere. Although the vapour pressure of the oil is low enough at the treatment temperatures and, normally, significant oil emissions are not expected, transformer oils may contain large amounts of hydrocarbon gases like methane, ethane, ethylene and acetylene which, due to its high greenhouse effect, must not be released to the atmosphere. To avoid such emissions, the vacuum pumps exhausts of treatment machines shall be connected to active charcoal filters.

Oil treatments produce waste, such as spent filters, oil-contaminated absorbents etc. It is therefore necessary to choose the best available technology to minimize production of waste or spent materials and to dispose of waste strictly according to local regulations. Special attention must be paid in the case of reclamation of PCB contaminated oils because the spent fuller's earths will inevitably be PCB contaminated.

If the treatment is performed on on-load equipment, strict safety measures must be taken to avoid risks to the workers. Also safety measures must be taken to avoid any damage to the equipment itself. In this case, the Risk Assessment must include also any risk to the equipment and the whole installation.

Due care should be taken when working with hot oil. Moreover, hot oil and its vapours may have a more sensitive dermatitis character. Workers should use appropriate personal protective equipment according to local regulations and the Risk Assessment.

7.1 Hazards associated with oil handling and processing

Oil handling and processing involves potentially hazardous activities. These hazards should be managed in accordance with the local Risk Management procedures. To provide guidance a checklist of the main hazards that are relevant to insulating oil and which may need to be addressed is given below. Advance planning of the work is essential to ensure compliance with the standards specified in this document.

7.1.1 Hazards to people

- Physical contact with or inhalation of oil and other chemicals.
- Noise and emissions from oil processing plant and other equipment.
- Mechanical failures of transformer components or oil processing equipment and associated pipes when under pressure or vacuum.
- Exposure of the body to high vacuum.
- Inadvertent removal of access covers under pressure.
- Slips, trips and falls.
- Excessively dry air.

7.1.2 *Environmental hazards*

- Oil spillage resulting from oil handling and processing.
- Leakage of oil from equipment.
- Atmospheric emissions and noise from oil processing plant.
- Oil process by-products and wastes.

7.1.3 *Hazards to the equipment*

- Over pressurisation and excess vacuum.
- Differential pressure across transformer components e.g. barrier boards, tapchanger drive linkage.
- Degradation of the electrical properties of the insulation, caused by sludge, moisture, fibres, entrained air.
- Overheating of the oil causing damage to insulation materials.

7.1.4 *Operational hazards*

- Spurious Buchholz gas alarms/trips.
- Contamination of the oil leading to insulation breakdown.
- Incorrect valve positions on return to service, or failure to remove all temporary blanking plates

8 GUIDANCE FOR DEVELOPING METHOD STATEMENTS FOR OIL HANDLING AND PROCESSING

In order to manage the identified hazards associated with oil handling and processing it is recommended that a method statement should be used to ensure that the correct sequence of work is followed. For routine maintenance activities generic method statements may be developed. It is essential that any generic method statement is modified to deal with any associated local site hazards. The following are recommendations:

- Obtain drawings and study the design of the asset to determine the parameters for each compartment i.e. the maximum flow rates, vacuum capability and temperatures for the activity to be undertaken. This will establish the need to equalise/isolate different compartments at various stages in the process.
- Prepare a method statement, including appropriate drawings, for every item of equipment. Where valve numbers are provided on drawings, these should be referred to in the method statement. For transformer main tank and selector switches, due to the value of the asset and the risks of the processes involved, which may have extreme consequences, the method statement should be subject to independent verification by someone who has had the appropriate level of training. Providing the work, equipment and site are the same the method statement can be reused without the need for reverification.
- Prior to use, any oil processing equipment must have been adequately maintained to ensure that it meets the required standard.
- For each activity the following basic steps should be followed to ensure technical compliance (Detailed notes which aid compliance are provided in italics):

8.1 Draining

a. Assemble and inspect the oil processing equipment.

b. Attach the processing equipment to the asset.

There may be valves specially provided for draining built into the asset which should be used in preference to other valves. These connections may be provided with an internal dip tube to facilitate the removal of all the oil and residues.

c. Attach flow, pressure and level measurement equipment.

Flow meters are required to ensure that the rate of draining does not exceed the venting capacity provided. Monitoring the level will indicate that oil is being removed at the requisite rate. Ideally the bottom of the level gauge should be fitted to a valve other than the drain valve. Where this is not possible and the gauge has to be connected to the drain connection the level will only be correct at zero flow. The level should also be monitored at the storage vessel to ensure no oil is lost to the environment. In addition it is also required to ensure that the oil is removed to the required level e.g. transformer oil retained above winding but below the access covers. When dry air is to be used a pressure gauge should be fitted to monitor the pressure on completion of draining.

d. Establish dry air system if required.

This is only required for all large power transformers when the windings are to be exposed. The capacity of the dry air machine/dehumidifier should match the flow rate of oil removal. Air supplied should meet a dewpoint requirement of -30°C at the output of the machine in order to maintain a dewpoint of -20°C in the transformer. If in doubt, specialist advice should be sought on the correct application of this technique.

e. Isolate compartment to be drained if required.

Care must be taken in isolating a compartment that adjacent compartments left full of oil have adequate means for oil expansion/contraction. If necessary, separate facilities for allowing this expansion/contraction should be provided. The power of sunshine should not be underestimated even on the coldest day.

f. Open vent and drain valves and commence draining at required flow rate using dry air if required. Check that the equipment is not leaking.

During draining it is essential that flow rates do not exceed the rates for venting in order to prevent unequal pressures damaging the asset. Initially the drain valve should be opened to allow oil to flow into the pipework under gravity. Following this the vent plug/valve should be fully opened before the pump is started. Following this sequence should ensure no spillage of oil and ensure no unequal pressures occur with adjacent compartments. Where there is difficulty in controlling the desired flow rate to match the venting capacity the asset should be gravity drained into a temporary break tank. ***Under no circumstances should a Drycol breather be considered adequate as a venting device - it is designed as a breathing device only.***

Guidance on specific flow rates for different equipment should be obtained from the manufacturer. Typical maximum rates are 5000 l/hour for transformer main tank and 2000 l/hour for selector compartments. If the permissible flow rates cannot be established with certainty then draining by gravity should be used.

g. Monitor flow rate.

The flow rate should be matched to the venting capacity. This may vary as oil levels drop and extra valves can be opened. In all cases it should not exceed the capacity of the dry air machine where fitted.

h. Close process down when asset is drained. Valves should be closed on completion and the dry air system shut down.

Maintenance of a slight pressure (max 0.5psig) is good practice to maintain the asset in a dry condition where windings have been exposed.

i. Access to compartment in order to carry out work.

Low pressures present a high level of stored energy when applied to large covers. Air pressure must be released before any covers are removed. A flow of dry air should be established where windings are exposed to minimise the ingress of moisture. It should be noted if access is requirement to a compartment in which a dry air flow has been established one of the requirements for air quality for breathing purposes is that the dew point of the air should not exceed -50 degrees Celsius at atmospheric pressure.

8.2 Vacuum treatment

a. Ensure the system can withstand the level of vacuum to be applied. Isolate sections which are not to be subject to vacuum.

Generally for older transformers the only sections which should be subject to vacuum are the main tank and selector switch. On newer transformers, the conservator is capable of full vacuum. It is not recommended that vacuum is applied to the coolers. Where the conditions cannot be easily established a transformer specialist should be consulted.

b. Establish vents on isolated sections.

This requirement is essential to protect compartments if isolating valves pass. These vents should be protected to prevent the ingress of moisture. Where these vents cannot be established separate vacuum gauges should be fitted to the isolated compartment.

c. Confirm valves on all the other sections are in correct position.

d. Assemble and inspect the processing equipment.

e. Attach vacuum gauge and level indicator to the equipment.

The vacuum gauge should be fitted at a position which is remote from the vacuum pipe. The level gauge must be capable of withstanding vacuum and be connected at both ends to permanent valves.

f. Attach vacuum pipework to equipment.

This should be at the highest point in the process to allow for filling above the level of the windings. Typically this could be the top of the main tank or the conservator tank.

g. Start vacuum pump and carry out a leak check when an appropriate vacuum level has been reached.

It is good practice to pull vacuum to 50% of the target level, close the isolating valve and then shut the vacuum pump down. The vacuum level should then be monitored to establish if any leakage is occurring. Leaks can normally be detected by listening to exposed joints around the transformer. The maximum acceptable leakage rate is 1% per hour

h. Once the leak rate is satisfactory the target vacuum should be pulled for the time required.

Guidance on this time should be sought from a transformer specialist.

8.3 Filling

a. Assemble and inspect oil processing equipment.

b. Attach oil filling equipment to asset.

There may be valves specially provided for filling built into the asset which should be used in preference to other valves. Where no other advice is available it is good practice to fill assets from the bottom thereby minimising aeration of the oil.

c. Attach flow, pressure and level measurement equipment.

Flow meters are required to ensure that the rate of filling matches the venting capacity provided. Monitoring the level should indicate that oil is being supplied at the requisite rate and to the correct level. Ideally the level gauge should be fitted to separate valves. Where this is not possible and the gauge has to be connected to the drain connection the level will only be correct at zero flow. When this is also monitored at the storage vessel it should ensure none is lost to the environment.

d. When filling is not being done under vacuum establish adequate venting.

This requirement is essential to protect compartments from over pressurisation during the filling process. These vents should be protected to prevent the ingress of moisture.

e. Commence filling at required flow rate. Check that the equipment is not leaking.

During filling it is essential that flow rates do not exceed the rates for venting in order to prevent unequal pressures damaging the asset. The vent plug/valve should be fully opened before the pump is started. Following this sequence should ensure no spillage of oil and ensure no unequal pressures occur with adjacent compartments. Where there is difficulty in controlling the desired flow rate to match the venting capacity the asset should be gravity filled from the conservator tank. ***Under no circumstances should a Drycol breather be considered adequate as a venting device - it is designed as a breathing device only.***

Guidance on specific flow rates for different equipment should be obtained from the manufacturer. Typical maximum rates are 5000 l/hour for transformer main tank and 2000 l/hour for selector compartments. If the permissible flow rates cannot be established with certainty then filling by gravity should be used. If filling is being undertaken through processing equipment, the temperature of the oil should be maintained between 65 and 70°C. Where these temperatures cannot be maintained due to site conditions, treatment temperatures should be discussed with a transformer specialist.

f. Monitor levels until the required level is reached.

The flow rate should be matched to the venting capacity. This may vary as oil levels rise and vent valves are closed.

g. Break vacuum (if applied).

Vacuum should only be broken when transformer windings are fully covered with oil. This should be done by using dry air or air supplied via a breather to ensure moisture is not pulled in. The air flow rate will require adjusting to match the equipment being used.

h. Complete filling process as required.

Deisolate and fill isolated sections. Filling of these to be controlled such that main core and windings are not re exposed and in line with the principles established above.

i. Bleed trapped air from all vent points.

After a power transformer is filled, circulating the oil using the main oil pumps to provide 100% flow will assist to remove any air trapped in the windings. Following this, operation of all the vents (eg coolers, selectors, bushings, blanking plates, pipework, bellows) should be checked to ensure that no air is trapped. This process may require repeating if significant quantities of air are removed. For other assets the requirements are not as stringent but final checks on vents should always be made before the equipment is returned to service.

8.4 Circulating oil

a. Assemble and inspect oil processing equipment.

b. Identify the compartments that require oil circulation and the sequence in which it will be carried out.

To minimise possible cross contamination of oil between compartments and pipework on a large transformer it is important that the correct sequence of oil circulation is observed. The main tank is usually circulated first, followed by coolers and selector switches in no particular order. Finally, the compartments and pipework are connected together such that the oil in both is common and the main oil pumps are run to mix the oil. Final circulation is then performed on the main tank until the required standard is achieved. During this final process it is necessary to run the main oil pumps periodically to continue to mix the oil. A balance has to be struck on the day as running the pumps cools the oil down which means the processing is not as effective. It is imperative that the method statement ensures that adequate provision for oil expansion and contraction is provided at all times during the oil processing.

c. Attach oil processing equipment to asset.

There may be valves specially provided for circulating oil built into the asset, which should be used in preference to other valves. Where no other advice is available it is good practice to circulate oil by feeding oil in at the top of the asset and removing it from the bottom of the asset. The latter should preferably be from the opposite side on large transformers in order to introduce a diagonal flow. More detailed guidance should be available in the manufacturer's manual or may be obtained from a specialist transformer engineer.

d. Open valves, carry out leak check, commence circulation and adjust flow rate.

The maximum flow rate should be adjusted to the size of the valves attached to the asset and to satisfy any pressure differential limits. When cold oil is being pulled into the oil processing equipment the flow rate may require reducing in order to achieve the necessary outlet temperature of between 65 and 70°C. This will ensure that the oil processing equipment is working at its most efficient to remove moisture and entrained gases. Where these temperatures cannot be maintained due to site conditions, treatment temperatures should be discussed with a transformer specialist.

e. Monitor process to achieve required standards.

Processing should continue until the standards set have been achieved. Routine oil samples should be taken every 4 hours and/or at the end of a particular circulation pass to monitor the oil process. On completion, final oil samples should be taken from the normal sampling points on the asset after final mixing of the oil by running the oil pumps once more. Where a service provider has carried out the circulation, one sample should be made available to the service provider and the other sent to an analytical laboratory. These oil samples are required as a cross check on the oil processing procedure and to set the datum for future DGA monitoring.

f. Close process down when desired oil quality has been achieved.

All valves should be returned to the service position and temporary pipework removed.

8.5 Topping up equipment

a. Assemble and inspect oil filling equipment.

b. Attach oil filling equipment to asset.

Temporary pipework used for topping up must always be securely connected to a filling point with a proprietary fitting. Wherever possible oil should be added above the level of any primary insulation and Buchholz relays when fitted in order to ensure that any air entrained in the oil is not released into the insulation. Where this is not possible the work must be carried out with the asset out of service.

c. Attach flow meter and level gauge if a permanent gauge is not provided.

Flow meters are required to ensure that the rate of filling matches the venting capacity provided. In addition if oil is being added to a transformer main tank before a Buchholz relay the flow should be restricted to prevent damage to the relay and also prevent a possible trip. Monitoring the level should indicate that oil is being supplied at the requisite rate and to the correct level. Ideally the level gauge should be fitted to separate valves. Where this is not possible and the gauge has to be connected to the drain connection, the level will only be correct at zero flow. When this is also monitored at the storage vessel it should ensure none is lost to the environment. Guidance on specific flow rates for different equipment should be obtained from the manufacturer. Typical maximum rates are 5000 l/hour for transformer main tank and 2000 l/hour for selector compartments. If the permissible flow rates cannot be established with certainty then filling by gravity should be used.

d. Provide adequate venting.

Venting of the asset must be provided to prevent over pressurisation and any consequent risk of Qualitrol operation or fracture of the bursting disc. ***Under no circumstances should a Drycol breather be considered adequate as a venting device - it is designed as a breathing device only.***

e. Pump oil at the required flow rate until the desired level is reached.

Oil must be supplied to the standards set down by local requirements

9 OIL RECONDITIONING / RECLAMATION

9.1 OIL RECONDITIONING

There are two types of physical oil reconditioning process: degassing and dehydration, which can be performed separately or together in the same process.

It is important to note that impairment of the insulation condition of a transformer begins at the time of transformer shipping. Shipping without oil results in de-impregnation of insulation and saturation with gas (nitrogen or carbon dioxide) and in some moisture ingress as well. Large amounts of rainwater can be sucked into a transformer in a very short time (several hours), when there is a rapid drop of pressure (after a rapid drop of temperature that can be induced by rain) combined with insufficient sealing. This phenomenon is especially of concern when transformers are stored partly filled with oil without their conservator preservation system. Direct exposure of the insulation to air cannot be avoided during installation procedures and special preservation measures should be used to mitigate adsorption of moisture and to protect insulation from rain, dust and other contaminants.

9.2 Guidelines for filling transformers

Ensure that the transformer and associated equipment is out of service, isolated and earthed.

If vacuum filling is going to be conducted make sure the main tank is designed for such vacuum.

For the oil filling procedure the hot oil outlet hose, from the oil processing plant, must be connected to a bottom valve on the chamber or tank being treated, with the oil processing plant inlet hose, connected to the lowest valve. The plant heaters thermostats should be set to raise the oil temperature to a maximum of 60°C and the degassing chamber must be evacuated to at least 1 mbar. The oil in the chamber or tank must be circulated for a minimum of three passes.

The calculation for the three passes is given below:

$$\frac{\mathrm{NumberofLitres} \times 3}{\mathrm{LitresperHour}} = \mathrm{Time}$$

Care should be taken that no volumes of oil are completely shut off during the oil circulation process. Hydraulic pressure may build up due to thermal expansion of the oil. Serious damage to the equipment could be caused if this is allowed to happen.

9.3 Guidelines for on site oil degassing and dehydration

9.3.1 Transformer Oil Dehydration

Moisture and dissolved gases in the oil may be removed by vacuum and heat treatment. The process is well known to the industry and used routinely. The equipment for this job is commercially available and used successfully. The process for removal of moisture can be performed at atmospheric temperature or at higher temperature depending on the type of equipment used. The most common one is based on heating the oil and subjecting it to vacuum to remove gases and moisture, followed by filtration to remove any particles. This process improves breakdown voltage of the oil and reduces moisture, dissolved gases and particles. The de-gasser dryer unit is used for filling a transformer either at factory or on site. This process may involve putting the transformer under vacuum for complete impregnation of the paper with oil. Care should be taken when applying vacuum, since not every transformer is designed to take vacuum. The dehydration unit is used to remove moisture from transformer paper by circulating the oil from the transformer to the unit. The process is more efficient at higher temperature. One major problem with such a process is the spread of PCB from one unit to another, since a quantity of oil remains in the unit at the end of the process and if the oil was contaminated with PCB then the next unit will be contaminated with PCB. Improvements in technology managed to overcome this problem by having a self-decontamination unit in the de-gasser dryer unit. At the end of each process the unit circulates the oil in a series of columns for destruction of PCB and removal of acids and polar compounds. Thus the unit is cleaned for the next job.

The oil feed pipe from the main tank to the conservator extends upwards into the bottom of the conservator to form a sump. Water and other impurities will lie at the bottom of the conservator sump and will therefore not enter into the main tank when the oil expands or contracts in the tank. Before any oil reconditioning and filtration takes place, it is important to remove all the deposits and contaminants from the conservator.

Due to the arcing that takes place during tap change operations, the oil in the tap changer conservator becomes severely contaminated and this oil must always be discarded when servicing the tap changer.

The different possible methods for transformer dehydration:

Vapour phase drying:

The vapour phase process is as today the standard drying process for the production of large power transformers. The process is based on the evaporation of a solvent that is sprayed on the assembly to utilize latent heat produced when the solvent vapour condenses. Since heating is effected deep inside, evenly and quickly, the transformer can be completely dried without causing damage to the insulation. The whole drying process takes place under vacuum without oxygen involved. This helps reducing paper degradation during the drying process.

Oil circulation and vacuum pulsation drying:
The oil treatment plant heats the transformer to approx.60-80 °C. Subsequently the oil is drained into a separate tank and the transformer evacuated. Whereby the water evaporates in the insulation and is pumped off through the vacuum pumps. Through the evaporation of the water, the insulation again cools down. Thus it might be necessary to repeat the heating cycle several times, depending on the size and voltage level of the transformer.

Oil spray drying:

The transformer is drained and evacuated. Hot transformer oil is sprayed over the active part. The oil heats the active part, as well as the insulation to the required drying temperature. Finally the oil is completely drained and the vacuum brought to the required level. Special preparation measures could be required to place the spray nozzles. The drying process occurs under the exclusion of oxygen, which has a positive influence on ageing.

Low frequency drying (LFH) with oil circulation:
The transformer which is filled with oil is heated by means of the oil treatment plant and the low frequency current heating. After the first temperature step is achieved, the oil is drained and the transformer evacuated. Further temperature increases are carried out only by means of current heating and under continuous vacuum.

Low frequency drying with oil spray:

In contrast to the combination LFH and oil circulation, with this method the oil is already drained at the beginning. Subsequently the active part is heated under vacuum with a combination of oil spray and low frequency current heating. Prior to the final temperature step, the oil spray process is stopped and the transformer will only be heated by means of LFH.

9.4 Reclamation for transformer oils

Reclamation is defined by the IEC as “a process that eliminates or reduces soluble and insoluble polar contaminants from the oil by chemical and physical processing”. The contaminants in question are mostly oxidation products from the oil and the solid insulation, especially the former. Chemical and physical processing is typically a combination of treatment with a sorbent material and filtering. Often degassing is performed at the same time, at least for on-line reclaiming.

International experience of oil reclamation is depends on whether inhibited or uninhibited oils are used. In general uninhibited oil may have shorter life after reclamation if inhibitor is not added. This is dependant on the degree of oil oxidation prior to reclamation. More oxidised oil will have shorter life after reclamation if they are reused as uninhibited oil.

Uninhibited oils have very different aging characteristics to their artificially inhibited counterparts, as they have a range of naturally occurring inhibitors already present in the oil, rather than a preferred and measurable single species added in large quantities and carefully monitored and controlled. Naturally inhibited oil quality must be controlled very strictly at all stages of oil life for best performance.

Same applies to passivated oils, i.e., oils to which a metal passivator has been artificially added to reduce or eliminate its potential corrosion activity.

As oil reclamation processes may partially or totally remove additives, antioxidants and passivators, it shall be necessary to re-additivate inhibited and/or passivated oils after the treatment

The actual reclamation process for oils is essentially the same for both inhibited and uninhibited oil. Off-line or on-line transformers are regenerated using a mobile unit containing a fuller’s earth mixture, or “clay”, through which warmed oil is pumped. The clay is a highly polar, granular matrix made from natural bentonite sepiolite or montmorillonite mixed with metal oxides, and “activated” (which may involve thermal dehydration and partial dehydroxylation) in order to increase the polarity, surface area and catalytic activity of the material. Other reclamation materials for have been tried, such as carbonaceous charcoals, sands, and other clays. Each has different properties and these affect the reclamation process in varying ways. In this report Fuller’s earth-based clays will be exclusively considered.

The reclamation process must be tightly controlled, as there are many factors governing the extent to which reclamation is effective. Primarily it is the material of which the clay is made which governs the efficacy of the process. Having a high proportion of highly polar material such as aluminium and silicon oxides will increase the polarity of the clay and increase the amount of polar material removed. Next to this the level of activation of the clay is important: the degree to which water and hydroxyl groups have been removed strongly affects the clay’s extraction properties. The next most important is the contact cross section of the oil through the clay beds, and the oil to clay ratio. The contact cross section depends on the granule size, the dimensions of the bed and the number of passes of the oil through the beds. A smaller granule size gives a longer contact time for the oil, increasing the extraction efficiency, but slowing the reclamation process, as a large force is required to move the oil through the clay. Longer clay beds also give more oil/ clay contact. Wider beds decrease the reclamation time. The temperature at which reclamation is performed is also important, as higher temperatures allow a higher flow, but less efficient retention of polar material.

It must be remembered that the system of reclamation, of a liquid phase flowing over a solid sorbent, has chromatographic properties, and this has impact on the period left before clay bed removal/ regeneration. As polar compounds are adsorbed onto the clay beds, there is an accrual of highly polar material at the entrance end, but less polar material may migrate down the column, albeit much more slowly than the bulk oil. If a very high contact cross section column is used, the first eluent will be almost devoid of all polar material, including, importantly much aromatic material.

Material removed includes (in rough order) any solids, polar material such as acids, alcohols, aldehydes, ketones, esters, soaps and aromatic material. This last is not so important if you are using artificially inhibited oil, but is critical when considering reclaiming uninhibited oil. Many oxidation inhibitors in naturally inhibited oil are aromatic in origin, with slightly polar functional groups capable of radical chain termination and other antioxidant functions. Their partial or complete removal, it is clear, will result in a reclaimed oil that satisfies many of the physical and electrical properties recommended for re-used oils, but cannot satisfy prolonged use inside an oxidising environment - for example inside a transformer. Currently it is not clear, using current chemical and physical testing methodologies, whether an oil is suitable for reclamation and re-use. Many oils put back into service following reclamation are found to have short service lives. The use of reclaimed naturally inhibited oil inside a transformer with many years before its planned replacement date is not one that should be taken lightly.

This being said it is frequently the case that reclaimed oil can perform successfully inside a transformer for many years, negating the need for oil replacement and saving money and resources in the process. However the choice as to which oil should be reclaimed should be an qualified one backed up by experimental data. To this end much work is being performed where transformer oils are being evaluated under conditions of accelerated aging, and tested according to a range of physical and chemical parameters. Though not a strict guide as to whether an oil will be useful inside a transformer, the IEC1125A, B and C tests are standards which may successfully be used when assessing oxidation stability. It has been found that oils at different stages of their lives perform differently in various chemical, physical and electrical tests, and monitoring their oxidation products may indicate a variation in species produced according to the life stage they appear to be at. This chemistry may in future lead to a test for “reclamation performance”, which may be applied to an oil prior to reclamation, in order to ascertain the likelihood of an operationally sound oil post reclamation. Prior to this chemical test, the suitability of an oil for reclamation may be ascertained empirically by observing oils that perform well and being consistent in your choice of new oil supplier. As satisfactory this may be in the long term, for short term decisions this is not a viable process since oil lifetimes are measured in decades.

It has not been investigated if the oxidation stability of all oils after reclaiming fulfils the requirements for new oil in IEC 60296. A study of reclaimed inhibited oils where the Rancimat, [21] method was used to measure oxidation stability indicated in general that the oxidation stability of reclaimed and reinhibited oil was very good. However, the correlation of the Rancimat method with IEC 61125 method C (test specified by IEC 60296) is not known. Oxidation stability will also depend on the composition of the original oil.

It could be argued that having the same requirements as for new oil does not really seem realistic. However, experience shows that IEC 60296 values are easily achieved unless the oil is in very poor condition before treatment. So why should an equipment user accept poorer results? In fact, there are operators of on-site reclaiming equipment that guarantee that values like those in IEC 60422 Table 4 still hold two years after the treatment.

9.4.1 Reclamation processes

Most commonly used processes involve contacting the oil in some way with a sorbent material, from which it is separated after a suitable treatment period. There are two basic approaches. The sorbent can be suspended in the oil while stirring, and subsequently separated from the oil, *e.g.* by filtration. This practice is sometimes referred to as contact processing. It is also possible to run the oil through percolating columns filled with the sorbent, either by gravity or by pumping the oil. International standards IEC 60422 and IEEE Standard 637 [23] describe in some detail several of the systems used.

9.4.1.1 Reclaiming by percolation

This process can either be carried out batch-wise, with disposal of the sorbent when it has been saturated, or in a semi-continuous mode, with in-situ reactivation of the sorbent. The main advantage of the latter is that it facilitates on-line processing. Typically, the on-line process is run in two alternating modes, treatment mode and reactivation mode. In the treatment mode, the oil is drawn from the bottom of the transformer tank, heated and pumped through the sorbent columns. Before it is returned to a top valve or the expansion vessel it passes a filter and degasser. The treatment stage may continue until the efficiency of the sorbent starts to deteriorate, or until it is convenient to switch to the reactivation stage. In the latter stage, the sorbent columns are by-passed, and the oil led directly to the filter-degasser. The sorbent is reactivated, *e.g.* by *in situ* incineration. After reactivation, the process switches again to treatment mode.

9.4.1.2 Reclaiming by the Contact Process

The contact process is not capable of use on-line, but may be a suitable option for large scale processing. It may also be used in lab-scale to test for feasibility of reclaiming for a certain oil.

9.4.2 Sorbent materials

Many different natural and synthetic materials have sorbent properties, and can be used for oil reclaiming. Some are briefly discussed below.

Fuller's Earth

The term *fuller's earth* refers to a class of naturally occurring adsorbent clays of varying mineral composition, as opposed to a specific species which may be used as bleaches, adsorbents, or oil reclamation compounds. Common mineral names are bentonite, montmorrillonite, and others, sometimes depending on the location of the mineral's source or the way in which the clay is treated prior to use. The main constituent is attapulgite clay, which has the ability to neutralise acids, adsorb polar compounds, and decolourise oils.

Several different clays are available that have proven suitable for these purposes. The most widely used are of the sepiolite, bentonite, attapulgite or montmorillonite type of which fullers's earth is the most commonly used. They are constituted of silicate anions $Si_2(O_5)n$ condensed with octahedral layers of the type $X(OH)_2$ where X may be magnesium, aluminium,etc. Normally, fuller's earth is treated to increase its specific surface area and the concentration and polarity of its Lewis acids. Fuller's earth can be used alone or in combination with other chemicals like trisodium phosphate, activated charcoal and sodium silicate. The retention of contaminants by adsorbent active sites is, generally, improved by temperature, thus the process normally takes place at 60ºC to 80ºC. The temperature of the oil circulating through the transformer should certainly be over its aniline point in order to dissolve the sludge.

Attapulgite is unique because of its crystalline structure. It is mined as a hydrated magnesium aluminium silicate. During processing, the clay is crushed, heat activated and ground. The temperature of the heat activation or drying stage determines the degree of internal porosity. Activation of Fuller's earth can be achieved by mild heating (70ºC to 140ºC) to remove water complexed within the mineral structure, or by more severe heating (450ºC plus) to chemically change the material by processes such as dehydroxylation. High temperature activation produces a low volatile matter (LVM) clay. This strongly adsorbs water, has high acid adsorption, but less than optimum decolourising efficiency. Lower temperature activation produces a regular volatile matter (RVM) clay. This has lower water adsorbing ability, but greater decolourising efficiency than LVM, while acid neutralisation is about the same.

It is an active material containing both internal and external polar active sites which allow the non-polar components of the oil to pass through without retention but which retains the polar contaminants or degradation compounds dissolved in the oil.

A further increase in activation can ensue if the Fuller's earth is acid treated, giving further increase in surface area and capacity for protonation or electron transfer. Clays also exhibit catalytic activity, the most well-known examples being dehydroxylation of sterols (aromatic alcohols) and cis- to trans- conversion of olefins (alkenes).

The following table shows the typical composition of Fullers earth

Table 9: Typical composition of Fuller's earth

SiO_2	66.1%
Al_2O_3	12.6%
Fe_2O_3	5.1%
MgO	9.8%
CaO	1.4%
K_2O	1.3%
TiO_2	1.0%
Other	2.7%

9.4.3 Other Adsorbents and reclamation processes

9.4.3.1 Carbonaceous

These are derived *from vegetable by-product charcoals*. They have a very strong affinity for aromatic materials but may introduce unwanted species into the reclaimed oils.

9.4.3.2 Alumina (aluminium oxide/ hydroxide).

Alumina (or bauxite) is a common adsorbent used for bleaching of engineering oils. It consists mainly of hydrated aluminium oxide, and is activated by thermal treatment alone. It is hard, durable, and can be regenerated and reused more often than clays. The strongest sorbent (giving the most severe treatment) is a fully dehydrated alumina. However the most common adsorbent in use today is fuller's earth.

9.4.3.3 Silica, Kaolin, sand

Silica (silicon oxide), Kaolin (*a clay*) and Sand (*sharp sand*) They essentially do the same job as fuller's earth but their varying strengths depends on their polarity, ie their bauxite/ silica content.

9.4.3.4 Molecular sieves

Molecular sieves are *synthetic aluminium silicates containing a variety of complexed metals for scavenging water and other polar molecules*). Molecular sieves belong to a class of materials known as zeolites. These are aluminosilicates, which are able to undergo dehydration with essentially no change in crystal structure. Type 4A is used to reclaim transformer oil and has an unusual affinity for polar compounds especially water. 4A is available in bulk, and can be regenerated. However it is significantly more expensive than other adsorbent materials.

9.4.3.5 Regenerative oil

Use of regenerative oil [24] is a temporary operation over 10-20 months where the transformer is placed under special control with a regenerative oil, for example oil with high aromatic content, in order to retrieve contaminants, then the transformer is drained and refilled with stable oil.

It is also possible to do on-line reclamation of liquid insulation by attaching a small adsorption tower to the tank of a power transformer[, therefore, the decay products are continuously removed of oil in a close loop. So, by using two mineral solvents that are recoverable by atmospheric distillation, the on-line reclamation procedure allows this mineral oil to be reactivated and successfully reused many times.

9.5 Oil reclamation Scenarios

When oil in a transformer reaches a stage, due to ageing process, which is not fit for the purpose then the oil must be changed or regenerated. There are several options available to equipment owner when it comes to oil reclamation. The choice of technique dependant on type of oil filled electrical equipment, economic, environment and local regulation.

9.5.1 On-site on-line

This type of oil reclamation is performed on site using live transformers. It is the preferred method as it can clean the solid insualtion since the internally produced heat from core and conductors of the unit is used for better movement of oil oxidation produtc from solid insulation. Care should be taken to avoid air entrying the system as it may destroy the transformer. The usuall method is to drain the oil from bottom main tank of the transformer and clean, hot reclaimed oil enters from top of the transformer.

9.5.2 On site off-line

It is similar to the above but using denergised transformer. It is mainly used to avoid removal and transport of the oil from transformer and also to reduce air contact with winding of the transformer.

9.5.3 *Tank to tank*

This technique is usually use at the a site when oxidised oil are transported to the site and stored in a tank until it reached a sizeable amount which is economic to start oil reclamation. The reclaimed oil is then stored in a clean tank.

9.5.4 *Large scale reclaiming*

This is reclamation in industrial scale and performed by some service providers by collecting used oil from asset owners and stored at their site in large tank for reclamation.

9.6 When to reclaim oil

The decision of when to reclaim an oil is not necessarily a straightforward one to make as two questions must be considered and compromise must be sought. The first is to examine the short-term risk of failure by asking "is the oil in such poor condition that it poses a threat to the safe operation of the equipment during the next few months or years?" With this perspective there is no need for very stringent requirements on oil condition, i.e. if the oil will continue to perform in the short term than there is no reason to reclaim. The limits set in IEC 60422 may serve well, even though in different countries the limits to apply may vary slightly.

The second question is to consider the transformer insulation in the long term and ask “how can the oil and paper be kept in good condition for many years?" The answer may be very different. In the latest editions of oil maintenance guides from the IEEE and IEC there is a shift towards the longer term perspective, with much more stringent requirements for several oil condition parameters. This is very much more the case with the IEC guide, and the same view is shared by many equipment users and service providers. Oil should be reclaimed without unnecessary delay when the test results for acidity, dissipation factor or interfacial tension are out the limits in IEC 60422. However, it is beneficial to reclaim the oil before it is in an unacceptably poor condition, and for this there are at least two reasons. It has been shown that the less degraded the oil is at the time of treatment, the better is the oil quality that can be obtained after treatment. Furthermore, to fully realize the potential of oil reclaiming to prolong life of paper insulation, one should not allow the oil to be acidic for any long period of time.

It is suggested that a set of action limits to be used as a rough guide, and that reclamation should be considered when any of the following criteria are met:

- Acidity 0.10 mg KOH/g or higher
- Interfacial tension lower than 32mN/m (this is also the IEEE limit for the highest voltage class)
- Dissipation factor higher than 0.050 (this is also the IEEE limit for the highest voltage class)
- When the "Oxidation Index" (interfacial tension divided by acidity) is below 300.

When it is known that a transformer is planned to be in service for many years more, it may be meaningful to reclaim the oil even before these criteria are met. This especially applies to the case where it can be assumed that a reclaiming means that the oil condition will be satisfactory for the remaining planned service life of the transformer.

9.7 Which oils are reclaimable

It is not obvious which oils are suitable for reclamation. It may depend on if we consider oil on its own, or if we consider oil in an operating transformer. An example of the former case is the re-use of oil from a scrapped transformer, one of the latter could be a transformer where on-site reclaiming is being considered.

In general, it can be stated that even severely aged oil can be restored to acceptable condition (see next sub-clause), provided of course that the oil was of good quality from the beginning. However, very acidic oils may require very long treatment times in order to get good long-term results. This particularly applies in the case of on-line treatment. Large amounts of oxidation products may be absorbed by paper and board, and there may even be sludge deposits. It may take a long time to dissolve sludge and desorbs harmful oxidation intermediates from cellulose materials. In the end it will be a question of economy. The cost to obtain an acceptable oil quality may become prohibitive. It is impossible to give any hard and fast rules for when this happens, since there may be large local differences in relative costs for different options. As a rough guide we suggest that for oils with an acidity higher than 0.5 mg KOH/g it should be carefully considered if on-line reclaiming really will be a cost-efficient option. This applies also to oil exchange: new oil will also become contaminated by residual oxidation products in the transformer.

If addition of oxidation inhibitor after reclaiming is not allowed, it may in many cases not be very meaningful to reclaim oil, unless a short additional service life is required. Regardless of if the oil was originally inhibited or uninhibited, it will become depleted of its content of natural inhibitors and after every use-reclaiming cycle the rate of oxidation will be higher than before.

Tests for oil´s suitability for reclamation usually consist of carrying out a lab-scale reclamation, followed by a check of all the usual oil quality parameters, including oxidation stability. Some proposed tests are described in Appendix A.

9.8 Requirements of reclaimed oil

It could be argued that the requirements for reclaimed oil should be the same as those for new oil, since these requirements are based on the functions the oil fulfils, and not on its history. For on-site reclaiming this means that the same requirements as those for new oil should apply before energizing (IEC 60422). With the exceptions of water content and oxidation stability this is easily accomplished. However, it would not be meaningful to have a requirement on water content of the oil after reclaiming. The bulk of the transformers' water content resides in the solid insulation. Even if oil reclaiming temporarily dries the oil, it can only achieve a partial drying of the solid insulation. PCB and particle content are similarly difficult to define.

It has not been investigated if the oxidation stability of all oils after reclaiming fulfils the requirements for new oil in IEC 60296. One study of reclaimed oils used the Rancimat method to measure oxidation stability. This indicated that in general the oxidation stability of reclaimed and reinhibited oil is very good [21]. However, the correlation of the Rancimat method with IEC 61125 method C (test specified by IEC 60296) is not known. Furthermore, the oxidation stability of reclaimed oil will depend partially on the composition of the oil when new. For this reason alone, it may not be meaningful to apply in every case the same oxidation stability requirements as for new oil.

It might also be argued that having the same requirements as for new oil (apart from PCBs, particles, water and oxidation stability) does not seem realistic. Experience in some countries does show that pass values are in fact easily achieved, unless the oil is in very poor condition before treatment. So there is little reason why an equipment user should accept poorer results. In fact, there are operators of on-site reclaiming equipment that guarantee that values like those in IEC 60422, still hold two years after the treatment.

10 OIL DEHALOGENATION

In the last 20 years, several methods for the disposal and elimination of PCBs have been developed and industrialised, such as controlled incineration, underground storage, bio-chemical transformation and chemical dehalogenation.

It is important to note that until 1996, the main technical option used in Europe to dispose of PCBs was thermal destruction and, since the only approved facilities were in France, the UK and Finland, these Nations had a virtual monopoly on the market. With the promulgation of Directive 59/96, decontamination processes have been introduced in the legislation.

Generally speaking the techniques on the market for the handling of PCBs can be divided into four categories: [25]

- Landfilling
- Thermal treatments, designated as “destructive techniques” since it is impossible to recover fluids and solids being treated
- Chemical-physical treatments, designated “as recovery techniques” since they provide, in most instances, a full or partial recovery of oil and equipment
- Re-filling or change of the initial fluid with a non-contaminated one.

Land filling and thermal treatment are not subject of oil treatment for this reason they are out of scope of this document.

10.1 Chemical-physical treatments of PCBs

Chemical-physical treatments of equipment and oils contaminated by PCBs have the purpose of removing the chlorine present in the molecules of the oil. Chemical-physical processes most currently studied are: *catalytic hydrogenation, decontamination by metallic sodium* and *continuous dehalogenation.*

The criteria for chemical-physical treatment operations are:

- Strict control must be undertaken in order to avoid cross contamination by PCBs.
- Strict control must be undertaken to avoid accidental spills and dangerous emissions into the environment.
- Pipes, pumps and hoses must be carefully inspected for tightness.

10.1.1.1 Decontamination of oils containing PCBs

There are several processes and techniques available for either on-site and off-site decontamination of PCB contaminated oils. These processes are based on chemical reactions between PCBs and the reagent to remove the chlorine present in the oil. Off-site techniques are limited by considerations for the safe transportation of contaminated equipment and liquid to the factory and are the subject of local regulations.

10.1.1.2 Catalytic hydrogenation processes

A very advantageous process for the destruction of chlorinated compounds is *catalytic hydrogenation*. This is performed in a hydrogen-rich reducing atmosphere and in the presence of a catalyst that resists chlorides so that it does not form oxygenated species such as PCDDs, PCDFs, sulphur oxides and nitrogen. The heat developed in the exothermic reaction is removed and partially re-used to pre-heat the inlet flow.

Hydrochloric acid formed during the reaction is abated with the formation of an acid water residue. Traces of acid not intercepted in this section are eliminated by a subsequent neutralisation section, with the production of a water solution and a hydrocarbon phase. Excess hydrogen that has not reacted, can be re-cycled into the inlet flow into the reactor. All catalytic hydrogenation processes follow, in their general lines, this scheme.

Two of these technologies had a large industrial application, one created by KTI Inc known as the Chioroff Process; the other developed by Manion.

The Chioroff process operates at high pressures of 50-60 bar and at temperatures of 250-200 °C with a catalyst, whereas in the Manion hydrogenation process the reaction occurs at a lower pressure and at a higher temperature (about 900° C), using a similar catalyst. Both processes proved to be effective, reaching destruction efficiencies of 99.9 % for PCBs. However, both process present some problems: they require catalysts and also, the Chioroff Process, using high pressure reactors, is considered a high risk for explosions and fires. The engineering is rather complicated, requiring high investment costs.

10.1.2 Decontamination by metallic sodium

The chemical destruction of PCBs by reagents based upon metallic sodium or its derived has a good level of efficiency if the oils and the equipment to be decontaminated have a low level of PCBs.

These processes are typically applied in batch and use reagents based on metallic sodium, sodium hydride, lithium hydride and additives for the dehalogenation of PCB in the oil.

The main problem of this process is the necessity to eliminate all traces of moisture and air from the reactor to prevent side reactions with the danger of explosions and fire. In fact the problem deriving from the safety of this technology has always been its major weakness, as documented by several accidents worldwide, with considerable damages to property and loss of lives. Also, due to the strong exothermal features of the reaction, very efficient cooling systems are required.

Several processes of this type have been developed. Among the most important must be mentioned: the “Goodyear Tyre Co” process, the “Pytlewski” process implemented at industrial level by Sunohio (PCBX), Enervac, “Fluidex” process and a process designed by Ecocalor based upon NaH (this compound is known as being critical because of severe health risks and associated risks of explosion and fire).

10.1.3 Dehalogenation processes using polyethyleneglycol and potassium hydroxide (KPEG)

This process, developed to overcome the problems associated with the use of metallic sodium, uses a liquid reagent based on polyethyleneglycol (PEG) and an alkaline metal hydroxide (KOH). This type of process, which is run at temperatures of 140C – 150 ºC, has a limited efficiency on some types of contaminants (e.g. Aroclor 1242). The technique also suffered from generating waste quantities of highly alkaline oily hazardous waste, which requires special disposal. The process was conducted at 150 C mixing oil and K-PEG which is above flash point of the oil.

Processes have been developed and implemented (i.e. SD Meyers USA, as PCB gone [25]) but only a few among the old chemical dehalogenation processes had a real industrial application, since almost all of them had really critical points [26, 27]]:

- High investment cost (1 million $ and up)
- High operating costs (several operators over 24 hours and use of expensive reagents)
- High disposal costs of the waist generated during the process
- Difficult access to the equipment
- Large dimensions of plants
- Critical process parameters (high temperatures and pressures)
- Risk of explosion and fires.

10.1.4 Dehalogenation in closed circuit

The most recent dehalogenation processes use reagents providing less critical reactions, ensuring, at the same time, higher efficiency and lower operating costs. Also they are capable of working on-site, both on large power transformers and medium/small size ones, and even when accessibility to the site is difficult, by using compact decontamination mobile units (DMU), without draining the oil.

A dehalogenation process in continuous mode designated the “CDP Process®” is a new technology developed for the on-site decontamination of equipment/transformers filled with insulating mineral oil contaminated by PCBs. It operates via closed-loop continuous chemical dehalogenation of the PCBs, without draining the equipment. The dechlorination of PCBs, PCTs, PCBTs, PCDDs, PCDFs in insulating mineral oils can be made both in continuous and batch modes.

Decontaminations in excess of 99 % are normally achievable in the continuous process, whereas they are even higher with the batch mode. In the specific case of chemical dehalogenation of PCBs, the change of oil and the creation of PCBs classified waste are prevented.

The reagent (a mixture of High Molecular Weight PPG and PEG, strong bases and a radicals source) fills modular configured columns into which the oil flows constantly at low temperature (80-100 °C). These features facilitate and simplify the on-site and on-line decontamination operations with the highest safety operational requirements. [26, 27].

An additional advantage of this technology is that, as the dehalogenation reagent is supported on the same material as used in depolarisation processes, the insulating oil, usually aged and contaminated by water and particles, became reclaimed and dehalogenated at the same time.

During the dehalogenation process the PCB content of the processed oil should be monitored regularly. The monitoring should be performed by implementation of a rapid and reliable method. For this reason total chlorine of the oil, before and during the process, can be measured using Dexsil chloride analyser or other equivalent method. Once the test indicated undetectable level of PCBs in the oil then the process can be stopped. This measurement also should be used for suitability of the decontamination reagent for further use or change of the reagent. The PCB content of the final products should be measured by method given in standard IEC61619 or EN12766 [28].

10.2 Refilling

Although this process does not comply with definition of “dehalogenation”, it is briefly described because is mentioned in European Directive 96/59 and is a common practice, despite that it does not fulfil the concept of “best available technology”.

With this process, the transformer containing PCB contaminated fluid is drained and refilled with a new, PCB free, fluid. This technique is very simple and can be performed by non specialised companies with scarce technological development but has a large number of disadvantages:

From a technical point of view, it is impossible to drain completely all the transformer oil because part of the oil remain adsorbed on the insulating paper. Depending upon the transformer design (shell or core type), it has been estimated that the total amount of oil which can not be drained is about 10 to 15 % of the overall, which means that the same proportion of PCB will remain inside the transformer and, in less than 3 months [will contaminate again the new oil.

From an economical point of view, either is the best solution because to the costs of the new oil and the refilling process itself, it is necessary to add the costs of transportation and elimination of the contaminated oil and the lost of profit due to transformer stop.

From an ecological point of view, this process shows a number of disadvantages:

- Consumes non-renewable resources (new oil);
- Risk of workers contamination by contact with contaminated oil (pouring of contaminated oil to storage tanks or cisterns);
- Large energy consumption during new oil production (oil refining);
- Risk of environmental contamination by traffic accidents during the transportation of contaminated oils to elimination plants (sometimes through several countries);
- Does not fulfil the European objectives of “proximity” (only few countries have incineration plants), “selfsufficiency” (large majority of countries do not produce crude oil) and “functional recovery of non-renewable resources” (final destination of PCB contaminated oil usually is incineration);

11 MANAGEMENT OF THE OIL

Waste oil is generally classified as special or hazardous waste depending upon the state of the oil and its PCB content. Unless a PCB analysis has been performed, it is prudent to assume that the batch of oil contains PCB and act accordingly. The management of used oil is a subject attracting increasing attention from regulatory authorities. It is become a major source of concern and added costs to industry as society's tolerance of unnecessary pollution decreases. Taking the economic situation in to account the equipment owner makes every effort to comply with legislation. Due to the dual use of PCB and mineral oil in the past, cross contamination of PCB spread widely in the electrical industry. This contamination is no longer acceptable under current legislation and a decontamination program should be implemented.

The first task for an asset owner and operator, is to identify equipment at risk of contamination i.e. with PCB levels at or greater than 50 mg/kg. Based on the volume of oil and type of equipment a decontamination program shall be implemented. Method statements together with risk assessment shall be prepared for transformer filling, oil replacement, on site oil reclamation and oil decontamination. Personal protective equipment shall be used for handling used and contaminated insulating. Control of substance hazard to health COSHH data sheets shall be prepared for working with used and contaminated insulating oil. The supplier usually supplies product safety data sheet with unused insulating oil.

12 SELECTION OF THE “BEST AVAILABLE TECHNIQUES (BAT)” AND “BEST ENVIRONMENTAL PRACTICE (BEP)”

Oil treatments generally produce a great deal of waste, especially in the case of PCB decontamination. In Europe, Council Directive 96/61/EC of 24 September 1996 concerning Integrated Pollution Prevention and Control (IPPC) establish the following general principles:

“General principles governing the basic obligations of the operator

Member States shall take the necessary measures to provide that the competent authorities ensure that installations are operated in such a way that:

(a) all the appropriate preventive measures are taken against pollution, in particular through application of the best available techniques;

(b) no significant pollution is caused;

(c) waste production is avoided in accordance with Council Directive 75/442/EEC of 15 July 1975 on waste(11); where waste is produced, it is recovered or, where that is technically and economically impossible, it is disposed of while avoiding or reducing any impact on the environment;

(d) energy is used efficiently;

(e) the necessary measures are taken to prevent accidents and limit their consequences;

(f) the necessary measures are taken upon definitive cessation of activities to avoid any pollution risk and return the site of operation to a satisfactory state”. (Article 3).”

For “Best Available Techniques” it shall be understood:

“Best available techniques (BAT): mean the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing in principle the basis for emission limit values designed to prevent and, where that is not practicable, generally to reduce emissions and the impact on the environment as a whole:

- 'techniques` shall include both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned,
- 'available` techniques shall mean those developed on a scale which allows implementation in the relevant industrial sector, under economically and technically viable conditions, taking into consideration the costs and advantages, whether or not the techniques are used or produced inside the Member State in question, as long as they are reasonably accessible to the operator,
- 'best` shall mean most effective in achieving a high general level of protection of the environment as a whole. (Article 2.11).”

Finally, this Directive also gives some guidelines for the election of the best available technique:

ANNEX IV

Considerations to be taken into account generally or in specific cases when determining best available techniques, as defined in Article 2.11, bearing in mind the likely costs and benefits of a measure and the principles of precaution and prevention:

- the use of low-waste technology;
- the use of less hazardous substances;
- the furthering of recovery and recycling of substances generated and used in the process and of waste, where appropriate;
- comparable processes, facilities or methods of operation which have been tried with success on an industrial scale;
- technological advances and changes in scientific knowledge and understanding;
- the nature, effects and volume of the emissions concerned;
- the commissioning dates for new or existing installations;
- the length of time needed to introduce the best available technique;

- the consumption and nature of raw materials (including water) used in the process and their energy efficiency;
- the need to prevent or reduce to a minimum the overall impact of the emissions on the environment and the risks to it;
- the need to prevent accidents and to minimize the consequences for the environment;
- the information published by the Commission pursuant to Article 16.2 or by international organizations.

The selection of the Best Available Techniques can be done by following the scheme indicated in Figure 20:

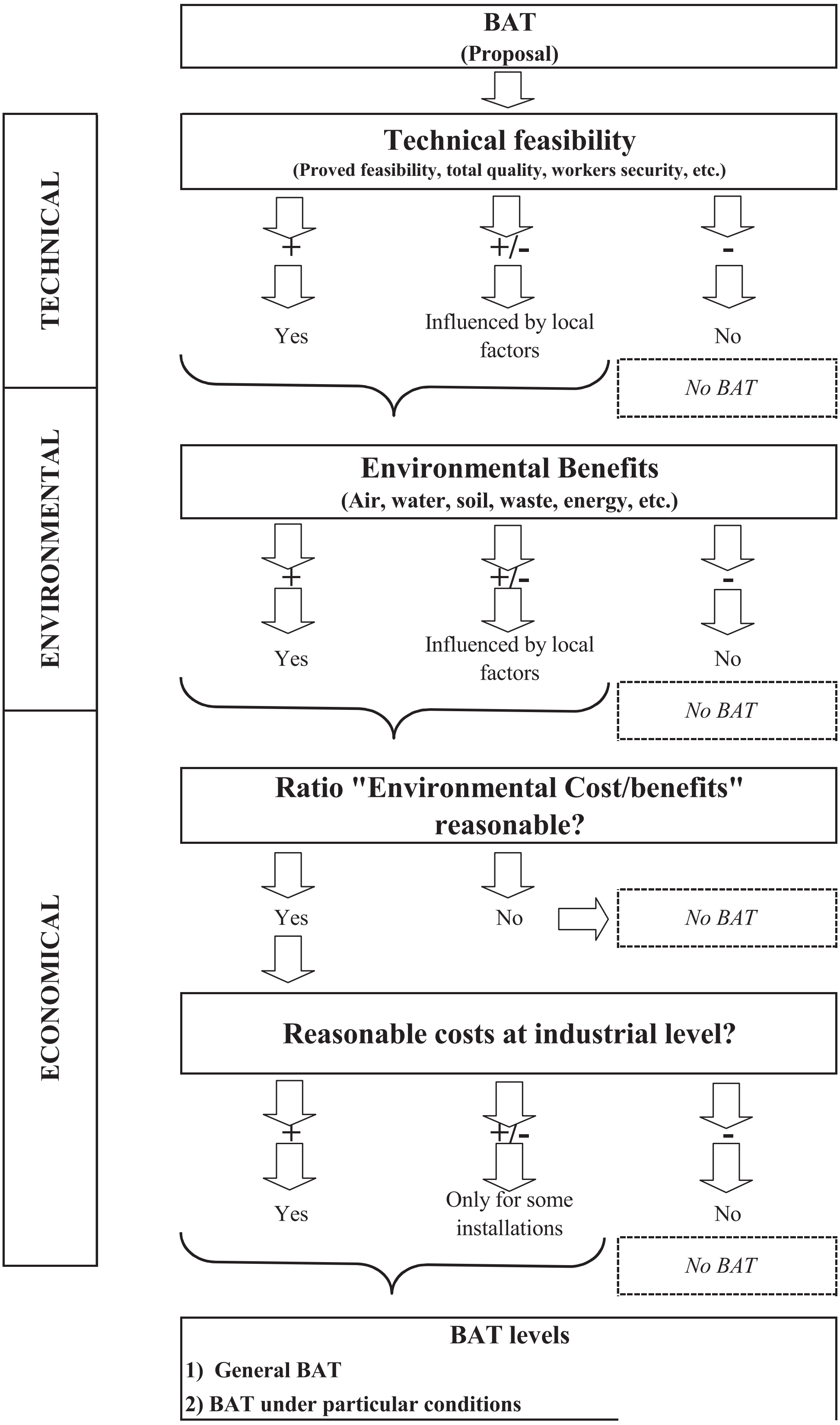

Figure 20.- Flow diagram for BAT election

On the other hand, the Stockholm convention (article 5.f) defines Best Environmental Practices (BEP) as the "application of the most appropriate combination of environmental control measures and strategies", so all measures to reduce or eliminate releases from unintentional contamination production are taken.

Dechlorination technologies must fulfil the following requirements:

- reduction of risks for workers, public health and environment, associated to faults and defects of electrical equipment which may produce a fire or an uncontrolled spill of dangerous and persistent products;
- “state of the art” application of the best available safety techniques and methodologies, favouring criteria of proximity, self-sufficiency and functional recovery;
- technical and economical feasibility of the proposed activity according with standards and local regulations.

13 BIBLIOGRAPHY

[1] CIGRE WG A2.18. Life management techniques for power transformers. Technical Brochure 227. June 2003.

[2] International Electrotechnical Commission. International Standard IEC 60296. Fluids for electrotechnical applications – Unused mineral insulating oils for transformers and switchgear. Geneva (Switzerland)

[3] International Electrotechnical Commission. International Standard IEC 60076. Power transformers. Geneva (Switzerland)

[4] International Electrotechnical Commission. International Standard IEC 61125. Unused hydrocarbon based insulating liquids - Test methods for evaluating the oxidation stability. Geneva (Switzerland)

[5] CIGRE JWG 12/15.13. Static electrification in power transformers Technical Brochure 170. 2000.

[6] International Electrotechnical Commission. International Standard IEC 60628. Gassing of insulating liquids under electrical stress and ionization. Geneva (Switzerland)

[7] International Electrotechnical Commission. International Standard IEC 60422. Mineral insulating oils in electrical equipment - Supervision and maintenance guidance. Geneva (Switzerland)

[8] W. G. Lawson, M. A. Simmons and P. S. Gale, Conf. Rec. IEEE Int. Symp. Electr. Insul., Vol. EI-12, 61 (1977).

[9] International Electrotechnical Commission. International Standard IEC 60450. Measurement of the average viscometric degree of polymerization of new and aged cellulosic electrically insulating materials. Geneva (Switzerland)

[10] American Society for Testing and Materials. Standard ASTM D-4243. Standard Test Method for Measurement of Average Viscometric Degree of Polymerization of New and Aged Electrical Papers and Boards. Philadelphia (USA).

[11] International Electrotechnical Commission. International Standard IEC 61198. Mineral insulating oils - Methods for the determination of 2-furfural and related compounds. Geneva (Switzerland)

[12] Burton, P. J., Graham, J., Hall, A. C., Laver, J. A. and Oliver., A. J., Recent developments by CEGB to improve the prediction and monitoring of transformer performance, CIGRE 1984 Session, Paris, Paper 12-09.

[13] Burton, P. J., Carballeira, M., Duval, M., Fuller, C. W., Graham, J., De Pablo, A., Samat, J. and Spicar, E., Applications of liquid chromatography to the analysis of electrical insulating materials, CIGRE 1988 Session, Paris, Paper 15-08.

[14] De Pablo, A., Andersson, R., Knab, H.-J., Pahlavanpour, B., Randoux, M., Serena, E. and Tumiatti, W., Furanic compounds analysis as a tool for diagnostic and maintenance of oil-paper insulation systems, CIGRE Symposium on Diagnostic and Maintenance techniques, Berlin 1993, Paper 110-09

[15] CIGRE Brochure 323, Ageing cellulose in mineral oil insulated transformer, TF D1.01.109, 2007

[16] Scroff, D. H. and Stannett, A.W., Review of paper ageing in power transformers, IEE Proc. 132(6), 312-319, 1985

[17] Scheirs, J., Camino, G., Tumiatti, W., Avidano, M., Study of the mechanism of thermal degradation of cellulosic paper insulation in electrical transformer oil. Angew. Makromol. Chem. 259 (1998) 19-24.

[18] CIGRE WG12.17. Effect of particles on transformer dielectric strength. Technical Brochure 157. 2000

[19] International Electrotechnical Commission. Technical Report IEC 62036. Development of an oxidation test method based on Differential Scanning Calorimetry (DSC) to assess the oxidation stability of mineral insulating oils. Geneva (Switzerland)

[20] Wilson 1980, Insulating liquids: their uses, manufacture and properties. Peter Pereginus Ltd, ISBN 0 906048 23 0

[21] Ø. Berg, K. Herdlevær, M. Dahlund, K. Renström, A. Danielsen, and U. Thiess, “Experiences from on-site transformer oil reclaiming,” in CIGRÉ Main Session 2002, Paris, France, Paper 12-103.

[22] Institute of Petroleum. Standard IP 346: Determination of polycyclic aromatics in unused lubricating base oils and asphaltene free petroleum fractions – Dimethyl sulphoxide extraction refractive index method.

[23] Institute of Electrical and Electronic Engineers IEEE. Standard 637. Guide for the Reclamation of Insulating Oil and Criteria for Its Use. Piscataway (USA).

[24] R.A. Lipshtein and M.I. Shaknovich, *Transformer Oil,* (2nd edition), translated from Russian, Israel Program for Scientific Translations, Jerusalem, 1970.

[25] UNEP. Inventory of worldwide PCB destruction capacity, United Nation, 1998.

[26] V Tumiatti, B Ruggeri, G Camino and S Dallo, A new technology for dehalogenetation of PCBs and other halogenated contaminants- Proceedings of the European meeting on chemical industry and environment- Girona Spain 2-4 June 1993

[27] V Tumiatti, S Dallo, P Aglietti and s Kapila – CDP process a new technology for continuous dehalogenation of PCBs in oil- Proceedings of the 10th international electric power research institute (EPRI) PCB seminar Boston, MA August 29, 1995

[28] European Committee for Standardisation. European Standard 12766. Petroleum products and uses oils – Determination of PCBs and related products. Brussels (Belgium).

[29] C.L. Coccio and C.W. Horneck, 87th Doble annual meeting section 10.301