

OIL: The Four R=s

Retain, Recondition, Reclaim, Replace

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I. Introduction

Fluids, liquids or gases, that are used in electrical equipment serve three essential purposes. These fluids must provide adequate insulation, efficiently transfer heat from the source to the atmosphere and quench arcs that may develop in the equipment. To meet these requirements the selected fluid must consist of non-polar molecules that are chemically stable. Viscosity, specific heat and thermal conductivity are properties that must also be considered when evaluating the ability of the fluid to conduct heat. Several liquids and gases that possess these attributes have been used as dielectric materials in electrical equipment. These liquids, such as mineral oil, are produced from natural sources or are chemically synthesized. Silicone dielectric fluids and perchlorethylene are examples of synthetic products.

In addition to the above required properties other factors that are considered in the selection of a dielectric fluid include: resistance to oxidation and other types of chemical degradation, stability at high temperature, flammability, solvent properties, toxicity and bio-degradability, cost and availability.

Oxidation of mineral oils results in acid production. Acid at any concentration attacks cellulose insulation and can lead to formation of sludge. Sludge can plug oil circulation pathways which can lead to overheating. Silicone fluids, in contrast, are resistant to oxidation and acid formation. High temperature stability is required so that the material does not undergo molecular degradation at anticipated operating temperatures. For safety reasons dielectric fluids should have high flash and flame points, especially if the equipment is located indoors. High flash point was a major factor that promoted the wide use of polychlorinated biphenyl (PCB) fluids before the environmental hazards were known. The selected dielectric fluid should not dissolve insulation materials or gaskets used in the construction of the electrical unit. It is for this reason that transformers that are retrofit with silicon fluids require replacement of the installed gaskets, that were not attacked by the original PCB fluid or mineral oil. Toxicity and bio-stability are increasingly important from an environmental and liability perspective.

II. Dielectric Fluid Categories

Mineral oil is the most widely used dielectric fluid in transformers, load tap changers, oil filled circuit breakers, bushings and oil filled cables. Mineral oil is a very complex mixture of aromatic, naphthenic and paraffinic compounds that is derived from a petroleum source. The major types of molecules found in mineral oil are shown in Table 1. High molecular weight hydrocarbon fluids, HMWH, are also derived from petroleum or are a synthetic mixture of hydrocarbons. HMWH, also designated less flammable hydrocarbons, LFH, contain the same molecular types as ordinary mineral oil except that more volatile and flammable hydrocarbons have been removed. Removal of these lower molecular weight compounds increases the flash point from 150° C to 300° C or higher and increases the fluid viscosity. Increased viscosity decreases the fluids ability to remove heat.

Silicone fluids are totally synthetic dielectric fluids that possess two major advantages, high flash point and resistance to oxidation and sludge formation. Silicone fluids do not remove heat as effectively as mineral oil or Askerals. Transformers that are retro-filled with silicone fluids must therefore be down rated by about ten percent. The structure of silicone fluids is shown in Figure 1. There are many other natural and synthetic liquids that have been employed as dielectric fluids. Table 2 is a listing of some of these fluid types and their properties.

Table 1
Molecular Components of Mineral Oil


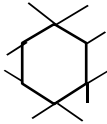
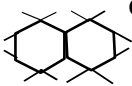
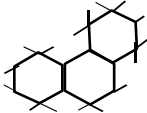

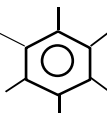
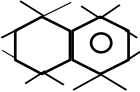
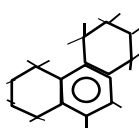
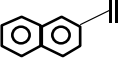
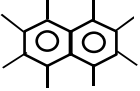
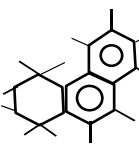
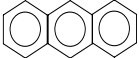
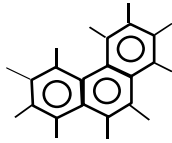
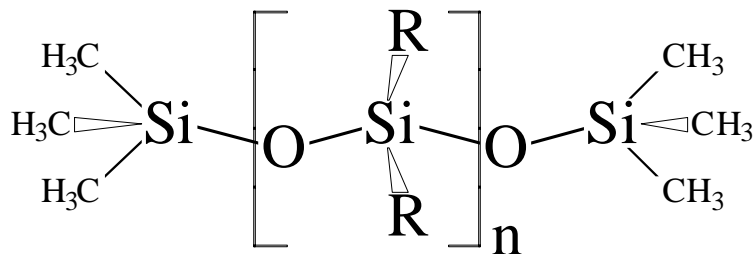
Molecular Types	Avg. Size	One Ring Compounds	Two Ring Compounds	Three Ring Compounds
Saturates 	25Å	 C_nH_{2n+1}	 C_nH_{2n+1}	 C_nH_{2n+1}
Mono Aromatics 	25Å	 C_nH_{2n+1}	 C_nH_{2n+1}	 C_nH_{2n+1}
Di-Aromatics 	19Å		 C_nH_{2n+1}	 C_nH_{2n+1}
Tri-Aromatics 	12Å			 C_nH_{2n+1}

Figure 1
Composition of Silicone Fluids



Where R can be any organic functional group.

Table 2
Properties of Dielectric Fluids

Property	ASTM Method	Mineral Oil	HMWH Fluids*	Silicone Fluid
Dielectric Strength (kV) (min)	D-877	30	25	35
Dissipation Factor (Power Factor) 25° C 100° C	D-924	0.0004 0.009	0.0001 0.004	0.0001 0.0015
Pour Point °C	D-97	-40	-15	-50
Specific Gravity 25° C	D-1298	0.875 - 0.910	0.869 - 0.910	0.957 - 0.964
Interfacial Tension (dynes/cm) 25° C	D-971	40	40	20.8
Viscosity 0° C 25° C 40° C 100° C	D-445, D-2161	76.0 max 14 - 16 12.0 max 3.0 max	2200 - 2900 350 - 379 120 - 140 13 - 19	81 - 92 47.5 - 52.5 35 - 39 15 - 17
Moisture Content (ppm) (max)	D-1533	35	35	50
Flash Point °C	D-92	150	238 (note)	268 (note)
Fire Point °C	D-92	160	311 (note)	371 (note)

*Note: The test limits shown in this table apply to HMWH fluids as a class. Specific values for each brand of fluid should be obtained from each fluid's manufacturer.

III. Degradation of Dielectric Fluids

Crude oil has remained intact in underground deposits for millions of years. This indicates that the molecular constituents of crude oil are chemically stable in the absence of oxygen. The implication is that under ideal conditions oil used in sealed equipment should last forever. Oxygen free environments are very difficult to maintain in electrical equipment which is subject to moisture and air intrusion. Impurities that originate from materials used in construction of the equipment can also mix and/or react with the oil. Oil degradation occurs because of these impurities. Oil properties, such as its dielectric strength, can be affected even by non-reactive impurities such as carbon or cellulose particles. Oil must therefore be periodically tested to ascertain whether or not chemical degradation or impurities have rendered it unfit to

adequately perform its functions.

Oxygen is detrimental to both oil and cellulose insulation. Hydrocarbons in the oil are oxidized when oxygen is present. The rate of oxidation depends on the oxygen level, temperature, moisture and other parameters. Hydrocarbons are oxidized to alcohols, aldehydes, ketones and finally acids. The structures of these organic functional groups are shown in Table 3. All of these oxidation products are polar in nature and will effect the interfacial tension, IFT, of the oil.

Figure 2 shows how the IFT decreases and the acid level increases as transformer oil ages. Transformer oil that was produced by acid refining retained the oxidation inhibiting compounds that are present in crude oil. Current refining methods remove these natural oxidation inhibitors and it is now common to add oxidation inhibitors to new transformer oil. The initial slow increase in acid level is due to the protective action of the oxidation inhibitors in the oil. When the oxidation inhibitors are depleted the oil is not protected and it is rapidly oxidized. For inhibited oils, monitoring the concentration of oxidation inhibitor and maintaining this concentration at recommended levels slows down the rate of oxidation. Figure 2 also shows that the IFT decreases with age. The IFT decreases rapidly before there is a large increase in the rate of acid production. This can be explained by the fact that the acid precursors listed in Table 3 are all polar molecules that lower the IFT. It is possible to determine the concentration of the carbonyl compounds, aldehydes and ketones, in the oil by infrared spectroscopy. Since the carbonyl precursors to acid formation will not be removed by Fuller's earth filtration, oil containing high carbonyl content will readily undergo further oxidation and acid formation.

Figure 2
Interfacial Tension and Acidity vs. Service Life of Oil

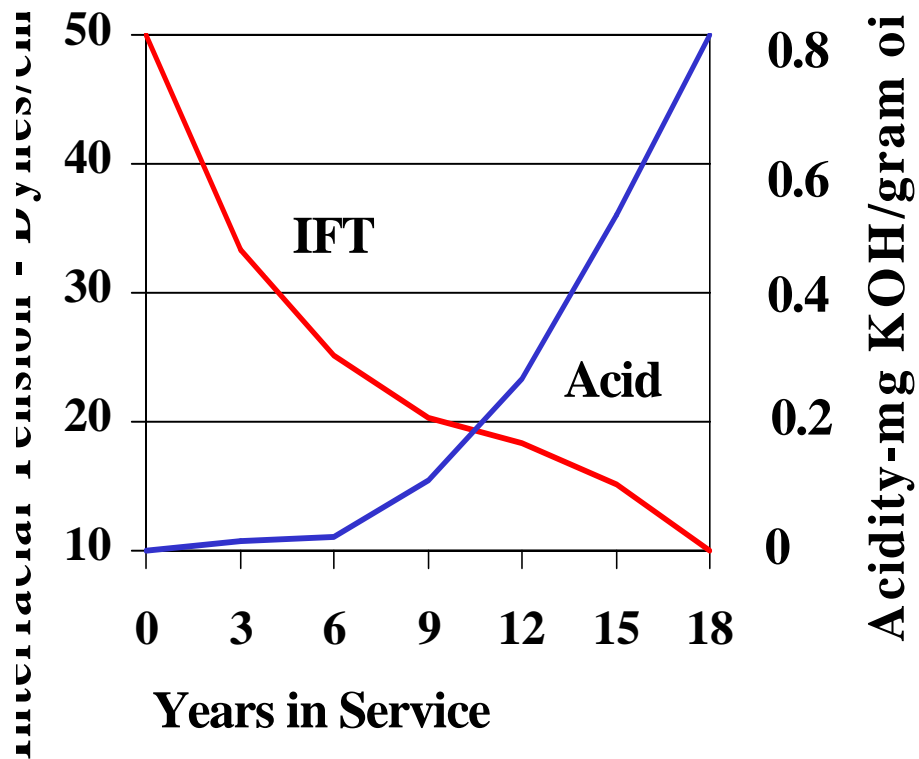


Table 3
Hydrocarbon Oxidation Products

Alcohols	R-O-R
Aldehydes	$\begin{array}{c} \text{H} \\ \\ \text{R}-\text{C}=\text{O} \end{array}$
Ketones	$\begin{array}{c} \text{O} \\ \\ \text{R}-\text{C}-\text{R} \end{array}$
Acids	$\begin{array}{c} \text{O} \\ \\ \text{R}-\text{C}-\text{OH} \end{array}$

Thermal and electrical faults result in a partial destruction of the insulation. Measurement of these fault gases is the basis of the dissolved gas method, DGA. The number of insulation molecules destroyed is small and the fault gases, listed in Table 4 are non polar or slightly polar molecules. These gases have very little, if any, impact on the insulation quality of the dielectric fluid.

IV. Oil Quality Assessment

The purpose of testing dielectric fluids is to determine if their physical and chemical properties are those that are required for the particular piece of equipment. Equipment of different voltage classes will require fluids that meet more stringent requirements as the voltage level increases. The ASTM tests listed in Table 5 are widely used to evaluate dielectric fluids. These tests can be characterized , as is shown in Table 6, according to the information they provide about the insulating fluids. For example some tests measure insulation quality, fluid characteristics, fluid degradation , impurity content, and properties related to the ability to conduct heat. Some tests give information that fits into multiple categories.

Table 4
Fault Gases Detected by DGA

Gas	Permanent Dipole Moment
Hydrogen	0
Carbon Monoxide	0.110
Carbon Dioxide	0
Methane	0
Ethane	0
Ethylene	0
Acetylene	0

Table 5
ASTM Oil Quality Tests

ASTM Method	Oil Quality Test
D-1533	Moisture in Oil
D-971	Interfacial Tension
D-974	Acid Number
D-1500	Color Number
D-877 and D-1816	Dielectric Breakdown
D-1298	Specific Gravity
D-924	Power Factor
D-6111	Aniline Point
D-92	Flash and Fire Points
D-88	Viscosity
D-97	Pour Point

Table 6
Characterization of Oil Quality Tests

Purity	Function	Composition
Color/Visual D-1500,1524	Pour Point D-97	Pour Point D-97
Interfacial Tension D-971	Flash Point D-92	Flash Point D-92
Neutralization Number D-974	Specific Gravity D-1298	Specific Gravity D-1298
Dielectric Breakdown D-877,D-1816	Dielectric Breakdown D-877,D-1816	Viscosity D-445
Power Factor D-924	Viscosity D-445	Aniline Point D-611
	Power Factor D-924	

V. Insulation Quality

The primary tests that measure insulation quality are ASTM D-877 and D-1816, Dielectric Breakdown Potential and ASTM D-924, Power Factor. The dielectric breakdown potential tests use two electrodes of fixed geometry and a specified separation. The electrode configurations and gap distance for these two methods are shown in Figure 3. D-1816 requires that the oil be stirred while the older method, D-877 does not require stirring. Flat electrodes with sharp edges are not representative of metal components in a transformer. Sharp edges or points are generally avoided in transformer design because corona is more likely to occur at points of high flux density. The semi-hemispherical electrodes used in D-1816 are more representative of internal surfaces in a transformer. The gap distance in D-877 is also greater than that used in D-1816. D-1816 is more sensitive to moisture in the oil and is the recommended method for fluid that is being processed into apparatus or contained in new apparatus. The relative responses of D-877 and D-1816 to moisture are shown in Figure 4.

Figure 3
Dielectric Cell Configurations

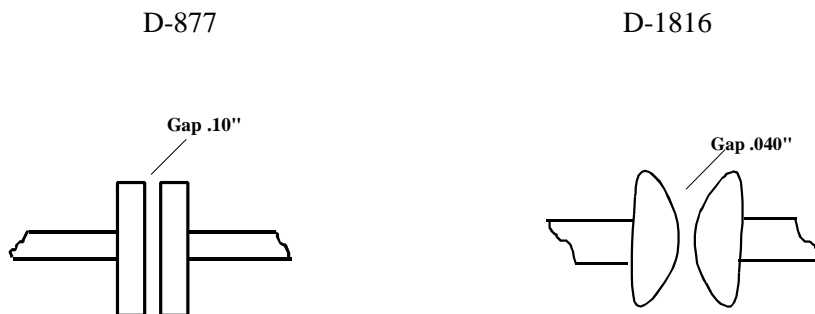
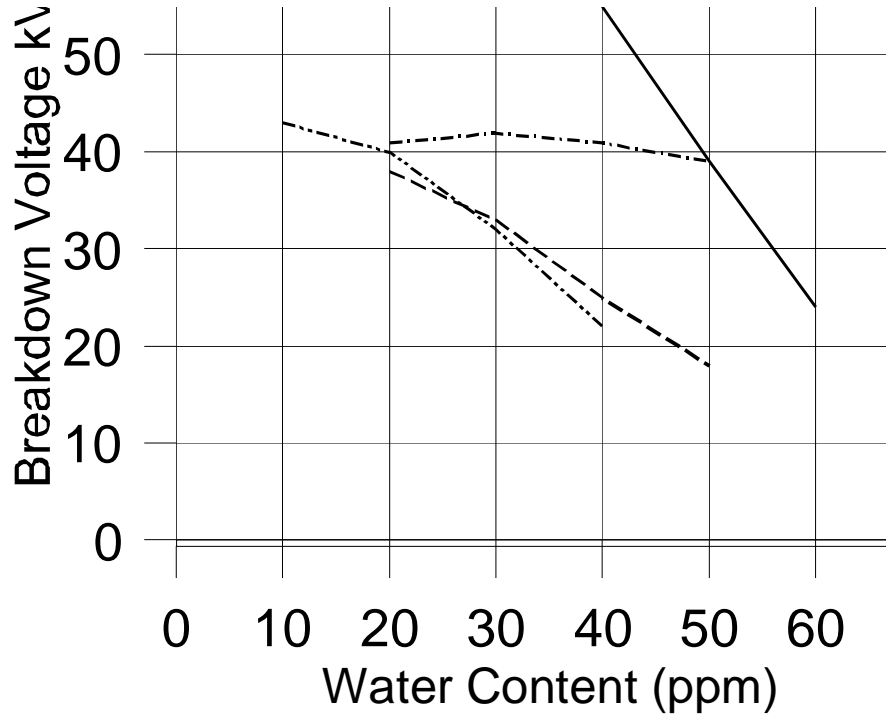


Figure 4
Relative Responses of D-877 and D-1816 to Moisture



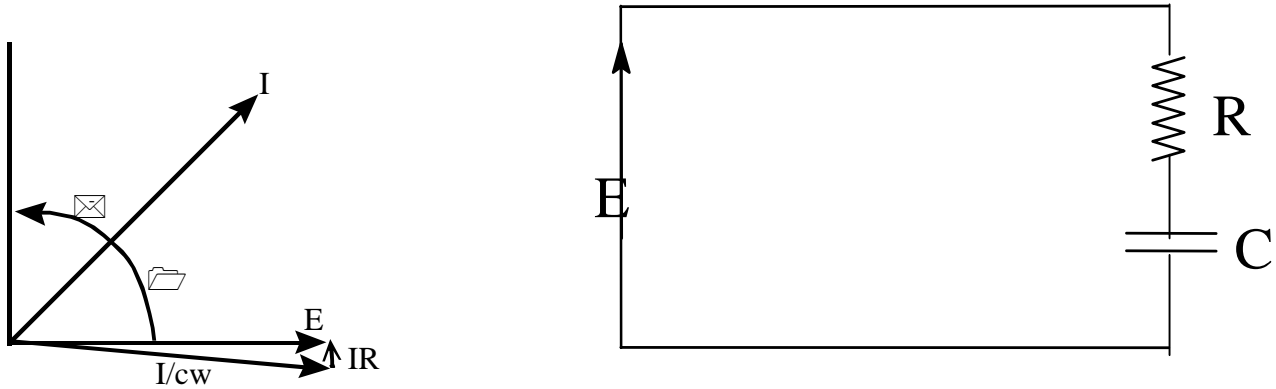
- VDE 0.080" ASTM D-1816
- Flat Disk 0.10" ASTM D-877
- - - - - VDE 0.040" ASTM D-1816
- Flat Disk 0.10" D-877 Stirred

A perfect dielectric material is one in which there is zero conductivity and no energy is absorbed when a voltage is impressed. The only perfect dielectric is an absolute vacuum. Dielectric materials have some of the properties of an insulator and vice versa, so these two terms are used interchangeably. An insulation system can be simulated by a simple equivalent series circuit as shown in Figure 5.

The phasor diagram for this circuit is also shown in Figure 5. The power factor (PF) is defined as follows.

$$PF = \cos \theta = \sin \delta = \frac{IR}{\sqrt{(IR)^2 + (1/c \cdot w)^2}}$$

Figure 5
Circuit Diagram and Phasor Diagram



The PF, $\cos \theta$ and dissipation factor, $\tan \delta$, are practically equal for values under 0.17 or 17 percent. A perfect insulator would act like a pure capacitance and θ would be 90° , $\cos 90^\circ = 0.00$ so $PF = 0$. Polar compounds dissolved in a dielectric fluid, change their orientation in an A.C. field, whenever the voltage polarity changes. The molecular friction associated with the dipole movement results in energy

dissipation in the dielectric. The increase in PF is thus reflective of polar impurities in the oil. If the P.F. measurement is made at 100EC instead of 25EC the observed values are generally greater at the higher temperature. The increase is due to a decrease in fluid viscosity at the higher temperature which allows more dipole movement, friction, and energy loss.

VI. Moisture Content

Mineral oil is hydrophobic and the amount of water that will dissolve in oil is very small. The solubility of water in oil is dependent on temperature as shown in Figure 6. It is commonly accepted that water that is dissolved in the oil has a minimum effect on the dielectric breakdown voltage. Free water, on the other hand significantly lowers the dielectric strength of the oil. The variation of dielectric breakdown potential with moisture is shown in Figure 7. Since the absolute amount of water dissolved in the oil is temperature dependent the percent relative saturation may be a more useful value to evaluate the condition of the oil. For example if the oil temperature is 65° C and the moisture content is 85ppm, the percent saturation is about 29%. If the oil temperature drops to 30° C, the percent saturation becomes slightly above 100 percent, the oil is now supersaturated with moisture and free water will come out of solution. Appendix A is a useful nomograph which was used to perform these calculations.

Cellulose insulation is hydrophillic so the bulk of the moisture that ends up in a transformer migrates into the cellulose insulation. Once the moisture is absorbed by the cellulose it is strongly held due to hydrogen bond formation. Figure 8 shows the equilibrium distribution of water in the oil and in the paper. These temperature dependent plots should be used with caution because it is very doubtful that equilibrium is ever achieved in a dynamic environment. It is nevertheless true that moisture will migrate between these two phases, oil and paper, as the temperature changes. The only way to really know how much moisture is in the paper is to experimentally determine it.

Moisture content in the oil or paper samples is measured according to ASTM D-1533. This titration method can be done with a reagent filled buret or the reagent can be generated electrochemically.

Figure 6
Effect of Temperature on Solubility of Water in Oil

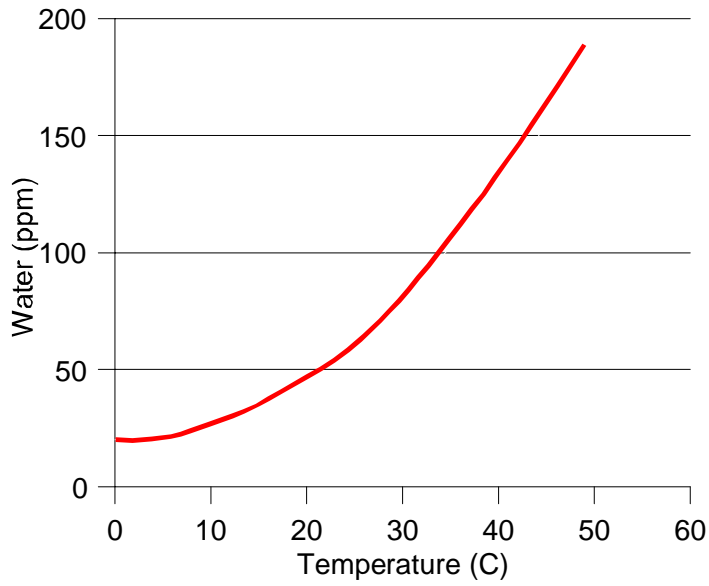


Figure 7
Relation Between Dielectric Strength and Amount of Emulsified Water

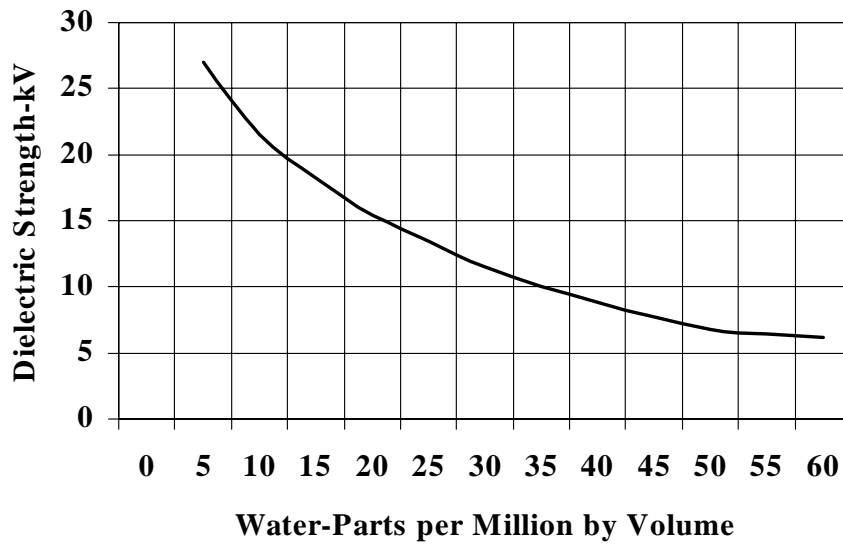
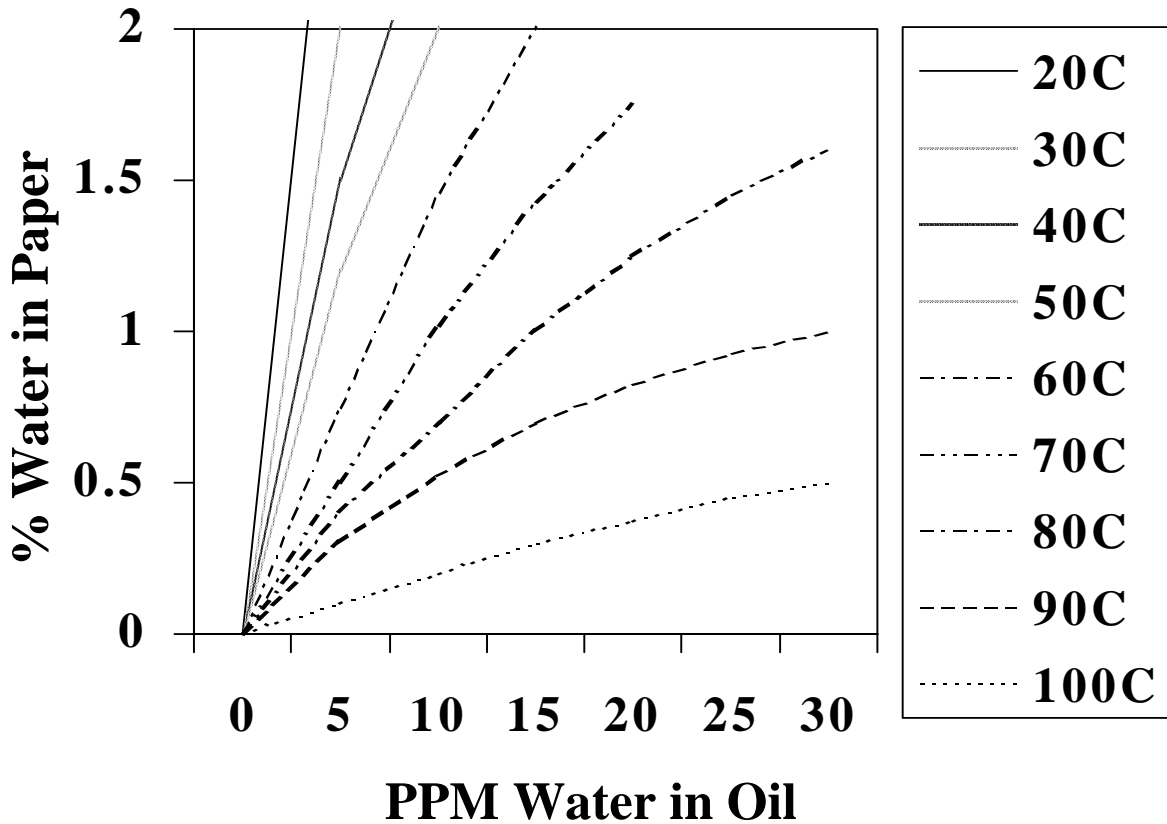


Figure 8
Equilibrium Distribution of Water Between Paper and Oil



VII. Acidity

Mineral oil will be oxidized when dissolved oxygen is present. The extent of oxidation can be determined by measurement of the acid concentration in the oil according to ASTM D-974. The acid is neutralized with a measured amount of a strong base, potassium hydroxide, and the completion of this neutralization reaction is observed with a color indicator. The results are reported in milligrams of potassium hydroxide required to neutralize the acid in one gram of oil. IEEE Guideline, C57.106-1991, gives recommended acid levels at which the oil should be reclaimed, reprocessed or replaced. Their recommendations are summarized in Table 6.

Table 6
Suggested Limits for Oil to be Reconditioned or Reclaimed

Test and Method	Group II	Group III
Acid Number (mgKOH/g, max.)	.2	.5
Interfacial Tension (dynes/cm, min)	24	16

From IEEE Guide for Acceptance and Maintenance of Insulating Oil in Equipment

Group I: This group contains oils that are in satisfactory condition for continued use.

Group II: This group contains oils that require only minor reconditioning for further use. (Mechanical removal of moisture and insoluble contaminants)

Group III: This group contains oils in poor condition. They should be reclaimed or disposed of, depending upon economic considerations. (Requires mechanical and chemical cleanup procedures.)

Group IV: This group contains oils that are in such poor condition that it is technically advisable to dispose of them.

VIII. Interfacial Tension

Measurement of the interfacial tension is completed according to ASTM D-971. The test procedure measures the force required to pull a platinum ring through the interface between the sample and distilled water. The interfacial tension is decreased by any polar compounds that are dissolved in the sample such as acids aldehydes, ketones, alcohols. Coatings used internally in equipment may also dissolve in the oil. These compounds may be polar and will also decrease the IFT. Generally the acid level increases and the IFT decreases as the oil undergoes oxidation. Occasionally the acid level is low and the IFT is also low. If this is the case, then the cause would have to be other polar compounds, rather than acid, in the oil.

IX. Color

Color determination according to ASTM D-1524 is a quick method to measure the extent of oxidation. Most organic compounds including those found in transformer fluids undergo oxidation. Oxidation is generally accompanied by a darkening of the oil.

X. Flash and Flame Points

Flash and Flame points are determined according to ASTM D-92. These measurements are important because of fire safety concerns. Mineral oil must have a minimum flash point of 150° C and HMWH must have a minimum flash point of 300° C. Flash point is a simple and effective way to determine if transformer oil is contaminated with more volatile components such as diesel fuel.

Ordinary mineral oil is completely miscible with HMWH but one should never add mineral oil to HMWH since this will lower the flash point below 300° C.

XI. Additional ASTM Tests

Table 7 is a tabulation of additional ASTM tests that are useful for further evaluation of transformer oil.

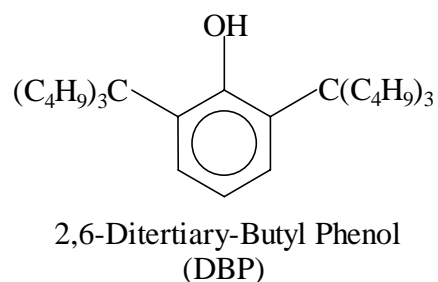
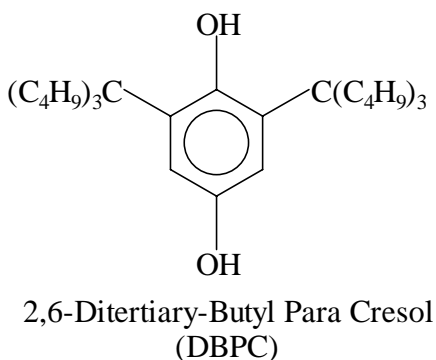
Table 7
Additional ASTM Tests

Test	ASTM Method Number
Aniline Point	D-611
Pour Point	D-97
Specific Gravity	D-1298
Viscosity	D-88
Visual Examination	D-1524
Corrosive Sulfur	D-1275
Oxidation Stability	D-2112

XII. Oxidation Inhibitor

The current methods used by refiners to produce transformer oil from petroleum unfortunately removes the natural oxidation inhibiting compounds present in the crude oil. Oxidation inhibitors are organic compounds that preferentially react with dissolved oxygen before the oil is oxidized. To alleviate this problem, it is common practice to add oxidation inhibiting additives to the uninhibited oil. The two additives that are most widely used as oxidation inhibitors are 2,6-Ditertiary-Butyl Para Cresol, DBPC and 2,6-Ditertiary-Butyl Phenol, DBP, shown in Figure 9.

Figure 9
Structure of Oxidation Inhibitors



The concentration of these two additives can be determined by infra-red spectroscopy according to ASTM D-2668. If the concentration is below the recommended value, approximately 0.15 percent by weight, it can be increased by addition of a measured amount of a concentrated solution of additive. It is not advisable to add these inhibitors, which are solids, directly because of their limited solubility. Concentrated solutions can be prepared by dissolving the solid inhibitor in heated and stirred new transformer oil.

XIII. Oil Maintenance, processing, and reclaiming

The IEEE has prepared extensive sets of recommendations regarding acceptable oil quality. The acceptable values depend on whether the oil is new or in service and on the voltage class of the equipment. Based on these values one can decide if a new oil shipment meets specifications and what actions should be taken with in service oil. The choices are to process, reclaim or replace the oil. Reprocessing refers to any mechanical process such as vacuum degassing or mechanical filtration. Vacuum degassing is effective for the removal of moisture, volatile impurities and dissolved gas. Reclaiming involves chemical processes such as filtration with Fuller=s earth or activated alumina. Reclaiming is effective in removing acids and other polar compounds. The U.S. Bureau of Reclamation has issued an excellent document that reviews the subjects of reprocessing and reclamation of transformer oils.

XIV. Laboratory Reports

ACTI has developed the software required to correlate oil quality assessment data with IEEE recommendations. Appendix B is a typical ACTI client report. The volume of oil required for each ASTM test are tabulated in Appendix C. ACTI provides suitable containers for client samples. These containers are not reused in order to avoid any possible cross contamination of samples.