

CHAPTER (4)

RESULTS AND DISCUSSIONS

4-1 Introduction

This chapter contains the experimental results, analyses and discussions of the results. Results are represented in tables and graphs forms.

4-2 Identification and characteristics of the used transformer oils

The characteristics of the used transformer oils UOT1 and UOT2 were determined according to ASTM/IP standard test methods. The experimental data presented in Table 4.1 reveals that the used transformer oils under investigation have boiling range of 300-355C° and 303-370C°. The physicochemical characteristics and structural group analysis of the waste transformer oils used throughout this investigation are shown in Table 4.1.

The experimental data in Table 4.1 show that the kinematics viscosities of UTO1 and UTO2 are 19 cSt and 21 cSt, density 0.8102 and 0.8159: total acidity 0.41 and 0.58: pour point -10 and -9: breakdown voltage 30 kV and 25 kV, dissipation factors 0.03 and 0.05, respectively. These results show that the used transformer oils are out of IEC 296 specification limits concerning tests, (Table 1.1).

This is attributed to moisture and the oxidation of oils which yields a variety of compounds that can be decorative during the service of oils.

Table 4.1 Physico-Chemical properties of the used transformer oils (UTO1 & UTO2)

CHARACTERISTICS	USED TRANSFORMER OIL	
	UOT1	UOT 2
Density, g/ml at 25°C	0.8102	0.8159
Kinematics viscosity, cst at 25°C	25	28
Kinematics viscosity, cst at 40°C	19	21
Pour point, °C	-10	-9
Carbon residue, wt%	0.71	0.82
Water, vol. %	0.02	0.05
I.b.p. °C	295	300
Recovery, vol.%		
10%	300	302
20%	305	305
30%	317	310
40%	320	318
50%	324	320
60%	330	340
70%	340	345
80%	350	360
90%	352	365
95%	355	370
Structural group analysis n.d.M		
% C _A	20	23
% C _P	52	52
% C _N	28	25
Flash point, °C (Closed), min.	178	180
Type of aromatic Monoaromatic, %	3.23	4.52
Diaromatic, %	4.27	5.37
Polyaromatic, %	12.50	14.21
Total acidity mg/KOH	0.41	0.58
Residue, vol %	5	6
Refractive index, n _D ²⁰	1.4720	1.4875
Density, 20/4 g/ ml	0.8102	0.8159
Average molecular weight	432	445
Tan (δ)	0.0085	0.010
Breakdown voltage (BDV) k Volt.	30	25

Also, the most important chemical aspect of transformer oils is the degree of the deterioration, which atmospheric oxygen can react with the oil under various operating conditions, since the degradation of transformer oil by oxidation can lead to the development of corrosive organic acids and insoluble resinous matter and a marked increase in viscosity, carbon residue

and total acid number, Table 4.1.

The used transformer oils UTO1 and UTO2 were characterized by high aromatic content 20 and 23 wt% and Conradson carbon residue 0.71 and 0.82 wt%, respectively. These undesirable constituents are the main factors for the poor quality and bad electrical properties of the transformer oil. Data in Table 4.1 show that the characteristics of this used transformer oil (high viscosity, low pour point, and high acid number) do not meet with the standard specifications.

The aromatic content of the used transformer oils have been separated into their classes: mono-, di- and poly-aromatics using silica gel chromatography and elution with n-pentane-benzene (95 : 5), n-pentane-benzene (85 : 15) and benzene – ether-methanol (20 : 20 : 60), respectively. The results obtained are presented in Table 4.1 which show that polyaromatics are predominant (12.5 and 14.12 wt%) while the mono- and diaromatics constitute the lower percentages of 3.23 wt% and 4.27 wt%, respectively.

It may be pointed out, therefore, that the polyaromatics contamination is one of the most common causes of deterioration in the insulating quality of oil. This contamination can be eliminated by treatment. More serious deterioration would result from the oxidation of the used transformer oil caused by oxidation polyaromatics with the formation of acids and sludge. Thus, the exclusion of polyaromatic is of prime importance.

The carbon distribution and structural group analysis reveal that the used transformer oils contain considerable portions of paraffinic compounds. The experimental data of the n-d-M method presented in Table 4.1 shows that the percentage of aromatic carbon ($\%C_A$) is 20 and 23, respectively. Meanwhile, the paraffinic carbon portion ($\%C_P$) of the molecules constitutes higher percentages 52 of each UTO1 and UTO2. The naphthenic carbon contents ($\%C_N$) of the molecules are 28 and 25, respectively.

As shown the separation of the aromatics into their classes by silica gel

column chromatography results in Table 4.1. It is clear that the monoaromatics and diaromatics are small class of aromatic compared with polyaromatics constitute. Correlation of the type of aromatics classes and n-d-M data reveals the complex nature of the used transformer oils (UTO1 and UTO2) under study.

The average molecular weight of the used transformer oils (UTO1 and UTO2) are 432 and 445, respectively. Correlation of the average molecular weights and the n-d-M data reveals the complex nature of the hydrocarbon molecules of the used transformer oils.

The new transformer oils contain practically no acids if properly refined. The acidity test measures the content of acids formed by oxidation. The oxidation products polymerize to form sludge which then precipitates out. Acids react with metals on the surface inside the tank and form metallic soaps, another form of sludge. Sludge has been found to begin when the acid number reaches or exceeds 0.4. New oil has an acid number of less than 0.05, the acid number (formerly referred to as neutralization number) equals the milligrams of KOH (potassium hydroxide) required to neutralize the acid contained in one gram of oil.

It is questionable whether oil that has deteriorated to the point where its acid number exceeds 0.6 can be put into lasting good condition by a single renovation. It is almost certain that two or more renovations, spaced six month to one year apart, would be necessary. In this respect, the experimental data presented in Table 4.1 shows that the high values of the total acid number for used transformer oils UTO1 and UTO2 are 0.41 and 0.58, respectively. It is clear that the oil UTO2 is more deteriorated than oil UTO1 this reveal that the potential power of the station.

The moisture contamination is one of the most common causes of deterioration in the insulating quality of oil. Table 4.2 shows that, the water content (volume percentage) for UTO1 and UTO2 are 0.02 and 0.05 vol%,

respectively. This percentage of water can be present in oils (a) in a dissolved form, (b) as tiny droplets mixed with oil (emulsion), or (c) in a free state at the bottom of the container holding the oil. Demulsification occurs when the tiny droplets until to form larger drops which sink to the bottom and form a pool of free water. This fact points to the importance of avoiding overloading of transformers, especially in this investigation.

Products of deterioration occur in oils as result of physical and chemical changes which lubricating oils undergo in the electrical station. Such changes are mainly those connected with decomposition caused by heating and those of oxidation. It has been demonstrated that only a low percentage of the oil is deteriorated while most of it remains unchanged.

Oxidation leads to the formation of various polymerized bodies resulting in a thickening of the oil. This is partially offset by dilution, hence the viscosity of a used oil cannot be used to indicate the effects of either dilution or oxidation while polymerization is taking place soluble and insoluble “sludges” are formed, in addition saponifiable matter or bodies of an aldehydic nature are formed, which in the presence of moisture lead to emulsions, soap, and acidic compounds^[98].

The Polycyclic aromatic hydrocarbons (PAHs) are hazardous organic compounds and are of particular importance as environmental contaminants. Most of them are toxic and those with four or more rings are often carcinogenic, Table 4.4. Owing to the increasing production of transformer oils, lack of proper treatment and disposal, the used transformer oils poses threat to our environment. A simple, fast, precise and efficient method to measure the levels of PAHs is of necessity both for the regulatory control of disposal of used oils, figures 4.6 and 4.7.

Qualitative and quantitative identification of the individual PAHs listed by the United States Environmental Protection Agency (US-EPA) for the studied used oils using HPLC is presented in figures 4.6 and 4.7. Careful examination

of these figures shows that the UTO1 and UTO2 are characterized by the absence of naphthalenes. This may be attributed to the increase in the concentrations of 5- and 6-membered rings the formation of which may be favored by the oxidation reactions which results from the arc during operation service.

4-3 IR spectral Analysis

Infrared spectroscopy provides important information concerning the function groups and their structural features in the studied samples. Figures 4.1 and 4.2 include the FT-IR spectra data of the UTO1 and UTO2 in the frequency range $4000\text{-}400\text{ cm}^{-1}$. The assignments of the vibrations of the functional groups are summarized in Table 4.2.

The spectra of used oil samples UTO1 and UTO2 show a weak band in the region $3600\text{-}3200\text{ cm}^{-1}$ indicating very low concentrations of OH and NH groups. The absence of a strong peak at 3600 cm^{-1} indicates the absence of free OH group. The spectra show a group of bands between 3000 and 2850 cm^{-1} , particularly three distinct bands at about 2950 , 2920 and 2850 cm^{-1} . These bands result from C-H asymmetric and symmetric stretching vibrations of methyl and methylene groups. All spectra showed a peak at about 1600 cm^{-1} , which is characteristic of the stretching vibration of C=C in aromatic system. The spectra also show a strong band at about 1460 cm^{-1} , which are due to asymmetric deformation of methyl and methylene groups. A small peak observed at about 1370 cm^{-1} may be attributed to methyl symmetric deformation. The appearance of a weak band at $1040\text{-}1030\text{ cm}^{-1}$ results from the aliphatic C-O, C-N and/or S=O stretching. Weak absorption bands, at $870\text{-}855$, $810\text{-}805$ and $780\text{-}740\text{ cm}^{-1}$, result mainly from the out-of-plane deformation of CH in aromatic rings. A weak band at about 720 cm^{-1} is due to CH_2 rocking in long chains, $\text{-(CH}_2\text{)}_n\text{-}$ where $n \geq 4$.

Infrared spectra of the UTO1 and UTO2 samples show a group of weak

absorption bands in the region 1850-1650 cm^{-1} , particularly four bands at about 1780, 1745, 1710 and 1655 cm^{-1} . These bands result from stretching vibrations of C=O of ester (1780 and 1745 cm^{-1}); ketones, aldehydes and carboxylic acids (1710 cm^{-1}) and highly conjugated carbonyls such as quinone-type structures and amides (1650 cm^{-1}). It is evident, therefore, that the oxidation reaction is favoured in electrical station.

Some ratios calculated from peak heights of selected infrared band allow for better comparison of the spectra (Table 4.3). The ratio of absorbance of CH_3 symmetric deformation at 1375 cm^{-1} to that of CH_2+CH_3 symmetric deformation at 1460 cm^{-1} (A_{1375}/A_{1460}) is a measure of chain length and/or degree of branching, but the ratio of CH_2 rocking at 720 cm^{-1} to CH_2+CH_3 or CH_3 symmetric deformation (A_{720}/A_{1460} or A_{720}/A_{1375})^(105,106). The data show that, for each oil, the ratios A_{720}/A_{1460} and A_{720}/A_{1375} of UTO2 oil is lower than that of the corresponding UTO1 oil. This indicates that the chain length decreases with time of the operation. The data also show that the ratio A_{1375}/A_{1460} is slightly increased the oil UTO1. This indicates that the degree of branching slightly increases and the chain length decreases with power of the voltage.

The degree of substitution in the aromatic structure is measured from the ratios of CH aromatic out-of-plane deformation of 2/3 or 4 adjacent free hydrogen atoms, at 810 or 770 cm^{-1} , respectively, to that one free hydrogen atom at 870 cm^{-1} ^[99], i.e. A_{810}/A_{870} or A_{770}/A_{870} . The data in Table 4.4 shows that, for each oil, the ratio A_{810}/A_{870} decreases with oxidation. This indicates that the degree of substitution on the aromatic structures is increased with oxidation. This is also conformed by the values obtained from the A_{770}/A_{870} ratio.

The percentage of aromatics to other hydrocarbons may be determined from the ratio of absorbance of C=C aromatic at 1600 cm^{-1} to the CH_2 rocking at 720 cm^{-1} i.e. A_{1600}/A_{720} . The data show that this ratio is generally increased

with time operation and the voltage power. Also, this indicates that the aromatic percentage increases with voltage power.

The proportion of carbonyl and/or carboxyl groups to aliphatic or aromatic proportion could be estimated^[99] from the ratios of absorbance of C=O in the region 1850-1650 cm^{-1} to the CH_2+CH_3 symmetric deformation at 1460 cm^{-1} or C=C aromatic at 1600 cm^{-1} , respectively

Correlation of the IR data (Table 4.3) and break down voltage (Table 4.1) for UTO1 and UTO2 the aromatic content (Table 4.1) reveals that the electrical properties of an insulating oils depends on its compositions. It is evident that the inducting impurities such dirt, sludge and polar compounds (compounds having -OH, C=O, -COOH and C=C aromatic) are attracted into the regions of high electric field and eventually form a bridge. It can be conclude that the oil UTO2 is more deteriorated than oil UTO1 this reveal that the potential power of the station.

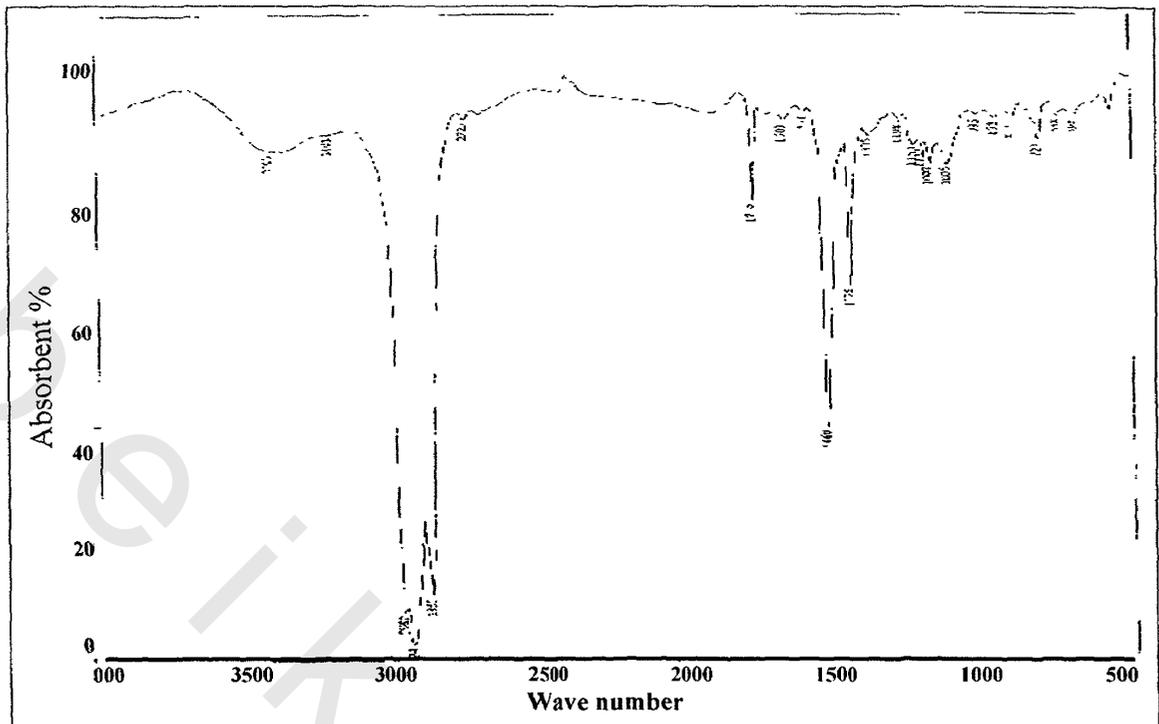


Figure 4.1 Infrared spectra for the first used transformer, UTO1

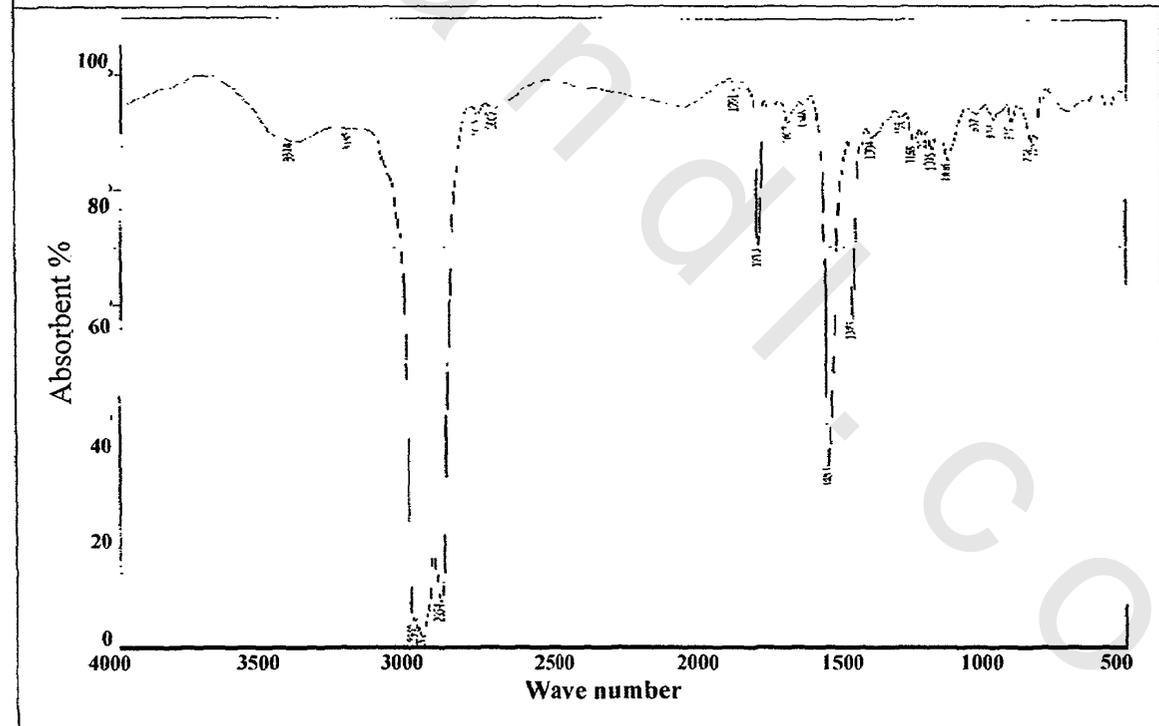


Figure 4.2 Infrared spectra for the second used transformer, UTO2

Table 4.2 Assignment of the vibration of the functional groups in the Infrared spectra of the used transformer oils

Wave numbers, cm^{-1}	Assignment of the Vibrations of the functional groups ⁽²⁰⁾
3600 – 3200	OH stretching; NH stretching
3100 – 3000	CH stretching in aromatic rings
2955 – 2945	CH ₃ asymmetric stretching
2930 – 2920	CH ₂ asymmetric stretching
2860 – 2850	CH ₂ symmetric stretching
2730 – 2725	CH stretching in aldehyde groups
2000 – 1800	Overtone of polycondensed aromatics
1780 – 1650	C=O stretching in carbonyl groups
1610 – 1590	C=C stretching in aromatic rings
1475 – 1450	CH ₂ and CH ₃ asymmetric deformation (scissoring)
1380 – 1370	CH ₃ symmetric deformation (scissoring)
1315 – 1300	CH ₂ wagging in long chain paraffins
1165 – 1155	(CH ₃) ₂ – C
1040 – 1030	C-O stretching; C-N stretching; S=O stretching
970 – 950	CH in naphthenic rings
945 – 910	OH out-of-plane deformation
890 – 860	CH aromatic out-of-plane deformation (1 free hydrogen atom)
815 – 805	CH aromatic out-of-plane deformation (2 or 3 adjacent free hydrogen atoms)
780 – 740	CH aromatic out-of-plane deformation (4 adjacent free hydrogen atoms)
730 – 720	CH ₂ rocking in long chains $-(\text{CH}_2)_n-$, $n \geq 4$

Table 4.3 Parameters calculated from the FTIR Spectra of the and UTO2

Oil sample parameters	UTO1	UTO2
A_{720} / A_{1375}	0.50	0.25
A_{720} / A_{1460}	0.20	0.13
A_{720} / A_{1375}	2.46	2.02
A_{720} / A_{870}	4.72	1.70
A_{720} / A_{870}	1.18	1.63
A_{720} / A_{810}	3.99	1.46
A_{1375} / A_{1460}	2.85	1.37
A_{1600} / A_{720}	1.23	1.09

4-4 Chromatographic Analysis

Gas chromatography (GC) plays an important role in the analysis of petroleum compounds especially paraffinic hydrocarbons. The distribution of hydrocarbons in the lubricating oils was performed using capillary gas chromatography (CGC), it gives qualitative and quantitative information^[100] concerning the types of hydrocarbons and their distribution. CGC gives a finger print for each lubricating oils as significance for the nature and type of such oil^[101]. Also it helps to distinguish the unresolved compounds representing the naphthene and polycyclic aromatic hydrocarbons^[102, 103]

The most widely used methods for the identifications of transformer oils are based on capillary gas chromatography. Interpretations of the chromatograms are to some extent a matter of comparison with chromatograms of the used transformer oils UTO1 and UTO2. The nature of transformer oils and the operation condition affect the chemical nature of the hydrocarbon products and can drastically alter the profiles of the chromatograms obtained. The gas chromatographic pattern of the studied samples UTO1 and UTO2 shows higher paraffin percentages, in other words the area of the unresolved component mixture (UCM) for UTO1 and UTO2 are 92.82 and 96.25, respectively. This may be due to the formation of polymeric materials in the region of UCM.

The carbon number distribution of the paraffinic hydrocarbons shown in Figure 4.5 reveals that the chain paraffinic hydrocarbons for UTO2 are lowest percentages than UTO1. Generally, the heavy hydrocarbons in all investigated UTO1 and UTO2 oils were degraded producing light hydrocarbons. While the formation of high percentages of polymeric compounds overtakes the produced light hydrocarbon during operation

Gas chromatographic analysis shows that the heavy fraction of paraffins in the case of the studied two samples was degraded after operation into the light fractions as given through the carbon number distribution in figure 4.5.

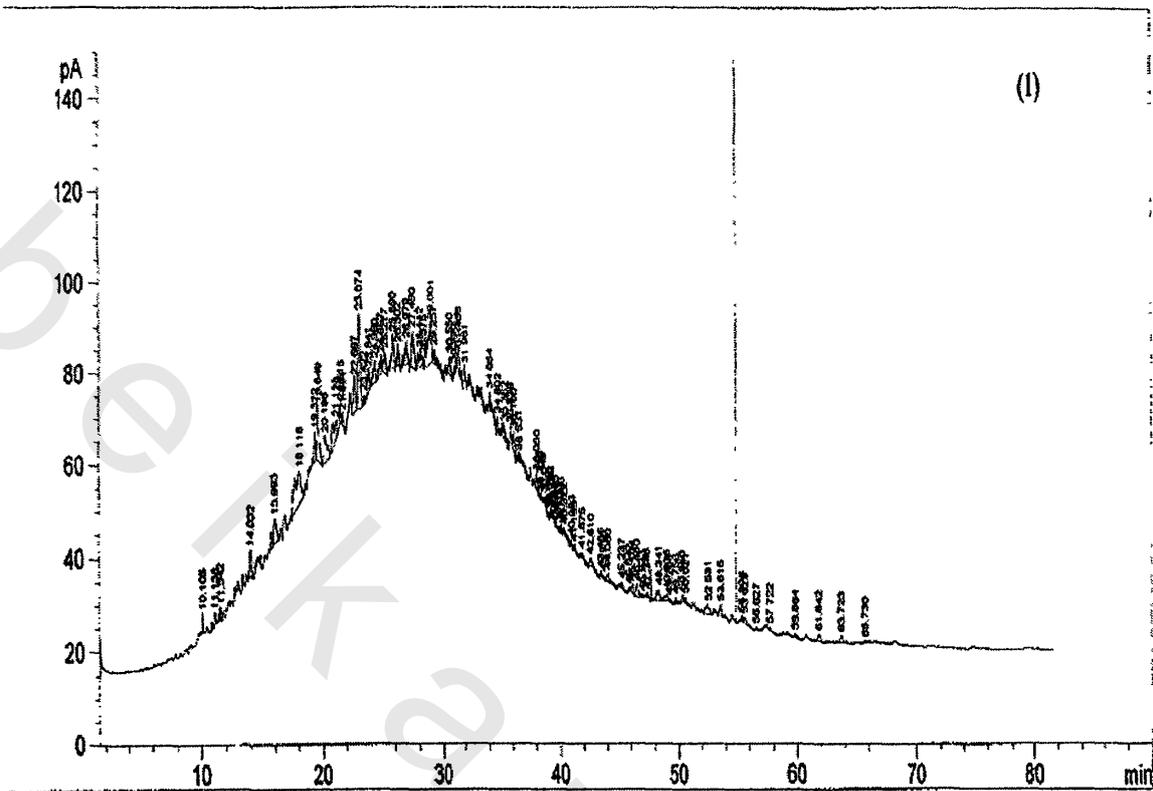


Figure 4.3 Gas chromatographic analysis of the first used Transformer oil, UTO1

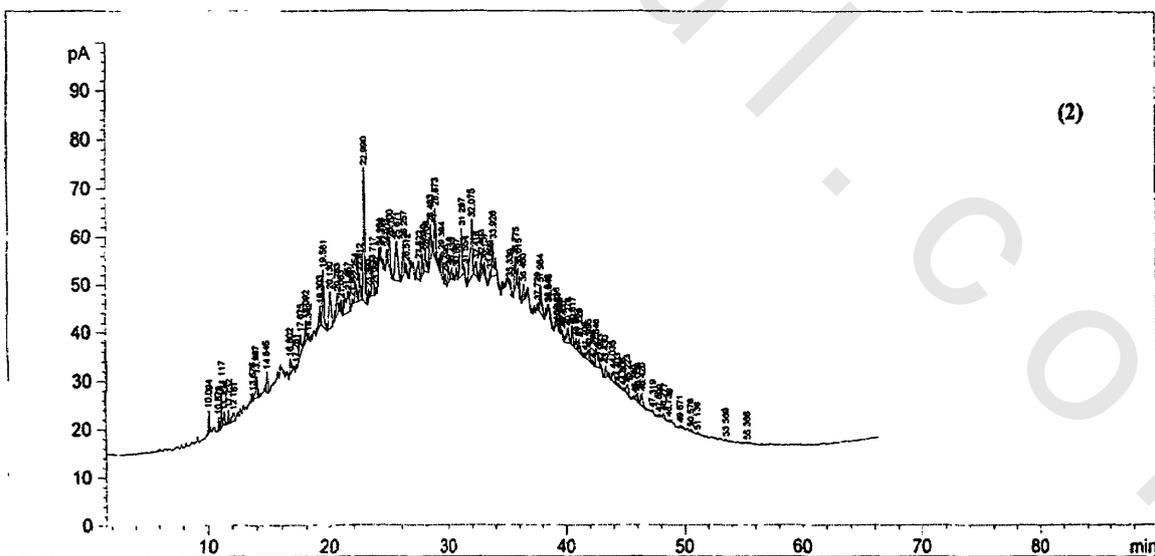


Figure 4.4 Gas chromatographic analysis of the second used Transformer oil, UTO2

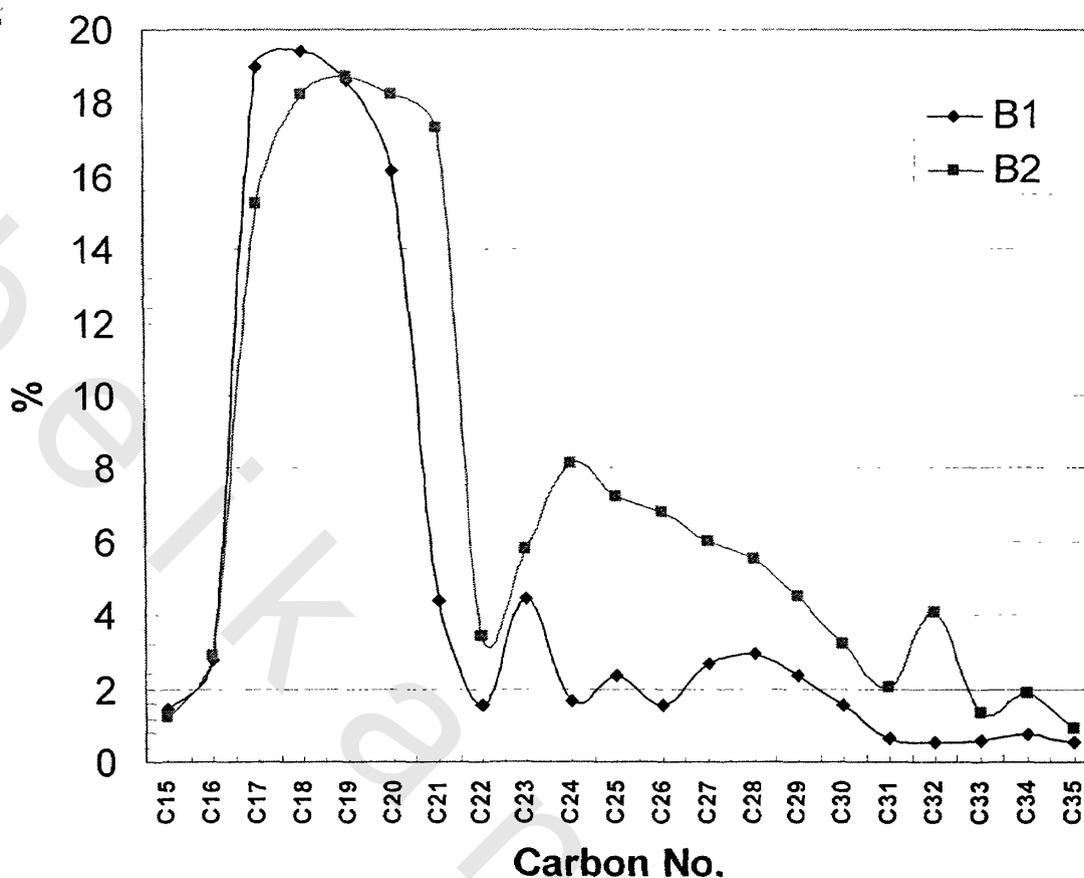


Figure 4.5 Paraffinic carbon distribution for used transformer oils, UTO1 and UTO2.

In the case of the studied two used transformer oils sample, the formation of light paraffins is a result of the oxidation of the unresolved compounds. During deteriorates there are many processes that occur such as thermal cracking, polymerization, cyclization and isomerization reactions. Accordingly, in the electrical station light paraffins, polycyclic hydrocarbons (naphthenes & aromatics) and some heavy components can be created. This finding is deduced from the chromatogram as a hump of unresolved complex mixture (Figures 4.3 and 4.4)

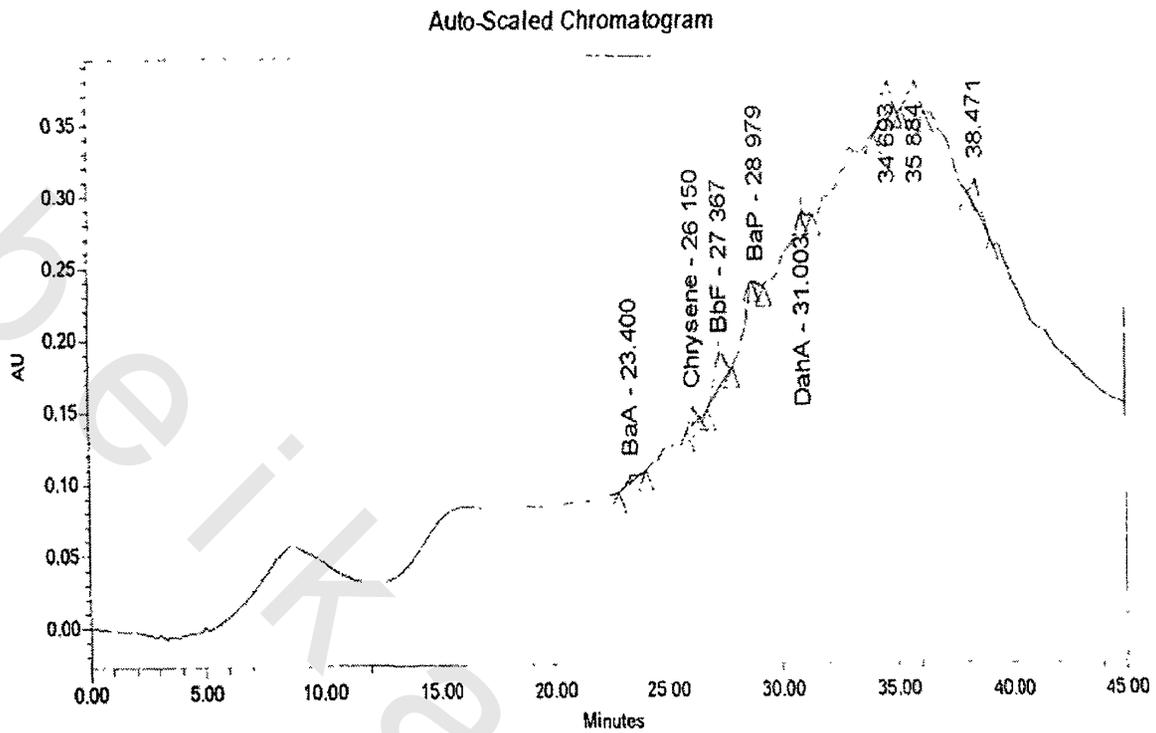


Figure 4.6 HPLC chromatogram of the UTO1

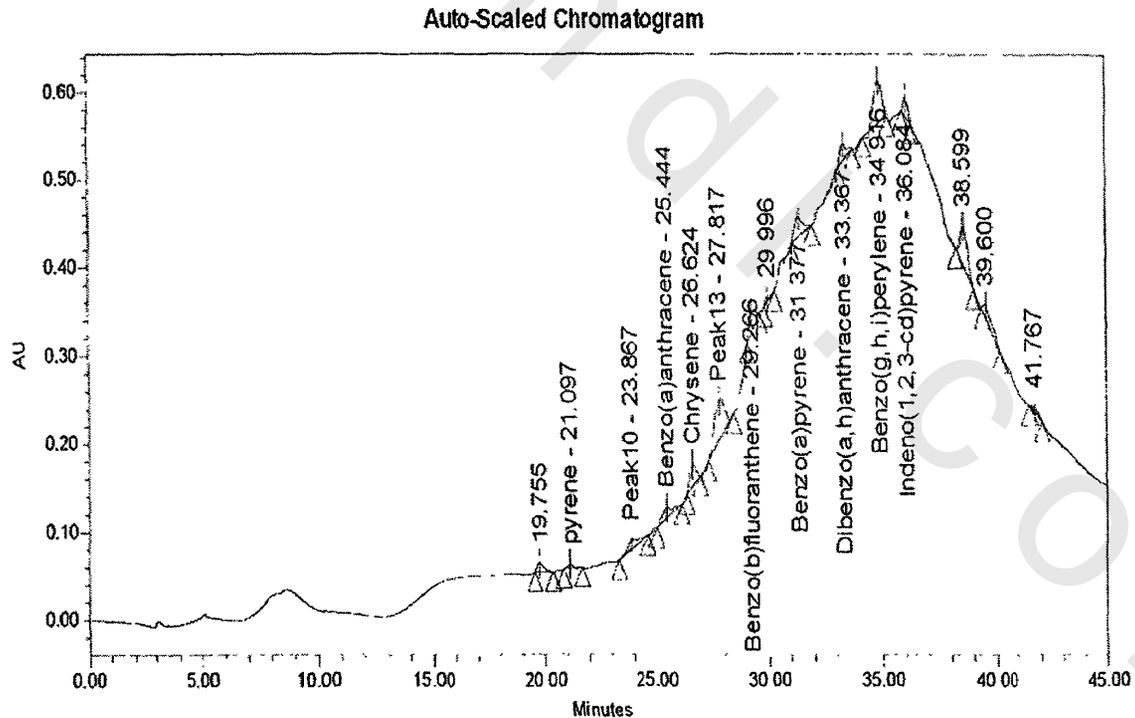
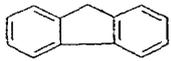
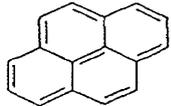
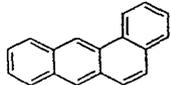
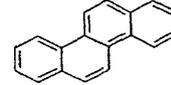
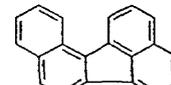
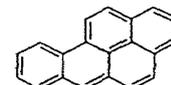
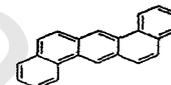
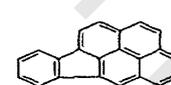
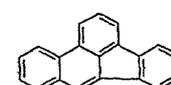
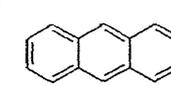
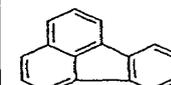
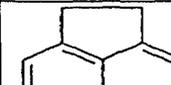
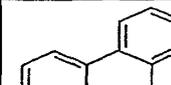


Figure 4.7 HPLC chromatogram of the UTO2

Table 4.4 Molecular weight and molecular formulae of some studied polyaromatic hydrocarbons

No.	Compound	Code	Molecular Formula	Molecular Weight	Toxicity
1	Fluorene	Fluo		166	Non toxic ⁺
2	Pyrene	Py		202	Very toxic ⁺
3	Benzo(a)anthraene	B(a)an		228	Very toxic ⁺
4	Chrysene	Ch		228	Moderately toxic ⁺
5	Benzo(k)fluoranthene	B(k)flu		252	Very toxic ⁺
6	Benzo(a)pyrene	B(a)py		252	Very toxic ⁺
7	Dibenzo(a,h)anthracene	Dib(a)an		278	Very toxic ⁺
8	Benzo(g,h,i)perylene	B(g,h,i)per		276	Very toxic ⁺
9	Indeno(1,2,3-cd)pyrene	I(1,2,3-cd)py		276	Very toxic ⁺
10	Benzo(b)fluoranthene	B(b)flu		252	Very toxic ⁺
11	Anthracene	An		178	Very toxic ⁺
12	Fluoranthene	Flu		202	Very toxic ⁺
13	Acenaphylene	Acena		154	Very toxic ⁺
14	Phenanthrene	Ph		178	Non toxic ⁺

4-5 By-pass Kiln Dust

The by-pass kiln dust, collected from Tourah Portland Cement Factory in Helwan was used in the present investigation as an adsorbent and neutralizing agent. This cementations by-product is largely available and its chemical composition (Table 4.5) is attractive for its utilization in recovering high quality transformer oils. In fact, this kiln dust constitutes a problem concerning the environment in Helwan district and the present study offers one of the promising approaches to overcome the serious problem.

The chemical analysis of the by-pass kiln dust (Table 4.5) reveals that contains low amount from both oxides Al_2O_3 (3.14 wt %) and Fe_2O_3 (2.84 wt%). Kiln dust is also enriched in CaO and Na_2O (53.1 and 2.5 wt% respectively), which causes the high alkalinity. This alkalinity of the by-pass kiln dust plays an important role in the eliminating the acidic compounds which cause the formation of emulsions with moisture in the transformer oil and also in bleaching the recovered transformer oil.

On the other hand, the cement industry produces a large amount of waste dust. This dust arises from two sources. Firstly, cement dust from the rotary kiln, known as kiln dust, that settles from the electrostatic precipitation used to purify the flue gases evolving from the kiln; and secondly, by-pass dust, which constitutes a "purge" from the kiln in order to minimize the amount of alkalis in the effluent flue gases from the kiln. The first type can usually be recycled to the kiln since its alkali content is usually low. By-pass dust, on the other hand can not be recycled to the kiln, its alkali content usually exceeding 10%. The present study is to investigate the possibility of using the by-pass kiln dust as an alternative to clay and solve pollution problem, for the reclamation of waste transformer oil.

Table 4.5 Chemical Analysis for by-Pass kiln dust

Oxides	Ratio	Oxides	Ratio
SiO ₂	13.40	SO ₃	5.50
Al ₂ O ₃	3.14	K ₂ O	2.65
Fe ₂ O ₃	2.84	Na ₂ O	2.50
CaO	53.10	Cl	3.90
MgO	1.35	Ignition loss	9.50

4-6 Sulphuric Acid Treatment and Mixing Time

Selections of treatment reaction conditions are based on capability to remove some of the impurities and undesirable components. Generally, transformer oil must have the following characteristics: low viscosity, low density, high electric strength, high impulse strength, high volume resistivity, low dielectric dissipation factor, high specific heat and thermal conductivity, low solvent power, excellent chemical stability, good gas absorbing properties and low volatility [104-105]. The used transformer oil must be regenerated by acid/kiln dust treatment to meet with these requirements. Basically, acid refining removes undesirable components from the oil by using sulphuric acid to cause the impurities to form sludge.

Data in Tables 4.6 and 4.7 show the effect of time of stirring with different weight percentages of sulphuric acid to select the optimum addition time. The reaction was carried out at different times of 30, 60, 90 and 120 minutes. It is obvious from these results that, the yield of the recovered oil, total acidity, total aromatics and flash point decrease by increasing mixing time at all dosages from sulphuric acid. The breakdown voltage increases with increasing the mixing time for sulphuric acid dosages of 3 wt% and 5 wt% but decreases at 7 wt% sulphuric acid on increasing mixing time. This could be attributed to the removal of sulphur, sludge oxidative and undesirable components by sulphuric acid.

In this respect, the time required to establish the equilibrium conditions depends on the intimacy of contact between the used oils and sulphuric acid. For complete separation of the phase in contact, the time depends on the nature of the used oils, acid weight percent, temperature and the degree of dispersion between oils and acid. The separation of phases carried out by settling and centrifuges.

Also, the efficiency of sulphuric acid increases by increasing the mixing time and dose percentage leading in turn to increasing the attacks on various compounds. These include oxygen compounds, asphaltic and resinous substances, in addition to other impurities such as sulphur-based compounds and soluble metallic components, while paraffinic and naphthenic hydrocarbons remain unaffected.

Concerning the total acid number, the acidic components are removed effectively when the used transformer oil has been treated with either percentage of 5 wt% or 7 wt% sulphuric acid. However, the yields of the treated oil decrease with such increase in the sulphuric acid percentage.

The correlation between this percentage and the acceptable limits of total acid number, taking into consideration the yields, reveal that 5 wt% of sulphuric acid is the optimum ratio with respect to both the quality and yield of the treated (processed) oil.

The AC breakdown voltage is a measure of the ability of oil to withstand electrical stress. The normal method of specifying AC breakdown voltage is IEC 156. Data in Tables 4.6 and 4.7 show the oil treated with 5 wt% sulphuric acid at mixing time of 30, 60, 90 and 120 minutes yields products having aromatic content of 10 wt% to 13 wt%. These aromatic percentages are the most favorable resulting in high breakdown voltage of 55 kV.

The oxidized and resinous components are actively adsorbed on the sulphuric acid. Worth mentioning is that decreasing the aromatic content below 10 wt% (with 7 wt% sulphuric acid ratio), as well as increasing the

aromatic above 13 wt% (using 3 wt% sulphuric acid) both result in negative impact on the breakdown voltage.

It may be concluded, based on the experimental data in Tables 4.6 and 4.7, that the acceptable balance between yield, aromatic content, total acid number and the breakdown voltage can be achieved using 5 wt% ratio of sulphuric acid at mixing time of 90 minutes.

4-7 Effect of the By-pass Kiln Dust

Experimental data in Tables 4.8 and 4.9 show the effect of by-pass kiln dust ratios (1, 3, 5, 7 and 9 wt%) on the properties of the treated transformer oils at selected weight percent sulphuric acid (5wt%) and ambient temperature. Its obvious from these data the by-pass kiln dust improving the colour, total acid number, kinematics viscosity, ash content, breakdown voltage and dissipation factor for both recycled transformer oils. The ranges of all these values (Tables 4.8 and 4.9) are within the acceptable limits. This reveals that the by-pass kiln dust is efficient as adsorbent and bleaching agent.

As well as, more active materials in oil are preferentially and selectively adsorbed on the surface of the by-pass kiln dust. The unsaturated compounds exert greatest attractive force for kiln dust followed in order by compounds containing oxygen and aromatic compounds. In each series the higher molecular weight hydrocarbons are adsorbed more readily. Thus, resinous and asphaltic materials which have high molecular weight are actively adsorbed.

Inspection of the data concerning the effect of by-pass kiln dust ratio on properties of treated oils shown in Tables 4.8 and 4.9 reveal the fact that the acidic components (total acidity) have been substantially reduced through the alkalies center in kiln dust.

In addition, kiln dust is the final finishing step in treatment to obtain specific desirable properties and/or to improve the characterizations.

Therefore it may be concluded that the most efficient weight percent from

by-pass kiln dust to recover high quality recycled transformer oils is 7 wt%. It may be significant to point out that the purpose of the kiln dust treatment is to decolourize the oils and to remove carbon, coke, resinous, water, polar compounds and suspended matter. A large portion of coloring matter is removed in the acid treatment process.

It is clear that the best condition for the recycled transformer oils obtained with 7wt% by-pass kiln dust, 5wt% sulphuric acid and 90 minute mixing time. This is due to the fact that the all polar, aromatic and unsaturated compounds in the used transformer oils were removed by acid/kiln dust treatment.

4-8 Electrical Properties

It is worth mentioning here that, the electrical properties of an insulating liquid are important to its function as an insulant. Their maintenance at an acceptable level ensures satisfactory equipment performance, reduce ohmic losses and limits discharge inception within the liquid. These properties are affected by the chemical constituents of the transformer oil, the presence of conducting contaminants such as fibers, water, particulate matter, dirt dipolar and ionic or dissociated compounds. The breakdown strength is the one of the most of important properties of transformer oils to be measured. The breakdown strength of the recycled transformer oils (RTO1 and RTO2) are normally specified using brass sphere shaped smooth electrodes with a gap distance of 2.5 mm at 50 Hz at 25°C.

It is apparent from the data in Table 4.6 the breakdown voltage for first recovered transformer oil (RTO1) at different weight percent of sulphuric acid and different stirring time is between 40-55 kV. Also, data in Table 4.7 show that the breakdown voltage for second recovered transformer oil (RTO2) at the same above conditions is 40-50 kV. This means that the breakdown voltage of the recycling used transformer oils depends on many factors such

as, time string, weight percent of sulphuric acid, service time and its composition.

Table 4.6 Effect wt% of sulphuric acid and mixing time on properties of the recovered transformer oil RTO1

Properties \ Ratio of II 2504	3 wt %				5 wt %				7 wt%			
	30	60	90	120	30	60	90	120	30	60	90	120
Stirring time (minute)	30	60	90	120	30	60	90	120	30	60	90	120
Yield wt%	88	86	85	84	87	87	85	83	81	82	79	76
Total acidity mg KoH/gm	0.1	0.06	0.04	0.03	0.03	0.02	0.02	0.01	0.03	0.01	0.01	0.01
Flash point °C	160	155	150	140	150	145	142	140	145	143	140	140
Pour point °C	-20	-25	-30	-32	-30	-33	-40	-41	-35	-38	-40	-42
Kinematics viscosity cSt	15	13	12	13	15	14	10	10	14	13	13	12
Total aromatic content, wt%	16	15	15	14	13	12	11	10	11	9	10	7
Conradson carbon	0.21	0.12	0.11	0.1	0.12	0.1	0.08	0.05	0.11	0.07	0.05	0.01
Break down Voltage, kV	42	43	45	46	45	48	55	55	50	41	42	40

Table 4.7 Effect wt% of sulphuric acid and mixing time on properties of the recovered transformer oil RTO2

Properties \ Ratio of II 2504	3 wt %				5 wt %				7 wt%			
	30	60	90	120	30	60	90	120	30	60	90	120
Stirring time (minute)	30	60	90	120	30	60	90	120	30	60	90	120
Yield wt%	87	86	86	85	90	89	87	85	84	82	80	78
Total acidity mg KoH/gm	0.1	0.06	0.04	0.03	0.03	0.03	0.02	0.01	0.03	0.01	0.01	0.01
Flash point °C	163	160	159	155	160	155	152	150	155	152	150	145
Pour point °C	-20	-20	-25	-28	-25	-28	-30	-30	-28	-30	-30	-32
Kinematic viscosity cSt	16	14	14	13	15	14	10	10	14	13	13	12
Total aromatic content, wt%	18	16	15	14	15	14	12	12	12	11	10	8
Conradson carbon	0.23	0.18	0.12	0.11	0.12	0.1	0.05	0.05	0.13	0.05	0.03	0.01
Break down Voltage, kV	40	44	45	45	48	48	50	50	48	45	40	40

Table 4.8 effect of the by-pass Kiln dust on the properties of the treated oil (RTO1) with 5% H₂SO₄ at 40°C

Properties	wt% by-pass Kiln dust				
	1	3	5	7	9
Relative density at 20°C	0.8823	0.8900	0.8912	0.8924	0.8891
Refractive index at 20°C	1.4731	1.4821	1.4803	1.4852	1.4795
Kinematic viscosity cSt, at 40°C	16	14	13	12	13
Pour point, °C	-30	-30	-32	-33	-33
Ash, wt %	0.04	0.03	0.02	0.01	0.01
Color	2.1	2.0	1.5	1.0	1.0
TAN mg KOH/g	0.10	0.06	0.03	0.04	0.04
BDV, kV	42	48	55	56	55
Tan δ	0.02	0.01	0.003	0.002	0.002
Yield, %	91	88	87	85	79

Table 4.9 effect of the by-pass Kiln dust on the properties of the treated oil (RTO2) with 5% H₂SO₄ at 40°C

Properties	wt % by-pass Kiln dust				
	1	3	5	7	9
Relative density at 20°C	0.8958	0.8943	0.8837	0.8804	0.8800
Refractive index at 20°C	1.4735	1.4788	1.4894	1.4859	1.4899
Kinematic viscosity cSt, at 40°C	17	14	13	13	12
Pour point, °C	-30	-30	-31	-29	-29
Ash, wt %	0.05	0.04	0.03	0.03	0.02
Color	2.5	2.2	1.5	1.5	1.0
TAN	0.10	0.08	0.05	0.03	0.03
BDV, kV	40	41	43	45	45
Tan δ	0.030	0.010	0.01	0.007	0.005
Yield, %	89	85	81	78	75

Table 4.10 Effect of mixing time on polyaromatics distribution at optimum conditions

Oil Sample	RUTO1					RUTO2					
	Mix. time, min.	30	60	90	120	150	30	60	90	120	150
Polyaromatics, wt%											
Pyrene	80.2	79.5	60.3	55.8	54.3	90.2	91.3	80.5	70.2	61.3	
Benz (a) anthracene	78.2	70.8	65.1	62.3	60.4	87.4	72.2	78.2	70.2	68.5	
Chrysene	15.2	14.5	10.1	9.8	9.5	12.4	11.5	11.3	9.2	9.1	
Benzo (b) flourathene	18.7	15.3	14.0	13.2	11.3	22.3	20.5	19.4	18.2	17.0	
Benzo (k) flourathene	-	-	-	-	-	10.8	9.7	9.0	8.2	8.0	
Benzo (a) pyrene	13.4	13.2	12.0	10.5	10.3	32.5	30.3	27.4	26.3	25.8	
Dibenzo (g,h) anthracene	21.4	20.8	19.2	17.7	17.0	12.3	11.4	10.0	9.6	9.0	
Benzo (g,h) perylene	17.0	16.8	15.2	15.0	14.2	22.4	21.5	19.4	18.0	17.8	
Indeno (1,2,3- CD) pyrene	10.2	9.8	9.0	8.4	8.0	28.5	25.3	22.0	21.0	20.3	

Where:

$$\text{Correct area} = \text{response factor} \times \text{area \%}$$

$$\% \text{ Concentration} = \frac{\text{Correct area} \times 100}{\text{Total Correct area}}$$

4-9 Breakdown Voltage as a Function of the Temperature

On the other hand, Figures 4.14 and 4.15 shows the effect of mixing time (30, 60, 90, 120 and 150 minute) on the breakdown voltage of the recycling used transformer oils at different temperatures (30, 40, 50 and 60°C). These Figures shows that increasing the BDVs by increasing mixing time and temperatures up to 120 minute and 40°C, respectively.

4-10 Dissipation factor as a function of the temperature

Dissipation factor is a measure of electrical energy dissipated as heat. This characteristic is expressed as a dissipation factor $\tan(\delta)$, where δ is the loss angle. The dissipation factor is quite sensitive to temperature changes and it is

proportional conductivity. It has not always been included in transformer oil specification; it appears for cables and capacitors oils. As $\tan \delta$ is always very low of a well recycled oil at optimum conditions (5 wt% H_2SO_4 , 7 wt% kiln dust, 90 minutes mixing time, 40°C temperature).

As shown in figures 4.16 and 4.17 $\tan \delta$ for RTO1 and RTO2 decreases by increasing temperature until 40°C and after that it gives plateau at 50 and 60°C, it can be concluded that the optimum temperature is 40°C. This data confirmed with breakdown voltage and (TAN) values. Also $\tan \delta$ decreasing by increasing mixing time in ranging (0.001 to 0.005).

4-11 Viscosity as a Function of Temperature

The most important properties of transformer oil are its viscosity and temperature characteristics. For most of the applications where boundary lubrication conditions are prevalent, it is the viscosity of the lubricating oil which determines to a large extent the uses to which the oil can be put. The viscosity of a fluid is that property which determines its resistance to shear; the way the molecules interact to resist motion. It is a vital property of a lubricant because it influences the ability of the oil to form a lubricating film.

In this respect, transformer oil must have low viscosity for easy flow and efficient heat transfer. The experimental data presented graphically in Figures 4.10 and 4.11, respectively at 5wt% sulphuric acid and 7 wt% by-pass kiln dust. It can be noticed that the viscosity of RTO1 and RTO2 are decreases with increasing temperature.

4-12 Yield as a Function of Temperature

The yield of the recovered transformer oils RTO1 and RTO2 obtained with different temperatures (30, 40, 50 and 60°C). The experimental data presented graphically in Figures 4.12 and 4.13, respectively at 5wt% sulphuric acid and 7 wt% by-pass kiln dust. These Figures give an overview on the effect of

temperature on the yield of processed oils. The general trend, the yield of the recovered oils is decreased with increasing temperatures. This attributed to the miscibility and adsorptive of the constituents with sulphuric acid and kiln dust are increasing with increasing temperature. It can be seen that, as the temperature is increased, the yield decreases with significant improvement in its physical and electrical properties and gives recycled oils of better quality.

4-13 Total Acid Number as a Function of Temperature

The neutralization number of oil not only shows the acidic or alkaline content of new oils but is also an indicator of the degree of oxidation of used transformer oils and its gives overview on the degree of reclamation.

Used transformer oils contain many ingredients which are either acidic or basic in nature. The ingredients considered to have acidic properties include organic acids, phenolic compounds, resin, esters, salt of heavy metals and inhibitors. All these compounds are created and present in transformer oils, as indicated the high value of total acid number for used transformer oils UTO1 and UTO2 Table 4.1.

Therefore, the use neutralization number as a guide for continued use or for reclamation of oil is easier and more accurate in large central recirculation systems where control may be optimized. Thus, it is more feasible to determine the condition of oil through neutralization number in transformer oils system.

It is to be noted that the total acid number is expressed in term of mg of KOH per gram of used or recycled transformer oils sample. This carried out through potentiometric titration method.

In this respect, anhydrous isopropyl alcohol is used in the preparation of alcoholic potassium hydroxide solution. The titration is carried out in a mixture of toluene and isopropyl alcohol containing a small amount of water using a glass indicating electrode and a calomel reference electrode. From the

inflexion points of the titration curve the total acid number is calculated.

From the experimental results it becomes clear that the reclamation with acid/by-pass kiln dust (5 wt% H₂SO₄, 7 wt% kiln dust and 90 minute) at different temperatures gives interesting improvements in the total acidity for RTO1 and RTO2, figures 4.8 and 4.9, respectively. It can be observed that as temperature increases, the total acid number of oils decreases up till 40°C, then there is reverses in trend. This can attributed to the fact that as the lower temperatures, ranging from 30-40°C, the increase the adsorption of the oxidizing compounds with sulphuric acid and kiln dust. At higher than about 40°C the effectiveness considerably reduced. Therefore it can be concluded that the effective temperature for reducing the total acidity of both used transformer oils under investigation is 40°C.

4-14 Effect of Polyaromatic Hydrocarbons

Correlation of the molar ratio of polyaromatic hydrocarbons data in Table 4.10, with data in figures 4.6 and 4.7, reveals useful information concerning the type of polyaromatic hydrocarbons in recycled oils (RTO1 and RTO2 and its electrophysical properties. Its clear that the breakdown voltage increases with decreasing polyaromatic hydrocarbons content. This means that the breakdown voltage of an transformer oils depends on its composition. Also, it is evident that the inducting of polyaromatic hydrocarbons are attracted into regions of high electric field and eventually form a bridge. Thus, it is important to decreasing these components.

4-15 Physicochemical Properties of Recycled Oils

The physico-chemical and electrical properties of RTO1 and RTO2 optimum conditions occurs at sulphuric acid 5 wt%, mixing time 90 minute, by-pass kiln dust 7 wt%, and temperature 40°C as represented in Table 4.11. It is clear that the recycled transformer oils have lower density, viscosity, pour

point and total acid number, as well as, remarkable improvements in the electrical properties. According to these data, the above reclamation conditions gives oils have good physical and electrical characteristics within the standard specifications required.

The experimental data of the carbon distribution and structural group analysis presented in Table 4.11 show that the low percentage of aromatic carbon ($\%C_A$) are 9 and 10 for the RTO1 and RTO2, respectively. Meanwhile, the paraffinic and naphthenic carbon portions have higher percentage.

It may be pointed out, therefore, that the acid/by-pass kiln dust method involves the treatment of used transformer oils with sulphuric acid, which preferentially attacks, aromatic, oxygen compounds and resinous substances (contaminant particles), while leaving paraffinic and naphthenic hydrocarbons essentially intact. In addition, hydrocarbon analysis of the recycled oils (RTO1 and RTO2) showed some selective removal of polyaromatic hydrocarbons and polar materials that are required for good insulation, as well as reduction of acid number and color bodies.

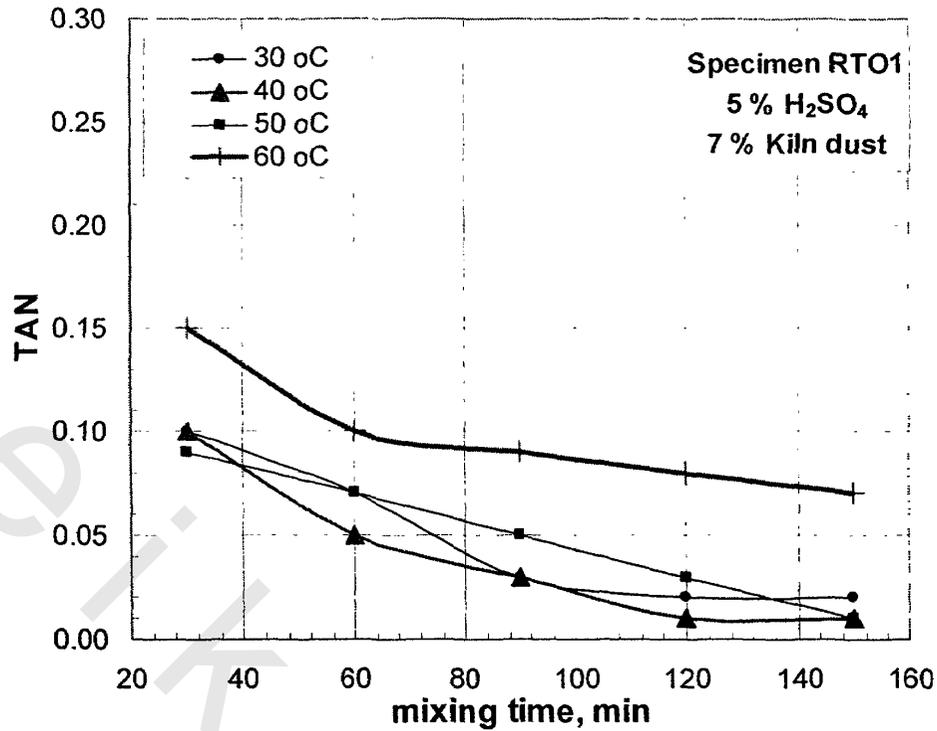


Figure 4.8 Effect of mixing time on the TAN at different oil temperature for RTO1

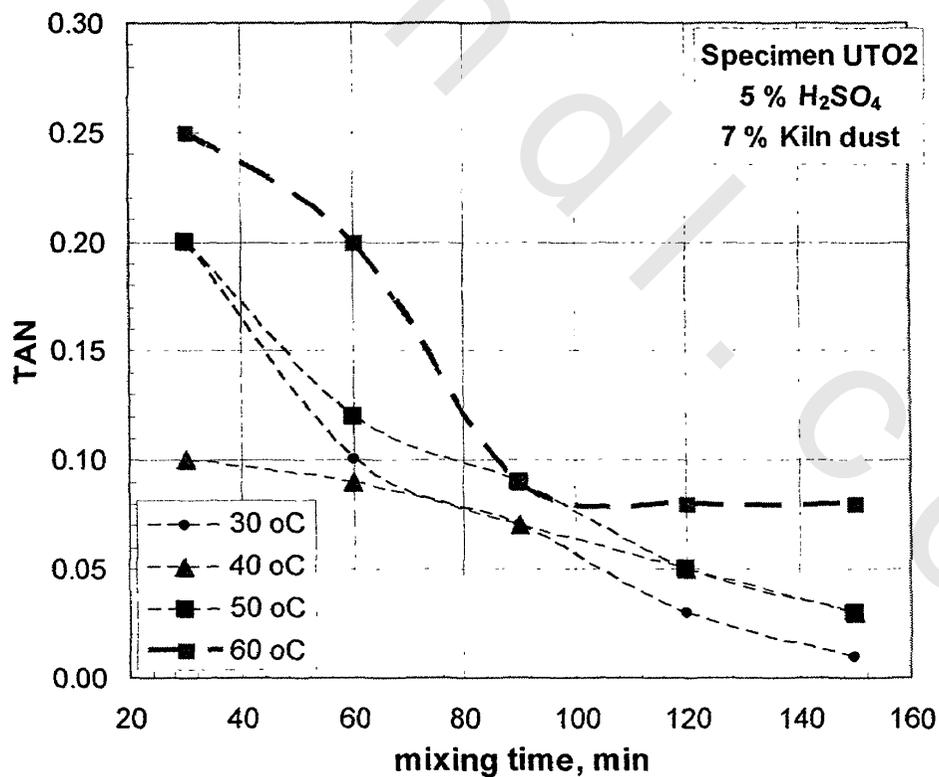


Figure 4.9 Effect of mixing time on the TAN at different oil temperature for RTO2

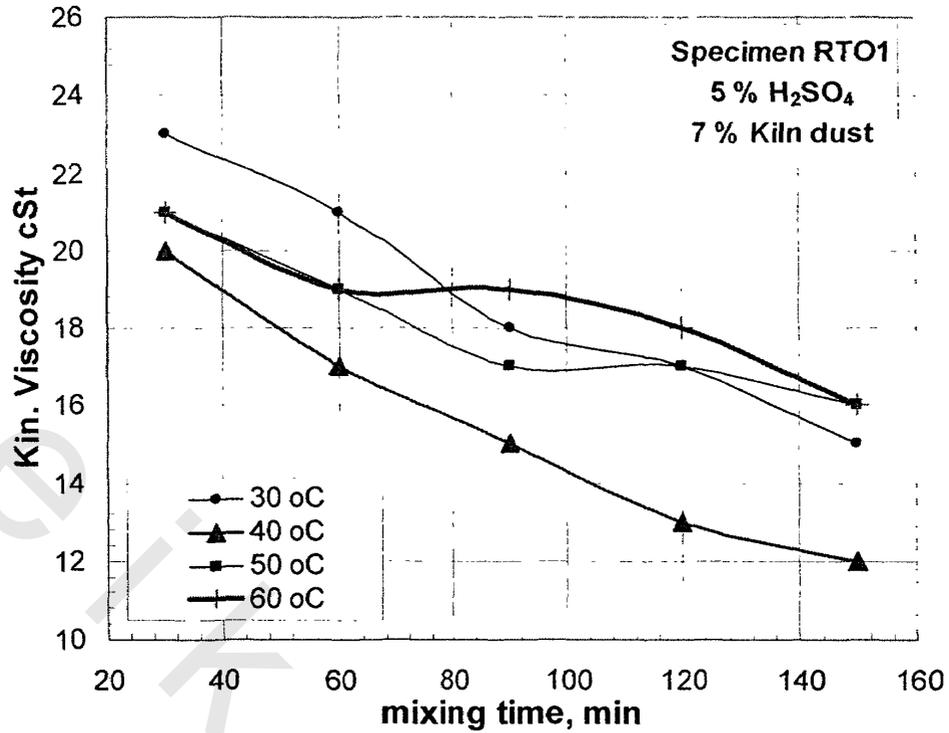


Figure 4.10 Effect of mixing time on the Kin. viscosity at different oil temperature for RTO1

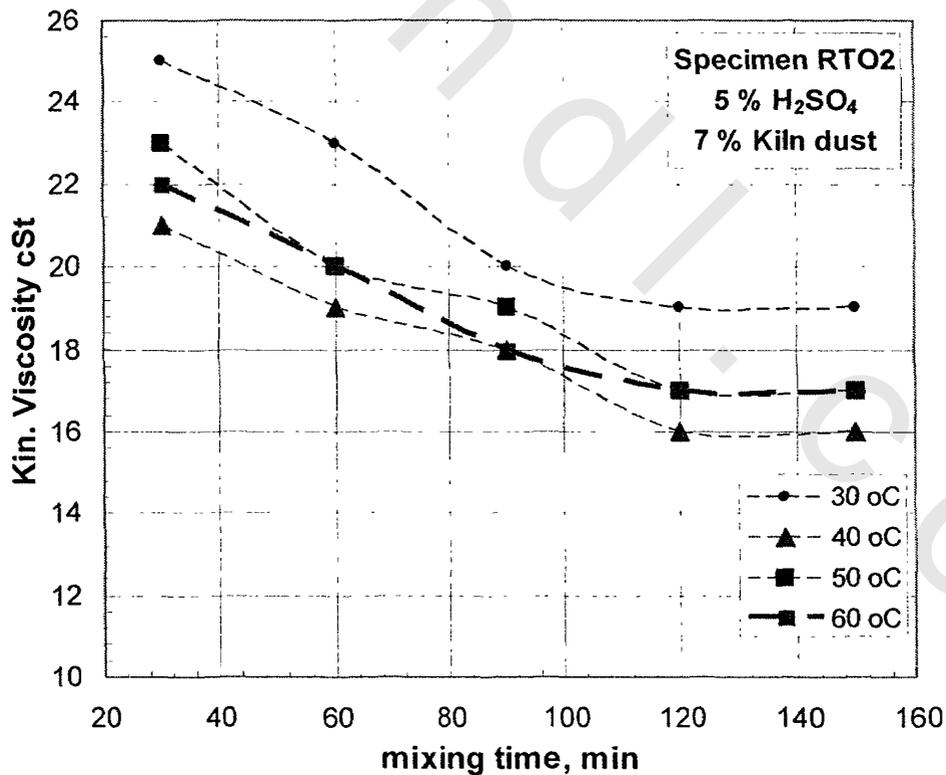


Figure 4.11 Effect of mixing time on the Kin. viscosity at different oil temperature for RTO2

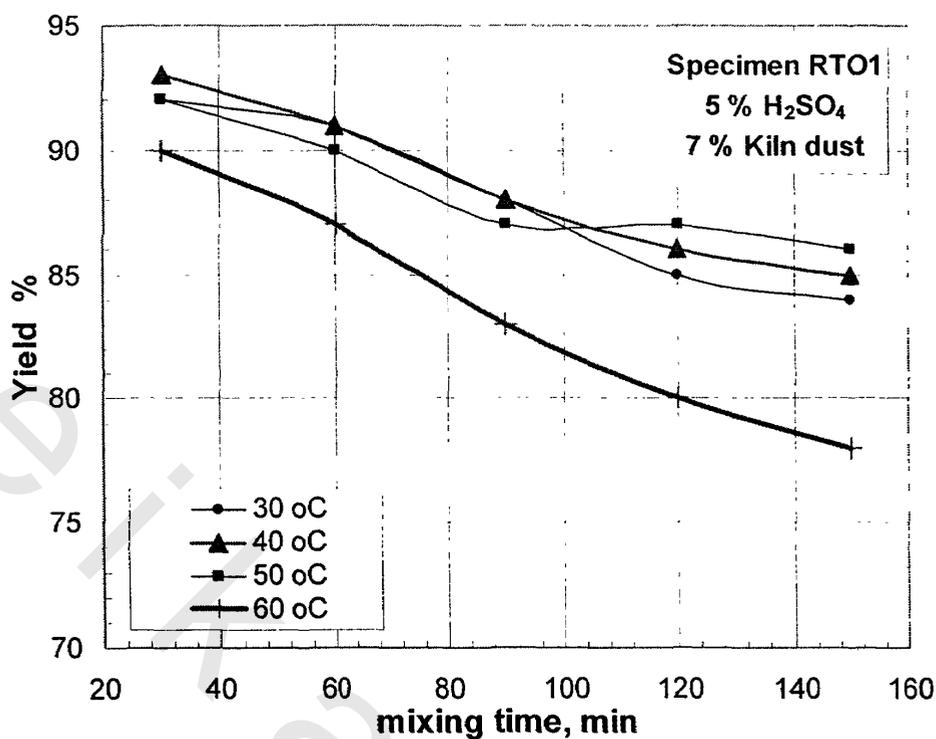


Figure 4.12 Effect of mixing time on the Yield at different oil temperature for RTO1

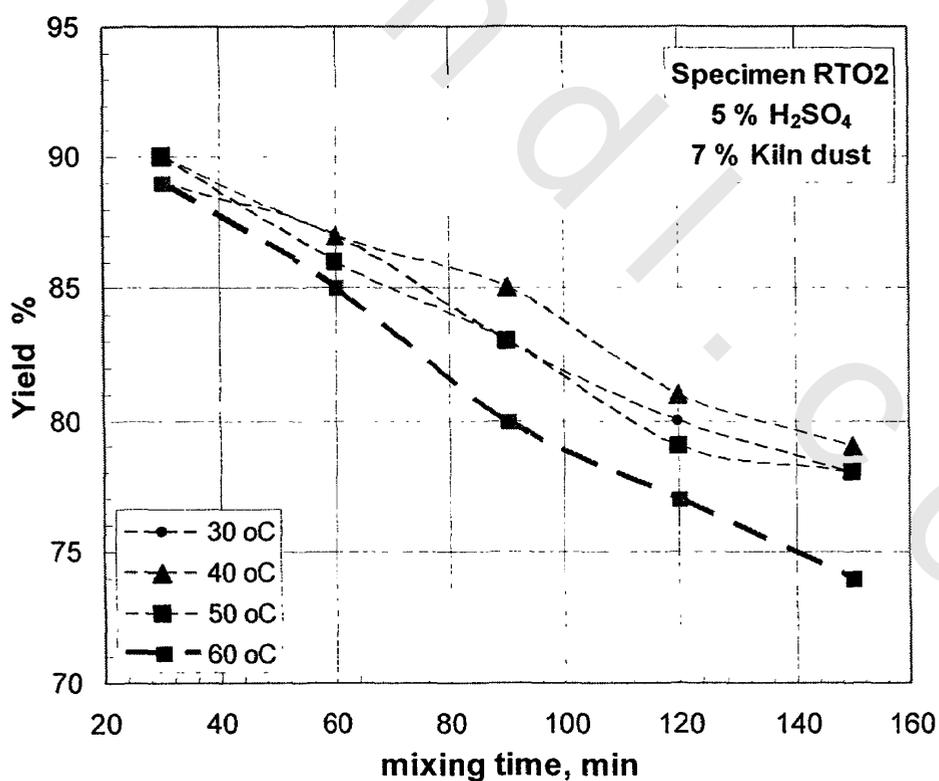


Figure 4.13 Effect of mixing time on the Yield at different oil temperature for RTO2

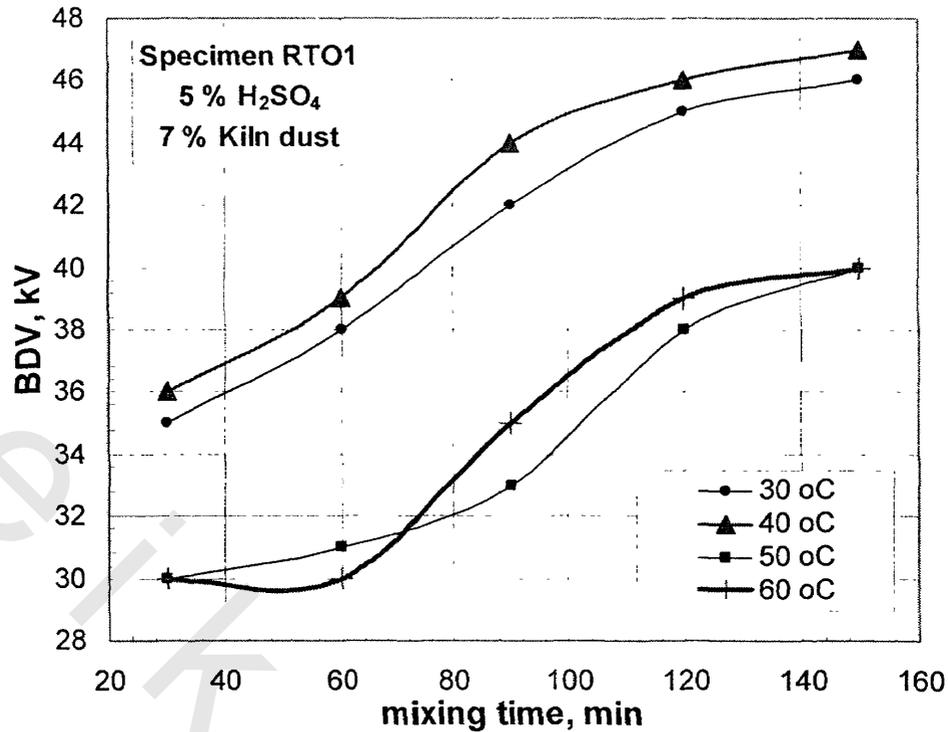


Figure 4.14 Effect of mixing time on the BDV at different oil temperature for RTO1

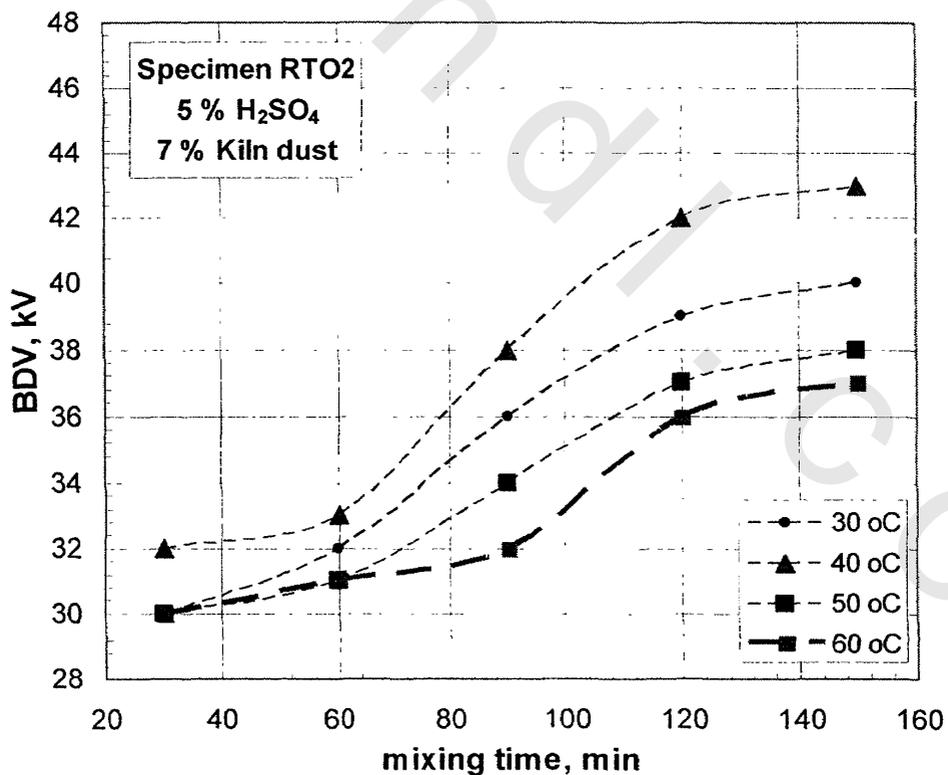


Figure 4.15 Effect of mixing time on the BDV at different oil temperature for RTO2

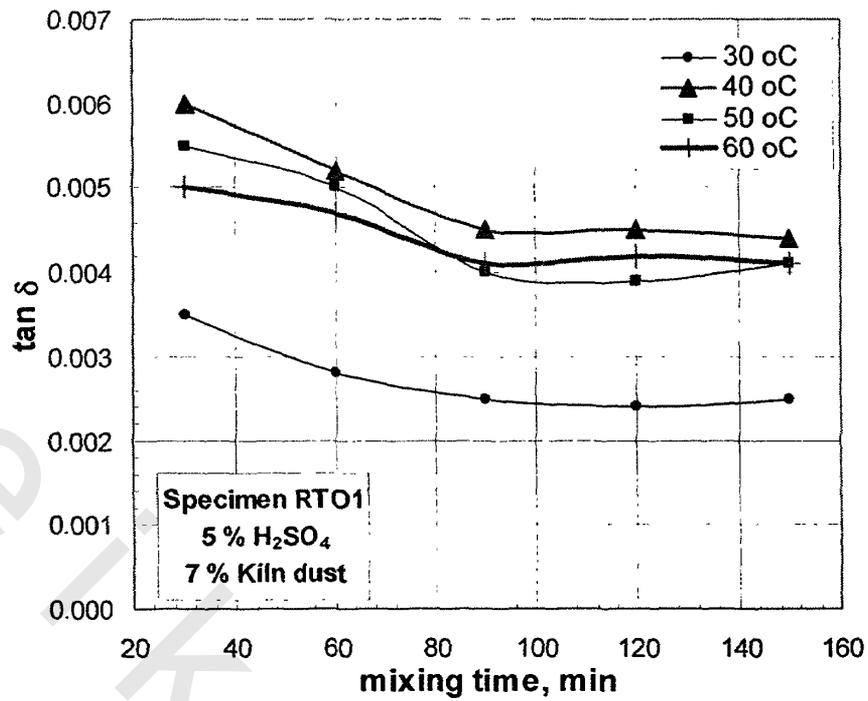


Figure 4.16 Effect of mixing time on $\tan \delta$ at different oil temperature for RTO1

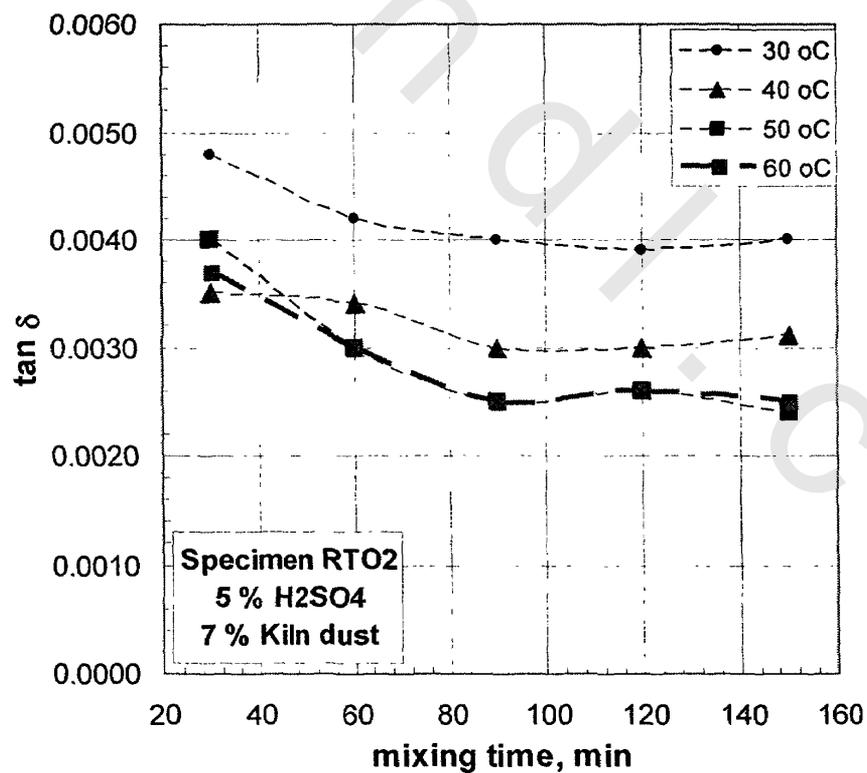


Figure 4.17 Effect of mixing time on $\tan \delta$ at different oil temperature for RTO2

Table 4.11 physico-chemical properties of the recycled transformer oils at optimum conditions

CHARACTERISTICS	Used Transformer Oil		Test method
	Ratio 1	Ratio 2	
Density, g/cm ³ at 20°C	0.8079	0.8100	ASTM.D-282-92
Refractive index at 20°C	1.4700	1.4782	ASTM.D-1218-92
Kinematic viscosity, cSt, at 40°C	10	11	ASTM.D-445-88
Pour point, °C	- 40	- 30	ASTM.D-97-88
Carbon residue, wt%	0.02	0.02	ASTM.D-482-91
Flash point, °C	140	143	ASTM.D-93
Total acidity, mg KOH/gm	0.02	0.02	ASTM.D-972-92
Break down voltage, kV	55	52	IEC-156
Dissipation factor	0.001	0.002	ASTM.D-1169
Colour, ASTM	1	1	ASTM.D-1500
<u>Structural group analysis n.d.M</u>			ASTM D 3238-74
% C _A	9	10	
% C _P	61	62	
% C _N	30	28	

4-16 Acid Sludge Disposal/Pollution Control

Sulfuric acid sludge treatment dissolves metal salts, aromatic and asphaltic compound organic acids, water, and other polar compounds. A phase separation occurs where by acid sludge settles and is removed from the treating vessel leaving relatively pure oil behind.

The acid sludge resulting from above processing is usually dumped in the open pit or into sea or burnt directly thus creating a lot of pollution hazard. Such a disposal system would require prior approval of authorities.

Combustion or incineration, even after neutralization, is undesirable due to the major amounts of sulfur oxides and very fine metal containing particulates which would be emitted

Basically, acid reclamation removes undesirable components from the oil

by using sulfuric acid to cause the impurities to form sludge. This process is costly, and disposal of the sludge has caused environmental concern and criticism.

Therefore, the objective in this section is to treat acid sludge with different inorganic formulations for the purpose of saving environment for hazards and reducing pollution problems.

Table 3.1 show that, the salts incorporated in the formulations S1-S6 stimulate the separation of aqueous phase from hydrocarbon phase. The preliminary tests showed that separation of the aqueous phase depends on the ratio of electrolyte, rate of stirring, temperature, rate of addition of formulation and the pH of the reaction medium.

By controlling the above mentioned parameters, the multi component resin (MCR) could be produced. It can be presumed that the separation of MCR can be achieved as shown in figure 4.18.

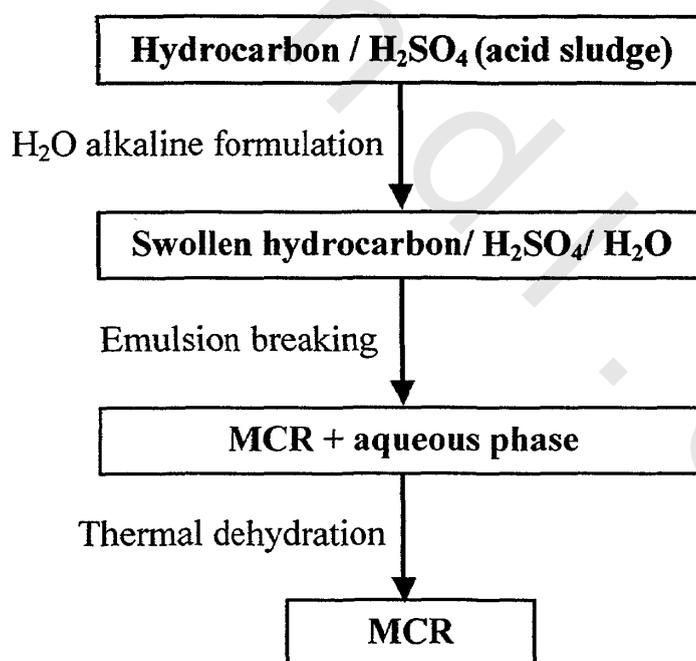


Figure 4.18 A mechanism for treating acid sludge

Sludge, soluble and insoluble in the used transformer oils, saponifiable matter, aldehydic bodies, acidic compounds, carbon, dirt, metallic particles

and moisture. Therefore, all these constituents form swollen with the formulations.

In addition, hydrocarbons and sulphuric acid are physically mixed by compatible force due to the high affinity of H_2SO_4 to the polarity of the unsaturated hydrocarbon and aromatic content. This causes a swelling of the hydrocarbon portion with water.

Hydrocarbon/ H_2SO_4 /acid sludge induces the main problem. The suggested formulations (S1-S6) act as a powerful emulsion breaker. The efficiency of different formulations for discharging the swelling medium and breaking the emulsion is illustrated in figure 4.18. The water content of MCR was determined by thermal treatment as described in the experimental section.

The data obtained Table 4.12 Show that the MCR prepared by utilizing different formulations possess water content varying between 10 and 15 wt%. The MCR obtained by using formulations S2 and S3 possess the lowest emulsified water (10 wt%) and higher yield. In addition to the lowest water content in the products, the quantity used of these formulates is the lowest compared with formulations S1, S4, S5 and S6.

Hence, we arrived at the conclusion that the most effective formulations are S2 and S3. In these formulations the concentration of both NaCl and sodium silicate range between 3 and 7 wt%. These formulations may give the best separation of the aqueous phase because they increase in the hydrophobicity of the MCR. When the concentration of Sodium Chloride increase at the expense of sodium silicate S6, the efficiency decrease and hence the water content of MCR increase to 17 wt%, as demonstrated by the results formulations S5 and S6

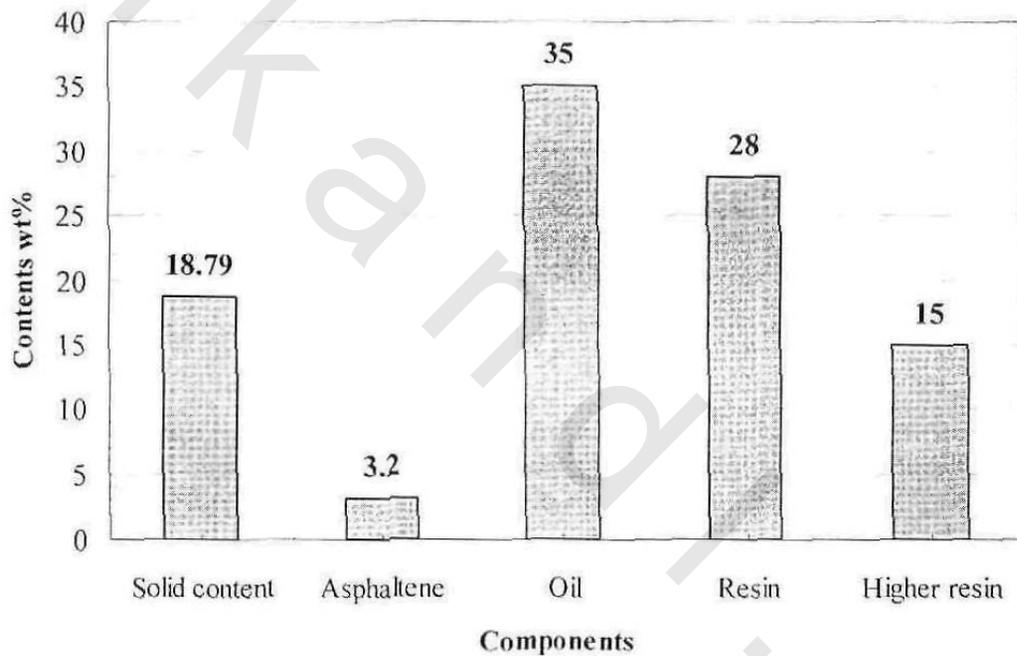
The above discussion leads to speculation that combination of the sodium chloride and sodium silicate within the specified ratios of S2-S3 causes a synergistic effect in the separation of the aqueous phase and produces a higher yield of MCR-1

Figure 4.19, illustrates the results of the hydrocarbon type analysis of the MCR. The presence of a relatively high quantity of resins, higher resins (57 wt%) and asphaltenes (2.37 wt%) this may be an indication of weathering of transformer oils . Also, its possible to propose that the asphaltenes comes as a result of the condensation reactions of aromatic compounds. This product is useful as plasticize for gilsonite varnish, as a water proofing compound and painting or coating material ^[106,107].

Solidification processes, now practiced on acid sludges provides a possible improvement over untreated disposal, but it is expensive. These are believed to be based on exothermic these are believed to be based on exothermic reactions, such as acid neutralization driving off water and forming low solubility salts. Acid sludge 1% is blended with asphalt 99% gave an acceptable industrial asphalt formulation. The criteria properties such as penetration, softening point, and ductility were not adversely affected by acid sludge and the adhesive and water proofing properties were excellent. The asphalt product would also not cause environmental pollution since free H_2SO_4 (<0.5%) were uniformly distributed and inherently absorbed by active ingredients of the asphalt, the sludge obtained by H_2SO_4 treatment of used mineral oil is processed by agitation with water, removal of the aqueous phase, neutralize with diluted NaOH removal of the aqueous phase, water washing, drying at 250°, and stripping at 240° and 40 mm. the product is useful as plasticize for bitumen's and as a water proofing compound and asphalted coating material.

Table 4.12 the efficiency test of formulation

Characteristic \ Sample of formulation	S1	S2	S3	S4	S5	S6
Sufficient amount add vol. %	100	70	80	65	75	80
PH medium	6.5-7.5	6.5-7.5	6.5-7.5	6.5-7.5	6.5-7.5	6.5-7.5
Aqueous phase separation observation	Poor	Good	Good	Poor	Poor	Good
Water content, wt%	80	10	10	15	15	17
MCR – Yield	85	90	90	85	80	80

**Figure 4.19** Component type analyses of MCR and hydrocarbon