

Laboratory Validation of Method of Solvent Extraction for Removal of Sulphur Compounds from Mineral Oil

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ABSTRACT

The presence of corrosive sulphur compounds in mineral oil is a serious problem affecting the life of transformers. There are several techniques available to remove corrosive sulphur and among them the method of solvent extraction is useful for complete removal of sulphur compounds. In this investigation, laboratory experiments were carried out to validate method of solvent extraction for removal of sulphur compounds like Dibenzyl disulphide and Mercaptan sulphur from mineral oil. The optimum oil to solvent ratio, solvent to co-solvent ratio are investigated and discussed. Efficiency of method of solvent extraction for removal of sulphur compounds is demonstrated on a laboratory scale and further improvements to properties of mineral oil is proposed by the use of conventional reclamation techniques.

Index Terms - N-methyl-pyrrolidone, DBDS, Mercaptan sulphur, total sulphur, copper corrosion, paper oil insulation, mineral oil reclamation.

1 INTRODUCTION

THE problems of corrosive and reactive sulphur components in mineral insulating oils are studied worldwide for understanding the basic chemical, physical, thermal and dielectric properties that undergo changes during service life of transformers [1-5]. Efforts are also made to combat the problems of corrosive sulphur by use of metal passivators like Irgamet 39 and benzotriazole (BTA) in oil to prevent sulphur attacks on copper surfaces [6-10]. Though metal passivation has been used by Power utilities, there are apprehensions about their depletion which can go undetected during service life of transformers or it can lead to hydrogen gas liberation in oil [11-12]. Therefore, scientists and engineers have been looking forward to alternatives for prevention or elimination of sulphur compounds in mineral oil.

There is very little published data on rate of depletion of metal passivators during the service life of transformers and it is necessary to closely monitor the concentrations of metal passivators in mineral oil. Further, the effect of sulphur species like mercaptan sulphur and DBDS leading to possible reduction of concentrations of metal passivators has to be well understood for preventing sulphur attack on copper conductors during service life of transformers.

There are some reported studies on the use of solvent extraction for removal of sulphur compounds from mineral oils [13-16]. These methods were suggested for preparation of oil sample for some chemical analytical tests.

Different polar solvents like methanol, acetonitrile, monomethyl formamide, dimethyl formamide, N-methyl-pyrrolidone (NMP), furfural, dimethyl sulfoxide and propylene glycol are used in extraction of sulphur compounds. Extraction with pyrrolidone followed by hydro treatment reduces the sulphur content to 0.01 mass % [15].

NMP is non-toxic in nature and has high solvent power, good selectivity and excellent thermal and chemical stability making it an attractive solvent for extraction [15]. A three stage extraction process is generally suggested for the removal of sulphur compounds using a mixture of NMP and water. Water increases the polarity and selectivity of the solvent and thus increases the solvent power.

In the present study, solvent extraction method is used for removal certain sulphur compounds like 2-mercapto benzothiazole (2MBT) and dibenzyl disulphide (DBDS). The ratio of water to NMP and oil to water in solvent mixture are varied to understand their effect on extraction process. The solvent extraction studies were carried out on mineral oil aged at elevated temperature to optimize the parameters of solvent

extraction. It was also intended to evaluate the efficacy of the extraction process on thermally aged mineral oil and to establish its correlation to concentration of sulphur in oil. The mineral oil recovered by solvent extraction method was assessed on the basis of its physical, chemical and dielectric properties to determine its suitability for reuse in transformers.

2 EXPERIMENTAL METHOD

This part gives the details of parameters of transformer oil which form the basis for sulphur removal. It also considers parameters which need special considerations during the process of solvent extraction. Further, experiments were also carried out on different concentrations of DBDS to understand as to whether the method is specific to DBDS concentration in oil.

DBDS is responsible for copper corrosion and hence different concentrations of DBDS in mineral oil from 30 to 670 ppm were used for understanding the complexities arising due to a wide range of DBDS concentrations. Further, as an extension of this work, efforts were made to (1) reduce moisture in recovered oil, (2) reduce the acidity of oil and (3) improve interfacial tension in order to bench mark the properties of oil for reuse in transformers.

Mineral oil containing DBDS of different concentrations were received from an oil manufacturer. The concentration of DBDS used is much above the normal range of concentration reported in literature. Higher concentrations of DBDS are observed during the service life of transformers and hence concentration of DBDS was deliberately kept high for understanding its impact on different parameters of solvent extraction. In order to understand the effects of other sulphur compounds in mineral transformer oil, in addition to DBDS, mineral oil containing 2MBT was also used as sulphur additive.

2.1 TRANSFORMER WINDING MODEL

For laboratory studies on chemistry of mineral oil, it is very difficult to work on large transformers. Hence only a laboratory model of transformer winding, which is conventionally called pigtail sample [17], was used in this study. The pigtail specimens are aged in oil containing different concentrations of DBDS and 2MBT, at a temperature of 140 °C for specified durations.

2.2 METHOD OF SOLVENT EXTRACTION

The flowchart of the method of solvent extraction is shown in figure 1. N-methyl-2-pyrrolidone (NMP) and deionized water are used as solvent and co-solvent in this study. Three different water concentrations namely 1, 2 and 3 wt. % are used to optimize water concentration over the range of DBDS concentration studied. The solvent to oil ratio was also varied from 0.5:1, 0.4:1, 0.3:1 and 0.2:1 respectively. The temperature of extraction was 40, 50, 60 and 70 °C for first, second, third and fourth extractions. The oil-solvent mixture was subjected to thermal conditioning with intense stirring for a period of 30 minutes at each of these temperatures. Fourth extraction was also carried out in few cases to completely eliminate the presence of sulphur compounds in mineral oil. Transformer oil containing DBDS and 2MBT were then treated with solvent mixture to remove sulphur compounds.

Solvent/co-solvent and oil/solvent ratios were modified for achieving better results.

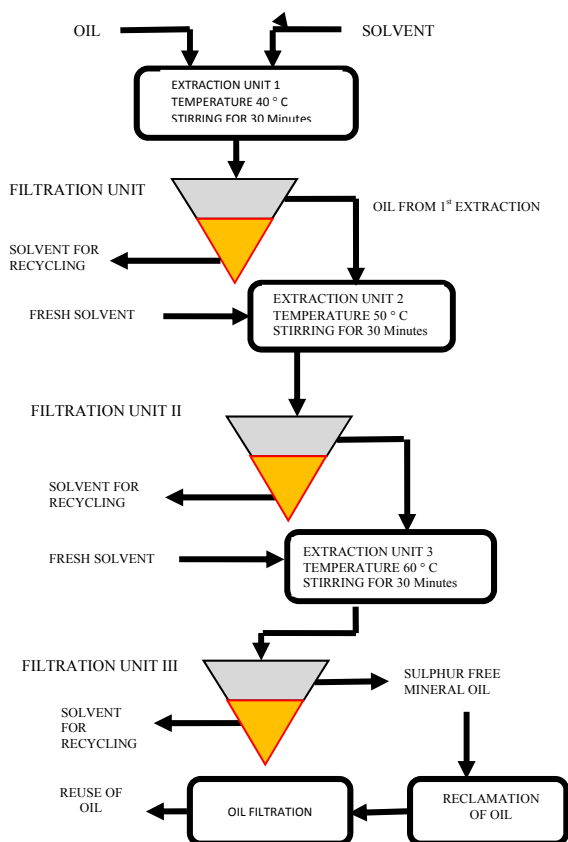


Figure 1. Flow chart of method of solvent extraction.

The efficiency of extraction process depends on complete mixing of oil with the solvent. Hence the mixture was subjected to intense stirring for a period of 30 minutes at 40 °C. After 30 minutes, oil was transferred into a separating funnel. An upper layer of refined oil and a lower layer of solvent containing extracted sulphur compound are formed. The two are separated and individually collected. The recovered oil from the first extraction is again treated with solvent mixture and the process is repeated at higher temperature of 50 °C for 30 to 40 minutes. As in the earlier case, upper layer of oil and a lower layer of solvent and sulphur compounds are formed. The third stage of extraction is similar but the temperature is increased to 60 °C. The extraction was also repeated for the fourth time at 70 °C in few cases. Thus the extraction process was standardized and it was used for removal of sulphur from oil containing different concentrations of DBDS and 2MBT. Table 1 gives the ratio of solvent to oil used for 1st, 2nd, 3rd and 4th stage of extraction. To begin with, the quantity of solvent used was 50% of the volume of oil and this was slowly reduced to 40, 30 and 20 % of volume of oil.

Extraction was also carried out on transformer oil samples containing DBDS which was aged at 140 °C for different durations in nitrogen atmosphere. Since majority of transformers work in sealed conditions, unlike the free breathing transformers, copper corrosion is reported to be more intense in case of sealed transformers [18]. In order to

Table 1. Solvent to oil ratio and temperature from stage 1 to Stage 4 of extraction.

Details of extraction	Stages of extraction			
	1	2	3	4
Solvent : Oil ratio	0.5:1	0.4:1	0.3:1	0.2:1
Temperature (°C)	40	50	60	70

replicate conditions that exist in sealed transformers, nitrogen was bubbled into transformer oil during aging.

In order to understand the effect of higher concentrations of DBDS, oil samples with DBDS concentration of 200 ppm was used. This oil sample was aged at 140 °C in presence of pigtail sample. The pigtail sample was then removed from oil and sulphur content of oil was estimated. The oil was then subjected to extraction again and then analyzed for its physical, chemical and dielectric properties.

The extracted oil was further aged under identical conditions of temperature using a fresh pigtail sample for a further period of 436 hours and properties of the oil were determined and compared with the normal oil aged under identical conditions. The experimental process flow chart of thermal aging and oil extraction are schematically shown in figure 2. In figure “A”, “B”, “C” and “D” refer to different stages of analysis of oil.

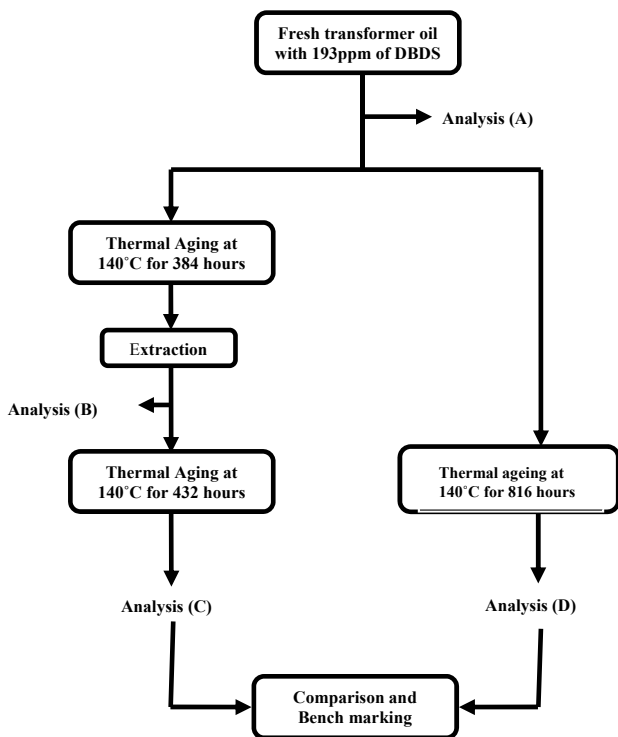


Figure 2. Flow chart of experimental method to study properties of extracted mineral oil

2.3PARAMETERS OF MINERAL OIL

The details of parameters studied, the experimental method used for evaluation and the values of these parameters are shown in Table 2. The base oil used is non-corrosive in nature and DBDS and 2MBT were added to oil to study the effects of different concentration of these sulphur compounds.

Table 2. Details of the parameter studied along with methods used for their estimation and their respective values.

Parameter	Test Method	Values
Appearance	-----	Clear, transparent and devoid of suspended particles
Density at 20° C	ISO 3675	0.8135 g/ml
Kinematic Viscosity at 27° C	ISO 3104	11.62 mm ² /s
Interfacial Tension	ASTM D971	48 mN/m
Flash Point	ISO 2719	156° C
Total Acidity (mg KOH/g)	IEC 62021	Nil
Water content	IEC 60814	11 mg/kg
Corrosive Sulphur	DIN 51353	Non-Corrosive
Mercaptan Sulphur Content	ASTM D3227-04a	Not detected
DBDS	IEC 62697 (Draft) [19]	Not detected
Total Sulphur Content	ISO 14596	9.83 ppm
Break down voltage	IEC 60156	61 kV
Dielectric Dissipation Factor at 90°C	IEC 247	0.00065
Resistivity @27 °C @90 °C	ASTM 1169-11	86 X 10 ¹⁴ ohm-cm 400 X 10 ¹² ohm-cm

3 RESULTS AND DISCUSSIONS

The effects of different parameters of extraction are discussed based on the end results of residual DBDS and mercaptan sulphur (MS) resulting from the addition of 2MBT.

The effect of different percentages of water in the solvent mixture for removal of sulphur by solvent extraction was studied in oil containing nominal DBDS concentrations of 300 and 350 ppm. The water concentration used was 1, 2 and 3 % of oil respectively. The measured values of DBDS concentrations before extraction were 290 and 340 ppm. The results of DBDS concentrations achieved after 1st, 2nd and 3rd extraction are shown in Table 3. The experiments were repeated a minimum of five times and the average concentration of DBDS are considered. The results showed good reproducibility and repeatability. Hence it was possible to carry out experiments with a satisfactory level of consistency.

It is observed from table 3 that with 1% water, 290 and 340 ppm of DBDS in oil are reduced to 63 and 81 ppm respectively after 1st extraction, 10 and 14 ppm after 2nd extraction and to 2 ppm after 3rd extraction. Similarly, with 2 and 3 % of water, DBDS is ultimately reduced to 2 ppm. Thus weight percentage of water does not have any significant influence on the end results. The extraction was repeated a number of times and the results were observed to be reproducible. The results are also applicable to lower concentrations of DBDS and the ultimate concentration of DBDS for such cases was 0.1 ppm which was the detection limit of the method used.

Table 3. Effect of water percentage on solvent extraction in terms of reduction in concentration of DBDS.

Details of oil sample	DBDS concentration in ppm for different weight percentages of water					
	1%		2%		3%	
	290	340	290	340	290	340
Concentration of DBDS (ppm)	290	340	290	340	290	340
After 1 st Extraction	63	81	61	80	64	79
After 2 nd Extraction	10	14	9	14	9	13
After 3 rd Extraction	2	2	2	2	2	2

3.1 EFFECT OF OIL TO SOLVENT RATIO

It is very essential to determine the optimum oil to solvent ratio in any industrial applications. In the first set of experiments, the ratio of oil to solvent was of 1:0.2. The extraction was carried out on oil containing 270 and 340 ppm of DBDS. The ratio was then changed to 1:1, 1:0.5, 1:0.4 and 1:0.3 and 1:2, 1:1, 1:0.5 to 1:0.4 respectively in second and third trials of solvent extractions.

It is observed that there is no significant effect on end result of extraction upon changing the solvent ratios. From the three cases, it is observed that after 4th extraction, residual DBDS in oil was 0.1 ppm which is the lowest detectable limit. Higher ratios of oil to solvent is observed to rapidly reduce the concentration of DBDS and second and third extractions adequately help in further reduction of DBDS levels to less than 0.1 ppm. Hence it is observed that 1:0.5, 1:0.4, 1:0.3 and 1:0.2 ratios for 1st, 2nd, 3rd and 4th extraction is the optimum ratio of oil to solvent for effective removal of sulphur compounds from oil. If the time at the disposal of Power utility to put the transformer back into service is a constraint, in such cases, higher oil to solvent ratio can be used. This is not a preferred method since long term performance of transformers would require total removal or reduction of DBDS to levels much below 1 ppm. Further, in such cases, more effort would be required to keep the level of moisture content to within acceptable limits. Their impact on acidity and interfacial tension would require more care and role of conventional reclamation methods would be crucial.

3.2 CORRELATION BETWEEN INITIAL AND RESIDUAL CONCENTRATION OF DBDS

It is observed from the study that the extraction is much easier when the oil contains lower concentration of DBDS. Hence the focus of this study was to assess the efficacy of the extraction method for higher concentrations of DBDS. Three cases of nominal DBDS concentrations of 175, 350 and 700 ppm were considered. The measured starting concentrations of DBDS were 175, 332 and 671 ppm respectively. The water concentration was 1 % and the oil to solvent ratio was 1:0.5, 1:0.4, 1:0.3 and 1:0.2 for 1st, 2nd, 3rd and 4th extractions respectively. The concentrations of DBDS after solvent extraction for this condition are shown in Table 4. The results clearly indicate that after four stages of extraction, irrespective of the initial concentration, DBDS is reduced to less than 0.1 ppm.

Table 4. Effect of variation of initial and residual concentration of DBDS after extraction (BDL: Below detection limit).

Stage of extraction	Initial concentration of DBDS (ppm)		
	175	332	671
1 st	65	35	81
2 nd	8	27	11
3 rd	2	3	2
4 th	BDL	BDL	BDL

3.3 CORRELATION BETWEEN INITIAL AND RESIDUAL CONCENTRATION OF MS

The permissible and acceptable level of mercaptan sulphur in mineral oil is less than 1 ppm. Hence the starting nominal concentrations of 2MBT considered for extraction were 5, 20 and 50 ppm respectively. With these concentrations, the oil was subjected to solvent extraction and the residual mercaptan sulphur after 4 stages of extraction are shown in Table 5. The actual concentration of MS before the commencement of extraction was measured to be 4.8, 18.3 and 44.5 ppm respectively.

Table 5. Effect of concentration of MBT on extraction.

Stages of extraction	Concentration of mercaptan sulphur (ppm)		
Before Extraction	4.8	18.3	44.5
1 st	0.5	0.1	0.6
2 nd	0.3	0.1	0.1
3 rd	0.2	0.07	0.1
4 th	0.06	0.07	0.1

Unlike DBDS, in case of 2MBT, after 1st extraction, the level of mercaptan sulphur goes down below 1 ppm. It reduces further, after 2nd, 3rd and 4th extraction. The final concentration of mercaptan sulphur for starting concentration of 4.8 ppm is 0.06 ppm and in case of 18.3 and for 44.5 ppm it is 0.07 and 0.1 ppm, respectively. Thus solvent extraction is observed to be equally effective in removing mercaptan sulphur when present in the form of 2MBT.

3.4 THERMAL STABILITY OF EXTRACTED MINERAL OIL

It is well known fact that DBDS undergoes cleavage [18] and has a tendency to reform during thermal ageing and during random temperature variations in a transformer. Hence it is very essential to understand the behavior of DBDS after thermal ageing as well as the implications of parameters of solvent extraction on thermal aging of oil. Ageing was carried out at 140°C for 708 hours on transformer oil with 600 ppm of DBDS. This study was carried out at 140°C since there is considerable information available at this temperature of ageing of oil containing DBDS in literature [16]. The DBDS and mercaptan sulphur concentration in oil just before aging were observed to be 565 and 0.06 ppm respectively. DBDS concentration and corresponding mercaptan sulphur concentrations at different durations of aging are shown in Table 6.

Table 6. Effect of aging on efficiency of extraction at ageing temperature of 140 °C (BDL: Below Detection Limit).

Aging duration (hours)	DBDS (ppm) Initial concentration : 565 ppm		MS (ppm) Initial concentration : 0.06 ppm	
	Before Extraction	3 rd Extraction	Before Extraction	3 rd Extraction
24	557	4	0.06	0.06
228	127	3	0.12	0.09
708	31	BDL	0.18	0.13

From the results of Table 6 it is observed that in case of mineral oil with initial DBDS concentration of 565 ppm, after 24 hours of thermal ageing, solvent extraction reduces the concentration of sulphur compounds from 557 ppm to 4 ppm. In case of 228 hours of aging, DBDS concentration is reduced from 127 ppm to 3 ppm. Further, in case of 708 hours of thermal ageing, DBDS reduces from 31 ppm to 0.1 ppm. The 4th stage of extraction was carried out in these cases to see if this residual DBDS will have an effect on thermal aging characteristics of mineral oil, since DBDS undergoes cleavage and has also a tendency to reform during thermal aging [18]. The DBDS concentrations were below the detection limit of 0.1 ppm. Thus solvent extraction is observed to be very effective in reducing the DBDS concentration, independent of effects of thermal ageing.

However, caution should be exercised in interpretation of this result, since in a transformer, thermal effects are random and temperature of oil would depend on transformer winding temperature which in turn is determined by other factors in-addition to the presence of Cu₂S in the paper layers and across the windings.

Further, in case of 2MBT, the concentration of mercaptan sulphur did not increase after 24 hours of thermal aging. After 228 hours of thermal aging, the MS concentration increased to 0.12 ppm which reduced to 0.09 ppm after 3rd extraction. Similarly, when mineral oil is aged for 708 hours at 140° C, MS increases to 0.18 ppm and after 3rd extraction it is reduced to 0.13 ppm. The 4th round of extraction was carried out and this resulted in further reduction in MS to 0.06 ppm. The results indicate that solvent extraction may not be necessary when MBT alone is present and its concentration is less than 1ppm.

Generally, both DBDS and mercaptan sulphur are present together in mineral oil [18]. In such cases, it is obvious that solvent extraction method is effective in reducing the levels of both DBDS and MS in mineral oil. It is further observed that the byproducts of thermal ageing do not affect the efficiency of extraction in terms of reduction in concentration of sulphur compound using solvent extraction. Hence it is possible to effectively use solvent extraction for removal of sulphur in mineral oil at any stage during service life of transformers. Since the health of paper insulation would depend on the extent of copper sulphide formation and its migration, this will

be the determining factor. If copper sulphide migration does not penetrate the deeper layers of paper insulation, in such cases it will be very effective in recovering the oil from sulphur compounds and this can contribute to the life extension of transformers.

The most important property of transformer oil is its ability to cool the transformer. The temperature of the transformer is dependent on the viscosity of oil. Since oil extracted by this method does affect the viscosity of oil, it is expected to perform satisfactorily as a coolant as well [20]. However, field studies on in-service transformer would be of vital importance for further confirmation of the efficiency of solvent extraction for removal of sulphur compounds.

3.5 EFFECT OF SOLVENT EXTRACTION ON PROPERTIES OF AGED MINERAL OIL

Transformer oil containing 200 ppm of DBDS was aged for 384 hours at 140 °C. The oil was extracted and its DBDS concentration was reduced to below detectable limit of 0.1 ppm and it was again aged for 432 hours. Total aging duration of the oil was thus 816 hours, considering the initial and subsequent aging periods of 384 and 432 hours. Properties of oil were compared with the oil aged for same duration without extraction and the results are discussed in the next section. The photographs of figure 3 depict the colors of oil after different stages of aging.



Figure 3. Photograph showing color of oils: (i) before aging (ii) after aging for 384 hours with 193 ppm of DBDS, (iii) aged for 384 hours and extracted, (iv) extracted oil aged for 432 hours and (v) oil aged for 816 hours without extraction (in order from left to right).

3.5.1 PHYSICAL, CHEMICAL AND DIELECTRIC PROPERTIES OF EXTRACTED OIL

Oil after different durations of thermal aging was analyzed for its appearance, physical, chemical and dielectric properties and the observed properties are discussed in this section.

3.5.1.1 PHYSICAL PROPERTIES

Thermal aging of oil at 140° C for 384 hours results in amber color with black precipitate at the bottom whereas it becomes colorless and clear after extraction. Aging of this extracted oil further, for a period of 432 hours changes the color to brown with suspended particles. Appearance of oil samples under thermal ageing for different duration at 140 °C is shown in Table 7.

Table 7. Appearance of oil under ageing for different durations at 140° C

Property	Oil before thermal aging (A)	Oil aged for 384 hours and extracted (B)	Extracted oil aged again for 432 hours (C)	Oil aged for 816 hours (D)
Appearance	Clear, transparent and free from suspended particles	Clear, lightly turbid and free from suspended particles	Dark yellow with small amount of black colored suspended particles	Amber colored with no suspended particles. Sludge formation at the bottom of the bottle

The results of density, viscosity and moisture are shown in Table 8. Oil density and viscosity exhibited only minor changes at different stages of thermal aging and after complete extraction. Hence, extraction does not affect density and viscosity of mineral oil.

Table 8. Density, Viscosity and Moisture of oil aged at 140° C

Property	Oil before thermal aging (A)	Oil aged for 384 hours and extracted (B)	Extracted oil aged for 432 hours (C)	Oil aged for 816 hours (D)
Density at 29.5°C (g/ml)	0.79	0.8	0.82	0.8
Viscosity at 40°C (cSt)	7.8	7.0	7.7	8.5
Moisture (ppm)	8.5	27.1	82.2	14.7

The moisture content of oil increases from 8.5 to 27.1 ppm after thermal aging and after extraction and it remains well below the permissible limits. But the extracted oil after thermal aging of 432 hours shows moisture content of 82.2 ppm which is much higher than the allowable limit of 50 ppm. Further, mineral oil aged for same duration has much lower moisture content. In order to reduce the moisture content, oil was subjected to filtration under vacuum at 90 °C. This reduced the moisture to a value much below the limit of 50 ppm.

3.5.1.2 CHEMICAL PROPERTIES

Results of some additional physical and chemical properties are shown in Table 9. Interfacial tension (IFT) reduces to 32 mN/m after 384 hours of thermal aging followed by extraction and then to 5.232 mN/m, after 432 hours of aging. Further, interfacial tension decreases to 10.132 mN/m in case of continuous thermal aging of 816 hours without extraction.

Hence decrease in IFT is more due to aging than the extraction process. However, it was possible to improve IFT by filtration using fuller's earth. Considering flash point of oil at different stages, there was not much of a deviation from the initial value. Hence the extraction process does not affect flash point of the oil.

Acidity of the oil increases from 0.0282 to 0.0412 mg of KOH/g on extraction after aging of 384 hours. It has a value of 0.400 mg of KOH/gram after aging of 432 hours. When mineral oil is aged continuously for 816 hours at 140° C, acidity was

observed to be 0.155 mg of KOH/g, which was much lower than that of the extracted oil. However, value of acidity exceeded its permissible limit in both the cases. Hence, conventional oil treatments were carried out to remove acidic components present in oil [1].

Mercaptan sulphur content in oil was well within the limits even after aging for 816 hours. However, MS value decreases from 0.18 ppm after 384 hours of ageing to 0.1 ppm after extraction. It remains around 0.16 ppm when oil is aged continuously for 816 hours.

DBDS content of the oil reduces to below detectable limit after extraction and it remains at this level even after thermal aging of 432 hours at 140°C whereas 72 ppm of DBDS is observed in case of oil which was subjected to uninterrupted thermal aging of 816 hours. Further, total sulphur content reduces from 62.237 ppm to 3.499 ppm after extraction. It increases to 58.163 ppm after its aging for 432 hours. Thus extraction is very useful in controlling the increase in concentration of DBDS due to thermal ageing.

3.5.1.3 DIELECTRIC PROPERTIES

The results of dielectric measurements are shown in table 10. Break down voltage in all the cases is above the minimum expected level of 50 kV for reclaimed oil. Dielectric dissipation factor and resistivity are also within the limits. Hence, extraction does not cause any adverse effect on dielectric properties of the oil. The dielectric parameters were evaluated using ten oil samples for each case of extraction and the values were observed to be highly consistent.

Hence, process of solvent extraction is observed to be efficient in removing sulphur compounds and in retaining the characteristics of mineral oil. Though the properties like moisture and acidity are above the prescribed limits and IFT is below expected levels, these properties can be improved by suitable conventional techniques.

Hence, process of solvent extraction is observed to be efficient in removing sulphur compounds and in retaining characteristics of mineral oil.

In addition to the general dielectric properties, evaluations were carried out using Frequency domain spectroscopy (FDS). Though the concentration of DBDS and MBT are reduced to below 0.1 ppm, the moisture content measured using FDS showed higher values.

Table 9. Physical and chemical properties of oil after thermal ageing and extraction.

Property	Oil before thermal aging (A)	Oil aged for 384 hours and extracted (B)	Extracted oil aged for 432 hours (C)	Oil aged for 816 hours (D)
Interfacial Tension at 27 °C(mN/M)	39	32	5.2	10.1
Flash Point °C	142	146	132	138
Total Acidity (No. of mg of KOH consumed per gram of Sample)	0.0282	0.0412	0.4	0.1550
Mercaptan Sulphur Content (ppm)	0.06	0.18	0.1	0.16
DBDS (ppm)	193	BDL	BDL	72
Total sulphur	62.237	3.499	58.16	87

Table 10. Dielectric properties of oil aged at 140° C.

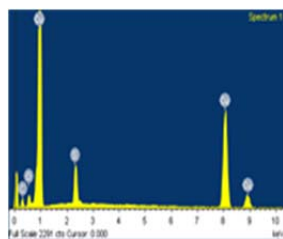
Property	Oil before thermal aging (A)	Oil aged for 384 hours and extracted (B)	Extracted oil aged again for 432 hours (C)	Oil aged for 816 hours (D)
Electric Strength – Break down Voltage (kV)	86.8	52.4	68.2	60.8
Dielectric Dissipation Factor at 90°C	14 X 10 ⁻⁵	9.35 X10 ⁻⁵	126 X10 ⁻³	0.14 X10 ⁻³
Resistivity (X 10 ¹² ohm-cm) @27 °C	724.00	13.50	0.15	16.80
@90 °C	49.00	1.40	0.92	1.75

Hence conventional methods of oil reclamation were used to improve the moisture content. Further, FDS measurements also showed that the oil conductivity was also observed to be within the safe limits. Hence integration of method of solvent extraction with conventional mineral oil reclamation methods is very essential for achieving optimum results.

3.6 EVALUATION BY ANALYTICAL METHODS

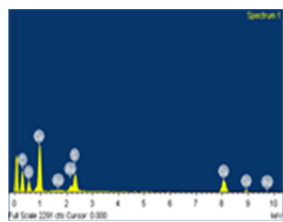
EDAX analysis of copper and paper aged in oil with 193 ppm of DBDS for 384 hours at 140°C before extraction is shown in Figure 4. Sulphur of 7.2 % is observed on copper conductor and 31.5% of copper as well as 8.23 % of sulphur are observed on paper.

This indicates dissolution of copper from conductor which is further established by oil analysis using atomic absorption spectroscopy. The copper ion concentration in oil is observed to vary from 2 to 20 ppm using Atomic absorption spectroscopy. Hence the result indicates that copper ions are released into oil and Cu₂S has diffused into paper.



Element	Weight %
C	3.00
O	5.10
S	7.20
Cu	84.70

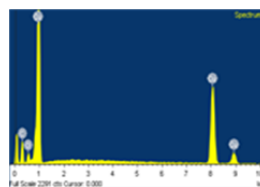
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Element	Weight %
C	29.74
O	30.54
S	8.23
Cu	31.50

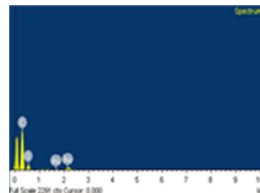
B

Figure 4. EDAX of (A) Copper and (B) paper aged in oil with 193 ppm of DBDS for 384 hours at 140 °C (before extraction).



Element	Weight %
C	7.85
O	4.99
Cu	87.16

A



Element	Weight %
C	48.77
O	51.23

B

Figure 5. EDAX of (A) Copper and (B) paper aged in extracted oil with no DBDS for 432 hours at 140 °C.

In Figure 5, the results of EDAX of copper conductor of pigtail sample and paper aged in extracted oil with traces of DBDS for a duration of 432 hours at 140 °C are shown. No sulphur is observed either on copper or on paper after extraction.

EDAX of copper and paper aged in oil with 193 ppm of DBDS for 816 hours at 140 °C without extraction is shown in Figure 6. The results indicate the presence of sulphur both on copper and paper insulation. It is interesting to observe 5.7 % of copper on paper layer, which is due to copper sulphide formation. EDAX study has clearly established that DBDS in oil leads to formation of Cu₂S and hence by using solvent extraction, DBDS can be removed and formation of Cu₂S can be successfully prevented

3.7 GENERAL REMARKS

The laboratory results of solvent extraction of mineral oil with DBDS and 2MBT have shown that these sulphur compounds can be effectively reduced to levels of 0.1 ppm and this method can be used any time during the service life of transformers. However, these experiments were carried out on laboratory scale, using 1000 ml of oil.

The results of mineral oil extracted are acceptable in terms of physical, chemical and dielectric properties and their thermal properties are also satisfactory. Since laboratory evaluations used very expensive chemicals, the process cost on laboratory scale is prohibitively higher. Hence pilot plant scale demonstration of the process and use of extracted oil on transformers would be absolutely necessary for further validation of the processes involved before it can be recommended for use by power utilities. It is clearly established that mere solvent extraction would be grossly insufficient and use of conventional reclamation methods are necessary for overall improvements with specific reference to moisture content, acidity and interfacial tension.

Loss of oil after three stages of solvent extraction was negligible. A maximum of 5 % loss may occur during the reclamation processes. In the present case, the yield of recovered oil was around 95 % or better in the laboratory scale experiments. However, the yield may decrease during reclamation process when large quantity of mineral oil is used.

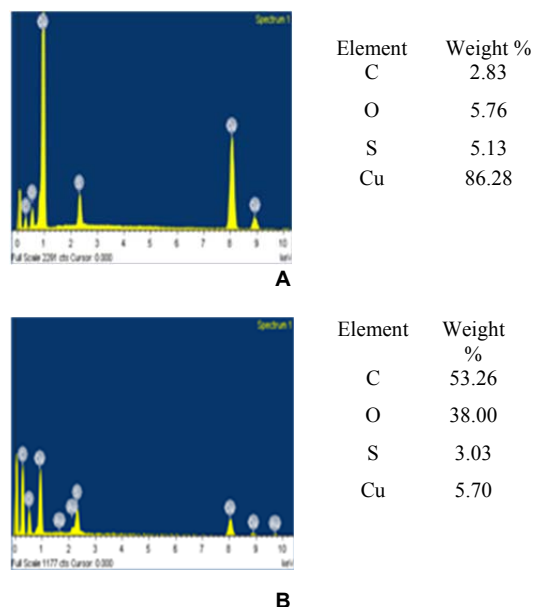


Figure 6. EDAX of Copper (A) and paper (B) aged in oil with 193 ppm of DBDS and aged for 816 hours at 140 °C (without extraction)

However, the yield would essentially depend on methods used for reclamation of extracted oil.

4 CONCLUSION

1. Recovery of mineral oil from sulphur compounds by solvent extraction method is efficient both at lower and higher concentrations of DBDS. Irrespective of DBDS concentration, three stage extractions would be sufficient for elimination of sulphur compounds.
2. Solvent extraction method of sulphur removal is also useful in removal of mercaptan sulphur from mineral oil.
3. The process of solvent extraction is effective in removal of both MBT and DBDS, when present individually or in combination.
4. The efficiency of extraction process does not improve significantly by increasing water percentage in the solvent mixture. Increasing water percentage only results in increase of moisture content of extracted oil. In such case moisture concentration should be reduced by conventional vacuum filtration.
5. Higher oil to solvent ratio is observed to reduce the concentration of DBDS much faster initially. However, third and fourth extractions help in reducing DBDS levels effectively to 0.1 ppm.
6. Solvent extraction process does not affect the physical, chemical and dielectric properties of the oil.
7. Mineral oil parameters after solvent extraction are comparable and even better than parameters of reclaimed oil without sulphur and the mineral oil parameters are within the range recommended values for new oil.
8. It is observed that flash point is not affected by oil extraction and this is a significant characteristic which permits reuse of mineral oil.
9. EDAX spectra clearly show the absence of copper sulphide formation on paper which was aged in extracted oil and this gives sufficient evidence of absence of sulphur compounds in oil after extraction.
10. Solvent extraction, as a process can be used any time during service life of transformer since it is effective in removal of sulphur compounds.
11. Total sulphur values show considerable increase in presence of DBDS and solvent extraction reduces the total sulphur values significantly. Thus additional evidence of removal of sulphur compounds is seen through reduction in total sulphur.
12. Extracted oil is thermally very stable and its performance in the laboratory is comparable to that of the virgin oil.
13. Extracted oil has very good dielectric properties and hence can be safely reused in transformers.
14. With the exception of the cost of chemicals, solvent extraction is observed to be a good and effective method for removal of sulphur compounds from mineral transformer oil.

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