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Decontamination of oils contaminated with polychlorinated biphenyls and dibenzyl disulfide using polar aprotic solvents

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Abstract – Extractions of PCB and dibenzyl disulfide (DBDS) from mineral and/or transformer oils into polar aprotic solvents acrylonitrile AC, dimethyl sulfoxide DMSO, dimethyl formamide DMF, N-methyl pyrrolidone NMP and propylene carbonate PC were performed in order to compare the extraction efficiencies. In a single-stage extraction performed at the room temperature, the efficiencies ranged from the highest to lowest as follows: NMP → DMF → DMSO → PC → AC. The highest efficiency, around 70 % in single-step extraction exhibited NMP. NMP was evaluated as having the best chance to be used in industry. It was shown that for some transformer oils the separation of corrosive sulfur with the common technique of filtration through a layer of commercially available sorbent (for example Fuller's earth) is totally inadequate. However, extraction efficiency of DBDS from contaminated transformer oil with the help of NMP is sufficiently high over 99 % and feasible in a fair time of about 20 minutes. The remaining concentration of DBDS after single-step extraction from transformer oil containing up to 100 ppm DBDS was low enough (approx. 0.1 ppm or non-detectable). Detection of corrosive sulfur in transformer oil after extraction with NMP has been also performed by Siemens test method (IEC 62535) and by updated ASTM 1275B proposed by CIGRE Covered Conductor Deposition test method and was negative. It is possible to consider the transformer oil after the extraction procedure as corrosive sulfur free. Traces of solvent in the oil after extraction were quantitatively separated from treated oil by purification via simple liquid-solid extraction with commercial Si-Al-Mg based inorganic sorbent containing attapulgite.

Index terms – corrosive sulfur, dibenzyl disulfide, polar aprotic solvents, transformer oils

I. INTRODUCTION

In the near past, transformer dielectric fluids were largely based on polychlorinated biphenyls (PCBs). After the production of PCBs was banned due to the concerns about their harmful effects on environment, many transformer dielectric fluids were fully or partially replaced by mineral oils. Since PCBs and mineral oils are highly miscible, contamination of oil-filled transformers and cleaning oils used to wash auxiliary equipment is a problem. Even now, there is a need to find an effective way to decontaminate such oils.

In recent years a significant volume of research has been undertaken in order to understand the recent failures in oil insulated power apparatus due to deposition of copper sulfide on the conductors and in the insulation paper. The sulfur compounds tend to react with the copper windings, forming harmful by-products such as Cu₂S. Dibenzyl disulfide (DBDS) has been found to be the leading corrosive sulfur compound in the insulation oil [1, 2].

A review of the literature indicates that DBDS is usually found in concentrations ranging from 10 to 100 mg/kg (ppm) in certain oils. Remedial processes such as adsorbents, absorbents, and oil change-out have been known to reduce the concentration of DBDS in the oil. Although several methods are provided in the published patents to produce reagents for PCB dechlorination, one seemed best suited for both PCBs and DBDS destruction [3, 4]. Particularly, the well-known reaction mixture of solid sodium hydroxide pellets and of 400 molecular weight polyethylene glycol has been effective to break down DBDS [5]. However, this reaction is very exothermic and it is difficult to control it in bigger volumes. Above all, the insulation properties of transformer oils have been partially changed. If not destroyed or removed DBDS below several mg/kg, breakdown of the DBDS to benzyl mercaptan or a DBDS-copper complex can still cause corrosion of copper and the formation of copper sulfide. The utilization of liquid-liquid extractions with organic solvents in the decontamination of oils polluted by PCBs (and lately DBDS) still represents a major challenge. This method has been known for decades [6, 7], but in practice was applied mainly as an auxiliary initial step in the analysis of PCBs in transformer oils [8 - 10]. A



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Volume 4, Issue 2, March 2015

way of removal of sulfur compounds from mineral insulating oil by extractive refining with n-methyl-2-pyrrolidone has been recently published [11, 12].

The utilization of liquid-liquid extractions with organic solvents in the decontamination of oils polluted by PCBs and DBDS still represents a major challenge.

Generally, extractive solvents such as methanol, acetonitrile, monomethylformamide, furfural, dimethyl sulfoxide and polyethylene glycols are often recommended [13]. If we exclude methanol due to its toxicity and polyethylene glycols [14] due to their low efficiency and poor quality of recycled oils, the suitable solvents that remain are most likely N- methyl pyrrolidone, dimethyldisulfide, dimethylformamide and acrylonitrile. All of these solvents can be classified as polar aprotic solvents.

The aim of this paper is to show examples of decontamination of mineral oils containing PCBs (mainly congeners with 3- and 4- Cl atoms) and dibenzyl disulfide (DBDS) using an effective and inexpensive method of their extraction of PCBs into selected polar aprotic solvents. Adsorption efficiency of a simple inorganic Si-A-Mg based sorbent (commercial Fuller's earth) in capturing the traces of polar aprotic solvents from transformer oils after their liquid-liquid operation treatment is illustrated. In addition results of experiments aimed at the separation of PCBs from the extracts are presented.

II. EXPERIMENTAL STUDIES

A. Analytical methods

PCB: Liquid samples of oils resp. solvents were extracted with hexane in a ratio of 1:100 (extractant to the liquid sample) in a linear shaker for two hours. Hexane layer was then separated, diluted 20 times, and chemically analyzed samples were analyzed on a Hewlett Packard gas chromatograph. The chromatograph was equipped with quartz capillary column HP-5MS of 60 m long with bonded phase 5% diphenyl and 95% dimethylsiloxan. Calculation of PCB content was performed for each indicator congener. The PCB contents of other congeners were assessed only in terms of relative changes of their normalized peak areas of the chromatograms.

DBDS: Analytical determination of DBDS was carried out in a similar procedure: Liquid samples of the transformer oil were extracted with iso-octane and the concentration of DBDS was analyzed on a Hewlett Packard gas chromatograph equipped with ECD detector. Preliminary detection of corrosive sulfur in the transformer oil has been performed by the Siemens test method (IEC 62535) and by updated ASTM 1275B proposed by CIGRE Covered Conductor Deposition test method.

B. Chemicals used

Two transformer contaminated (corrosive) oils, Czech Republic with the inlet DBDS concentration at 65.2 mg/kg (A) and Poland with the inlet DBDS concentration at 71.5 mg/kg (B) were tested. Their basic physico-chemical characteristics are summarized in Table 1. Propylene carbonate, anhydrous, 99.7%, Sigma-Aldrich; Dimethyl sulfoxide (methyl sulfoxide, 99.9%, A.C.S. reagent, Aldrich; N,N-dimethyl formamide, 99.8%, A.C.S, Aldrich; 1-Methyl-2-pyrrolidone, anhydrous, 99.5%, Aldrich; Acetonitrile, anhydrous, 99.8%, Sigma Aldrich; Dibenzyl disulfide 98%, Sigma Aldrich were used as other chemicals. Fuller's earth, Baron, USA, Model Ba-CL, in particles cca. 1 mm was used as sorbent for adsorption of NMP from oil. Copper beads 2-8 mm, electrolytic iron, powder, Sigma Aldrich together with copper sheets and cast iron particles were used as reagent sorbents.

C. Extraction of PCBs and/or DBDS from contaminated transformer oil

Extraction experiments with oils contaminated PCBs were performed with the real transformer oils with low content of PCBs in the range of 20 mg/kg to 4000 mg/kg (expressed as the sum of indicative congeners PCB 28, PCB 52, PCB 101, PCB 153, PCB 138, PCB 180). Samples of oil with various content of PCBs were mixed in the weight ratio of 1:1 or 1:2 with NMP, DMF, DMSO, PC, and AC as representatives of polar aprotic solvents. Parameters such as the extraction efficiency, the cost, the convenience in handling large volumes of the solvents and their environmental impacts determined the selection. Extraction was performed at room temperature 18 °C to 22 °C by mixing the oil with the solvent in a 500 mL Erlenmeyer flask. The samples were shaken in a laboratory shaker at the frequency of 2 swings/sec for 10, 20, 30 and 120 minutes. After the specified extraction



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Volume 4, Issue 2, March 2015

period, the samples were poured into a separatory funnel. In all experiments, a clear interface between the two liquid phases was established within 5 minutes. Samples of two phases were then taken for analysis of content of the PCB congeners. Similarly, extraction experiments with oils containing DBDS were performed with the real transformer oils A and B.

D. Recovery of oil after the extraction of PCBs and corrosive sulfur

Recovery of N-methyl pyrrolidone dissolved in oil (3.9 wt %) was done by filtration through a column filled by Fuller's earth. During standardized procedure oil was dripped through a column filled with loose sorbent bed (200 mm in height and 50mm wide). The mean lag time of the oil in the column was 40 minutes. Residual concentrations of impurities in the oil were measured in the effluent at the exit from the column. The flow of oil through the layer was uniform across the width of the bed without any channelling (the calculated mean residence time of flow calculated with the help of the flow rate and the porosity of the bed t_{calc} and statistically determined mean residence time t_{stat} obtained from the integration of the residence time distribution did not differ by more than 2%).

E. Separation of PCBs and DBDS from NMP

Separation of extracted PCBs from NMP was done by distillation and rectification. The apparatus consisted of a 500 mL still pot, a condenser, a distillate receiving flask and a vacuum pump. The process took place at a reduced pressure of 150 mbar. Out of the initial batch of 300 mL of the treated solution, the total volume of the initial portion of the distillate that was sampled and analyzed amounted to 100 mL.

A method that took into account the works focused on the determination of corrosive sulfur via the reaction of sulfur with metals was applied [15 - 17] for DBDS separation. The bimetallic catalyst Cu-Fe was manufactured by pushing particles of gray cast iron into strips of a copper sheet. The graphite content in the gray cast iron was about 4 %; the particles had sharp edges and measured 1- 2 mm; the thickness of the copper strips was 0.6 – 0.8 mm; the weight ratio Cu: Fe was about 1:1 [18]. A 200 mL flask was charged with 100 mL of solvent obtained from the extraction of corrosive sulfur from oil and 20 g of the bimetallic catalyst. Temperature of the mixture was kept under stirring at 150°C for 1 to 96 hours. Samples of the solvent were regularly collected. Collected samples were cooled, centrifuged to remove small solid particles of cast iron and graphite released from the catalyst, and then analyzed for the content of DBDS. Alternatively, experiments were carried out with copper beads and electrolytic iron powder.

III. RESULTS AND DISCUSSION

A. Separation of DBDS from selected contaminated transformer oil by adsorption of Fuller's earth

Results are summarized in the Table I. *Oil A*: Solid-liquid extraction of DBDS, e.g. forcing oil through the Fuller earth sorbent (usually used in practice), residence time of oil on sorbent approx. 60 minutes, the content of DBDS was not detected. *Oil B*: Forcing oil through the same Fuller earth at the same condition, the remaining concentration of DBDS was 12.8 mg/kg and does not changed with following cycles of sorption.

Separation of DBDS by current adsorption on commercial Fuller's earth cannot be by a long site consider as a universal method for decontamination of oils contaminated by DBDS (and/or by corrosive sulfur).

Table I: Separation efficiency of Fuller's earth of two oils with different physic-chemical characteristics

Oil	Viscosity 40°C mm ² /s	Density 20°C g/cm ³	Contact angle °	Saturated hydrocarbons %	Mono- aromates %	Di-aromates %	Polyaromates %	Corrosivity after adsorption ASTM
A	8.50	0.8825	9 ¹	81.6	16.6	1.7	0.1	Non- corrosive
B	9.74	0.8836	18 ¹	77.6	15.9	5.6	1.2	Corrosive

B. Extraction of PCBs and/or DBDS from contaminated transformer oil

a) Extraction of PCB from the mineral oil with the help of selected aprotic solvents

The results are summarized in Table II-IV. Only NMP and DMF evidence the value of distribution coefficient $K > 1.5$; both solvents have to be considered as suitable means for extraction of PCBs from contaminated oils. The time course of the extraction efficiency of individual solvents is depicted in Fig. 1.

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Volume 4, Issue 2, March 2015

Table II: Efficiency of extraction of PCB from contaminated oils with NMP. 20 minutes of extraction, ratio of both phases was 1:1, temperature 20 °C, concentration of PCB was in mg/kg

Oil	PCB28	PCB52	PCB101	Total PCB	Efficiency [%]
Initial concentration (mg/kg)	49.3	8.5	2.1	59.9	
After extraction with DMF	18.4	3.2	1.0	22.6	62.3
After extraction with DMSO	32.2	5.5	1.5	39.2	34.7
After extraction with PC	38.4	6.7	1.8	24.2	21.8
After extraction with NMP	14.3	2.4	0.65	17.4	71.0

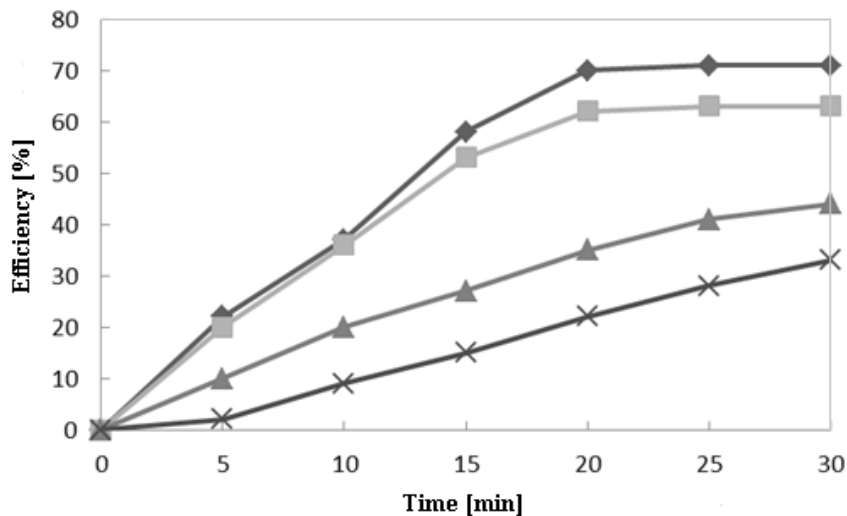


Fig. 1: Efficiency of extraction of PCBs from contaminated oil by extraction with polar aprotic solvents. ♦ NMP, ■ DMF, ▲ DMSO, × PC

Table III shows single-stage batch extraction efficiencies of contaminated oils having different initial concentrations of PCB. Table III also lists the concentrations of the individual indicative congeners in the oil and the solvent. Efficiency in % has been calculated as $100[(C_{\text{initial}} - C_{\text{after extraction}})/C_{\text{initial}}]$, where C were concentrations of the PCBs in the oil.

Table III: Efficiency of extraction of PCBs from contaminated oil with NMP, DMF, DMSO and propylene carbonate PC. Initial concentration of Σ PCBs in contaminated oil was 59.9 mg/kg, ratio of oil: solvent = 1:1, time of extraction was 20 minutes, T = 22 °C. Results from 3 independent experiments

Contaminated oil, initial concentration	Sample	Σ PCB	PCB 28	PCB 52	PCB 101	PCB 153	PCB 138	PCB 180
1502.3	Oil	438	336	73	20.7	2.6	4.2	1.35
	NMP	1064	771	218	64.6	3.6	5.1	1.3
2849.8	Oil	590	454	100	28.4	3.1	3.4	1.2
	NMP	2259	1645	442	147.6	8.8	11.5	3.5
4112.4	Oil	879	673	150	42.3	5.7	5.7	1.8
	NMP	3233	2372	627	200.2	8.9	11.8	3.1
Average ratio of PCB concentrations in NMP:oil			3.19	3.96	4.36	1.91	2.06	1.86

The efficiencies of all the measured samples ranged from 70 % to 78 %, and document high efficiency of the extraction of PCBs in a wide concentration range of PCBs from tens to thousands mg/kg. It can be also concluded that the lower chlorinated congeners extract into the solvent preferentially.



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ISO 9001:2008 Certified

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Volume 4, Issue 2, March 2015

Table IV presents the efficiencies of PCB extraction from oils with the help of aqueous solutions of NMP. The solvent recovery can sometimes lead to the water enrichment of NMP. It is therefore useful to quantify the degree of negative influence of the presence of water in the polar aprotic solvent on the extraction efficiency.

Table IV: Extraction efficiencies when using N-methyl pyrrolidone NMP (anhydrous NMP, 0% H₂O) and NMP mixtures with water (10% H₂O and 60% H₂O). Concentration of the sum of indicative congeners in the contaminated oil was 83.6 mg/kg. Efficiency was calculated as the ratio between the sum of PCB congeners extracted into the solvent to the original sum of congeners in the oil. Extraction time 120 minutes, temperature 20 °C, ratio of phases: 150 ml oil: 150 ml solvent (pure or with water). The table shows the concentrations of PCBs in the solvents measured in mg/kg and given as the averages of three independent measurements. ND – not detected

Solvent	Σ PCB	PCB28	PCB52	PCB101	PCB153	PCB138	PCB180	Efficiency [%]
Oil	83.6	68.6	11.8	3.2	ND	ND	ND	
NMP,0% H ₂ O	57.7	48.3	7.7	1.8	ND	ND	ND	69.0
NMP,10% H ₂ O	39.4	32.6	5.4	1.4	ND	ND	ND	47.2
NMP,60% H ₂ O	4.7	3.7	0.8	0.2	ND	ND	ND	4.6

Table V shows the concentrations of the indicative congeners after the first, second, third and fourth extraction steps. The extraction conditions in all the steps were identical, i.e., the ratios of n-MP to oil were 1:1.

The “total” concentration of PCB was calculated based on the sum of six indicative PCB congeners by multiplication with the value of four, which corresponds to the theoretical contribution of those congeners to Aroclor 1254 (see e.g. [19]) and determined as $\Sigma PCB_{regulated} = 4 \Sigma$ concentrations of the indicative congeners. It is apparent that after the fourth extraction the Σ of the concentrations of PCB ($4 \times 11.79 \text{ mg/kg} = 47.2 \text{ mg/kg}$) is close to the regulation value. The overall efficiency after four extraction steps was 99.2 %.

Table V: Concentrations of the indicative congeners in the oil phase after the extraction with NMP performed under the same conditions as described in Table II (1:1 in weight, the oil leaving an extraction step was contacted with the same amount of pure NMP). The initial concentration of ΣPCB entering the extraction cycle was 1502.3 mg/kg. All concentrations in the table are given in mg/kg

Congener PCB Number	Output from 1. extraction = input to 2. Extraction	Output from 2. Extraction = input to 3. Extraction	Output from 3. Extraction = input to 4. Extraction	Output from 4. extraction
28	336.5	94.20	23.54	9.41
52	73.0	16.82	4.20	1.47
101	20.7	4.10	1.02	0.35
153	2.6	0.91	0.23	0.08
138	4.2	1.49	0.61	0.42
180	1.35	0.54	0.25	0.06
Σ	438.4	118.06	29.85	11.79

Our optimization studies showed that the ratio of NMP:oil = 1:1 worked best. After the first cycle of extraction with NMP about 70 % of ΣPCB s congeners were separated. Only a few extraction steps are needed to virtually complete the separation of PCBs from the oil. The products of the separation are the decontaminated oil (with



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International Journal of Engineering Science and Innovative Technology (IJESIT)

Volume 4, Issue 2, March 2015

traces of PCBs) and the solvent containing the extracted PCBs. The interface between the phases after the extraction is very sharp and the oil can be quantitatively separated from the solvent.

b) Extraction of DBDS from contaminated transformer oil with N-methyl pyrrolidone

The results concerning of the oil A are summarized in Table VI, which shows single-stage batch extraction efficiencies of DBDS from contaminated oil. The results of extraction of DBDS from oil B are depicted in the Fig.2.

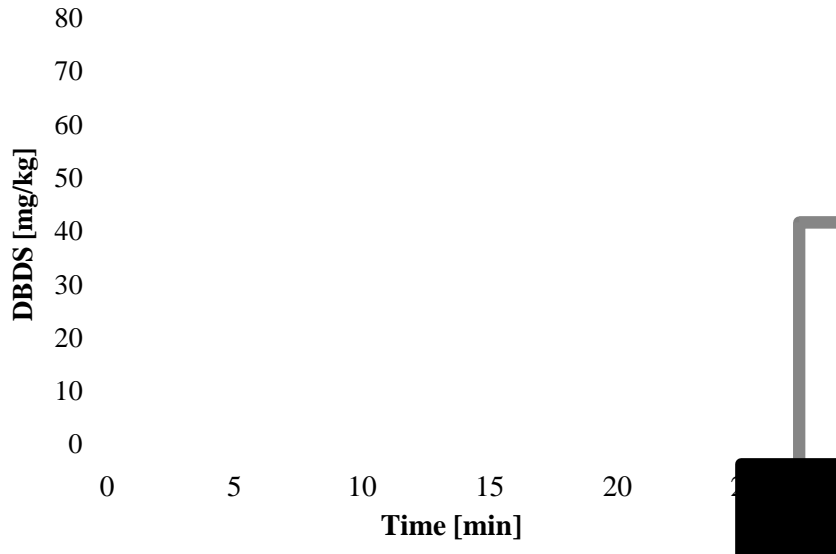


Fig. 2: Extraction of DBDS from Oil B. ■ DBDS

Table VI: Efficiency of extraction of DBDS from contaminated transformer oil A with NMP. Initial concentration of DBDS was 65.2 mg/L, ratio of oil: solvent= 1:1, course of time extraction between 0-45 minutes, T = 22 °C. Measured in triplicate. ND – not detected

Time [min]	Average content of DBDS
0	65.2
15	2.1
30	0.1
45	ND

While extraction of PCBs from oils to concentrations that met mandatory environmental limits required at least 4 extraction steps, extraction of DBDS from used transformer oil with a relatively high content of DBDS was remarkably efficient even in one extraction stage and under moderate mixing. The test for corrosive sulfur in a sample taken after 30 minutes of the treatment was negative. This is the most important proof of the suitability of extraction with the help of NMP. In practice, oils containing corrosive sulfur but no PCB may be treated with high efficiency by extraction with polar aprotic solvents, especially NMP in a simple mixer-settler extractor. Oils containing corrosive sulfur and PCBs require multi-stage extraction.

C. Simple distillation and rectification of PCB from NMP

Table VII shows the comparison of the PCB concentrations of the original sample, the initial portion of the distillate after simple distillation, and the initial portion of the distillate after rectification.

From the results it is clear that it is possible to use rectification to separate PCBs from NMP with high efficiency. The obtained NMP may be recycled.



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International Journal of Engineering Science and Innovative Technology (IJESIT)

Volume 4, Issue 2, March 2015

Table VII: Results of the separation of PBC from N-methyl pyrrolidone via simple distillation and rectification.

Congener PCB	Concentration initial [mg/kg]	Concentration after rectification [mg/kg]	Concentration after distillation [mg/kg]
28	54.1	0.4	1.9
52	7.9	0.1	0.3
101	0.7	0	0.1

D. Recovery of oil using Fuller's earth

During the extraction of corrosive sulfur from oils with the help of N-methyl pyrrolidone, a portion of NMP dissolves in the oil. Traces of solvent in the oil substantially negatively influenced the dielectric properties of the transformer oil, mainly: Breakdown Voltage, Acidity (Neutralization Value), Dielectric Dissipation Factor and Resistivity. At a temperature of 25°C the equilibrium concentration of NMP in the treated transformer oil was 3.9 wt% (determined according to the detected concentration of N in the oil). Therefore, it is preferable to work at low temperatures when using N-methyl pyrrolidone to extract PCBs from oils. After filtering the oil through commercially available Fuller's earth no DBDS was detected in the sample of the oil. Technological characteristics of such treated oil after the extraction of NMP and subsequent recovery (mainly separation of NMP) were tested and met all the requirements of the first-class transformer oils.

E. Separation of DBDS from NMP with Cu-Fe catalyst

During the first 12 hours of the treatment the concentration of DBDS fell from its initial value of 62.7 mg/kg to almost negligible value of 1.2 mg/kg. The solution also contained dibenzyl. According to our preliminary results, the bimetallic catalyst was more reactive than the particles of electrolytic iron and the beads of reactive copper. Residual concentrations of DBDS after 24 hours of treatment with copper alone, and electrolytic iron particles alone were 12.8 mg/kg and 45.7 mg/kg respectively. The contact of iron with copper apparently synergistically activated the iron particles. This method of reducing the content of sulfur compounds in polar aprotic solvents appears as a promising technology. Given the new findings, however, further research in this direction is necessary.

IV. CONCLUSIONS

Among all the tested polar aprotic solvents (AN, DMF, DMSO, NMP a PC), NMP and DMF proved to be the most efficient. Extraction efficiencies of PCBs in a single step extraction with the help of NMP and DMF are rather high and range from 63 % to 78 %. Moreover, extraction efficiency of DBDS from contaminated transformer oil with the help of NMP is sufficiently high (over 99 %) and feasible in a fair time. The remaining concentration of DBDS after single-step extraction was low enough and it was possible to consider the transformer oil after the extraction procedure as free from corrosive sulfur.

Oil containing traces of the solvent, which impair its dielectric properties can be recovered with high efficiency simply by filtration through conventional sorbents, such as Fuller's earth; this is critical knowledge enabling the application of liquid-liquid extraction for the removal of corrosive sulfur in cases where conventional cleaning with sorbents fails. Polar aprotic solvents (PAS) may be recovered and recycled with the help of vacuum rectification. Experiments with NMP showed that the rectification works with high efficiency. The small residue of PAS with the extracted PCB may be sacrificed to incineration.

DBDS could be quantitatively separated from NMP in reasonable time with the help of a reaction with particles of graphite gray cast iron on Cu sheet at 150 °C. Further research on the separation of corrosive sulfur from polar aprotic solvents is necessary.

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