The Effect of Composition and Trace Contaminants on the Electrical Properties of Insulating Oil*

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Summary: The authors studied factors influencing the dielectric behaviors of insulating oil by investigating its hydrocarbon composition and trace of impurities picked up during the process of refining.

The raw transformer oil distillate was separated into varied group of hydrocarbon by means of chromatographic adsorption and their electrical properties examined.

It was found that the polycyclic aromatics imparted the most unfavorable properties and resins also had a deleterious effect on the electrical properties of the oil.

On the authors' assumption that the trace of impurities could be metallic soap, numerous metallic soaps prepared in the authors' laboratory were added to the refined oil in minute quantities and its effect on the electrical properties of the oil studied.

The result of the study revealed that metallic soap not only degraded the electrical properties but caused poor stability of the oil against oxidation.

From these observations, some suggestions for improving the properties of insulating oil are given.

Introduction

There are various factors which influence the electrical properties of insulating oil. One of them is the chemical composition of oil, and others are moisture, fibrous contaminants, dusts and so on. In this paper, the authors report the result of studies on the effect of composition of hydrocarbons and trace of metallic soaps on the electrical properties of insulating oil.

Already, R. N. Hazelwood¹⁾ separated transformer oil into naphthenic and aromatic fractions by percolation through silica gel, and determined d-c conductivity and other physical and chemical properties of these fractions. He discussed the behavior of these fractions in an electric arc with respect to the formation of gases and structural changes of molecules.

A. W. Thompson²⁾ showed that oils containing soluble metallic naphthenates might give a low resistivity. These metallic soaps deteriorate not only the electrical properties but the oxidation stability. For example, J. C. Wood-

Mallock³⁾ has described that transformer oils, which has high ash content predominately consisting of calcium sulphonates, has very low oxidation stability.

For the purpose of improving the properties of insulating oils, the authors attempted to investigate the electrical properties of the hydrocarbons and trace of impurities which make up the composition of the oil.

Experimental results and discussion

1. *Electrical properties of each components of raw transformer oil distillate:* Raw transformer oil distillate was separated into saturates, aromatics, mono and dicyclic aromatics by silica gel chromatography and activated alumina gel chromatography. The electrical properties of these components were then determined. Resins were added to some cable oils which have good electrical properties and the properties of these oils determined. Flow sheet indicating the separation procedure is given in Fig. 1.

The raw transformer oil distillate was separated into saturates, aromatics, and resins, by silica gel chromatography. In this case, 10 gr. of sample distillate was taken and gel/oil ratio was 10:1 by weight. Applying petroleum ether,

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Fig. 1 A Flow Sheet of Separation Procedure

benzene, and methyl alcohol as the eluent successively, three components were desorbed and recovered separately. A necessary quantity of each fraction was obtained by repeating the same procedure. From each collected fraction, the solvent were removed by vacuum distillation.

The saturates (S-2) was analysed by similar chromatographic method, and it was found that the saturates consisted of 99.2% of paraffin and naphthen hydrocarbons, aromatics only 0.8% by weight. While the aromatics (S-3), owing to the activated alumina gel chromatographic analysis, gave 80.9% by weight of the portion desorbed with petroleum ether. This desorbed portion was separated into 10 equal portions by dividing the chromatographic column packed with alumina into 10 pieces. Ultraviolet spectra of these 10 portions are shown in Fig. 2.

From the observation of the positions and intensities of characteristic absorption peaks, it was concluded that these aromatic portions are composed of mono and dicyclic aromatics (benzene and naphthalene type). Accordingly, the aromatics (S-3) was separated into three main fractions of mono and dicyclic aromatics,

Fig. 2 Ultraviolet Spectra of Petroleum Ether Cut of S-3

polycyclic aromatics, and resins, by means of the same procedure described above, applying alumina gel. About 10 gr. of the aromatics (S-3) was weighed out in every manipulation. By repeating the same procedure, sufficient quantity of these three fractions were collected. The physical and chemical properties of sample oils, the components, raw distillate, and transformer oil, are given in Table 1. From Table 1 it can be seen that polycyclic aromatics has the highest viscosity among the oils and its specific gravity greater than 1.0.

Acidic matter is concentrated in resins (S-4). It is quite interesting to know that the sulphur are predominately concentrated in the polycyclic aromatics in comparison with other component and the saturates contains only 0.8% of aromatics contains still more 0.07% of sul-

Table 1 Physical and Chemical Properties of Sample Oils

No.	Sample	Viscosity (cst)		Specific Gravity d_4^{20}	Refractive Index n_D^{20}	Sulphur Content wt. %	AV KOH mg/g		Remarks
		100°F	210°F				After Clay Treatment		
S-1	Raw distillate	9.71	2.28	0.9065	1.5029	0.58	0.83	0.58	Silica gel chromat
S-2	Saturates	8.83	2.19	0.8621	1.4687	0.07	<0.02	<0.02	
S-3	Aromatics	13.48	2.49	0.9806	1.5585	1.20	<0.02	<0.02	
S-4	Resins	—	—	—	—	1.17	23.7	22.8	
S-5	Mono and Dicyclic Aromatics	12.10	2.63	0.9594	1.5400	1.03	—	—	Alumina gel chromat
	Polycyclic Aromatics	21.23	2.87	1.0687	1.6323	1.58	—	—	
	Resins	—	—	—	—	1.12	—	—	
	Transformer Oil Products	9.40	2.28	—	—	—	—	—	

phur.

Each separated component was treated with activated clay (5 % weight) and filtered through a glass filter (G 4) before testing its electrical properties. In Fig. 3, 4 and 5, numerical valu-

es of the electrical properties of each component together with raw distillate and finished product, and their changes with temperature are shown.

Fig. 3 Variation of Resistivity of Sample Oil

Fig. 4 Variation of Power Factor of Sample Oils

Fig. 5 Variation of Dielectric Constant of Sample Oils

In the experiment, the electrical properties were measured according to the Japanese Industrial Standard Methods (JIS C-2320, 1955), viz. resistivity by comparison method applying the specified galvanometer, power factor and dielectric constant, by Shering bridge at a potential of 1,000 volts and a frequency of 60 cycles per second. The test cell used comprised of two concentric cylindrical electrodes, the gap between the cylinder walls being 1 mm, and outside diameter and height being 84 mm and 111 mm respectively. The capacity was 90 pF. This test cell is available at Yokogawa Electric Works Ltd. (OE-2 type).

From the results of this experiment, following deductions were made:

1) Among the oil samples tested, there are significant differences in electrical properties. The value of resistivity becomes higher in the following order: aromatics < raw distillate < mono and dicyclic aromatics < transformer oil finished products < saturates. The value of power factor decreases in the order of: aromatics > raw distillate > mono and dicyclic aromatics > transformer oil finished products > saturates. For every oil sample, the resistivity decreases with temperature, and the power factor increases with temperature.

2) The dielectric constant of all oil samples decrease slightly with temperature. The value of aromatics is the highest, and decrease in the order of mono and dicyclic aromatics, raw distillate, transformer oil and saturates.

3) From these results, it can be seen that polycyclic aromatics rank below mono and dicyclic aromatics in electrical properties.

4) The transformer oil ranks next to the saturates in electrical properties. Such being the case, it can be concluded that a greater

part of aromatics and resins should be removed in refining process, namely sulphuric acid treatment and caustic soda neutralization and so on.

2. *Effect of resins on the electrical properties.* The electrical properties of resins itself could not be determined because of its viscous tarry property. Hence, the cable oil containing resins were tested.

As shown in Fig. 6, the addition of resins up to about 50 p.p.m. does not cause remarkable change in power factor in comparison with the base oils, but when the quantity of resins increased to 1,000 p.p.m., a marked increase of power factor is observed.

Fig. 6 Effect of Resins on the Electrical Properties

3. *Effect of sulphonates on the electrical properties:* It is a well known fact that any contamination of oil with sulphonates as well as naphthenates results in deterioration of the electrical properties of oil. It might be quite possible that some sulphonic acid produced during the sulfuric acid treatment of oil combines with calcium compound, present in the process water, to give calcium salts, and with sodium hydroxide, during the neutralization process, to give sodium sulphonates. Some trace of these salts would remain in the finished oil product even if the oil had been treated with great care during the finishing stage of refining.

The authors prepared some calcium sulpho-

nates and sodium sulphonates by extraction and conversion from the oil solution of "Calcium Sulphonate Neutral" manufactured by L. Sonneborn Sons Inc. and carefully purifying them. These sulphonates, so obtained, were added to cable oil in concentrations of 10, 50, and 100 p.p.m. The sulphonates were first dissolved in a small quantity of cable oil, heated to about 70°C and diluted to designated concentration.

The oil samples were filtered through a glass filter (G-4) to eliminate any moisture and insoluble matter immediately before testing its electrical properties to avoid the influence of moisture from the ambient air. The addition of these sulphonates showed marked effects on the electrical properties of oils as shown in Fig. 7.

Fig. 7 Effect of Sulphonates on the Electrical Properties

4. *Thermal stability-test of oils containing trace of metallic soaps:* Trace of sulphonates (as described above) and some metal naphthenates (prepared from naphthenic acid, "Shell Naphthenic Acid" manufactured by Shell Petroleum Company, in the authors' laboratory) were added to cable oils and transformer oils. These oils were subjected to thermal stability test (beaker test according to Pirelli General Method, viz. sample quantity 500 cc, copper wire catalyser 1.6 mm ϕ $\times$ 1 yard, 100°C $\times$ 96 hrs.) and the aged oils measured for electrical properties and acidity. The results are given in

Table 2 Thermal Stability Test of Oil Containing Various Metallic Soaps

Sample Oil	Before Test		After Test		AV	Remarks
	$\tan \delta$ (%)	ρ (Ω cm)	$\tan \delta$ (%)	ρ (Ω cm)		
Cable Oil (1)	0.006	3.40×10^{14}	2.42	9.36×10^{11}	0.02	After filtration with glass filter (G 4) 100°C × 96 hrs
(2)	0.005	6.47×10^{14}	4.58	4.40×10^{11}	0.02	
+Na-n 10 p.p.m. (1)	0.268	2.09×10^{14}	6.90	4.14×10^{11}	0.03	
	0.124	1.54×10^{14}	4.41	4.99×10^{11}		
	0.105	2.01×10^{14}				
+Na-n 50 p.p.m. (1)	0.627	2.76×10^{13}	4.92	5.11×10^{11}	0.04	Measuring temp. 80°C
	0.600	3.10×10^{13}				
	0.600	1.71×10^{13}				
+Na-n 100 p.p.m. (1)	4.81	5.26×10^{11}	2.95	6.36×10^{11}	0.06	Ca-S: sulphonate Na-n: Na naphthenate
	4.84	7.67×10^{11}	2.78	6.48×10^{11}		
+Ca-S 10 p.p.m. (1)	0.305	5.25×10^{13}	3.09	9.06×10^{11}	0.02	
+Ca-S 100 p.p.m. (1)	3.27	7.80×10^{12}	>11.1	2.58×10^{11}	0.05	
			>11.1	2.56×10^{11}		
Transformer Oil (1)	0.082	2.04×10^{14}	4.37	6.48×10^{11}	0.02	After filtration with glass filter (G 4)
(2)	0.074	4.04×10^{14}	5.90	3.54×10^{11}	0.02	
(3)	—	—	10.44	1.92×10^{11}	0.02	
(4)	—	—	9.97	2.24×10^{11}	0.04	
(5)	—	—	(8.96)	(2.79×10^{11})		
+Ca-n 10 p.p.m. (1)	0.170	3.70×10^{14}	>11.1	1.12×10^{11}	0.09	* After filtration with glass filter (G 4)
	0.200	1.48×10^{14}	>11.1	1.69×10^{11}	0.04	
	0.459	1.36×10^{14}	(10.41)	(2.35×10^{11})		
+Ca-n 100 p.p.m. (1)	>11.1	1.01×10^{12}	9.24	2.33×10^{11}	0.06	* After filtration with glass filter (G 4)
	>11.1	8.98×10^{11}				
	>11.1	9.09×10^{11}				
(2)	>11.1	6.95×10^{11}	>11.1	2.26×10^{11}	0.05	

Note* Subjected to the oxidation stability test specified in JIS.

(1)(2) and etc. indicate the repetition of the same test.

Table 2.

As shown in the table, the oils with and without addition of metallic soaps showed about the same degree of deterioration in electrical properties after the thermal stability test. The power factor were higher than 1 % and resistivity $10^{11} \Omega$ cm. The acidities of the aged oils containing trace of metallic soaps, however, showed higher values than those of base oils.

The oxidation stability test specified in JIS C-2101 were taken up as a reference test. As Table 3 shows, the oils containing metallic soaps, at a concentration of 100 p.p.m., were strongly oxidized. In comparing Table 3 and Table 2, it can be seen that the oxidation

Table 3 Oxidation Stability Test Containing Various Metallic Soaps

Sample Oil	SI %	AV	Remarks
Transformer Oil (1)	0.14	0.23	Mean value of 3 samples
(2)	0.13	0.31	
+Ca-n, 10 p.p.m.	0.17	0.32	
+Ca-n, 100 p.p.m. (1)	0.22	0.32	
(2)	0.21	0.54	
+Ca-S, 10 p.p.m.	0.16	0.35	
+Ca-S, 100 p.p.m. (1)	0.40	0.70	
(2)	0.30	0.83	

Test Method; Specified in JIS C-2101-1955, 120°C × 75 hrs.

stability test specified in JIS C-2101 evaluates the sludge formation and acidity development of oils after considerable deterioration of electrical properties.

5. *Effect of metallic soaps on interfacial tension, steam emulsion number, and friction coefficient*: In order to examine the effect of oils contaminated with trace of metallic soaps on the surface chemical properties, the authors observed the interfacial tension (IFT), steam emulsion number (SEN), and friction coefficient. Friction tester used was a pendulum

Table 4 Effect of Metallic Soaps on Interfacial Tension, Steam Emulsion Number, and Friction Coefficient

Sample Oils	Interfacial Tension dyne/cm 25°C	SEN sec.	Friction Coefficient* μ	
			Room temp. 27°C	100°C
Cable Oil	42.6	37	0.28	0.21
+Ca-S 10 p.p.m.	45.6	38	0.28	—
+Ca-S 100 p.p.m.	35.5	>1800	0.28	0.18
+Na-n 10 p.p.m.	46.5	35	—	—
+Na-n 50 p.p.m.	42.3	38	—	—
Transformer Oil	45.9	20	0.39	0.29
+Ca-n 10 p.p.m.	44.0	38	0.38	—
+Ca-n 100 p.p.m.	44.0	<20	0.38	0.29

* Tester being of the pendulum type.

type originated by Dr. N. Soda. The results obtained are given in Table 4. The IFT for all the oils were about equal to the base oil except for oil containing 100 p.p.m. of calcium sulphonates which was slightly lower. As for SEN, the oils containing 100 p.p.m. of calcium sulphonates were highly emulsified. Except for the different values obtained from the two base oils, no difference was noted in the friction coefficient between the base oil and the oil contaminated with metallic soaps.

Conclusion

1. Out of many presumable factors controlling the electrical properties of insulating oils, the present investigation was carried out to find the effect of hydrocarbon component of the oil, and the metal sulphonates and naphthenates contamination on the properties of insulating oil.

2. It is apparent that polycyclic aromatics and resins imparted the most deleterious effect on the electrical properties of insulating oils. For this reason, the elimination of these compounds would improve the electrical properties of the finished products. On the other hand, there are some aromatic compounds which are natural inhibitors and suppress evolving of gas, hence, the elimination of aromatics should be selective and retention of some aromatics is necessary.

3. Trace of sulphonates, prepared in authors' laboratory, were added in cable and transformer oils. When electrical properties of these oils were determined, the addition of sulphonates gave notable effect. Addition of 100 p.p.m. of various sulphonates degraded the electrical properties of the oil to the limit of permissible degree specified by the thermal stability test for cable oils. After 96 hrs. the power factor of the aged oils were higher than 1 % and resistivity $10^{11} \Omega \text{ cm}$. It was found that the oils containing 100 p.p.m. of sulphonates lost considerable stability in JIS oxidation stability test. Moreover, it is a characteristic phenomena that the oil containing 100 p.p.m. of calcium sulphonate is highly emulsified.

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