Improvement of Oxidation Stability of Mineral Oil using Jojoba Oil

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Abstract: The production of insulating mineral oil from naphthenic fraction (b.r. 300-420°C) was carried out by furfural solvent extraction. The refined oil and its binary mixtures with jojoba oil at different concentrations 20, 50, and 80 vol % have been employed as synthetic insulating oil in a wide variety of electrical equipment. The physico-chemical properties of the refined oil as well as the electrical properties of the mixtures were determined. The oxidation stability of original oil, refined mineral oil and its binary mixtures with jojoba oil with different concentrations was studied. The stability of oxidation by adding different concentrations of 2,6,-di-tertiarybutyl phenol inhibitor to binary mixture containing 20 vol % jojoba oil was studied. It is found that the maximum stability is obtained by adding 2 wt % of inhibitor.

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1. Introduction:

Insulating oils should have stable high-quality properties, not only in the original state, but also during the up time in operation. The oxidation stability of insulating oils has an elementary meaning during operation, because they work under high temperatures usually in the presence of oxygen, so they should resist oxidation.

The oxidation of oil increases its acidity and the content of sediments. Low sediment values indicate high oxidation stability, leading to long oil life. Minimizing the creation of sediments, the dielectric dissipation factor, corrosion of metals,
electric failures maximize the insulating stability of oil[1].

Oxidation stability is an indicator that allows us to set stricter limits for oils in special applications. In some countries, striker limits or other requirements and tests are imposed [2].

In order to settle down the environmental and sustainable issues, people started to look for alternative sources for insulating oil. The latest insulating oil implementation is vegetable oil-based fluid which is known as the most potential source to replace the mineral oil because of its biodegradability characteristic. The first vegetable oil was used for capacitor insulation in 1962 and gave a good match with cellulose due to its higher dielectric constant [3,4].

Jojoba oil has potential as a substitute for some of the petroleum-derived products. It is observed that jojoba oil as a component enhances and also imparts certain properties to the base oil which otherwise can only be realized by doping with additives, thereby helping partially to substitute mineral oil base stocks and to reduce or eliminate the use of some of the additives.

Pure Natural Jojoba is structurally and functionally much different than any other botanical product. Its unique array of pure mono unsaturated liquid wax esters, consisting of long chains of fatty acids and alcohols is very unlike the large branched triglyceride molecules of all other seed oils. The extraordinary oxidative stability and non-occlusive moisture control of jojoba esters provides a highly safe [5, 6]. Jojoba oil has good lubricity and can be utilized as a component. Jojoba oil is an ester of fatty alcohols and fatty acid as shown in its molecular structure [17]

$$CH_3\ (CH_2)_6\ CH_2CH{=}CH\text{-}CH_2(CH_2)n - C(=O) - O - CH_2\ (CH)m - CH_3$$

Where ,
n= 7,9,11 and m = 6,8,10,12

The physicochemical properties of the oil when compared with those of mineral base stocks showed that the pour point, acid value and oxidative stability were the limiting factors in its use as a base stock [7].

Jojoba oil is unique because it is wax ester instead of a typical triglyceride. Jojoba wax esters are similar to those in sperm whole oil and can be utilized in areas, where sperm whole oil has been used in the past. Jojoba liquid wax is stable lipophilic, nontoxic oil obtained frm the desert plant jojoba. This liquid wax differs from common vegetable oils and animal fats in its composition mainly of linear wax esters (97 %).Jojoba being stable to oxidation, may remain chemically

unchanged for years. The wax and its derivative have potential commercial uses in a variety of fields including pharmaceuticals and lubrication [8 - 10].

Mineral oil insulating fluids undergo oxidative degradation in the presence of oxygen to give a number of oxidation products. The final products of oxidation are acidic materials that can affect the characteristics of the insulating fluid as well as cause damage to the components of the electrical unit. Oxygen is a di-radical species and the reactions of the oxidative process are complex but they do involve free radical reactions. One way to prevent these types of reaction is to incorporate an oxidation inhibitor that will interrupt and terminate the free radical process of oxidation. Phenolic materials are quite good for this purpose and the two most commonly used inhibitors are 2,6-ditertiary-butylphenol (DBP) and 2,6-di-tertiary-butyl-4-methylphenol or 2,6-di-tertiary-butyl-paracresol (DBPC) [11-13].

This paper deals with the study of oxidation stability of a naphthenic mineral oil, its rafinate obtained from furfural extraction with solvent/oil ratio 4:1 and binary mixtures of jojoba oil.

2. Experimental:

1- Preparation of the tested oil sample.

The naphthenic acid fraction from suez Co. b.r. 300 – 420^{o}C was refined by using furfural extraction process to prepare raffinate of varying quality. A glass double jacketed mixer settler unit having 0.5 litre capacity was used. The oil fraction and furfural solvent mixed at ratio 4: 1vol was stirred for a period of time (one hour) at 70 ^{o}C then settled for the same time before separate the two phases.

The solvent was removed from raffinate phase by washing with distilled water and dried over anhydrous calcium chloride.

The raffinate oil obtained was mixed with Jojoba oil at different concentrations 20, 50 and 80 vol%. These mixtures were evaluated for improving the characteristics of the mineral oil for insulating performance.

2- Physico–chemical properties Determination

The physico–chemical properties of the naphthenic fraction, its refined oil and its binary mixtures with Jojoba oil were determined according to the standard methods in IP [14] and ASTM [15].

The electrical properties power factor (tan δ) for the previous samples were measured using “HIO KI 3532 Z high Tester” [16].

The naphthenic oil fraction and its refined oil were separated into their hydrocarbon components by using silica gel column chromatography [15].

Oxidation Test:

The oxidation stability of the refined oil produced by furfural extraction and its binary mixtures with jojoba oil with concentration 20, 50, and 80 vol %, were tested according to the oxidation test method ASTM D-1313 and IP-307[15].

The tested samples (40ml for each) were oxidized at 120^{o}C using copper coil as a catalyst. Pure gaseous oxygen (purity 99.9%) flow was adjusted to 2.5 liter/hrs. For the analytical program and the oxidation test was continued up to 210 hrs.

The rate of oxidation was measured by the increase in total acid number, sludge formation and change in power factor.

The binary mixtures of refined oil containing 20 vol.% of Jojoba oil were oxidized using various concentrations of 2,6-Ditert-butyl-phenol-0.5 wt% - 2wt%).

3. Results and Discussion:

The physico-chemical properties of the naphthenic mineral oil fraction and the rafinate used in this work are shown in table (1).Table (1) shows that the tested oil fraction are characterized by pour point (21 ^{o}C), density (0.8958 mg/cm^{3}), below viscosity (1327 cSt), viscosity index(111.2), refrective index(1.4877), viscosity garvity constant(0.45), high aromatic content (50wt%), high sulfur content(2.20wt%), nitogen content(0.123wt%) and total acid number(0.05 mgKOH/g) sample.

Table (1) shows that refining process causes a decrease in physical constants. It is clear that the viscosity of refined oil does not exceed the limits of standard specifications. The viscosity index (V.I.) increases from (111.2) for naphthenic oil to (140.5) for the rafinate. The total acid number of the refined oil decreased after solvent refining to zero value , giving good oil.

The precentage of the removal of aromatics content is 50%, of sulfur content is 63wt% and nitrogen content is 80.48%.The Refining process decreases mostly the aromatic hydrocarbons in the form of di-and polycyclic aromatics while the monocyclic aromatics are not affected to a big extent as given in Table (1). It is observed that the polycyclic aromatics are completely removed. The refining process removes 80% of dicyclic aromatics.

Table (1): Physico-chemical properties of refined mineral oil sample obtained from Suez fraction (b.r.300-420°C) by furfural extraction process:

Physical properties	Method	Origin	Furfural raffinate 4:1
Yield,wt%		-	50.9
Density,g/L,15.56°C	IP-190	0.8958	0.8510
Refractive index,70°C	ASTM D-1747	1.4877	1.4696
Pour point,°C	ASTM D-97	21	30
Mean Molecular weight		228	350
T.A.N.,mg KOH/g	ASTM D-664	0.05	nil
Sulfur content,wt%	ASTM D-	2.2	0.8
Nitrogen content, wt%	ASTM D-	0.123	0.024
Kinematic viscosity, cSt @40 @100 Viscosity index, V.I.	ASTM D-445	 13.27 3.24 111.2	 11.27 3.09 140.5
Flash point,°C	ASTM D- 92	180	188
Hydrocarbon components			
Saturates, wt%		60.00	81.8
Monocyclic aromatics, wt%		14.0	15.2
Dicyclic aromatics, wt%		16.0	3.2
Polycyclic aromatics, wt%		10.0	0.0

Oxidation Stability:

The data presented in Table 2 and Figs. (1-3) illustrate the oxidation stability of the original oil, refined oil and its binary mixtures with different volume percent of Jojoba oil. It is found that the rate of increase in total acid number, sludge formation and tan δ is small in the initial stage of oxidation till (140hr).The reverse occurs at the advanced stage of oxidation. This is due to the fact that the accelerating effect of the oxidation products at this period.

Table (2) and Figs. (1-3) show that the oxidation stability of the original sample is lower than that of the refined mineral oil which is detected from the high sludge formation (1.03-3.0 wt%) as well as the increase in total acid number (0.38-1.17 mg KOH/gm) for the original oil as compared with that of the refined oil where sludge increases from (0.00035-0.0025 wt%) and T.A.N. increases (0.39-0.96 mgKOH/gm) at all times of oxidation process. This due to the presence of high percentage of aromatics, sulfur and nitrogen contents which effect the oxidation rate of the original oil as compared with that of the refined oil as shown in Table (1). The effect of mixing of refined oil with different volume percent of Jojoba oil (20, 50 and 80 vol%) has been studied. The data in Table (2) indicate that blending of Jojoba oil improves the oxidation stability of refined oil to some extent and improve tan δ. The oxidation stability reaches a maximum value by adding 80 vol.% of Jojoba oil. This may be attributed to the high stability of Jojoba oil.

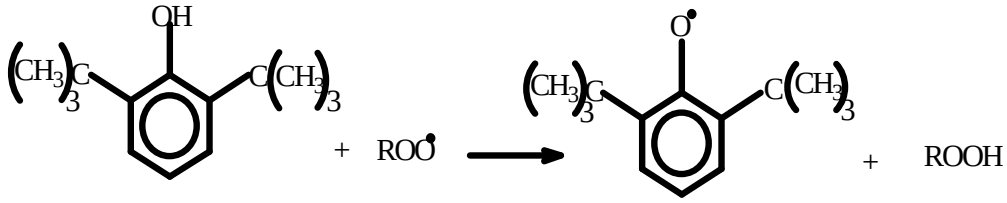
The results in Table (2) indicate that the power factor (tan δ) rises slowly with oxidation time. The value of tans δ of the original oil is higher than that of refined oil. It increases by time (0.62-0.78) for original oil while reaches to 0.67 for refined oil. This is due to the fact that the solvent refining removes the polycyclic aromatic which contain some type of sulfur and nitrogen compounds which effect tan δ. The power factor values of binary mixtures show lower values by oxidation due to the high insulating properties of Jojoba oil and high its stability.

Table (2): Effect of oxidation on the properties of Suez oil fraction, Refined Mineral oil, Pure Jojoba Oil, and its binary mixtures with Refined Oil.

Tested sample	Zero	70 hours			140 hours			210 hours		
	T.A.N.	T.A.N.	Sludge	tan δ	T.A.N.	Sludge	tan δ	T.A.N.	Sludge	tan δ
Original	0.05	0.38	1.03	0.62	0.72	2.01	0.67	1.17	3.0	0.78
Refined Mineral Oil	Nil	0.39	0.00035	0.61	0.48	0.001	0.63	0.96	0.0025	0.67
Pure Jojoba Oil	0.07	0.11	Nil	0.48	0.15	Nil	0.54	0.23	0.0001	0.57
20% Jojoba Oil	0.02	0.21	Nil	0.43	0.34	0.001	0.45	0.71	0.0014	0.51
50% Jojoba Oil	0.04	0.13	Nil	0.72	0.24	0.0004	0.30	0.52	0.0012	0.51
80% Jojoba Oil	0.06	0.08	Nil	0.7	0.19	Nil	0.9	0.34	0.0001	0.26

Effect of Inhibitor on the Oxidation Stability:

An inhibitor material that has found almost universal approval is known chemically as 2,6-Di-tert-butyl phenol was used. This material is very desirable inhibitor and has outstanding properties which even in small concentrations are stable and effective as oil antioxidant. A concentrations ranging from (0.5- 2 wt%) of inhibitor were used with the original oil, refined oil and its binary mixture (20 vol%) with Jojoba oil tt reduces the alkylperoxy radicals and alkyl hydroperoxide as observed by the following equation:



The rate of oxidation as shown in table (3) and Figs. (1-3) decreased in all samples which is detected from the low values of total acid number for original oil, refined oil and binary mixture with Jojoba respectively, this is due to the termination of the chain reaction of oxidation by the action of hydroxyl group in inhibitor which is suggested to absorb oxidation radicals. The maximum stability is obtained by adding 2% of inhibitor. This means that the effect of inhibitor on stability of oil depends on its concentration and also on the degree of refining.

Table (3): Effect of Inhibitor on the Oxidation stability of Suez oil fraction, Refined Mineral oil, Refined Mineral Oil with 20 vol% Jojoba Oil

Tested sample	T.A.N, mg KOH/g								
	70 hours			140 hours			210 hours		
	0.5%	1%	2%	0.5%	1%	2%	0.5%	1%	2%
Original	0.34	0.28	0.23	0.63	0.54	0.41	0.98	0.83	0.71
Refined Mineral Oil	0.30	0.25	0.17	0.40	0.32	0.26	0.81	0.74	0.60
20% Jojoba Oil	0.18	0.13	0.10	0.30	0.21	0.16	0.61	0.50	0.39

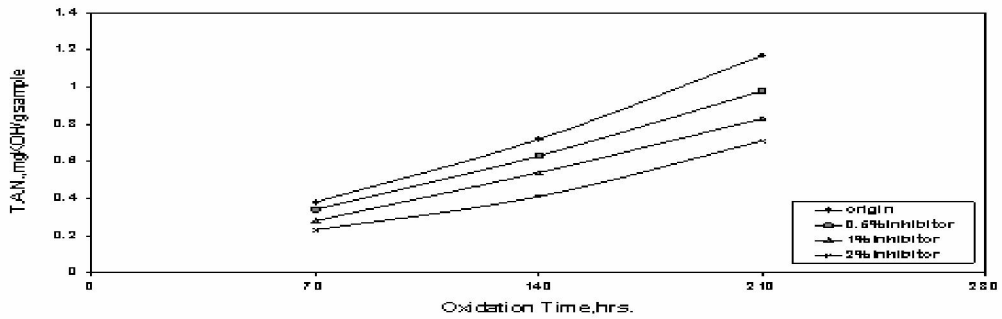


Fig. (1): Effect of DTBPh Inhibitor on the T.A.N. of the Suez Naphthenic Oil Fraction

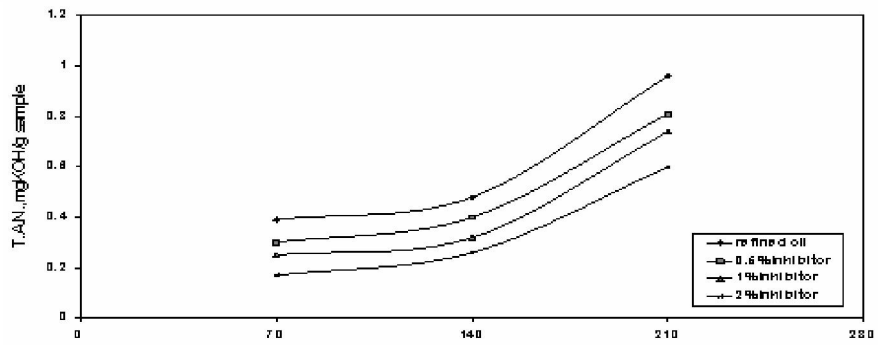


Fig. (2): Effect of DTBPh Inhibitor on the T.A.N. of the Refiend Mineral Oil

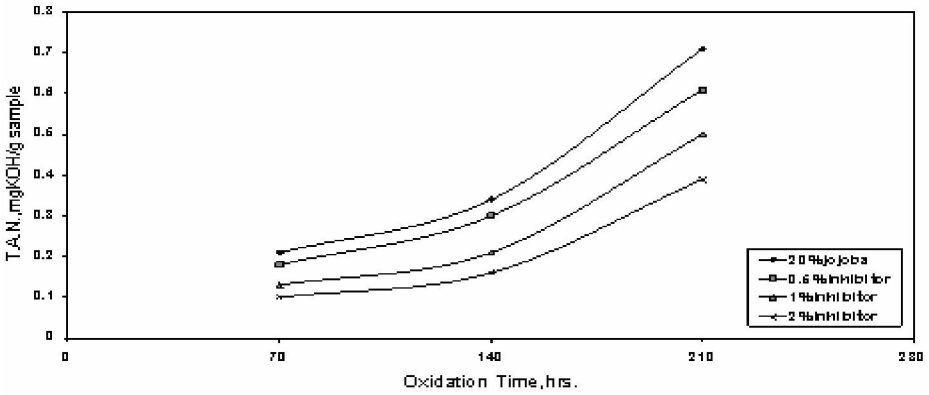


Fig. (3): Effect of DTBPh on T.A.N. of the Refined Mineral oil with 20 Vol % Jojoba Oil.

4. Conclusion:

- The refining processes increase the oxidation stability of the oil.
- The oxidation stability of the binary mixtures is highly improved by increasing the volume percent of jojoba oil.
- The values of power factor (tan δ) for binary mixtures show lower values by oxidation due to high insulating properties of these oils.
- The maximum stability reaches by adding 2 wt % inhibitor to 20 vol % binary mixture of jojoba oil with refined oil.

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