

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231372585>

# Thermo-Oxidative Stability of Mineral Naphthenic Insulating Oils: Combined Effect of Antioxidants and Metal Passivator

ARTICLE *in* INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH · OCTOBER 2004

Impact Factor: 2.59 · DOI: 10.1021/ie049645o

CITATIONS

37

READS

92

9 AUTHORS, INCLUDING:



**Raimundo Crisostomo Rabelo Neto**

Instituto Nacional de Tecnologia

19 PUBLICATIONS 137 CITATIONS

SEE PROFILE



**Celio Loureiro Cavalcante Jr.**

Universidade Federal do Ceará

148 PUBLICATIONS 1,361 CITATIONS

SEE PROFILE



**Diana Azevedo**

Universidade Federal do Ceará

132 PUBLICATIONS 1,457 CITATIONS

SEE PROFILE

## APPLIED CHEMISTRY

## Thermo-Oxidative Stability of Mineral Naphthenic Insulating Oils: Combined Effect of Antioxidants and Metal Passivator

R. Crisóstomo Rabelo Neto, Daniel O. Lima, Thauzer D. S. Pinheiro, Rômulo F. Almeida,<sup>†</sup> Tereza N. Castro Dantas,<sup>†</sup> Michelle S. G. Dantas,<sup>‡</sup> M. Adelina S. Araújo, Célio L. Cavalcante, Jr., and Diana C. S. Azevedo\*

GPSA (Grupo de Pesquisas em Separações por Adsorção), Department of Chemical Engineering, Universidade Federal do Ceará (UFC), Campus do Pici, bl. 709, Fortaleza, CE, 60.455-900, Brazil

The oxidation of mineral oils is the most important cause of poor power transformer performance. High voltages, high temperatures, and the presence of oxygen and metallic surfaces are some of the factors that may trigger oxidation reactions. The use of antioxidant additives and metal passivators in insulating oils has the purpose of improving their performance, by increasing their stability to oxidation so as to ensure a more reliable operation of the transformer. This work presents a kinetic experimental study of the oxidation reactions of a naphthenic mineral oil (with and without additives) as a function of temperature. Oil samples were doped with phenolic antioxidants (AOX), a metal passivator (MPA), and combinations of these (AOX and MPA) in order to verify the efficiency of such additives in increasing thermo-oxidative stability. All doped and nondoped oil samples were submitted to an accelerated oxidation test according to modified ASTM D-2440 method. The level of degradation was assessed by monitoring the area under the carbonyl band (around 1713  $\text{cm}^{-1}$ ) in the FTIR spectrum and comparing it to that obtained for the new nonoxidized oil. The results obtained for the oxidation of nondoped oil samples showed that the kinetic behavior may be well represented by a first-order homogeneous reaction rate law, with energy of activation around 10 kcal/mol. Our results also show that hindered phenolic antioxidants significantly reduce the formation of oxidation products. The addition of a metal passivator, even at very low levels (8 ppm), causes a synergetic effect with all antioxidants tested, leading to a significant improvement in the resistance of the oil against oxidation.

## Introduction

Mineral oils used for electrical insulation are complex mixtures of linear saturated hydrocarbons (paraffins), cyclic saturated hydrocarbons (naphthenes), aromatic hydrocarbons, and a small fraction of non-hydrocarbons, with hundreds of individual compounds. These oils may be classified as paraffinic or naphthenic, depending on the predominant class of hydrocarbons, paraffins, or naphthenes.<sup>1</sup> Insulating oils, also called transformer oils, should have a high dielectric breakdown voltage and allow fast dissipation of heat.<sup>2</sup> In the dielectric function, the oil insulates the bare metallic surfaces of the power transformer, fills up the voids between the energized parts, and impregnates the paper linings, preventing the formation of a voltaic arc between conductors that present electric potential difference. In the function of heat dissipation, the oil acts as a

transport fluid for the heat generated in the spirals due to the process of energy conversion.<sup>3</sup>

The commercially available insulating oils are produced from base oils, mainly of mineral origin. Norm ASTM D-3487<sup>4</sup> classifies new mineral isolating oils in two types, regardless the origin of the crude oil and the refining process. Oils of type I are moderately resistant to oxidation whereas those of type II present a high resistance to oxidation. The oils of type I are commercialized without antioxidant addition, since they contain natural inhibitors. On the contrary, artificial inhibitors must be added to oils of type II in order to enhance their oxidation stability.<sup>5</sup>

Insulating oils are susceptible to oxidation, which leads to the formation of compounds such as acids, aldehydes, esters, ketones, peroxides, and alcohols. These products not only affect the insulating properties of the oil, but also form sludge, which modifies the heat transfer properties of oil. This harms seriously the performance of the transformer, reducing its service life.<sup>6</sup> Oxidation is mainly caused by exposure to high temperatures in the presence of oxygen, metals (Cu and Fe), and humidity. The oxidation of the oil results in the formation of polar (oxygenated) compounds, which are responsible for the increase in acidity of the oil, and consequently decreases the dielectric breakdown voltage

\* Corresponding author. E-mail: dianacsa@ufc.br.

<sup>†</sup> Current address: Department of Chemistry, Universidade Federal do Rio Grande do Norte, Lagoa Nova, s/n, Natal, RN, 59.072-970, Brazil.

<sup>‡</sup> Current address: Universidade Corporativa—PETROBRAS, Rua General Canabarro, 500, 4° andar, Maracanã, Rio de Janeiro, RJ 20.271-900, Brazil.

**Table 1. Properties of the Mineral Naphthenic Oil**

appearance	clean
chlorides	absent
color	3.0
density at 20/4 °C (g/cm <sup>3</sup> )	0.8918
corrosive sulfur	noncorrosive
total sulfur by X-ray fluorescence (%)	0.0178
dielectric dissipation factor at 90 °C (%)	0.30
total acidity (mg KOH/g)	0.000
refractive index at 20 °C	1.4628
aniline point (°C)	75.67
pour point (°C)	-32
flash point (°C)	164
dielectric breakdown voltage (kV)	36.3
interfacial tension at 25 °C (mN/m)	42.33
water content (ppm)	55.34
viscosity at 40 °C (cSt)	9.7001

and increases the interfacial tension. Attempts have been made to increase the resistance to oxidation by tailoring the refining process, but sometimes the upgrading obtained is not sufficient to reach the desired performance. Another way of inhibiting oxidation reactions is the addition of antioxidants, which ensures a high oil oxidative stability.

2,6-Di-*tert*-butyl-4-methylphenol, also called 2,6-di-*tert*-butyl-*p*-cresol (DBPC), is the most frequently used antioxidant in insulating oils. Its action consists of capturing the free radicals generated by heat. Metal deactivators and passivators can also be added to the insulating oil together with antioxidants in order to improve the resistance of the oil to oxidation.<sup>6–8</sup>

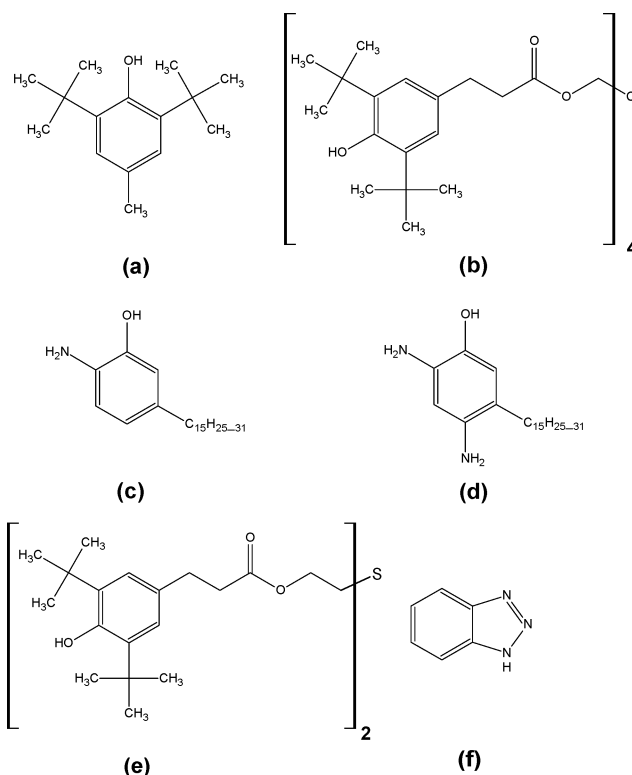
In this work, accelerated oxidation tests were carried out for a naphthenic mineral oil without additives at different temperatures in order to establish an oxidation reaction rate law. The same experimental procedure was applied to oil samples doped with antioxidants (AOX), metal passivator (MPA), and combinations (AOX + MPA) thereof. The synergism between phenolic antioxidants and a metal passivator was investigated with the purpose of improving the oxidative stability of the insulating oil.

## Experimental Section

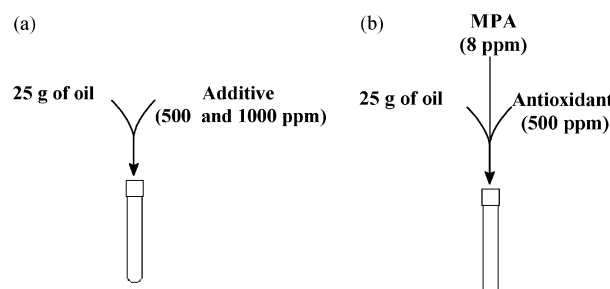
**Materials.** All experiments were performed with a naphthenic mineral oil processed by hydrotreating a vacuum gas oil from the crude Bachaquero (Venezuela). Samples were kindly supplied by Lubrificantes e Derivados de Petróleo do Nordeste, LUBNOR/PETROBRAS (Brazil). Table 1 summarizes the main properties of this oil.

The insulating oil was doped with five different phenolic antioxidants, 2,6-di-*tert*-butyl-4-methylphenol (AOX1), tetrakis[methylene(3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate)]methane (AOX2), 2-amino-5-pentadecylphenol (AOX3), 2,4-diamino-5-pentadecylphenol (AOX4), and thiodiethylenebis(3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate) (AOX5), and with the metal passivator *n*-(1,2,3-benzotriazole) (MPA). Antioxidants AOX3 and AOX4 were obtained from cashew nut shell liquid, whereas the others are commercially available. The chemical structures of these substances are presented in Figure 1.

**Accelerated Oxidation Tests.** Experiments were carried out in a bench-scale oxidation apparatus, with simultaneous capacity for 12 samples. Each oil sample was placed in a 100-mL vessel of glass, kept at constant temperature, in the presence of a copper wire spiral that acts as a catalyst and is under constant flow of oxygen,



**Figure 1.** Structures of antioxidants AOX1 (a), AOX2 (b), AOX3 (c), AOX4 (d), and AOX5 (e) and of additive metal passivator MPA (f).



**Figure 2.** Doping of the insulating oil with the individual additives (a) and with antioxidant and MPA (b).

as described in modified ASTM D-2440 method.<sup>9</sup> The nondoped oil was oxidized at 90, 100, 110, and 120 °C. Samples were collected at regular time intervals and analyzed by FTIR spectroscopy.

For the tests with doped oil samples, each of the five antioxidants and also the metal passivator alone was added to oil in the proportions of 500 and 1000 ppm, as shown in Figure 2a. Following the tests with individual additives, the oil samples were doped with 500 ppm of the antioxidant and 8 ppm of the metal passivator (MPA) in order to analyze the synergic action of the two species (see Figure 2b).

After doping, the samples were submitted to the accelerated oxidation test for 164 h, under an oxygen flow of 1.0 L/h, in the presence of a copper wire spiral that acts as catalyst, at 100 °C, in accordance with the method ASTM D-2440 modified<sup>9</sup> (see Figure 3). After the oxidation, the samples were filtered in order to separate the insoluble oxidation products. The filtrate was kept in a sealed vial at 4–8 °C, so as to interrupt the oxidation reactions, before the analytical procedures could be performed.

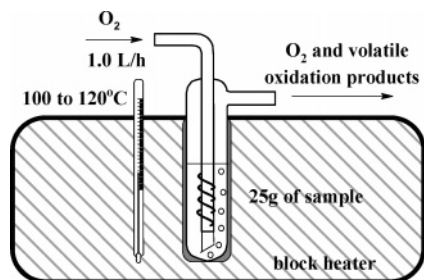


Figure 3. Schematic representation of accelerated oxidation test.

#### Fourier Transform Infrared Spectroscopy (FTIR).

Oxidized oil samples were analyzed by infrared spectroscopy. In this study, a BIO-RAD FX-3000 spectrophotometer was used, equipped with a DTGS cooled detector and KBr beam splitter. Wavelengths were scanned in the range  $400\text{--}4000\text{ cm}^{-1}$ , with a resolution of  $4.0\text{ cm}^{-1}$ . The samples were analyzed in a standard cell with an optical path of  $2.0\text{ mm}$ . The oxidation of the oil samples was quantified by calculating the area of the spectral band around  $1713\text{ cm}^{-1}$ , measured from  $1639$  to  $1835\text{ cm}^{-1}$ . This band is characteristic of the axial deformations of carbonyl bonds ( $\text{C}=\text{O}$ ), present in the majority of the oxidation products, as illustrated in Figure 4. According to several authors,<sup>10–14</sup> this technique is acknowledged as a satisfactory measure of the level of oil degradation, since the carbonyl band is not found in the spectrum of fresh oil. For the calculation of the area under the carbonyl band, the spectrum of oxidized oil is subtracted from that of the fresh oil. The band is centered at approximately  $1713\text{ cm}^{-1}$ , and the baseline is defined from  $1635$  to  $1835\text{ cm}^{-1}$ .

#### Kinetic Model for Oxidation Reactions

The reaction mechanisms proposed in the literature for the oxidation of mineral oils involve numerous steps.<sup>8,13–19</sup> The reactivity of each intermediary species is different, and hence, establishing a detailed kinetic law is not a simple task. Alternatively, simple and straightforward reaction models may be applied to experimental data in order to find parameters of practical relevance, such as rate constants and energies of activation. This work proposes to assemble all hydro-

carbons susceptible to oxidation as a theoretical component A and the oxidation products (containing the carbonyl group) as component B, so that all the complex oxidation reactions may be represented by a simple homogeneous irreversible first-order kinetic law:



The following assumptions are taken into account: isothermal system; perfect mixing;  $\text{O}_2$  in excess; hydrocarbons susceptible to oxidation initially present in finite concentration,  $C_{A0}$ ; irreversible first-order homogeneous reaction; constant volume,  $V$ . Applying a mass balance for component B leads to the following equations:

$$\frac{dC_B}{dt} = kC_A \quad (1)$$

$$\frac{dC_B}{dt} = k(C_{A0} - C_B) \quad (2)$$

$$\int_0^{C_B} \frac{dC_B}{(C_{A0} - C_B)} = \int_{t_{\text{ind}}}^t k dt \quad (3)$$

$$C_B = C_{A0}(1 - e^{-k(t - t_{\text{ind}})}) \quad (4)$$

where  $t_{\text{ind}}$  is the induction period and  $k$  is the kinetic rate constant. It should be a function of temperature according to Arrhenius equation, eq 5. Hence, the energy of activation may be easily obtained from values of  $k$  obtained at different temperatures.

$$\ln(k) = \ln(k_0) - \frac{E_a}{R} \frac{1}{T} \quad (5)$$

#### Results and Discussion

**Accelerated Oxidation Tests of Nondoped Oil Samples.** Figure 5 shows a magnified region of the FTIR spectra obtained for the nondoped oil samples submitted to the accelerated oxidation test. As the oxidation proceeds and the temperature increases, the area of the band at  $1713\text{ cm}^{-1}$  becomes wider and

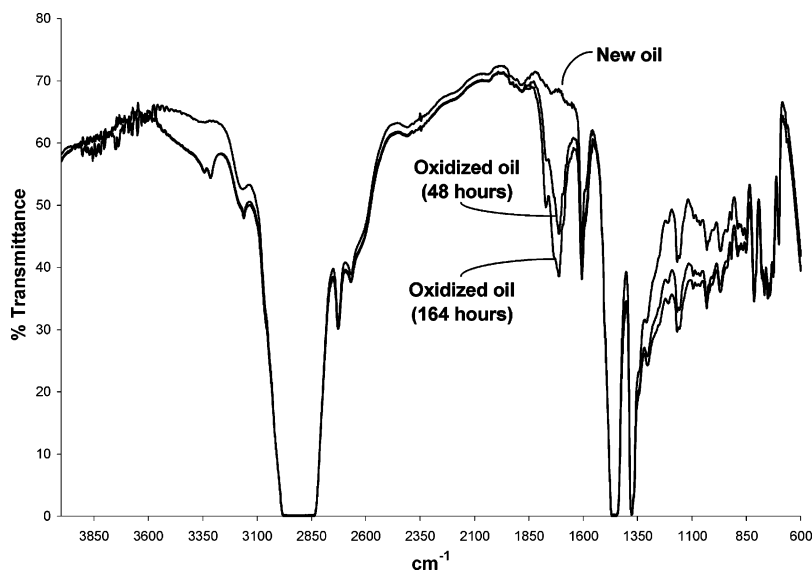
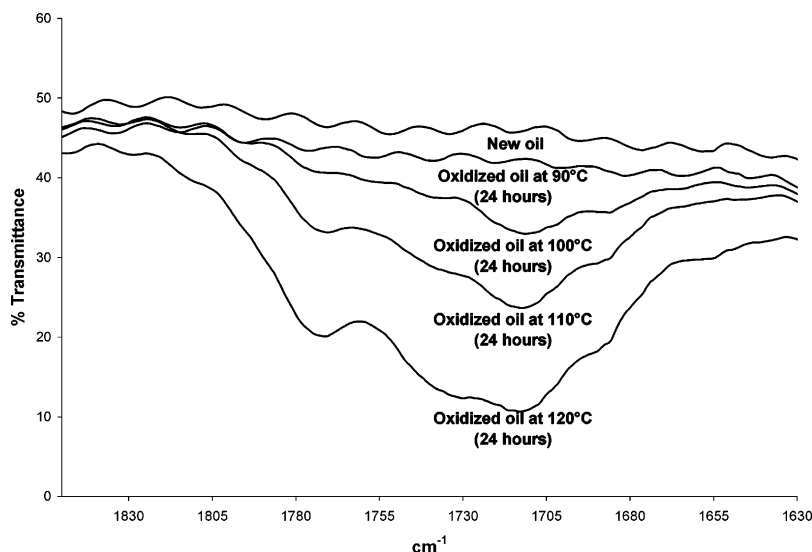
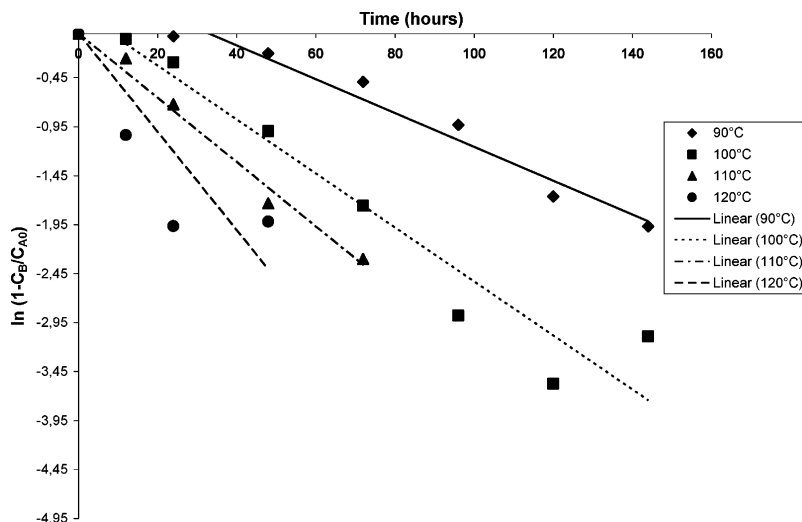


Figure 4. Infrared spectra of oil samples at different times of oxidation,  $100\text{ }^{\circ}\text{C}$  under oxygen flow rate  $1.0\text{ L/h}$ .



**Figure 5.** Magnified region of carbonyl in FTIR spectra of a nondoped oil sample submitted to the accelerated oxidation test at the temperatures of 90, 100, 110, and 120 °C.



**Figure 6.** Plot of  $\ln(1 - C_B/C_{A0})$  against time of oxidation for the tests with nondoped mineral oil at 90, 100, 110, and 120 °C in the presence of a copper spiral and oxygen flow rate of 1.0 L/h.

deeper, indicating an increasing level of degradation and also a greater variety of oxidation products.

Samples of nondoped oil were collected at 12, 24, 48, 72, 96, 120, 144, and 164 h at four different temperatures. Figure 6 shows the evolution of the area of the carbonyl band in the FTIR spectrum of each of the collected samples. At 90 °C, the carbonyl band was only detected to an appreciable level after the first 24 h. The period where no appreciable degradation is observed is called period of induction,  $t_{ind}$ . The higher the temperature, the shorter the induction period becomes. At 110 and 120 °C, an appreciable amount of oxidation products is detected only 12 h after the start of the oxidation tests.

Figure 6 shows  $\ln(1 - C_B/C_{A0})$  versus  $t$  for the oxidation tests of nondoped mineral oil at 90, 100, 110 e 120 °C.  $C_B/C_{A0}$  was taken as the ratio between the carbonyl band area obtained for a sample at a given time and that obtained after 164-h oxidation at the same temperature. Note that, for all temperatures studied, the FTIR carbonyl band areas reach a constant size before 164 h. This fact supports the assumption that all initially oxidizable hydrocarbons have reacted after 164 h in all cases studied. If the proposed model

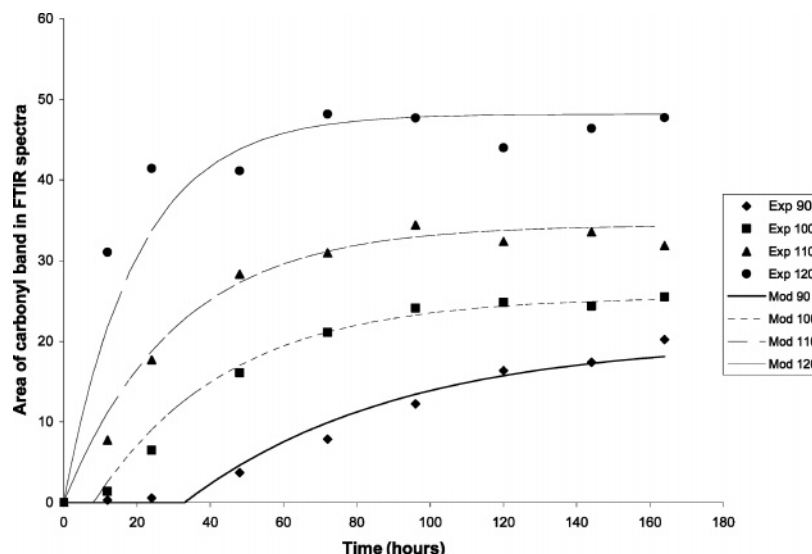
**Table 2.** Reaction Rate Constant ( $k$ ), Induction Period ( $t_{ind}$ ), and Correlation Coefficient ( $R^2$ ) Calculated Assuming a Homogeneous First-Order Irreversible Rate Law

temp (°C)	$k \times 10^3$ (h <sup>-1</sup> )	$t_{ind}$ (h)	$R^2$
90	17.3	33.0	0.961
100	27.6	8.1	0.924
110	32.8	0.0	0.987
120	48.1	0.0	0.917

adequately represents the experimental data, one should obtain straight lines, with slope equal to the rate constant  $k$ . The points where the lines intercept the abscissa are the induction periods for each temperature. Table 2 summarizes the values of  $k$  and induction period obtained for each temperature.

Applying the Arrhenius equation, eq 5, to the rate constant values obtained for four different temperatures, the energy of activation for the oxidation reaction of nondoped oil was found to be 9.56 kcal/mol. This is consistent with the value of 11 kcal/mol, reported by Krishnamoorthy et al.<sup>20</sup> for insulating paraffinic mineral oils. Other authors<sup>10,13,21</sup> have also reported activation energies between 11 and 15 kcal/mol for several lubricant oils.





**Figure 7.** Theoretical curves and experimental FTIR carbonyl band areas obtained for nondoped oil samples at different temperatures.  $O_2$  flow rate of 1.0 L/h.

**Table 3. Normalized Carbonyl Band Areas Obtained for Doped Oil Samples Using Individual Additives<sup>a</sup>**

additive	additive content (ppm)	normalized carbonyl band area ( $A_d/A_{nd}$ )
none	0	1.000
AOX1	1000	0.285
	500	0.629
AOX2	1000	0.000
	500	0.551
AOX3	1000	0.423
	500	0.574
AOX4	1000	0.404
	500	0.589
AOX5	1000	0.000
	500	0.077
MPA	500	1.153

<sup>a</sup> Test conditions: 100 °C,  $O_2$  flow rate of 1.0 L/h, 164 hours.

Figure 7 shows the experimental kinetic curves (points) as compared to the curves obtained from eq 4, using the values of  $k$  and  $t_{ind}$  shown in Table 2. The theoretical curves satisfactorily match the experimental data. The very reasonable agreement between the calculated energy of activation and those reported in the literature shows that, despite its simplicity, a first-order homogeneous reaction model may be used for preventive and corrective procedures in transformer oils.

**Effect of Individual Additives in the Oxidation Tests.** Table 3 shows the results of the oxidation tests for individual additives with doped and nondoped oil at 100 °C after 164 h. The results are expressed as the ratio between the area of the carbonyl band obtained for the doped ( $A_d$ ) and nondoped ( $A_{nd}$ ) oil samples under the same experimental conditions.

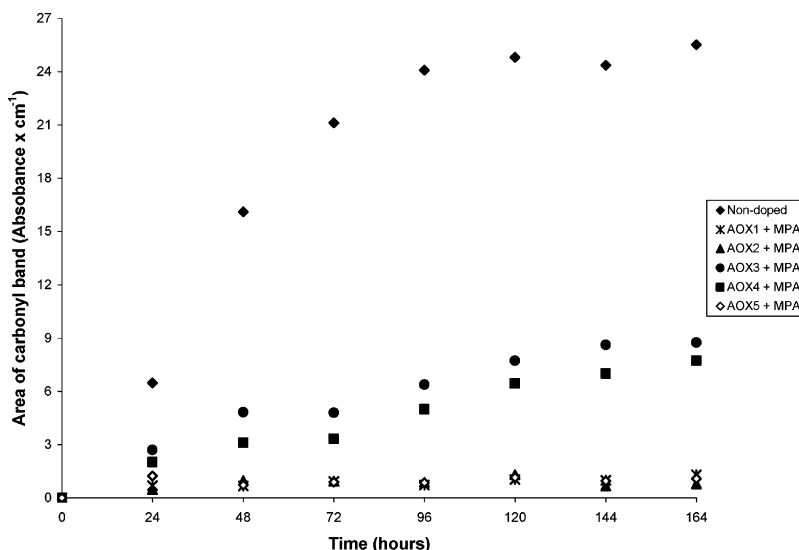
As discussed before, oxidation products containing the carbonyl group appear in the nondoped oil to a significant extent. Doping the oil with phenolic antioxidants caused a marked reduction in the intensity of the spectral band around  $1713\text{ cm}^{-1}$ , mainly for the highest concentration of antioxidant (1000 ppm), indicating the inhibition of the oxidation by these substances. However, doping with only metal passivator (MPA) did not show the same effect. On the contrary, a more pronounced degree of oxidation was observed. Note that, in the tests with antioxidants AOX2 and AOX5, the final level of degradation was lower to that of the nondoped

oil even at the concentration of 500 ppm. When the oil samples were doped at 1000 ppm, no oxidation was observed after 164 h. The additives AOX1, AOX3, and AOX4 were less effective than AOX2 and AOX5. The carbonyl band area was significantly reduced as compared to that for the nondoped oil; however, oxidation levels were much higher than for AOX2 and AOX5, even at 1000 ppm.

**Synergetic Effect of Antioxidants and Metal Passivator.** After the evaluation of the individual action of antioxidants, oxidation tests were carried out with a combination of antioxidant and metal passivator under the same operating conditions as for the previous experiments. The evolution of the carbonyl band area with time is shown in Figure 8. For all five antioxidants, the addition of MPA delayed the oxidation process, which is clear evidence of the synergetic effect between antioxidants and metal passivator by isolating the catalytic effect of the metal surface. This effect was more pronounced for antioxidants AOX1, AOX2, and AOX5. Even after 164 h, the carbonyl spectral band had a practically constant and reduced area, indicating incipient degradation.

Regarding the tests with additives AOX3 and AOX4, the addition of MPA reduced the levels of oxidation as compared to the antioxidant itself. For both, a mild and approximately constant oxidation rate was observed between 72 and 144 h. At the end of the experiment (164 h), the degradation levels were lower than those obtained for AOX3 and AOX4 without MPA. Table 4 summarizes the normalized carbonyl band areas, obtained for each case after 164 h, and the percent reduction in the level of oxidation of the insulating oil with the addition of MPA.

The results of Table 4 show that the combined use of antioxidants and metal passivator led to an expressive improvement of the resistance to oxidation, even in low concentrations of antioxidant, providing evidence that the protection of the metallic surface delayed efficiently the formation of free radicals (initial stage of the oxidation). The antioxidants act, initially, by donating a protonic hydrogen, which links to hydrocarbonic radicals, such as hydroperoxides and/or other radicals that promote the oxidative process of decomposition of oil. The efficiency of these antioxidants is closely related



**Figure 8.** Transient evolution of the area of the carbonyl FTIR spectral band for oil samples doped with antioxidant (500 ppm) and metal passivator MPA (8 ppm) as compared to a nondoped sample. Experimental conditions: 100 °C and O<sub>2</sub> flow rate of 1.0 L/h.

**Table 4. Evaluation of the Synergism between Antioxidant Additives and the Metal Passivator in the Oxidation Tests at 100 °C and Flow of O<sub>2</sub> of 1.0 L/h**

sample	ratio between band areas ( $A_d/A_{nd}$ )	reduction in the level of oxidation with the use of additives (%)
nondoped oil	1.000	0.0
Antioxidant (500 ppm) + MPA (8 ppm)		
AOX1 + MPA	0.051	94.1
AOX2 + MPA	0.000	100.0
AOX3 + MPA	0.342	65.8
AOX4 + MPA	0.302	69.8
AOX5 + MPA	0.000	100.0
Antioxidant (500 ppm)		
AOX1	0.629	37.1
AOX2	0.551	44.9
AOX3	0.574	42.6
AOX4	0.589	41.1
AOX5	0.077	92.3

to the characteristics of the groups linked to the aromatic ring. The electron donor character of the substituent can increase the electronic density of the phenolic oxygen or nitrogen atoms,<sup>22</sup> allowing the antioxidant to most readily inactivate the radicals.

It has been reported that benzotriazole (MPA) can be chemisorbed onto copper metallic surfaces to form polymeric films.<sup>23</sup> Hence, the polymeric film covering the metallic surface prevents oxygen from being adsorbed, which attenuates the catalytic role of the metal surface in the formation of oxidation products.

The combined effect of these two types of action reduces the speed of propagation of the chain reactions by preventing the formation of new radicals at the same time that the catalytic action of the metal is attenuated. Therefore, the overall concentration of radicals in the oil is drastically reduced, which increases the period of induction and the stability of the oil to oxidation.

## Conclusions

The experimental data for the accelerated oxidation of a mineral naphthenic oil were well adjusted by a simple reaction rate model assuming a pseudo-homogeneous, first-order, irreversible reaction rate law. Although this model oversimplifies the actual reaction mechanisms involved, it may be useful to predict the

degree of degradation of the soluble phase of an oil as a function of time for corrective and preventive purposes. Not only was the agreement between experimental and theoretical data satisfactory, but also the estimated energy of activation was found to be consistent with data previously reported. The study with doped samples showed that AOX2 and AOX5 antioxidants were the most effective in preventing oxidation, perhaps because their chemical structure is more sterically hindered than the others. The metal passivator alone did not reduce the levels of degradation. Nevertheless, the synergism between metal passivator and antioxidant effectively increased the resistance against oxidation of the mineral insulating oil as compared to the isolated action of the antioxidants. The addition of as little as 8 ppm of metal passivator caused a decrease in oxidation levels of 94%, 100%, and 100% in the presence of AOX1, AOX2, and AOX5 antioxidants as compared to the nondoped oil. On the basis of these data, this concentration (500 ppm) of the alternative antioxidants should be enough to achieve higher oxidation stability.

## Acknowledgment

The authors thank FINEP, Petrobras, ANP, and CNPq for grants and financial support.

## Literature Cited

- (1) Erhart, L.; Rey, E.; Sutter, H. Recherches Nouvelles Concernant les Huiles Isolantes à l'aide des Méthodes Chromatographiques Modernes. In *Proceedings of CIGRÉ SESSION 1996*, Paris, 1996, p 21.
- (2) Clark, F. M. *Insulating Materials for Design and Engineering Practice*. J. Wiley and Sons: New York, 1962.
- (3) Dhiba, D. Étude du Vieillessement de l'isolation Papier/huile dans les Transformateurs de Puissance: Influence des inhibiteurs d'Oxidation. D.Sc. Thesis, Institute National Polytechnique de Toulouse, Toulouse, 1995.
- (4) ASTM D-3487. Specification for Mineral Insulating Oil Used in Electrical Apparatus. *1998 Annual Book of ASTM Standards, Petroleum Products and Lubricants (I)*; 1998.
- (5) Sierota, A.; Rungis, J. Electrical Insulating Oils Part I: Characterization and Pretreatment of New Transformer Oils. *IEEE Electrical Insulation Magazine* **1995**, 11, 8.
- (6) Krishnamoorthy, P. R.; Vijayakumari, S.; Sankaralingam, S. Effect of Antioxidant and Metal Deactivator on the Oxidation of Transformer Oil. *IEEE Trans. Electr. Insul.* **1992**, 27, 271.

- (7) Lamarre, C.; Duval, M.; Crine, J. P. Conduction and Breakdown in Dielectric Liquids. *Proceedings of the 10th International Conference on ICDL*; 1990, p 510.
- (8) Lipshtein, R. A.; Sharhnovick, M. L. *Transformer Oil*; Israel Program for Scientific Translations Ltd.: Jerusalem, 1970.
- (9) ASTM D-2440. Standard Test Method for Oxidation Stability of Mineral Insulating Oil. *1998 Annual Book of ASTM Standards, Petroleum Products and Lubricants (I)*, 1998.
- (10) Adhvaryu, A.; Perez, J. M.; Singh, I. D.; Tyagi, O. S.; Sharman, Y. K. Spectroscopic Studies of Oxidative Degradation of Base Oils. *Energy Fuels* **1998**, *12*, 1369.
- (11) Araújo, M. A. S. Adsorção Aplicada ao Rerrefino de Óleos Lubrificantes Usados. D.Sc. Thesis, COPPE, Universidade Federal do Rio de Janeiro, Rio de Janeiro, 1996.
- (12) Bowman, W. F.; Stachowiak, G. W. Determining the Oxidation Stability of Lubricating Oils Using Sealed Capsule Differential Scanning Calorimetry (SCDSC). *Tribol. Int.* **1996**, *29*, 27.
- (13) Koh, C. S.; Butt, J. B. Experimental and Modeling Study of Kinetics and Selectivity in the Oxidation of a Poly( $\alpha$ -Olefin) Lubricant. *Ind. Eng. Chem. Res.* **1995**, *34*, 524.
- (14) Naidu, S. K.; Klaus, E. E.; Duda, J. L. Evaluation of Liquid-Phase Oxidation Products of Ester and Mineral Oil Lubricants. *Ind. Eng. Chem. Res. Dev.* **1984**, *23*, 613.
- (15) Rabelo Neto, R. C. Estudo e Avaliação da Oxidação em Óleo Mineral Isolante Naftênico. M.Sc. Dissertation, Programa de Pós-Graduação em Engenharia Química, Universidade Federal do Ceará, Fortaleza, 2004.
- (16) Blaine, S.; Savage, P. E. Reaction Pathways in Lubricant Degradation. 2. n-Hexadecane Autoxidation. *Ind. Eng. Chem. Res.* **1991**, *30*, 2185.
- (17) Korcek, S.; Johnson, M. D.; Jesen, R. K.; Zinbo, M. Determination of the High-Temperature Antioxidant Capability of Lubricants and Lubricant Components. *Ind. Eng. Chem. Prod. Res. Dev.* **1988**, *25*, 621.
- (18) Lamare, C. *Resistance to Oxidation of Reclaimed Transformer Oils*; Report 202 T444; Canadian Electrical Association: Montreal, 1986.
- (19) Maleville, X.; Faure, D.; Legros, A.; Hipeaux, J. C. Oxidation of Mineral Base Oils of Petroleum Origin: The Relationship between Chemical Composition, Thickening, and Composition of Degradation Products. *Lubr. Sci.* **1996**, *9*, 60.
- (20) Krishnamoorthy, P. R.; Vijayakumari, S.; Krishnaswamy, K. R.; Thomas, P. Effect of benzotriazole and 2,6 ditertiary butyl paracresol on the accelerated of new reclaimed transformer oils—a comparative study. *Proceedings of the 3<sup>rd</sup> International Conference on Properties and Applications of Dielectric Materials*; 1991, p 732.
- (21) Natarajan, S.; Olson, W. W.; Abraham, M. A. Reaction Pathways and Kinetics in the Degradation of Forging Lubricants. *Ind. Eng. Chem. Res.* **2000**, *39*, 2837.
- (22) Castro Dantas, T. N.; Dantas, M. S. G.; Dantas Neto, A. A.; D'ornellas C. V.; Queiroz, L. R. Novel antioxidants from cashew nut shell liquid applied to gasoline stabilization. *Fuel* **2003**, *82*, 1465.
- (23) Xue, G.; Lu, Y.; Shi, G. SERS studies of synergetic effect in corrosion inhibition for Cu by a two-component inhibitor system of polyvinylimidazole and benzimidazole. *Appl. Surf. Sci.* **1994**, *74*, 37.

Received for review April 30, 2004

Revised manuscript received August 17, 2004

Accepted August 26, 2004

IE049645O