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STUDY OF AGEING AND PROTECTING FACTORS CONCERNING THE PAPER/OIL INSULATION

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Abstract - An original approach based on the method of experiment design in dynamic mode is proposed in order to study the effect of ageing factors on the paper/oil insulation in power transformers. The relevant calculations are described. The influence of the effects of each factor (temperature, oxygen pressure, catalyst and antioxidant) is quantified and discussed. Finally, a comparative study of three classes of antioxidant (phenols, amines and thiols) enabled the classification of these additives according to their reactivity and their efficiency with respect to the protection of mineral insulating oils and the depolymerization mechanisms of paper.

1 INTRODUCTION

Protection against the ageing of paper/oil insulation has always been a preoccupation for manufacturers and users. The use of inhibited insulating oils has been known since 1940. However, the compatibility of oxidation inhibitors with cellulose insulation remains controversial. Indeed, WILPUTTE [1] showed that the degradation of the Kraft paper used in transformers of a power exceeding 1 MVA can be slowed down in the presence of DBPC (2.6-di-tert-butyl-p-cresol). SCHÖBER [2] and SALOMON [3] revealed the problems raised by using inhibited oils and showed the advantages they offer. For WALDON [4], on the other hand, the utilization of DBPC is not recommended in the field of sealed distribution transformers. This interview is confirmed by the tests done by THIBAULT [5] who observed that DBPC accelerated the degradation of paper. Similarly, D.H. SCHROFF and A.W. STANNETT [6] noted the negative effects of inhibitors in certain tests on mock-ups or on transformers without any clear explanation being found. Thus, the effect of inhibitors on the ageing of the paper/oil complex does not always appear to be as positive as in oxidation tests on oil alone. Owing to these divergent points of view, we have conducted a comparative study on three classes of antioxidant, looking not only at their effects on the stability of liquid insulation as regards oxidation but also their role with respect to solid insulation. The first phase of this work led us to draw up an accelerated ageing protocol more suitable than the standards in force for the study of paper/oil insulation and which indicates the effects of the main factors influencing the ageing of the paper/oil insulation. In fact, amongst all the factors likely to affect the phenomenon studied (T°, Cu, O_2, DBPC, H_2O, etc.),we consider that it is of interest to answer the following questions:

- What are the factors having a significant influence ?
- What part of the insulating material do the factors act on ?
- Does this influence vary in the course of time ?

For this purpose, we propose an original approach based on the method of dynamics experiment design. This is a methodological procedure intended for the experiment planning purposes. It is especially well suited to the systematic study of the simultaneous effects of several factors acting on a process. The complete factorial design applied in relation to time allows the above-stated questions to be answered in an optimum manner.

2 EXPERIMENTAL

To study the influence of p factors $X_1 \dots X_2 \dots X_p$, on a response Y taking the values y_i (i = 1 ... N) for N experiments, we define a response function f such that :

$$y_i = f(x_{i1}, x_{i2}, \dots, x_{ip}) + e_i \qquad \text{(I)}$$

where e_i is the experimental error of y_i measurement.
If we assume that f is continuous and indefinitely derivable, we can then perform a Taylor's development in the region of a centre of interest :

$$Y = b_0 + \sum_{i=1}^{p} b_i X_i + \sum_{i=1(i<j)}^{p} b_{ij} X_i X_j + \sum_{i=1(i<j<k)}^{p} b_{ijk} X_i X_j X_k + .. + e \qquad \text{(II)}$$

This polynomial constitutes a good model for the response function, particularly as its degree is high and the experimental space is not very wide. In a limited space, we can perform linear approximation but we can no longer extrapolate. In the case of a very wide space we will be led to use a model with a high degree and, thus, seek many coefficients by conducting numerous experiments. If we limit ourselves to a first degree model and to the principal terms, the relation (II) will be written as follows :

$$Y = b_o + \sum_{i=1}^{p} b_i X_i + e \qquad \text{(III)}$$

i.e. in a matrix form :

$$[Y]=[X][B]+[e] \qquad \text{(IV)}$$

$[Y]$: single-column matrix of responses.

$[X]$: matrix of model.

$[B]$: single-column matrix of model coefficients.

$[e]$: single-column matrix of experimental error.

The answer function is obtained by determining the matrix $[B]$. The coefficients are estimated by the method of least squares : $\sum e_i^2$ must be minimal which entails estimating $[B]$ by means of $[\hat{B}]$ such that :

$$[\hat{B}]=\left([X]^t[X]\right)^{-1}[X]^t[Y] \qquad \text{(V)}$$

$[X]^t$: transposed by $[X]$.

$[\hat{B}]$: matrix of coefficient estimators.

$\left([X]^t[X]\right)^{-1}$: scatter matrix.

The estimate is more satisfactory if the scatter matrix is diagonal. This is the case where $[X]$ is a HADAMARD matrix: $[X]^t[X]=N[I_N]$. Equation (V) is then written as follows :

$$[\hat{B}]=\frac{1}{N}\left([X]^t[Y]\right) \qquad \text{(VI)}$$

The complete factorial design [7] is a model whose matrix is a HADAMARD type. The matrix of experiments, for a complete factorial design with four factors : X_1, X_2, X_3 and X_4 defines the $2^4 = 16$ tests to be performed. Each line represents an experiment where the factors assume two levels corresponding to the limits selected for the study. To allow a simpler representation, the variables Xi are centred and reduced. Their codes are then (+1) and (-1), respectively, at the upper and lower levels :

Factors				Response
X_1	X_2	X_3	X_4	Y
-1	-1	-1	-1	y_1
+1	-1	-1	-1	y_2
-1	+1	-1	-1	y_3
+1	+1	-1	-1	y_4
-1	-1	+1	-1	y_5
+1	-1	+1	-1	y_6
-1	+1	+1	-1	y_7
+1	+1	+1	-1	y_8
-1	-1	-1	+1	y_9
+1	-1	-1	+1	y_{10}
-1	+1	-1	+1	y_{11}
+1	+1	-1	+1	y_{12}
-1	-1	+1	+1	y_{13}
+1	-1	+1	+1	y_{14}
-1	+1	+1	+1	y_{15}
+1	+1	+1	+1	y_{16}

According to relation (VI), the estimator for coefficient b_i will be obtained by the linear combination of responses assigned by the signs of the i^{th} column of the matrix $[X]$ divided by the number of experiments N. This estimator is also defined as half of the main effect of factor X_i, which is the difference between the mean values observed at the upper (+1) and lower (-1) levels of the factor considered.

2.1 Factors and experimental space studied

In order to choose the space of study, we took the basis of the technical specifications most commonly used to evaluate the stability of insulating oils as regards oxidation. Being an uncontrollable factor, water content was not retained in our study. Table 1 summarizes the factors studied and the limits of the experimental space.

Table 1 : Factors and experimental space

Factor	Units	Symbols	Codes	Min.(-)	Max.(+)
Temperature	°C	T	X_1	100(1)	120(2)
Oxygen	bar	pO_2	X_2	0.2(3)	1.0(4)
Catalyst	cm^{-1}	S_{Cu}/V_{oil}	X_3	0.32(5)	0.96(6)
Inhibitor	%	DBPC	X_4	0(7)	0.15(8)

(1) : value for tests CEI 74 [8] and EDF HN 27-S -02 [9].
(2) : value of tests CEI 474 and 813 [8].
(3) : obtained by synthetic air stream at 20% in oxygen.
(4) : obtained by pure oxygen stream.
(5) : value of tests ASTM D2440 [10] and CEI 74 [X].
(6) : value of tests CEI 474 and 813 [7].
(7) : non-inhibited oil.
(8) : minimum for an inhibited oil.

2.2 Responses studied

- Response Y_1: Total acidity number (TAN) which indicates the ageing of the paper/oil complex.
- Response Y_2: Degree of polymerization (DP), the decrease of which indicates the degradation of the paper.

3 RESULTS AND DISCUSSIONS

3.1 Experiment design with oil

The first experiment design concerns only the oil component. This is a non-inhibited paraffinic insulating oil with the following composition : 59% paraffinic carbon, 28% naphthenic carbon, 13% aromatic carbon. The test duration is 400 hours. The results of this test are summarized in Figure 1. We observe two types of curves : three curves with positive effects and one curve with a negative effect. These effects vary during the ageing process. As concerns temperature and copper, these variations are quasi-linear. In the first phase of ageing, a "thermo-oxidizing" effect is observed. The thermal effect becomes preponderant in the second phase. It should be noted that the curve of the effect of oxygen shows a maximum which can be attributed to the formation of intermediate products (hydroperoxides), resulting in kinetics of order 2. Furthermore, the effect of the antioxidant tends towards zero as it is consumed during ageing.

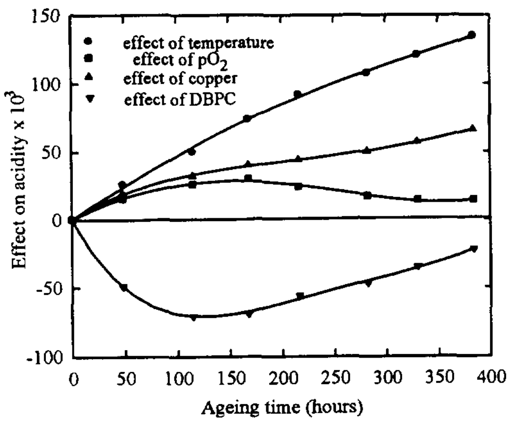

Figure 1.

Experimental design with oil : variations effects on acidity of oxidation factors versus ageing time.

3.2 Experiment design with paper/oil complex

An analogous study was carried out on the paper/oil complex. The paper used is 100% KRAFT paper, 50 µm thick and with a density of 35 g/m^2. The oil is of the same type as that used in the previous experiment design.

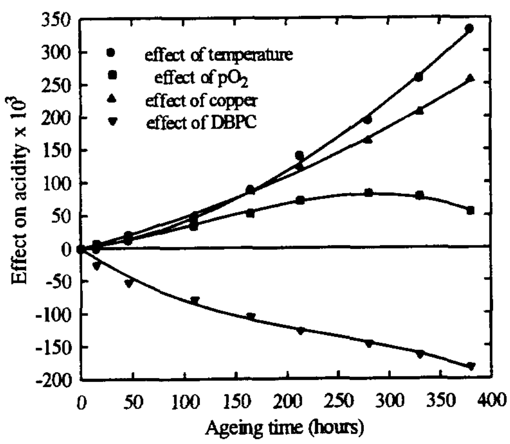

Figure 2.

Experimental design with oil/paper : variations effects on acidity of oxidation factors versus ageing time.

Figure 2 shows the effects variations of factors versus time. Again, two types of curve can be distinguished. In addition, we note that the effects of the four factors, in terms of absolute value, are more pronounced than in the case of oil alone. This observation is explained by the fact that the paper contributes to increasing the acidity. In the presence of paper, copper exerts a strong action on the oxidation of the oil with kinetics practically of order 1, comparable with the situation for temperature. For oxygen, the kinetics remain of order 2 with a maximum value that is offset in time compared with the previous case. It should also be noted that, in the presence of paper, the antioxidant has a more pronounced protective role. It should therefore play an active part with regards to protecting the paper.

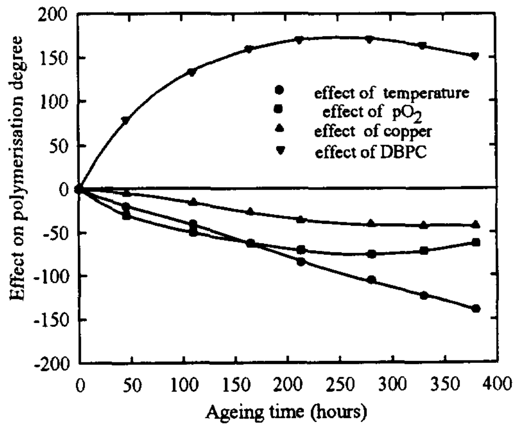

Figure 3.

Experimental design with oil/paper : variations effects on depolymerization of oxidation factors versus ageing time.

Figure 3 shows the variation in these effects on the degree of polymerization of the paper with respect to time. Two types of curve are still found, with their signs inverted, as the answer studied is inversely proportional to the degradation of the paper. Of the four factors studied, DBPC has the greatest effect in this case which allows us to state that it provides considerable protection of the cellulose insulation by slowing down the depolymerization kinetics. The effects of temperature and copper remain practically similar to their effects in the case of oil. The effect of oxygen shows two slight maxima which correspond, in terms of time, to the two types of kinetics for the depolymerization of the paper. This depolymerization is, thus, mainly the result of an oxidizing mechanism. This mechanism is clearly accentuated by the effect of temperature.

A detailed description of the first order effects as well as the interaction effects will be published subsequently in a full paper.

3.3 Comparative study of three classes of antioxidant

This study was conducted in the following experimental conditions :

- temperature : 120°C,
- partial oxygen pressure : 0.2 bar
- area of Cu/volume of oil : 0.96 cm^{-1},
- weight of paper/weight of oil : 0.95,
- antioxidant : 0.15% (by weight) in oil,
- using the same type of oil as previously.

The three classes of antioxidant studied are :

- Phenols, represented here by DBPC,
- Aromatic-amines represented here by PBN,
- Thiols, represented here by decanethiol (RSH).

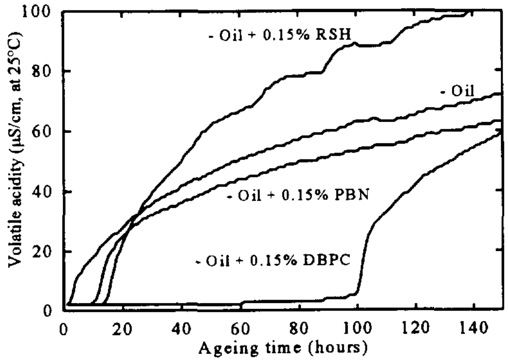

Figure 4.

Volatile acidity versus ageing time, at 120°C.

Figure 4 shows the variations of volatile acidity (measured by conductimetry) versus time. We observed :

- in the absence of antioxidant : a characteristic curve of auto-inhibited oxidation kinetics. The oil studied therefore contains natural inhibitors.
- in the presence of antioxidant : an induction period more or less long according to the nature of the antioxidant. This corresponds to the difference in efficiency of the three antioxidants used. It should be noted that the induction period for DBPC increases in the presence of paper.

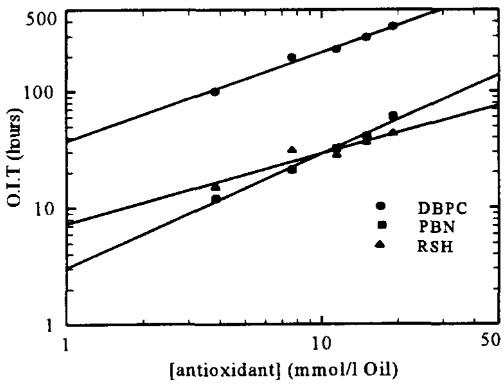

Figure 5.

Oxidation induction time (O.I.T) at 120°C versus antioxidant concentration.

Figure 5 shows the induction period in relation to the concentration of each antioxidant in the oil. At a given concentration, DBPC is by far the best oxidation inhibitor. The performances of PBN and RSH are comparable.

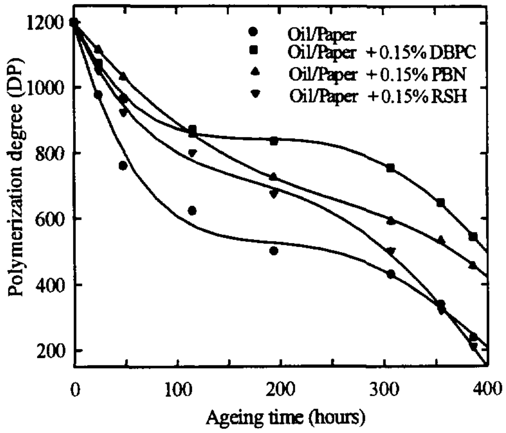

Figure 6.

Polymerization degree variations versus ageing time, at 120°C. Influence of the antioxidant type.

Figure 6 illustrates the influence of the three antioxidants on the depolymerization and, thus, on the degradation of the paper. In the case of a non-inhibited oil, the DP dropped quickly from 1200 to 500. This depolymerization is much less pronounced in the presence of one of the antioxidants. With DBPC in particular, the DP is stabilized at 900 for a long period.

In conclusion, the utilization of antioxidants not only protects the oil against oxidation but also stabilises the depolymerization of the cellulose and leads to a thermally upgraded paper. The efficiency of this protection depends, however, on the type of antioxidant used. Of the three antioxidants studied, DBPC allows the best compromise between protection of the oil and the paper.

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