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FURANIC COUMPOUNDS ANALYSIS AS A TOOL FOR DIAGNOSTIC AND MAINTENANCE OF OIL-PAPER INSULATION SYSTEMS

by

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ABSTRACT

Thermal degradation of cellulosic materials present in electr; cal equipments with oil-paper insulation systems yields different amounts of furanic derivatives. In this report, latest results obtained during laboratory tests are discussed, as well as the effect of temperature, water and oxygen. The relationship between furanic compounds evolution and the change in degree of polymerization is also taken into consideration.

Analysis of furanic compounds dissolved in the oil of transformers in service with a well known thermal history are presented, as well as an statistical survey on the analysis results of some 5.000 transformers in service in several European countries, indicating that furfuraldehyde is the main degradation by-product.

This contribution is a brief summary of the work carried out by CIGRE Task Force 15.01.03 since 1989.

<u>Keywords:</u> Furans, Cellulose, Insulation, Oil, Transformer, Diagnostic, Maintenance condition, Monitoring.

1. INTRODUCTION

During the last years, dissolved gas analysis (DGA) has been one of the most widely used techniques for in service transformers condition monitoring. Usually, carbon monoxide and carbon dioxide concentrations have been associated with cellulosic (paper, pressboard and wood) insulation condition, but these results are not reliable, because these gases can be produced by other sources, as well. Furthermore, gases are rather volatile and are vented off to the atmosphere at a rate depending on their oil solubility and the amount of available mass transfer. This effect is particularly important in open breathing transformers subjected to load cycling. The result is that, on some occasions, paper and related compounds ageing can not be detected unless timely analysis are performed.

On the other hand, it is very easy to take oil

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samples from transformers in service for further analysis of their physico-chemical properties but, although several attempts have been made during the last years [1], this is almost impossible to do with paper, due to its inaccessibility to the outside of the electrical equipment.

For the first time, Burton et al.[2] reported that thermal degradation of insulating cellulosic material yields different amounts of furanic derivatives, like (2FAL), 2 - furfuraldehyde 5 hydroxymethyl furfural dehyde (5HMF), acetylfuran 5-methylfurfuraldehyde (2ACF), (5MEF), furfurylalcohol (2FOL) and furoic acids. These compounds, like water, distribute themselves between the paper and the insulating oil, and can be analyzed by means of High Performance Liquid Chromatography (HPLC) after extraction from the oil by one of the two methods described in a previous paper [3], and now being standardized by IEC. The main advantage when using this technique as a tool for diagnostic and maintenance of oil-paper insulating systems is that these compounds are degradation by-products specific to the paper, and can not be produced by the oil.

2. THERMAL DEGRADATION OF INSULATING CELLULOSIC MATERIALS

It is well known that paper is a mat of cellulose fibres extracted from wood and other vegetable sources. Cellulose is a linear polymer consisting of D-anhydro-glucopyranose units (often abbreviated to anhydroglucose units or even to glucose units) joined together by β -1,4-glicosidic bonds. A number of these chains held together by hydrogen bonds, in which the hydroxyl groups are involved, form a single cellulose fibre.

The thermal degradation mechanism of cellulose molecules is quite complex and it will not be discussed in depth here, but it is generally accepted to be influenced by water (hydrolytic degradation) and oxygen (oxidative degradation), both present in amounts enough in electrical equipments in service.

The combined effect of temperature, water and oxygen produces the breakage of the glicosidic bond with

loss of one hydroxyl group yielding an unstable intermediate called levoglucosane, which evolves towards more stable chemical products like furanic derivatives, gases (carbon oxides) and sugars.

However, experimental results demonstrate that (i) furfuryl alcohol is unstable and quickly evolves towards more stable compounds, (ii) furoic acids are almost insoluble in mineral oil and they remain adsorbed onto the paper surface and (iii) to the best of our knowledge methods for the analysis of sugars in mineral oils have not been developed, but one can assume that their behaviour, in terms of solubility, will be identical than furoic acids.

Depletion in the degree of polymerization is another important consequence of cellulose thermal degradation. Such depletion does not affect much at the dielectric properties of paper, at least during the first degradation steps, but it does affect its mechanical properties, increasing the risk of catastrophic failure if small pieces of paper block the transformer cooling conducts.

On some occasions [2-4] a semilogarithmic relationship between furanic derivatives production and degree of polymerization depletion has been reported, but it seems to be better to introduce the "Knosp's Degradation Factor", which can be related with the degree of polymerization by the following formulas:



where N is the number of bond splits, D_i is the initial degree of polymerization, D is the degree of polymerization at any time, and DF is the degradation factor.

A series of cellulose ageing tests [5] have been performed by heating oil and paper in theratio of 100:1 in 50 ml glass syringes. All samples were analyzed for furans content; dissolved gas; moisture and degree of polymerization. Test variables included:

- temperature: 120ºC and 130ºC
- moisture in paper: 0,2 % and 8 %
- oxygen level in oil: air saturated or completely degassed oils.

These variables lead to the following codes: 120 dd (1209C, dried paper (0,2% water) and degassed oil); 120 du (1209C, dried paper and air saturated oil); 120 8d (1209C, wet paper (8% water) and degassed oil); 120 8u (1209C, wet paper and air saturated oil) and 130 dd (1309C, dried paper and degassed oil). These codes are used throughout table 1 and figures

1 to 3 below, where results of the analysis carried out on samples taken from time to time during the 2000 hours which experiments took long, are shown:

test and an

TABLE 1

Efficiency of by-products formation

| CODE | 00 | യു | 2FAL | 5HMF |
|-------------|------|------------|--------------------|------|
| | a | -21.4 40.0 | | |
| 120 dd | 0,26 | 6,6 | 0,30 | 0,04 |
| - 120 du | 0,26 | 6,2 | 1,20 | 0,02 |
| 120 8d | 0,07 | 2,7 | 0,92 | 0,26 |
| 120 8u | 0,12 | 4,3 | 2,45 | 0,52 |
| 130 dd | 0,13 | 3,0 | 0,28 | 0,05 |
| Control and | | | - 40 I SI - 62 _ 5 | |

Units: Average number of moles formed per chain rupture.



Figure 1.- Relationship between CO evolution and Degradation Factor



Figure 2.- Relationship between CO₁ evolution and Degradation Factor





Figure 3.- Relationship between furfuraldehyde evolution and Degradation Factor

Calculation of test results as average number of moles formed per chain rupture enables to interpret changes in degree of polymerization and by-products evolution in terms of degradation mechanism. So, from the data in table 1, the following conclusions can be drawn:

- Thermal degradation of cellulose is strongly influenced by the amounts of available water and oxygen, not only because higher concentrations of these two compounds lead to higher degradation rates, but also because they determine the relative concentrations of byproducts formed during degradation.
- When the amount of available water is low (120 dd and 120 du) oxygen does not affect very much to carbon oxides formation, but it does affect by a factor of 4 to furfuraldehyde formation.
- On the other hand, an increase of 10°C (130 dd) has not important consequences to the formation of furanic derivatives, except for a short initial period during which oxygen is depleted, but carbon oxides are formed at a lower relative rate.
- Large amount of water (120 8d and 120 8u) leads to significatively lower amounts of carbon oxides increasing the formation rate of furanic derivatives. In this case, the presence of oxygen contributes to higher amounts of all four compounds.

These differences in the formation rates of carbon oxides and furanic derivatives, can be responsable of the lack of success when trying to correlate their concentrations in transformers in service.

Finally, figures 1 to 3 show a reasonable linear relationship between by-products evolution and thermal degradation of cellulosic papers. Such a linear relationship has been found also in other series of quite different experiments.

In effect, a thermogravimetric analyzer to measure thermal degradation of several cellulosic insulating papers by weight loss, was used [6]. These

experiments were carried out under both dynamic (heating samples from 50 to 600 °C) and isothermal (heating samples 2 hours at several selected temperatures) conditions. In both cases, air (thermooxidative degradation) and nitrogen (pure thermal degradation) atmospheres were used. During isothermal experiments, a disposable cartridge packed with silica gel was fitted to the analyzer gas outlet. At the end of every test, the cartridge was washed with methanol and analyzed by HPLC to measure the amount of retained furfuraldehyde. The results obtained with one of the papers are shown in figures 4 and 5. It can be seen that the Arrhenius plots of thermal degradations have the same slope than the Arrhenius plots of furfuraldehyde evolution. In the three cases, dynamic, isothermal and furfuraldehyde evolution, activation energies are in the range from. 90 to 120 kJ/mol. depending upon the papers. (Other furanic derivatives can be found retained on the cartridge, but only at the highest temperatures, and in so low amounts, that it was not possible to calculate their kinetic parameters).



Figure 4.- Arrhenius plots for the thermal degradation of a cellulosic paper under nitrogen.



Figure 5.- Arrhenius plots for the thermal degradation of a cellulosic paper under oxygen.

In figures 4 and 5 K is reaction rate, Y is the number of molecules not yet decomposed [7] and [2FAL] is furfural concentration.

3. AGEING OF TRANSFORMERS IN SERVICE. SOME CASE HISTORIES

A few case histories may serve to illustrate the usefulness of furfural as an indicator of cellulose degradation resulting from localized hot spots or more general overheating.

Periodic analysis at one year interval on a 30 MVA station transformer showed an increase of furfural from "not detectable" to 0.6 ppm. Infrared inspection revealed a loose point at a 6 kV bushing with the overheating involving an internal insulated busbar. In another case, a 70 MVA OFAF step-up transformer operated at nearly full load without forced cooling for approximately 6 hours. Winding temperature was calculated at 150-1802C using equations from the industry loading guide. 0,5 ppm furfural was measured on oil sampled on the next day. Follow-up analysis showed essentially stable values with a slight tendency to decrease in the long term. On both cases, degradation of paper was clearly indicated also by ordinary DGA through the sharp increase of carbon oxides.

The following data (table 2) were obtained from a 7.2 MVA power station exciter feeder. Soon after startup, unusually high top oil temperature called for more detailed investigations. Oil analysis at 1600 hours showed very high levels of CO, CO, and furans, suggesting rapid insulation ageing. An average winding temperature rise of 759C was measured under actual operating conditions as opposed to a 60°C rise design rating. Forced air cooling was fitted to the transformer which caused a drop of 12-159C in top oil temperature. Subsequent oil checks tend to confirm the improved situation although a moderate rise of furfural content is still apparent. The decreasing concentration of hydroxymethylfurfural may be explained as the combined effect of its decomposition and re-absorption onto the solid insulations at the lower operating temperatures. It is important to emphasize the rapid loss of CO and CO, to levels that at 5000 hours are quite in the normal range in contrast to furfural.

TABLE 2

Analysis results of an exciter feeder

| SERVICE (hours) | SAMPLING TEMP.(9C |)α | တ္ | 2FA | l 5HMF |
|--------------------|----------------------|-----|-------|-----|--------|
| 1600 | 83 | 770 | 13900 | 4.5 | 0.73 |
| 1956 | 78 | 560 | 11000 | 5.2 | 0.63 |
| 2935 | 46 | 310 | 5700 | 4.6 | 0.44 |
| 4970 | 69 | 270 | 2800 | 5.8 | 0.33 |

Next example corresponds to a 110 kV, 90 MVA transformer built in 1957. Six months after the last DGA analysis, there was a failure in the 100 kV network and, after several hours under no-load-working, Buchholz alarm took place. DGA did no show proofs of bad paper constitution, even carbon oxides concentrations decreased during this period. However, analysis of an oil sample taken from the bottom of the transformer main tank immediately after the Buchholz alarm indicated 1,7 mg/Kg furfuraldehyde and traces furfurylalcohol. Degree of polymerization

measurements indicated a very bad condition of the paper: 251 at high voltage cable phase W, 117 at selector-circuit phase V, 61 at low voltage cable phase U and 84 at cable to inductance coil.

Although furanic compounds analysis have been applied mainly to power transformers, a few examples about their utility to instrument transformers , have been identified. For instance, table 3 gives the analysis results of four instrument transformers installed in the 50's. After taking the four transformers out of service, transformer 3 in the table was dismantled, and it was found that the inner layers of paper, about 20% of the overall, were burnt; furthermore, the degree of polymerization of the outermost layers of paper was only 300.

| TABL | E 3 | 3 |
|------|-----|---|
|------|-----|---|

Analysis results in instrument transformers

| TRAFO | C0 | C0, | 2FAL | 5HMF | 5MEF |
|-------|-----------|------|------|------|------|
| 1 | 737 | 3630 | 16.3 | 3.4 | 1.4 |
| 2 | 1470 | 8160 | 7.4 | 2.3 | 4.7 |
| 3 | 421 | 2710 | 7.0 | 2.0 | 1.0 |
| 4 | 534 | 3090 | 11.3 | 1.3 | 0.6 |

Finally, furanic compounds analysis have been successfully applied for controlling factory tests of large power transformers [8].

4. STATISTICAL SURVEY

An statistical survey with the analysis results of oil samples taken from 5.005 transformers in service in five European countries has been carried out. Such data has been reported by six laboratories. The number of transformers analyzed by the different laboratories ranges from 140 to 2160 being 87,5 % of the data provided by laboratories D, E and F, as it is shown in table 4.

It can be seen that the two laboratories with the lowest number of results, laboratories A and B, did not report any transformer with more than 5.01 ppm furfuraldehyde. Laboratory C reported nine transformers with furfural concentrations over than 5.01 ppm without indicating if any of these results was over 10 ppm, so these nine results were considered in the range 5 to 10 ppm.

One contributor reported separate statistics for free-breathing and membrane sealed conservator transformers. The latter group contains less frequent and considerably lower levels of furans which can be interpreted as a significant support for the oxygen effect shown by the laboratory tests.

Main differences from laboratory to laboratory can be found in the percentage of transformers with furfuraldehyde content no more than 0,1 ppm (45,3 to 71,8) but if these percentages are summed to the percentage of transformers in the range 0,11 to 0,50, such differences are reduced indicating that the 0,1 ppm level is too low to establish differences.

The 95 % level is located in the range 1 to 5 ppm in all laboratories except in laboratory B which is in the range 0,5 to 1 ppm. The 99 % level is located in the range 1 to 5 ppm for laboratories A and B, in the 5 to 10 ppm range for laboratories C, D and F, and just in 10 ppm for laboratory E.

More interesting seems to be, however, to sort the

| TABLE | 4 |
|-------|---|

Statistical Survey. Number of transformers. Into brackets the relative percentage

| FURFURAL | LAB A | LAB B | LAB C | LAB D | LAB E | LAB F | TOTAL |
|---------------------------------------------------------------------------|---------------------------------------------------------------|----------------------------------------------------------------|----------------------------------------------------------------|----------------------------------------------------------------------|--------------------------------------------------------------------------|--------------------------------------------------------------------------|----------------------------------------------------------------------------|
| TOTAL D | ATA | | | | | | |
| < 0,10 0,11- 0,50 0,51- 1,00 1,01- 5,00 5,01-10,00 > 10,00 | 93(66,4) 25(17,9) 9 (6,4) 13 (9,3) 0 (0) 0 (0) | 140(60,1) 79(33,9) 11 (4,7) 3 (1,3) 0 (0) 0 (0) | 130(51,0) 56(22,0) 20(7,8) 40(15,7) 9(3,5) 0(0) | 583(71,8) 102(12,6) 53 (6,5) 65 (8,0) 8 (1,0) 1 (0,1) | 637(45,3) 363(25,8) 175(12,5) 201(14,3) 15 (1,1) 14 (1,0) | 1117(51,7) 722(33,4) 147 (6,8) 144 (6,7) 25 (1,2) 5 (0,2) | 2700(54,0) 1347(26,9) 415 (8,3) 466 (9,3) 57 (1,1) 20 (0,4) |
| - | Sorted by < 70 | VOLTAGE <u>kv</u> | | | - Sorted < 5 y | by AGE ears | |
| < 0, 0,11- 0,51- 1,01- 5,01-1 > 10 | 10 0,50 1,00 5,00 0,00 ,00 | 1216(47, 740(28, 254 (9, 307(11, 43 (1, 15 (0, | 2) 7) 9) 9) 7) 6) | < 0,11 0,51 1,03 5,01 > | 0,10 - 0,50 - 1,00 - 5,00 -10,00 10,00 | 277(73, 64(17, 17 (4, 16 (4 0 (1 (0, | 9) 1) 5) ,3) 0) 3) |
| | 70-15 | 0 kV | | | 6-10 | years | |
| < 0 0,11- 0,51- 1,01- 5,01- > 1 | ,10 0,50 1,00 5,00 10,00 0,00 | 731(58, 307(24, 94 (7, 101 (8, 7 (0, 4 (0, | 8) 7) 6) 1) 6) 3) | < 0,11 0,51 1,01 5,01 > | 0,10 - 0,50 - 1,00 - 5,01 -10,00 10,00 | 311(74, 72(17, 24 (5, 10 (2, 1 (0, 0 (| 4) 2) 7) 4) 2) 0) |
| | > 150 | kV | | | <u>11-15</u> | years | |
| < 0,11 0,51 1,01 5,01 > | 0,10 - 0,50 - 1,00 - 5,00 -10,00 10,00 | 600(66, 235(26, 39(4, 23(2, 1(0, 1(0, | 7) 1) 3) 6) 1) 1) | <pre>< 0,11 0,51 1,01 5,01 > 1</pre> | 0,10 - 0,50 - 1,00 - 5,00 -10,00 0,00 | 311(58, 142(26, 37 (6, 38 (7, 7 (1, 0 (| 1) 5) 9) 1) 3) 0) |
| | - Sorted by < 30 1 | Y POWER | | | <u>16-20</u> | years | |
| < 0,11 0,51 1,01 5,00 > | 0,10 - 0,50 - 1,00 - 5,00 -10,00 10,00 | 1193(45, 841(31, 258 (9, 301(11, 36 (1, 16 (0, | 1) 8) 8) 4) 4) 6) | < 0,11 0,51 1,01 5,01 > | 0,10 - 0,50 - 1,00 - 5,00 -10,00 10,00 | 372(52, 169(23, 55 (7, 6(13, 8 (1, 7 (1, | 6) 9) 8) 6) 1) 0) |
| <u>30-100 MVA</u> | | | | 21-30 | years | | |
| <pre>< 0,11 0,51 1,01 5,01 ></pre> | 0,10 - 0,50 - 1,00 - 5,00 -10,00 10,00 | 331(53, 184(29, 45 (7, 48 (7, 5 (0, 2 (0, | 8) 9) 3) 8) 8) 3) | <pre></pre> | 0,10 - 0,50 1,00 - 5,00 -10,00 10,00 | 560(47, 351(29, 121(10, 121(10, 18 (1, 6 (0, | 6) 8) 3) 3) 5) 5) |
| | > 100 M | <u>/A</u> | | | > 30 y | ears | |
| <pre>< 0,11 0,51 1,01 5,01 ></pre> | 0,10 - 0,50 - 1,00 - 5,00 -10,00 10,00 | 483(63, 195(25, 39 (5, 32 (4, 7 (0, 1 (0, | 8) 8) 2) 2) 9) 1) | <pre>< 0,11 0,51 1,01 5,01 </pre> | 0,10 - 0,50 - 1,00 - 5,00 -10,00 10,00 | 258(39, 181(27, 88(13, 105(16, 13 (2, 4 (0, | 8) 9) 6) 2) 0) 6) |

transformers depending upon other characteristics like voltage, power and age. Laboratory A did not sort their data, laboratory B only provided data corresponding to transformers higher than 150 kV and 100 MVA without sorting them by age, laboratories C and F only sorted partially their overall data and laboratory D did not sort their data by power.

It can be seen that the highest is the voltage and the power the highest is the number of transformers with very low concentrations of furfural, indicating that bigger transformers, which in most cases are the most important, more cares are taken during their operation in service, in order to ensure a more reliable function. That is the reason why the results of laboratory B provided the lowest furfuraldehyde concentrations and laboratory E the highest ones.

When transformers are sorted by age, the table indicates that, with the exception of the data reported by laboratory E, which deals mainly with low voltage and low power transformers, the condition of most transformers with less than 10 years in service seems to be very good, and the few exceptions can easily be related with thermal defaults, involving the insulating paper.

High furfural concentrations in older transformers can be due to the combined effect of both, thermal defaults and ageing, depending on the furfural concentration and the transformer age, but there is an abnormal and sudden increase in furfural concentration in transformers older than 16 years and up to 30 years. Such an increase can not be explained only by the transformer age, but could be related to the change during the early 60's from Disk type to Lyer type transformers.

5. CONCLUSIONS

Although furanic compounds analysis is a technique described only a few years ago, it seems to be of a great interest as a tool for the diagnostic and maintenance of oil-paper insulating systems, and now is routinely used by many laboratories all around the world. This new technique is not intended to replace DGA, but it could be an interesting complement to identify some problems where cellulosic materials are involved.

Laboratory tests indicated that at least in a temperature range, furanic compounds evolution is directly related to paper ageing. Such direct relationship can be found both using the degree of polymerization depletion or the weight loss, which take place during paper ageing.

Analysis of transformers in service indicate that this method can be successfully applied to identify certain thermal defaults in which cellulosic papers are involved after a sharp increase of furfural content or when such content is in the range 1 to 5 ppm or higher. REFERENCES

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RESUME

La dégradation thermique des matériaux cellulosiques (papier, carton et bois) utilisés dans les systèmes d'isolation des transformateurs produit des quantités variables de dérivés furaniques tels que: le 2furfural (2FAL), le 5-hydroxyméthyl-2-furfural (5HMF), le 2-acétylfurane (2ACF), le 5-méthyl-2furfural (5MEF), le 2-furfurylalcool (2FOL) et des acides furoiques.

Les dérivés furaniques, dont une grande partie reste absorbée dans le papier, sont néanmoins légèrement solubles dans l'huile. Ils peuvent être analysés par chromatographie liquide à haute performance (HPLC). Leur présence peut être utilisée comme outil de diagnostic pour les transformateurs de puissance et de mesure et apporter un complément d'information à l'analyse des gaz dissous.

Le rapport présente les résultats d'essais réalisés dans différents laboratoires européens. L'influence des facteurs suivants sur la dégradation du papier et la production de dérivés furaniques a été étudiée:

- * humidité
- * température
- * oxygène

Ces essais ont montré que le 2FAL est le produit de décomposition prépondérant, que les acides furoiques sont pratiquement insolubles dans l'huile et qu'ils restent absorbés dans le papier et enfin que le 2FOL este instable et se décompose rapidement en d'autres substances. Des relations entre le facteur de dégradation du papier et les concentrations en 2FAL, CO et CO₁ dissous dans l'huile sont proposées.

L'évolution des concentrations en dérivés furaniques dans l'huile de certains transformateurs en service ayant subi des échauffements anormaux est également discutée.

Enfin des études statistiques de la distribution des concentrations en dérivés furaniques, conduites dans plusieurs pays européens, sont également présentées. Il en ressort que le 2FAL est le produit de dégradation principal accompagné de 5HMF et 5MEF et que les concentrations les plus faibles sont associées aux transformateurs de tension et puissance les plus élevées.

Ce rapport est un résumé des travaux du Groupe d'Action CIGRE 15.01.03 entrepris depuis 1989.