Influence of Chemical Structure Changing on Lubricants Behaviour in Service

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This study aimed to highlight the correlation between the changes occurring in the oils chemical structure and the evolution of specific functional characteristics of lubricating oils, during their service cycle. The study focused mainly on turbine oils type that has special requirements in terms of quality performance and also exigent requirements in terms of usage period which must be very long - over 5000 h of operation. For this purpose, it have been tested more features associated with the lubricant's chemical structure and composition and have been highlighted their correlation with the oil performance along its service-life. In fact, there were tested representative functional characteristics of turbine oil type. The research study was developed based on the testing and evaluation results of two turbine oils that were monitored in working conditions, for a period of 12 months. The experimental results emphasized the influence of oil chemical structure changes on the specific characteristics as well as interesting and useful correlations between the evolutions of different characteristics. All the obtained results and conclusions of the turbine oils study allow assessing more effective the lubricants behaviour along their period of use.

Keywords: lubricants, chemical structure, lubricants assessing

The specific consumption of lubricants for a power plant is very high, especially for the turbine oils type. The turbine machines and equipment used for producing energy have a high capacity, so the required oil quantities serving these equipment are very large: a benchmark of 10000 L is a typical one [1].

These important charges of turbine oils involve high financial efforts; therefore it is essential for these lubricants to have a long period of usability, which implicitly assumes a high level of quality. So these lubricants are characterized by a suitable viscosity and viscosity index, high flash point and low pour point, a very good capability of water separation (demulsibility), good protection to corrosion and rust, proper antitrust capacity (low wear scar diameter), very good oxidation resistance (long time for oxidation reaction induction) and high capability of air separation (foam tendency/stability).

In the table no.1 are presented typical characteristics of turbine oils that are specified by different quality standards [2 - 5].

In order to accomplish all these requirements, the turbine oils have to be manufactured from selected base oils and suitable additives.

Considering the severe conditions of turbine oils applications, another very important item in the operation of these oils correlated with the aspects described before, is the ensuring of very careful maintenance and monitoring of their behaviour in service.

That may prevent the occurrence of adverse events in the operation of equipment and allow identifying any problems during of turbine oils service period, in a due time.

Degradation of lubricants quality could have many causes and sources: accidentally blending with another type of lubricant, contamination with dust or water, changing of the oil chemical structure etc.

Considering the permanent progress concerning the equipment design and performance as well as the lubrication management efficiency, the possibility of contamination by different compounds is very low. The main factor which impacts on the lubricant quality is the modification of their chemical structure during the service.

Actually, the oxidation is the most important parameter responsible for the oil degradation and that affects many other representative characteristics like: viscosity, acidity, flammability, foam tendency and stability, demulsibility, cleanliness etc [6, 7].

Therefore, in order to have accurate and representative information about the turbine oils quality level along their period of use, they are tested periodically in conformity with an adequate maintenance program, based on the representative characteristics analysis.

Testing schemes have to highlight the evolution of chemical and physical characteristics with a significant impact on the oil behaviour.

Modification of these characteristics in time, over certain limits, can lead to malfunctions or accidents in equipment operations, so is important to clearly state the accepted range of the characteristics modification.

Setting of the acceptable limits of characteristics variation in accordance with an adequate oil behaviour in the system is not an easy matter to do. Therefore, several parallel tests are needed to analyze the changes of oil characteristics and its influence on the equipment operating parameters.

Starting from these definite aspects, the main purpose of this study was to determine a relevant and efficient method for assessing the lubricant degradation stage by analyze of representative physical, chemical and functional characteristics and to identify the correlations between these characteristics, in order to reduce the number of necessary tests for lubricants quality monitoring.

In this respect, the behaviour of two turbine oils in operation was monitored, for a period of 12 months. These two lubricants had the same initial quality level (the same

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characteristics), were working in similar equipment and conditions, specific for high capacity power plant and they were evaluated in conformity with the same testing program, by analyzing specified representative characteristics.

**Experimental part**

As the volume of analysis for the complete characterization of turbine oils is very high (as could be seen in table 1), a total of four representative features was selected for providing relevant information on chemical structure and behaviour of these oils. The selection of analytical scheme was based on literature data and previous experimental performed studies [8 10].

The evolution of the following characteristics were monitored:

- kinematic viscosity;
- oxidation resistance;
- acidity index;
- foaming properties.

A summary description of the characteristics importance as well as specific testing methods used for their study and control are presented below.

**Viscosity** is the most important characteristic of lubricant oils; the viscosity has to be maintained at almost the same level during the oil service. The significant change of the viscosity could indicate the degradation of the base oil (modification of the chemical structure), the degradation of the viscosity improver additives, the contamination with other compounds etc.

The test method used for viscosity analyzing, during the experimental study, was ASTM D 445. This test method specifies a procedure for determination of the kinematic viscosity by measuring of time for a volume of liquid which flow under gravity through a calibrated glass capillary viscometer [11].

**Oxidation resistance** of oils gives information about their capacity to keep undamaged the chemical structure of the components. Measuring of oxidation is an important task for oil condition monitoring programs. Oxidation of oil is responsible for the occurring of acid components as well as of heavy component structures; this phenomenon has unfavourable consequence on the oil service conditions, generating the compressibility increasing, affecting the effective pressure of the system, the heat transfer and the lubrication capability of the oil [10, 12].

Serious operational problems can occur over oil service time from varnish and sludge formed from oxidized lubricants, as these coatings can obstruct proper cooling of equipment and bearings.

Oxidation resistance capacity of oil can be assessed by various testing methods, some considered “fast”, which have a shorter testing time, and others with an extended duration of testing time.

Rotary bomb method, in conformity with ASTM D 2272 standard, is a relatively fast method, with a quite high degree of accuracy, allowing a proper assessment of oxidation resistance.

This test method utilizes an oxygen-pressured vessel to evaluate the oxidation stability of new and in-service turbine oils, in the presence of water and a copper catalyst coil, at 150°C. Test result consists in measuring the time length in minutes, in which the pressure is maintained constant, at a certain level, in the vessel. When the pressure decrease is considering that the oxidation reactions are starting and the oil chemical structure is changing [13].

**Acidity Index** is also an important parameter in tracking the behaviour of oils in service. Increasing of oil acidity indicate changes of oil chemical structure and occurrence of acidic compounds. These compounds have negative consequences on the oil ability related to corrosion protection ensuring, they have negative influence on the foaming properties and even on the oil lubricating properties. This feature is also in close correlation with the oxidation resistance of the oil.

The testing method used for analyze of oil acidity was ASTM D 974. This test method covers the determination of

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>ISO-VG 32</th>
<th>ISO-VG 46</th>
<th>ISO-VG 68</th>
<th>Test Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density at 15°C, max</td>
<td>0.895</td>
<td>0.895</td>
<td>0.895</td>
<td>ASTM D1217</td>
</tr>
<tr>
<td>Viscosity at 40 °C, cSt</td>
<td>28.8 - 35.2</td>
<td>28.8 - 35.2</td>
<td>61.2 – 74.8</td>
<td>ASTM D445</td>
</tr>
<tr>
<td>Viscosity Index, min.</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>ASTM D 2270</td>
</tr>
<tr>
<td>Flash point, °C, min.</td>
<td>200</td>
<td>200</td>
<td>210</td>
<td>ASTM D 92</td>
</tr>
<tr>
<td>Pour point, °C, max.</td>
<td>- 20</td>
<td>- 20</td>
<td>- 15</td>
<td>ASTM D 97</td>
</tr>
<tr>
<td>Demulsibility, minutes</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>ASTM D 1401</td>
</tr>
<tr>
<td>Copper corrosion</td>
<td>1b</td>
<td>1b</td>
<td>1b</td>
<td>ASTM D 130</td>
</tr>
<tr>
<td>Rust prevention</td>
<td>pass</td>
<td>pass</td>
<td>pass</td>
<td>ASTM D 665</td>
</tr>
<tr>
<td>4-Ball Test : scar diameter (20 daN, 100 min) mm, max.</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>ASTM D 4172</td>
</tr>
<tr>
<td>Rotary Bomb, minute, min.</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>ASTM D 272</td>
</tr>
<tr>
<td>Foam Tendency/Stability, at:</td>
<td></td>
<td></td>
<td></td>
<td>ASTM D 892</td>
</tr>
<tr>
<td>- 24 °C, ml/ml, max.</td>
<td>100 / 0</td>
<td>100 / 0</td>
<td>150 / 0</td>
<td></td>
</tr>
<tr>
<td>- 93.5 °C ml/ml, max.</td>
<td>50 / 0</td>
<td>50 / 0</td>
<td>100 / 0</td>
<td></td>
</tr>
<tr>
<td>- 24°C ml/ml, max.</td>
<td>100 / 0</td>
<td>100 / 0</td>
<td>150 / 0</td>
<td></td>
</tr>
</tbody>
</table>

Table 1

**CHARACTERISTICS OF TURBINE OILS**
acidic or basic constituents in petroleum products and lubricants, soluble or nearly soluble in mixtures of toluene and isopropyl alcohol. New and used petroleum products can contain basic or acidic constituents that are present as additives or as degradation products formed during service, such as oxidation products. The relative amount of these materials can be determined by titrating with acids or bases, specified by testing method [14].

Foaming properties are expressed by tendency and stability of the oil foam. The foaming can generate serious problems in the lubrication systems of turbine oils, high-speed gearing, hydraulic pumps, engine oils etc. Inadequate lubrication, cavitation and overflow loss of lubrication could lead to mechanical failure. The foaming could be caused by polar compounds, by dirt, water etc. The polar compounds formed in the oxidation process could also lead to the formation of polar byproducts that increase the foaming tendency and stability.

Foam tendency and stability of turbine oils was tested in conformity with ASTM D 892 standard method. This test covers the determination of the foaming characteristics of lubricating oils at two reference temperatures, 24 and 93.5°C [15].

As has been previously shown, in order to appreciate the evolution of these features and the correlation between their changes during the oils service, was necessary the study of oils behavior over an extended period of time, on real working conditions. Therefore the experiments were conducted in parallel, on two turbine oils, during a significant long period of time (12 months).

In order to obtain accurate and relevant information, the sample of oils were collected in accordance with a very rigorous procedure: the oil sample was representative, taken from key point of the system, collected in clean vessels, in conditions of system operation [16].

The experimental results, the evolution of the features and related comments are presented further.

### Results and discussions

All the samples of turbine oil were tested in conformity with the analytical established scheme. In this respect the samples collected every each month, for both turbine machines, 1 and 2, were analyzed by testing kinematic viscosity, acidity index, oxidation resistance and foam tendency/stability.

The related results of these characteristics are presented in the table number 2 – for turbine oil 1 and in table number 3 – for turbine oil 2.

For a more conclusive representation of oil behaviour, the evolution of each tested characteristics was represented in parallel, for the both turbine oils, in the diagrams shown in the figure 1, 2 and 3.

It is important to specify that the foam characteristics were represented based on the results related to foam tendency at 24°C (seq.I).

Evaluating the obtained results and related diagrams of monitored characteristics, the evolution of studied oils is presented as follows.

#### Kinematic viscosity

For turbine oil 1, the range of values was between 29.74 cSt to 30.20 cSt and for turbine oil 2, between 29.78 cSt to 30.14 cSt.

It could be said that this feature had a very little variation, which indicates that the oils had not undergone major structural changes, such as cracking of hydrocarbon molecules, nor was contaminated with other components with different viscosities from those of the tested oils. On the other hand, even very low, the slight increase of viscosity could indicate the beginning of oxidation reaction.

#### Acidity number

The values of this characteristic have varied as following: from 1.05 mg KOH/g to 0.094 mg KOH/g corresponding to turbine oil 1 and from 0.99 mg KOH/g to 0.078 mg KOH/g, for turbine oil 2.

<table>
<thead>
<tr>
<th>Testing date</th>
<th>Kinematic viscosity at 40°C, cSt</th>
<th>Acidity Index, mg KOH/g</th>
<th>Oxidation stability, minutes</th>
<th>Foam tendency/stability:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Fresh oil</td>
<td>29.74</td>
<td>1.05</td>
<td>460</td>
<td>100 / 0</td>
</tr>
<tr>
<td>Month 1</td>
<td>29.86</td>
<td>0.87</td>
<td>450</td>
<td>100 / 0</td>
</tr>
<tr>
<td>Month 2</td>
<td>29.91</td>
<td>0.62</td>
<td>440</td>
<td>110 / 0</td>
</tr>
<tr>
<td>Month 4</td>
<td>29.89</td>
<td>0.15</td>
<td>410</td>
<td>130 / 0</td>
</tr>
<tr>
<td>Month 6</td>
<td>30.12</td>
<td>0.081</td>
<td>390</td>
<td>160 / 0</td>
</tr>
<tr>
<td>Month 8</td>
<td>30.14</td>
<td>0.076</td>
<td>360</td>
<td>210 / 0</td>
</tr>
<tr>
<td>Month 10</td>
<td>30.17</td>
<td>0.073</td>
<td>310</td>
<td>280 / 0</td>
</tr>
<tr>
<td>Month 12</td>
<td>30.20</td>
<td>0.094</td>
<td>250</td>
<td>410 / 0</td>
</tr>
</tbody>
</table>

Table 2
EVOLUTION OF TURBINE OIL 1 CHARACTERISTICS ALONG OF 12 MONTHS PERIOD
That evolution could be confusing for the evaluation of the oil behaviour because normally, during his operation in the system, total acidity index should increase, due of the occurrence of acid components resulted from the oxidation process. In fact, the modification of acidity must be analyzed in relation with baseline acidity of the oil. The decreasing of the turbine oils acidity index values within the first ten months can be explained by the consumption of antioxidant additive that has own intrinsic acidity. But, starting from the eleventh month, a slight increasing of acidity has been recorded and that could be correlated with the enhancement of oxidation process and consumption of additive.

**Oxidation stability**

The oxidant resistance corresponding to turbine oil 1 had specific values between 460 min and 240 min and, for turbine oil 2, specific values between 480 min and 305 min.

Oxidation resistance has remained at high absolute values but a significant decrease was recorded and that could be correlated with the additive consumption, reflected by acidity index decreasing. Dropping of oil oxidation resistance have also to warn about the occurrence of acid compounds in its composition.

**Foam tendency and stability**

Oil tendency to foaming have shown a noticeable increase, starting from the first interval of 7-8 month that was characterized by a slow and constant growing of the foam tendency and continuing with the last 4 months when a significant increasing of foam volume values was recorded. This tendency can be well correlated with the decreased resistance to oxidation and the occurrence of acidic compounds in oil: the acids are surface-active compounds that favour the oil capacity for air retention and, as consequence, the foaming phenomenon is intensified.

Reviewing of the experimental results and related diagrams allows concluding that the changes of tested characteristics were very similar for both studied turbine oils.

The graphics represented evolution of acidity, oxidation resistance and foam tendency during the 12 month are almost overlapped, as could be seen in the figure no.1, 2
Fig. 3. Evolution of turbine oils foam tendency

and 3. This similarity of the characteristics evolution demonstrates the general tendency of turbine oils behaviour, in real conditions of service.

Conclusions

The results and information resulted from the research and monitoring study of turbine oils behaviour, within 12 months of service, allow formulating following conclusions.

Decreasing of oxidation resistance, tested by Rotary Bomb Oxidation Test, was highlighted by the recorded values of oxidation time that were getting smaller during the monitoring period. This was in a straight correlation with the oil acidity that had the following evolution: decreasing of acidity index as consequence of the antioxidant additive consumption during the first ten month, and a slight increasing of acidity done by the occurrence of the acid compounds resulted from the oils oxidation reactions, noticed from the eleventh month.

The oil foam tendency recorded a continue increase during the whole period and that was a consequence of the oil chemical structure modification.

The acid compounds that occurred from oil oxidation have a polar character and influenced on the foam characteristics of oils. As much as the polar compounds concentration was rising, the higher oil foaming tendency became.

The slight viscosity increasing recorded for the both turbine oils, could indicate the occurrence of higher molecular weight compounds, generated by combination of by-compounds resulted from oil oxidation reactions.

That study of the turbine oil investigation during a twelve month period, has emphasized some concrete correlations between oxidation resistance and acidity number, foam tendency and acid number, or oxidation resistance and foam tendency. Defining of the correlation between the evolutions of different oil characteristics, during the service life, could offer the possibility of a more efficient and selective control.

A proper understanding of different parameters interdependencies could provide an advanced capability of products quality diagnose and less time necessary to doing testing and analysis.

The experimental study will be continued with more detailed tests that will highlight the changing of chemical structure during the oil life-service.

References

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