Research of Turbine Oil Varnish in Generator Unit

Haoya’nan*, Li Qiang, Yu Naihai, Qi Guodong, Qi Qiubo and Shang Panfeng
Shandong Electric Power Research Institute, State Grid, Jinan, China
*Haoyanan@sd.sgcc.com.cn

Abstract. In recent years, due to the fact that thermal power generating units have been deeply involved in the peak shaving work of the power grid, the frequent start and stop operations of the units and rapid load-carrying operations have made the operating conditions of the units very bad. In large-scale thermal power generation units, shutdown accidents caused by varnish failures are becoming more common. Take the serious varnish failure of Unit 3 in a domestic power plant as a case for analysis. The steam turbine oil after the varnish is formed is fully analyzed and tested and the metal ion content test is carried out. The changes in the physical indicators of the steam turbine oil during the formation of the varnish are studied to determine the influence of the steam turbine oil on the physical indicators of the steam turbine oil during the formation of the steam turbine oil. The operation and maintenance personnel can detect the varnish in advance through the daily sampling and analysis of the steam turbine oil, and timely take treatment measures to remove the varnish components in the oil to ensure the safe and stable operation of the unit. This article summarizes the reason for the formation of varnish and the detection method of varnish. It is of great significance to effectively discover and control the production of varnish during the operation of the generator set, to study the formation mechanism of varnish and to find an effective method to remove varnish. This article also introduces the commonly used paint film treatment methods for the convenience of electric power technicians.

1. Introduction
In recent years, a large number of new energy sources have been connected to the power grid. Generator units have begun to participate in deep peak shaving. The units quickly start and stop and cut in and out of the load, which brings more operational risks to the operation of the unit. With the increase of the operating temperature of the generator set, the use conditions of the turbine oil are becoming more and more severe. The service life of the operating turbine oil is also rapidly decreasing. The more obvious indicators include a series of problems such as excessive consumption of antioxidant content, increased sludge precipitation, and accelerated chroma increase, among which the varnish problem is particularly prominent [1-2]. Many serious failures caused by varnish have been reported at home and abroad, which seriously affects the economic efficiency and safety of power generation enterprises.[3-4] Lubricating varnish is a high molecular hydrocarbon polymer. The typical element analysis is as follows: C 81~85%, H 7~9%, O 7~9%, N 2~3%. Its color ranges from light brown, brown to tan, and is named because its appearance resembles the varnish of anticorrosive paint. The main reasons for the formation of varnish are oil oxidation, local high temperature degradation and micro-combustion, and the influence of oil refining process [5-6]. The formation of the varnish on the bearing bush reduces the bearing bush clearance, increases the friction between the bearing bush surface and the shaft, and increases the temperature of the bearing bush.
A power plant #3 unit with a capacity of 350MW combined heat and power unit was put into operation in December 2006. The unit used No.32 turbine oil. Two weeks after the chroma exceeded the standard, the lubrication failed and the engine tripped. For this reason, the steam turbine oil is sampled and analyzed. Open the bearing and check that the varnish on the bearing and the bearing bush is serious. Show in Figure 1.

2. **Instruments and test methods**

In order to have a comprehensive understanding of the oil quality, the abnormal oil samples were fully analyzed. The physical and chemical analysis items, methods and instruments are shown in Table 1.

| Project                  | Instrument and model                                      | Method        |
|--------------------------|----------------------------------------------------------|---------------|
| Exterior                 |                                                          | DL/T 429.1    |
| Chroma                   | Colorimeter PFXi-195/2                                    | GB/T 6540     |
| Particle pollution level | Particle size counter SBSS-C                              | DL/T 432      |
| Rotating Oxidation stability(150℃)/min | Lubricating oil oxidation stability tester ZHXY2100       | SH/T 0193     |
| Viscosity(40℃)/(mm²/s)   | Automatic kinematic viscosity tester SVW3001              | GB/T 265      |
| Acid value(In KOH)/(mg/g)|                                                          | GB/T 264      |
| Demulsification degree(54℃)/min | Petroleum and synthetic liquid water separation tester DH 5 | GB/T 7605    |
| Liquid phase corrosion   | Corrosion meter ZHX1201                                   | GB/T11143(A法) |
3. **Analysis of physical and chemical properties of turbine oil**

In order to analyze the cause of the failure, the #3 turbine oil was fully analyzed and tested. The test results are shown in Table 2.

**Table 2.** Turbine oil analysis data of unit #3

| Project                        | Results        | Standard                                      | Conclusion   |
|--------------------------------|----------------|-----------------------------------------------|--------------|
| Exterior                       | Transparent    | Transparent, no impurities or suspended matter | qualified    |
| Chroma                         | 6              | ≤5.5                                          | unqualified  |
| Particle pollution level       |                | ≤8                                            | qualified    |
| Rotating Oxidation stability(150℃)/min | 138      | ≥100                                          | qualified    |
| viscosity(40℃)/(mm²/s)         | 33.01          | Not more than ±5% of the measured value of new oil | qualified    |
| acid value(In KOH)/(mg/g)      | 0.15           | ≤0.3                                          | qualified    |
| Demulsification degree(54℃)/min | 20.2          | ≤30                                           | qualified    |
| Liquid phase corrosion         | No rust        | No rust                                       | qualified    |
| Sludge precipitation           | No sludge      | No sludge                                     | qualified    |
| Open flash point /℃            | 220            | ≥180                                          | qualified    |
| Varnish tendency index         | 33.44          | 0≤MPC<15 normal                               | unqualified  |
| Moisture /(mg/L)               | 26             | ≤100                                          | qualified    |
| Air release value(54℃)/min     | 7.2            | ≤10                                           | qualified    |
Foaming (foam
tendency/foam
stability)/(mL/mL)/(mL/mL)

| Temperature | Foaming Tendency | Foam Stability |
|-------------|------------------|---------------|
| 24°C        | 350/0            | ≤500/10       |
| 93.5°C      | 70/0             | ≤100/10       |
| Later 24°C  | 420/0            | ≤500/10       |

Through the detection and comprehensive analysis of the steam turbine oil samples, it can be known from the test data in Table 2, and the temperature monitoring of the bearing bush, it is known that the bearing bush temperature has not exceeded the standard, and it can be known that the formation of the varnish is due to oxidation. The operating oil temperature of the power plant #3 steam turbine is 42°C. The oil sample is transparent in appearance, free of impurities, and periodic physical and chemical analysis of moisture and particle size is normal, so the influence of temperature, moisture and impurities can be excluded. Turbine oil has been in a forced circulation state for a long time, and it will gradually age under the influence of heat, oxygen, water vapor, impurities, etc. during operation, and produce a small amount of degradation products, some of which are dissolved in the oil to cause the oil to darken in color, and some are not dissolved in the oil in, a small amount of sticky deposits are produced. The polar viscous precipitate will have better adsorption to metal devices, and will form a varnish on the metal surface over time.

4. Metal element analysis
In order to understand whether the bearing bush and bearing are worn out after the varnish is formed, the metal elements in the oil are analyzed in Table 3.

Table 3. Metal element content in steam turbine oil

| Element name | Content μg/g | Element name | Content μg/g |
|--------------|--------------|--------------|--------------|
| Al           | 1.0          | Na           | -            |
| B            | 2.6          | Si           | -            |
| Ba           | -            | Ag           | -            |
| Ca           | 0.599        | Ti           | 0.14         |
| Cr           | -            | Mg           | -            |
| Cu           | -            | Mn           | -            |
| Fe           | -            | Mo           | -            |
| Pb           | 5.3          | Ni           | 9.1          |
| P            | -            | V            | -            |
| K            | 0.66         | Zn           | 0.316        |
| K            | 0.66         | Zn           | 0.316        |

From the results of the metal element data, the production of the paint film did not cause wear to the bearing bush and the bearing. Since the particle size in the oil does not exceed the standard, no larger particles cause wear to metal components. It can be seen from Figure 1 that the problem of the paint film on the bearing and the bearing bush of the turbine is very serious. A thicker carbonized layer has been formed on the metal surface. The existence of the paint film not only makes the gap between the bearing and the bearing bush. The gap becomes smaller, so that the lubricating oil cannot form an oil film for lubrication when the rotor is rotating. At the same time, because of the thick paint film, the bearing and the bearing bush will not have more serious direct contact friction, so from the analysis of the metal element content in the oil According to the data, the metal content in the oil has
not exceeded the standard. The existence of paint film affects the lubrication effect of metal components, and will cause local high temperature, making paint film problems more serious. Since the product at the beginning of the paint film formation is difficult to find through conventional testing, and because its particle size is at the sub-micron level, the particle size test during operation cannot be detected, so the paint film tendency detection system is urgently needed to be established.

5. Varnish tendency index detection needs attention
As the average peak-to-valley difference between my country's power grids is getting bigger and bigger, the task of peak shaving has gradually increased, and the number and scale of large-scale peak shaving units have also increased. Serious failures caused by varnish on the unit are not uncommon. However, many power plant managers fail to attach great importance to this issue. As there is still a gap between my country’s technical standards and international standards, the varnish is not covered in GB/T 7596-2017 "Quality of Turbine Oil in Power Plant Operation" and GB/T 14541 "Guidelines for Maintenance and Management of Mineral Turbine Oil Used in Power Plants" Propensity index makes testing requirements. The varnish is very harmful to the unit, which should arouse the attention of managers and strengthen the management of lubricants.

6. Reasons for the formation of varnish
The varnish is the product of the oxidation and degradation of oil. After a series of chemical reactions in the oil, the varnish is finally formed. The formation process of the varnish is that the hydrocarbon compounds are excited by energy and the valence bonds are broken to form free radical groups with relatively small molecular mass. These hydrocarbon groups will recombine with oxygen, nitrogen and other elements to form polar compounds. Polar organic molecules with a smaller relative molecular mass can be soluble in oil. As the polar organic molecules interact, they can form more polar compounds. Large polar molecules will gradually exceed the saturated melting point of the oil, at which time the polar organic macromolecules will precipitate out of the oil. Since the polar organic compounds have van der Waals force with the metal surface, they can better adhere to the metal surface. After a period of time, the polar organic compounds will form a film on the metal surface, carbonize and become difficult to remove.

There are several reasons for the formation of varnish.
A. The formula of steam turbine oil
Turbine oil is a blend of base oil and additives. Refineries usually do not directly produce finished lubricants, but directly produce base oils, because the output of lubricants accounts for about 2% of the entire refinery. At present, base oils are mainly divided into Type Tintype II and Type III, Among which Type II and Type III are obtained by hydrorefining. The traditional Type I base oil is a physical treatment method, which is obtained through solvent refining, solvent dewaxing, and clay supplement refining. Type II and Type III base oils are obtained by hydrofining. In 2019, the hydrorefined base oil accounted for about 60%. Its advantage is that it has a higher viscosity index, excellent thermal stability and oxidation stability. Compared with Class I base oils, almost all aromatic compounds are removed. The solubility of polar substances is not ideal, the compatibility with addition and addition has also become relatively poor, and its light stability is also poor. In order to improve its anti-oxidation and high-temperature operation performance, two or more composite additives are added to the steam turbine oil. After such additives are cracked, it is easy to produce sludge and form a varnish.[7]

B. Oxidative cracking
Turbine oil will undergo oxidation during normal operation, and its service life is usually more than several years. However, different brands of steam turbine oil have different formulas, so their antioxidant capacity is different. High-temperature oxidation is an important factor in the deterioration of oil products. When the operating temperature reaches 60°C, the rate of oil deterioration doubles when the temperature increases by 10 degrees. When there is a certain amount of water in the oil, the oil oxidation rate can be Increase by 10 times.
C. Pyrolysis and micro-chamberization [8]

Under anaerobic conditions, when the temperature of steam turbine oil exceeds 200 °C, the base oil and additives will be thermally cracked, and the cracked products will form a varnish on the metal surface. In addition to high temperatures, the lubricating oil is also subject to adiabatic compression (micro-dieselization). This happens when the bubbles in the oil flow from the low-pressure part to the high-pressure part, the outside is doing work on the bubble, the volume will decrease sharply, the temperature around the bubble will rise rapidly, and the hot spot temperature will reach 766 °C or even higher. Locally causing "micro-burning" will cause sludge in the turbine oil, leading to varnish.

D. Electrostatic discharge

Electrostatic discharge is a high-energy release, which can also cause micro-burning of the oil locally, resulting in varnish. The high-speed flow of steam turbine oil can generate static electricity through the friction between molecules and the friction between the fluid and the metal surface. When the static charge accumulates to a certain extent, the discharge site will occur. A large amount of energy is generated during discharge to crack the oil.

7. Detection method of varnish

The varnish is a soft pollutant at the beginning of its formation. It is composed of sub-micron products produced by the cracking of steam turbine oil. The particle size is usually less than 0.08 μm, which cannot be detected by traditional particle detection equipment. The predecessor of the varnish is the oxidation product of the oil. Usually the antioxidant content and the varnish have a certain correlation, but the hydrefined base oil used in the current steam turbine oil still has a good rotation even when the antioxidant content is unqualified. Oxygen bomb value. Therefore, the varnish has already appeared when the routine test items are all qualified. It is undoubtedly difficult to find the tendency of varnish formation through the daily test items.

At present, the United States, Europe, Japan and other countries have done a lot of research on the mechanism, detection, prevention and removal of turbine varnish formation, and some relevant standardized documents have been formed. Foreign research institutions have developed several new methods for evaluating the tendency of varnishes, of which the filter membrane colorimetry (MPC) is the most widely used. It has been widely recognized in actual use. The American Society for Testing and Materials (ASTM) has also formed a new standard ASTM D7843 for varnish tendency detection on the basis of this method [9]. Some domestic research institutions have also conducted in-depth research on the filter colorimetric method. Among them is the GB/T 34580-2017 "Determination Method of Insoluble Colored Substances in Operating Turbine Oil-Diaphragm Colorimetry Method" drafted by the Guangdong Electric Power Research Institute. This standard is promulgated and implemented for the majority of power plant oil personnel to provide test methods.

8. Methods of controlling and processing varnish

The varnish seriously threatens the safe operation of the unit, so an effective method of removing varnish becomes very important. First of all, the predecessor of the varnish is a soft organic matter with a small particle size, so it is difficult to remove it by mechanical oil filtering.

A. Oil selection

There are many types of lubricants in the market. In addition to the major domestic brands Kunlun and Great Wall, there are joint venture or foreign brands such as Uni-President and Shell. Different brands of lubricants have different formulations. The base oils and additives used are quite different. The oxidation products of oil are the direct source of varnish formation, so the hydrefined lubricating oil and suitable antioxidants (not easy to form sludge) can be used as the basis for selection by manufacturers.

B. Oil change

Some power plants will deal with varnish problems through partial and full oil changes. This method has a high processing cost. At the same time, the partial oil change effect will not greatly extend the service life of the oil. The oil that has not been replaced still contains oxidation products, which will
accelerate the oxidation of the new oil, which still cause varnish problems. However, when all the oil is changed, the entire oil system needs to be cleaned. The process is cumbersome and new pollutants will be introduced when the cleaning department is thorough. This treatment effect is not ideal.

C. Balanced charge purification technology

The key point of the balanced charge purification technology is that the sub-micron soft organic particles are repelled by the same sex and the opposite sex through the charge, so that they form large particles, and then go out through filtration. However, this method has its limitations. Because the particles are soft substances, their solubility is higher when the temperature is too high, and the filtering effect is not ideal. Therefore, this kind of purification technology is suitable for offline processing.

D. Electrostatic particle purification technology

Electrostatic spark discharge is an important factor in the production of varnish. Therefore, reducing the accumulation of static charge and speeding up the dissipation of static charge are a major means to avoid the formation of varnish. The new type of anti-static filter material has an obvious effect on alleviating and eliminating the discharge of static electricity. [10] Some domestic scholars have also done a lot of research on anti-static filter materials. [11] Through the regeneration technology of polar alumina adsorbent, the oil quality has been greatly improved.

E. Ion exchange resin method

The ion exchange resin method is to selectively adsorb polar substances through a specially made ion resin to reduce the tendency of the varnish. This method is not limited by temperature and can be carried out at runtime. Due to the selective adsorption, the purification effect can be better when the oil temperature is higher. Due to the high cost of this purification method, it has limitations.

9. Conclusion

There is still a lack of emphasis on varnish in my country, and many countries such as the United States, Japan and Europe have conducted more research. Many domestic scholars are actively studying the treatment technology of varnish and have achieved some results. The problem of varnish is still lacking in mechanism research. The research on its formation mechanism requires progressive exploration.

Periodic inspection of varnish should be established. At present, the standards for the management of new oil, operating oil, and steam turbine oil used in domestic power plants all provide for varnish detection. The formation of a varnish detection system is of great significance.

New varnish treatment technology is in urgent need of research. Because the particle size of the steam turbine oil cracked product is small and it is a soft organic matter, it is difficult to remove it by means of fine filtration. The development of high-efficiency, low-cost, selective adsorption materials is the focus of current research.

References

[1] WANG Juan, AN Jinmin, LIU Jie, et al. Cause analysis of sudden deterioration for turbine oil and treatment thereof[J]. Thermal Power Generation, 2010, 39(4): 58-61.
[2] WANG Xiaowei, YANG Jun, WANG Juan, et al. Cause analysis and treatment for abnormal color of turbine oil in service[J]. Thermal Power Generation, 2013, 42(9): 139-140.
[3] WU S T, WANG P P, HAO J. The difference between gas turbine and steam turbine[J]. The Guide of Science & Education, 2015(5): 154-155.
[4] FANG S, GEN X L. Managing varnish of turbine oil[J]. Advanced Materials Research, 2014, 842: 341-344.
[5] Han Xu, Lu Haidi, Yan Hongzhen, etc. The cause of lubricating varnish and its elimination method. Lubricant, 2020, 35(01), 21-24.
[6] WANG J X. Formation mechanism and removal countermeasures of lubricating oil varnish[J]. Petro & Chemical Equip-ment, 2015(5): 76-78.
[7] Wang Hui, Sun Daxin, Cheng Liang. Sludge analysis of steam turbine oil[J]. Lubricants, 2014, 29(1): 7-11.
[8] Yi Meirong. Causes and solutions of varnish during gas turbine operation [J]. Petroleum Business Technology, 2009, 27(1): 42-45.

[9] Standard test method for measurement of lubricant generated in-soluble color bodies in in-service turbine oils using membrane patch colorimetry: ASTM D7843-12[S].

[10] KAN C, LI J, CHRISTIAN B, et al. Mitigation of triboelectric charging in paper machine hydraulic and lubrication fluids [J]. Light Industry Machinery, 2011, 29(2): 45-48.

[11] WANG B, YU Y. Cause analysis and treatment on bearing pad fault of 650 MW steam turbines [J]. Electric Power, 2014(9): 42-45.