Combustion behavior of mineral insulating oil with addition of flame retardants

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Abstract. Mineral oil is the most commonly used liquid insulating material in oil-immersed transformer. Improving the fire performance of mineral oil can not only greatly reduce the probability of fire in transformer system, but also reduce the risk of fire. In this paper, the flash point tester, cone calorimeter and thermogravimetric analyzer were used to study and analyze the mineral oil and modified samples. The results show that the fire resistance and thermal performance of the modified insulating oil are improved.

1. Introduction

Since its good dielectric properties and low price, which plays a role of cooling and insulation, mineral oil is widely used in oil immersed equipment. However, its poor fire-proof performance can lead to disastrous fire when transformer system fails. In order to overcome the shortcomings of mineral oil, natural esters with high biodegradability and high ignition point have been widely studied as substitutes for mineral oil. Mazzaro M, Bartolomeo D D, Bemporad E et al studied the effect of ester insulating oil on reducing the fire of distribution transformer through the external fire source combustion test of ester insulating oil transformer and the fire simulation test caused by the internal discharge fault of natural ester insulating oil transformer[1]. Pompili M, Calcara L, Sturchio A also show that natural ester insulating oil is an effective method to reduce transformer fire[2]. CETC has carried out comparative tests on fire safety parameters such as flash point, ignition point and explosion limit of natural ester insulating oil and mineral insulating oil, as well as metal hot surface test and combustion disk comparison test of natural ester insulating oil and mineral insulating oil [3]. However, due to the monopoly of foreign technology, the research of natural ester insulating fluid in China is still in the initial stage, and the research of new fire-resistant insulating fluid has not been reported.

Adding flame retardant is an economic and effective way to improve the fire performance. A large number of reports have been reported on the use of flame retardant additives to improve the safety of lithium-ion batteries. Most of the additives are organophosphorus and halogenated compounds, among which organophosphorus compounds, due to their strong ability to capture free radicals, have been proved to effectively improve the flame retardancy of electrolyte. Feng Guo, Yu Ozaki compared the effect of additives on the combustion performance of the electrolyte by using the wick LOC method,
which proved that the organophosphorus flame retardant effectively reduced the flammability of the lithium electronic electrolyte[4]. Xi Li, Weikang Li studied the excellent flame retardancy of ethoxy (pentafluoro) cyclotriphosphazene (PFPN) through self-extinguishing and oxygen index experiments[5].

In this paper, the method of flame-retardant additive in mineral oil is applied for the first time. Through the thermal performance experiment, it is found that the modified insulating liquid with flame retardant has better fire-retardant performance than mineral oil.

2. Experimental materials
The advantages of low smoke, low toxicity and high efficiency of phosphorus flame retardants make it one of the most widely studied flame retardants[6]. The flame retardant mechanism of organophosphorus flame retardant mainly includes[7]: Gas phase flame retardant mechanism, condensed phase flame retardant mechanism, and synergistic flame retardant mechanism. The research of organophosphorus flame retardants mainly focuses on phosphate, phosphonate, phosphine oxide, polyphosphate, phosphine and organophosphate. In this study, four kinds of phosphorus flame retardants and one kind of halogen flame retardants were selected in terms of comprehensive performance, solubility in mineral oil and environmental protection. Dimethyl toluene phosphate (CDP) and tripropylphenyl phosphate (IPPP) are phosphate flame retardants, both of which have high flash point boiling point, excellent electrical insulation performance, low viscosity, low toxicity, stable and non-volatile. IPPP is an alternative product of DPK flame retardant in Germany, CDP is a replacement product of trimethylbenzene phosphate (TCP). Daiying Zhoul found that the self-extinction time of electrolyte in lithium-ion batteries with 5wt.% CDP was reduced from 60s to 47s[8]. Qingsong Wang found that adding IPPP to the electrolyte can reduce the starting temperature of self-extinguishing[9]. Dimethyl methyl phosphonate (DMMP) and diethyl ethyl phosphonate (DEEP) are phosphonate flame retardants. Their phosphorus content is outstanding while their flash point is not very high. The phosphorus content of DMMP is as high as 25%. Excellent flame retardant effect can be obtained by only a small amount of DMMP. H.F.Xiang first added DMMP additive to the electrolyte of lithium-ion battery, only 10wt.% DMMP can make the electrolyte nonflammable[10].

Halogenated flame retardants are still one of the largest organic flame retardants in the world [11]. Chlorinated paraffin, decabromodiphenyl ether, tetrabromobisphenol A, trisiscyanate are commonly used. Among them, chlorinated paraffin flame retardant can be dissolved in various mineral oils. The insulating oil for experiment is provided by Hunan electric power company. The flame retardant for experiment is as follows: CDP, Shanghai bide Pharmaceutical Technology Co., Ltd; IPPP, Shanghai McLean Biochemical Technology Co., Ltd; DMMP, deep, Yangzhou Chenhua New Material Co., Ltd; CP42, Jiangsu Shengkai plasticizer Technology Co., Ltd.

There are five modification schemes of mineral oil used in this paper, covering 12 ratios, as shown in Table 1.

| Component     | MASS FRACTION RATIO |
|---------------|---------------------|
| Mineral oil-CDP | 4.0 cm              |
| Mineral oil-IPPP | 2.7 cm              |
| Mineral oil-CP  | 2.5 cm              |
| Mineral oil-DEEP | 2.5 cm              |
| Mineral oil-DMMP | 0 cm                |

The flame retardant is added to the pure mineral oil and placed on the surface of the magnetic stirrer and stirred at room temperature.

3. Experimental instruments and test methods
The main instruments and models used in the experiment are shown in Table 2.
Table 2. Main instruments used in the experiment.

| Experimental instrument                  | SPECIFICATION     |
|------------------------------------------|-------------------|
| Martin closed cup flash point tester     | SCKB3000          |
| Cone calorimeter                         | I-CONE CLASIC     |
| Thermogravimetry                         | SDT Q600          |
| Magnetic stirrer                         | MS-H280-Pro       |
| Sony HD digital video recorder           | HDR-PJ30E         |
| Electronic analytical balance            | BSA124S           |

3.1. Martin closed cup flash point tester

3.1.1. Instrument and equipment. The closed flash point tester is mainly used for light petroleum products with large evaporation, such as transformer oil, fuel oil, solvent oil, etc.; the open flash point tester is mainly used for lubricating oil and heavy petroleum products. In consideration of universality and applicability, Martin closed cup flash point tester is selected as the test equipment for research, and the test temperature is from room temperature to 299.9 °C.

3.1.2. Test method. The flash point was measured by Martin closed cup flash point tester (GB-T 261-2008). First, wash the test cup with ethanol acetone mixed solution, dry it naturally in the air, and inject the sample into the oil cup to the scale line position. Then place the test cup in the heating chamber. Adjust the flame size of the test fire source to 3mm ~ 4mm, and set the pre-flash value. Conduct ignition experiment, and start ignition at 23 °C below the pre flash point. When a flash of blue flame appears above the sample liquid level for the first time, the instrument automatically stops testing. If the difference between the thermometer reading and the starting ignition temperature is within the range of 18 °C ~ 28 °C, it is regarded as the effective closed flash point value.

3.2. Cone calorimeter

3.2.1. Instrument and equipment. In this paper, I-cone class produced by British FTT company is used. The radiation intensity of cone calorimeter is 25kW /m², referring to international standard ISO 5660-1.

3.2.2. Test method. Inject 50ml sample into the 100 × 100 × 15mm³ combustion plate, place it on the heating table with the liquid level 25mm away from the conical heater, remove the baffle plate of the heating chamber, move the electric spark igniter to the center of the combustion plate, and remove the igniter after the liquid is ignited. Stop the test after the heat release rate returns to a stable value close to 0. Close the baffle plate of heater, remove the combustion box, clean it after the combustion box cools, and repeat these steps for the next test.

3.3. Thermogravimetry

3.3.1. Instrument and equipment. In this paper, SDT Q600 was used for the experimental analysis. Two kinds of curves can be obtained by TGA under the set program: one is TG curve, which represents the relationship between the weight of the measured object and the temperature change under a certain temperature, the abscissa is the temperature, and the ordinate is the weight loss percentage. The other is the derivative of TG curve to time and temperature, which represents the relationship between the change rate of sample weight and temperature. The abscissa is the temperature, and the ordinate is the change rate of weight.

3.3.2. Test method. Weigh 15-17mg of sample at a time, with the heating rate of 10K / min, rise from room temperature to 500 °C, select air for purging gas and nitrogen for protection gas.
4. Results and analysis

4.1. Closed flash point measurement

The closed flash point of transformer oil is an important index to characterize the risk of power equipment fire[12]. Flash point is the minimum temperature of fire source combustion when sufficient vapor is generated on the surface of combustible liquid and air is mixed to form combustible gas under specified test conditions. Flash point indicates the flammability and danger of flammable liquid. The lower the flash point, the greater the danger of liquid. Therefore, if the flash point of transformer oil can be increased, its safety can be improved accordingly. The flash point of binary mixture of mineral oil and another high flash point insulating liquid has been studied. China Electric Power Research Institute [13] has tested the open and close flash point of mineral oil and FR3 produced by Cooper in the United States and NP produced by Henan Enpai Electric Power Technology Co., Ltd. It has been proved that mixing with natural ester can improve the flash point of mineral oil.

First of all, we are concerned about the influence of different flame retardants on the flash point of pure mineral oil under the same mass ratio. The test results are shown in Figure 1. Considering the solubility of each flame retardant in mineral oil, the upper limit of its solubility in mineral oil except DMMP is 1.5wt%. The solubility of other flame retardants is more than 5wt%. We expect that a group of tests can clearly distinguish the performance differences of different flame retardants. Therefore, 5wt% is selected as the unified addition mass fraction for four flame retardants except DMMP, and the flash point under the upper limit of 1.5wt% is tested for DMMP.

| Flame retardant | Closed flash point(℃) |
|-----------------|-----------------------|
| CDP             | 232                   |
| IPPP            | 174.3                 |
| DMMP            | 93                    |
| DEEP            | 68.89                 |
| CP              | 298.4                 |

The flash point of binary organic mixtures follows four rules[14]: 1) minimum flash point behaviour; 2) gradual change behaviour; 3) constant flash point behaviour; 4) linear change behaviour. The closed flash point of the original pure mineral oil was 135.5 ℃, and the flash point of the modified mineral oil was increased to 137.5 ℃, 136.5 ℃ and 140 ℃ respectively after adding 5 wt.%
CDP, IPPP and CP. CDP and IPPP were high flash point flame retardants, and the closed flash points were 232 °C and 174.3 °C respectively. When flammable solvent is added, whether the flash point can be increased depends on the molecular interaction between the two flammable liquids. Only when the force is greater than the molecular attraction of the pure component liquid, the flash point will be increased. When adding the flame retardants deep and DMMP whose flash point is lower than that of mineral oil, the flash point of the mixed liquid is lower than that of DMMP whose flash point is lower than that of mineral oil, especially when the amount of DMMP is only 1.5wt%. Therefore, in the actual production, the liquid with low flash point should not be mixed with insulating oil.

In the first group of tests, we found that under the same amount of additives, the improvement of flash point value by different flame retardant to mineral oil was not obvious, and there was little difference between flame retardants, the minimum increment was 2 °C, the maximum was 4.5 °C. Therefore, we continue to adjust the proportion of each flame retardant, in which every 2.5wt.% of CDP and IPPP is an interval, and every 5wt.% of CP is an interval, in order to find out whether different mass addition will affect the change of flash point. The solubility of CDP and IPPP in mineral oil is limited, and the test range is from 0 to the upper limit of the solubility of each flame retardant. Considering the influence of the addition of flame retardant on the dielectric properties of mineral oil, the viscosity of chlorinated paraffin is large, so the upper limit of CP addition is set to 20wt%.

![Figure 2. Flash point of insulating oil with different mass fraction of flame retardant.](image)

Figure 2 shows the flash point curves of mineral oil modified by CDP, IPPP and CP. In all the ratios in the experiment, the modified insulating oil is higher than pure mineral oil. Therefore, we can confirm that the flash point of CDP, IPPP, CP mixed with mineral oil is higher than that of pure
mineral oil. In Figure b), with the increase of IPPP mass fraction, the flash point of the modified oil shows a linear upward trend, in which the flash point is 139.5 °C at the concentration of 10wt.% and 12.5wt%. In figures a) and C), there is no obvious linear trend. The solubility of CDP and IPPP in mineral oil is limited. In the range of maximum solubility limit, when the amount of CDP is 7.5wt%, the maximum flash point is 140 °C, and when the amount of IPPP is 12.5wt%, the maximum flash point is 139.5 °C. The flash point of CP decreased with the increase of CP addition.

4.2. Cone calorimeter

4.2.1. Heat release rate per unit area HRR. The heat release rate (HRR) refers to the heat released by the combustion of materials per unit area in a unit time. It is considered to be the most important characteristic parameter of the combustor in a fire. Generally speaking, in a small-scale fire, the larger the HRR, the shorter the ignition time, the faster the material burns, the faster the fire spread, and the greater the fire risk. Jim goudie. used cone calorimeter to test the change of fire behavior of mineral oil after mixing silicone oil in 1992 [15]. Through the experiment of cone calorimeter, the heat release rate of mineral oil and modified oil per unit area can be obtained. The experimental results are shown in Figure 4.

Figure 3 shows the flame diagram of mineral oil and modified insulating oil burning at 150s after ignition. According to Figure 4, under the condition of 25kW / m² thermal radiation intensity, the curves of heat release rate of combustion per unit area of four samples with time are given. The curves of heat release rate time are single peak curves for both pure mineral oil and modified oil. Take mineral oil as an example: mineral oil samples are exposed to strong radiation, and heat accumulates continuously, so as to ignite. After a short pre-combustion phase, the oil tank enters a stable
combustion phase, at which time the fuel combustion is calmer. After a period of combustion time, the heat release rate suddenly increases, reaching the peak value, and then gradually decreases. The peak value of heat release rate of pure mineral oil reached 1198.65 kW/m². After treated with flame retardant, the heat release rate of mineral oil decreased greatly. The peak value of thermal release rate of mineral oil decreased to 819.31 kW/m² and 68% of pure mineral oil with the addition of 12.5wt.% IPPP. 7.5wt.% CDP reduced the peak heat release rate of mineral oil to 969.78 kW/m² and 81% of pure mineral oil. CP is not as effective in testing as IPPP and CDP. This shows that the addition of IPPP and CDP is not just a dilution effect. The flame-retardant mechanism of organophosphorus system has been explained in detail by predecessors. The natural radicals (such as PO · etc.) of flame retardant combustion decomposition can capture hydrogen radicals (H ·), thus slowing down the combustion chain reaction process.

4.2.2. Total heat release per unit area THR. Total heat release per unit area (THR) refers to the total heat released by a unit area material from ignition to complete extinction under a preset heat radiation intensity. The gradient of THR curve represents the velocity of flame propagation.

![Figure 5. Total heat release - time curve.](image)

Figure 5 shows the THR curve of mineral oil treated by IPPP, CDP and CP. It can be seen from Fig. 5 that the THR of mineral oil is the largest, 200-210 MJ/m²; the THR of mineral oil treated by 12.5wt.% IPPP is the smallest, 150-160 MJ/m². During the period from the ignition of mineral oil to the peak of the maximum heat release rate, the total heat release rate increases rapidly, and when the peak of the heat release rate changes, the change rate is the fastest. After adding flame retardant, the curve of the total heat release rate was more gentle, and the increase rate of the total heat release rate decreased. From Figure 5, it can be seen that the flame propagation speed of mineral oil is the fastest, and the fire risk is the largest. The flame propagation speed of modified oil added with IPPP is the slowest, and the fire risk is the lowest.

| insulating oil | pkHRR (kW/m²) | THR (MJ/m²) | TTI (s) |
|---------------|---------------|-------------|--------|
| Mineral oil   | 1198.65       | 204.21      | 27     |
| 12.5%IPPP     | 819.31        | 159.37      | 32     |
| 7.5%CDP       | 969.78        | 162.99      | 30     |
| 20%CP         | 923.83        | 162.50      | 30     |

4.2.3. Ignition time TTI. According to table 4, the comprehensive maximum heat release rate (pkHRR), total heat of combustion (THR) and ignition time (TTI) can quantitatively evaluate the performance of flame retardant. The ignition time of mineral oil and modified oil are: mineral oil 27s; IPPP, 32s; CDP, 30s; CP, 30s. Compared with the pure mineral oil, the ignition time of the modified insulating oil is longer. The ignition time of mineral oil is 27s. The addition of 12.5wt.% IPPP makes the ignition time longer.
delayed by 5S. The addition of 7.5wt.% CDP and 20wt.% CP also makes the ignition time of mineral oil delayed by 3S. The delay of ignition time can obtain valuable time for timely extinguishing the fire and reduce the fire risk.

4.3. Thermogravimetric analysis
Thermal analysis technology is a technology to study the change of material properties with temperature. Two kinds of modified flame retardants with better effect and pure mineral oil are analyzed by comprehensive thermal analyzer in the air atmosphere. The combustion characteristics of different insulating oil are compared and TG and DTG curves are obtained.
It can be concluded from Figure 6 that the change rate of thermal weight of the three insulating oils is relatively similar, with the total weight loss rate of 100%. The DTG curve of mineral oil and the two modified DTGs is single peak, and the DTG curve reaches the peak value near 250 °C, at this time, the decomposition rate is the largest, and the weight loss temperature range is similar. The weight of mineral oil and modified oil has been reduced to 0 before 300 °C. The initial decomposition temperature of mineral oil is the same as that of modified mineral oil with flame retardant, and the initial decomposition temperature of three groups of samples are all around 100.17 °C. When the residual mass fraction of the sample is 0.1%, the temperature of the mineral oil is 244 °C, the temperature of the mineral oil added with 12.5wt.% IPPP is 256 °C, and the temperature of the mineral oil added with 7.5wt.% CDP is 256 °C, which shows that under the same weight loss rate, the combustion temperature of the modified mineral oil is higher, the heating capacity of the pure mineral oil is larger and the combustion is more intense. The DTG curve of the modified oil with IPPP shows an unobvious peak near 270 °C, which indicates that two substances in the modified oil lose weight successively, the mineral oil components decompose first, IPPP decomposes later, and the initial decomposition temperature of IPPP is much higher than that of mineral oil. Therefore, the thermal stability of modified mineral oil is higher than that of pure mineral oil, because the combustion risk of modified oil is reduced.

5. Conclusion
- Adding high flash point flame retardant to mineral oil can improve the flash point in a certain range. Adding a small amount of flame retardant with flash point lower than mineral oil will greatly reduce the flash point of mineral oil. In practical production, low flash point liquid should be avoided mixing with insulating oil.
- The addition of 12.5% IPPP can reduce the maximum heat release rate of insulating oil by 32%, which is about one third of pure mineral oil. At the same time, compared with the same volume of mineral oil, the ignition time was delayed 5 s.
- The modified oil improves the thermal stability of mineral oil and gives rise to complete weightless temperature.
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References

[1] Mazzaro, M. et al. (2017). Power transformer fire and environmental risk reduction by using natural esters. J. IEEE 19th International Conference on Dielectric Liquids (ICDL), Manchester, pp:1-4.

[2] Mazzaro, M. et al. (2019) Fire simulation tests of mineral oil and natural esters transformers. J. IEEE 20th International Conference on Dielectric Liquids (ICDL), Roma, Italy, pp:1-4.

[3] Cai, S., Shao, M., Chen, C., et al. (2018) Fire Performance Test of Natural Ester Insulating Oil-Immersed Transformer. J. Transformer, 55(05):56-60.

[4] Feng, G., Yu, O., Katsunori, N., et al. (2020) Influence of lithium salts on the combustion characteristics of dimethyl carbonate-based electrolytes using a wick combustion method. J. Combustion and Flame, 213:314-321.

[5] Li, X., Li, W., Chen, L., et al. (2018) Ethoxy (pentafluoro) cyclotriphosphazene (PFPN) as a multi-functional flame retardant electrolyte additive for lithium-ion batteries. J. Journal of Power Sources, 378:707-716.

[6] Zhou, Y., Yang, L., et al. (2009) The Present Situation and Prospect of Phosphorus Flame Retardants. J. Tianjin Chemical Industry, 23(01):1-4.

[7] Li, B. (2010) The Mechanism and Application Progress of Phosphorus Flame Retardants. J. Chemical Engineering & Equipment, (11):122-123+93.

[8] Zhou, D., Li, W., Tan, C., et al. (2008) Cresyl diphenyl phosphate as flame retardant additive for lithium-ion batteries. J. Journal of Power Sources, 184(2):589-592.

[9] Wang, Q., Sun, J. (2007) Enhancing the safety of lithium ion batteries by 4-isopropyl phenyl diphenyl phosphate[J]. Materials Letters, 61(16):3338-3340.

[10] Xiang, H., Xu, H., Wang, Z., et al. (2007) Dimethyl methylphosphonate (DMMP) as an efficient flame retardant additive for the lithium-ion battery electrolytes. J. Journal of Power Sources, 173(1):562-564.

[11] Tang, G., Huang, Z. (2012) Perspectives of Halogenated Flame Retardants. J. Bulletin of Science and Technology, 28(01):129-132.

[12] Liu, X., Wu, H., Feng, Z. (2011) Summarization of Closed-cup Flash test for Transformer Oil. J. Jiangxi Electric Power, 35(05):21-24.

[13] Kou, L., Wang, J., et al. (2017) Experimental Study on Properties of Different Mixed Insulating Oils. J. Insulating Materials, 50(02):76-80.

[14] Li, G., Pan, Y., Jiang, J. (2013) Experimental study on flash points of binary organic mixtures. J. Chemical Engineering, 41(01):28-31+36.

[15] Goudie, J., Buch, B. (1992) Combustion properties of contaminated dielectric fluids as determined in the cone calorimeter. C. Electrical Insulation, Conference Record of the 1992 IEEE International Symposium on. IEEE,