Study of the thermal stability of process lubricants for heavy-duty modes of contact friction

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Abstract. Results of research of thermal stability of the lubricants used in industrial technologies related to heavy-duty modes of contact friction are given. Certain mathematical models of thermal destruction of lubricants process allow to give approximate quality assessment. Considering complexity of process of thermal destruction experimental studies are necessary and orientation for them is offered. The two-stage process of thermal destruction of lubricants is shown; the rate of pyrolysis is studied. The conclusion is drawn on the influence of flying products of thermal decomposition of lubricants on a tribological situation in the zone of contact friction.

Thermal stability being a functional property of process lubricants (PL) plays the most important role in heavy-duty modes of boundary contact friction, which is characteristic of technological processes (forging, rolling, abrasive machining, etc.) Nevertheless, insufficient attention has been paid to the study of thermal stability in scientific and technical literature, and methods of quantitative and qualitative assessment of thermal stability of PL are not standardized. Therefore, the purpose of this study which is to consider theoretical and applied aspects of PL behavior in high-gradient temperature fields typical of heavy-duty conditions of contact friction, seems actually relevant.

Thermal decomposition of any PL, especially hydrocarbon ones, is a series of variable and sequential chemical reactions with the formation of a large number of volatile and residual products. Intense thermal effect on the boundary layer of the PL is produced by the heated metal and the heat of friction and by plastic deformation [1].

According to the generally accepted point of view, the reason for the thermal decomposition of PL is an increase in the energy of vibration motion of the parts of molecules relative to each other with the rise of temperature. The energy of the oscillatory motion is evenly distributed over all the bonds in the molecules. At a certain temperature, the average energy of vibrations becomes greater than the strength of the weakest bonds, which leads to their breaking. Further temperature rise may cause stronger bonds destruction. Breaking of the bonds in a molecule leads to formation of "fragments" with unsaturated valency - free radicals, with high reaction capacity. As a result of recombination and repeated interactions of radicals, a radical-chain reaction develops. Due to the continuous interaction of radicals with stable molecules, new decay products and new radicals are formed. The complexity of the mechanism of thermal decomposition explains the complexity of the resulting gaseous mixture composition.

Thermodynamic and kinetic calculations of modern PL pyrolysis are impossible due to the exceptional complexity of the accompanying processes.
Approximate and empirical dependencies are also of little value for thermal stability of PL assessment, since, one hand, they comprise many empirical coefficients, and, on the other hand, they describe pyrolysis for a specific situation. Thus, in [1], the dependency for calculating the burnout rate of oils is proposed:

\[ U_v = \frac{0.001 \alpha (T_c - T_{boil}) M}{\rho_l (\Delta H_{vap}^0 + C_p (T_{boil} - T_0))} \]  

where: \( U_v \) is the burnout rate of the liquid; 
\( \alpha \) - the heat transfer coefficient from the heated body to the liquid; 
\( \rho_l \) - density of the liquid at the initial temperature \( T_0 \);  
\( C_p \) - average heat capacity of liquid in the temperature range from \( T_0 \) to \( T_{boil} \);  
\( \Delta H_{vap}^0 \) - heat of evaporation of the liquid.

For a specific lubricant the values of \( \alpha \), \( C_p \), \( T_{boil} \), \( \Delta H_{vap}^0 \) are unknown and difficult to find. In this regard, the main means of identifying the thermal stability of PL is to conduct an experiment with special equipment in conditions as close as possible to real ones.

Experimentally, thermal stability of PL is estimated indirectly by the parameters of the gas mixture resulting from pyrolysis. Here two approaches are possible. On the one hand, it is possible to consider thermal stability as a significant physical and technical property of a lubricant. On the other hand, thermal stability can be considered as a result of the process of contact interaction of heated surfaces separated by a PL layer. In both cases, thermal stability is considered as a gas-making ability of PL subjected to high temperature exposure.

In the first approach, the specified volume of lubricant is loaded into metal capsule, after which the capsule is sealed and placed in a temperature-controlled heating device. The working cavity of the capsule is connected with a highly sensitive manometer through a capillary. The gaseous products resulting from the pyrolysis of PL cause an increase in pressure in the capsule cavity, which is recorded by a pressure gauge with accuracy of \( \pm 0.4\% \). A capsule with a working volume of 0.048 m\(^3\) was used for the experiment conducted with the use of this technique. The chamber of the capsule stored 5g of lubricant. The maximum heating temperature of the capsule was 1100°C.

To implement the second approach, a plant has been developed, the scheme of which is presented in figure 1.

![Figure 1. Plant diagram for the study of thermal stability.](image-url)
is placed, is fixed on small protrusions in the case. After installing the sample 8, the connector is sealed and the magnetic plate is turned off. The lubricated bottom die 5 is released and with the help of springs forces the heated specimen 8 to the device cover. The lubricant layer burns out (the process of pyrolysis). The pressure and temperature of the resulting gas mixture are registered by a miniature sensor 9. Due to the presence of gas leaks, the accuracy in defining thermal stability in the plant is ± 10% with confidence level of 0.95.

For a quantitative assessment of the gas-making ability of PL, it is advisable to use the U parameter, called the decomposition rate of PL and defined by the formula:

\[ U = \frac{P_f - P_s}{m(T_f - T_s) (kPa/g°C)}, \]  

where: \( P_s \) and \( P_f \) are the initial and final values of the pressure of gaseous products of thermal decomposition;
\( T_s \) and \( T_f \) - absolute temperatures of the beginning and end of thermal effects on the PL;
\( M \) – is the mass of lubricant in the tribo-active zone.

It has been established that lubricants for hot stamping of leading foreign firms are characterized by high gas-generating value [3]. The results presented in figure 2 indicate that gas pressure in the stamping zone can reach values comparable with deformation energy. Substantial nonlinearity of gas pressure dependence on temperature during punching and on the composition of the lubricant was also confirmed.

![Figure 2. Dependence of gas pressure on temperature during punching.](image)

Release of volatile components of the PL pyrolysis is of particular interest. There is every reason to believe that in some cases, the volatile components of thermal destruction of PL can have a radical impact on the tribological situation in the zone of loaded content [1].

Volatiles components composition depends on many factors: on the initial chemical composition of the lubricating film, on the kinetics of the pyrolysis process, on temperature gradients, on the catalytic action of juvenile metal surfaces.

Typical yields of pyrolysis products of organic compounds under various process conditions are presented in table 1. Sometimes hydrogen and CO are found in volatile products. As can be seen, even
insignificant heat exposure time (0.1 s) causes formation of considerable amount of volatile components. Relative volatile yield can be calculated by the formula [4]:

\[ \xi = 1 - \exp \left[-\tau k_0 \exp \left(-\frac{E}{RT_4}\right)\right] \]  

(3)

where:
- \( \xi \) is relative yield of volatiles;
- \( k_0 \) is the rate constant for the reaction of thermal decomposition. We believe that it is subject to the dependence of Arrhenius;
- \( \tau \) is the time of heat exposure;
- \( R \) is the universal gas constant;
- \( E \) – activation energy, KJ / mol;
- \( T_4 \) – maximum process temperature, K.

This dependence can be used for the qualitative analysis of the process of pyrolysis of PL. Given the complexity and multicomponent structure of real lubricants, experimental identification of \( k_0 \) and \( E \) constants is extremely difficult.

| Table 1. Typical yields of organic pyrolysis products. |
|------------------------------------------------------|
| Product | 785÷800°C | 815÷840°C | 840÷870°C | 870÷925°C |
| Product Yield (%) under various conditions |
| Product | 1,2 c | 0,05c | 0,35c | 0,1c |
| CH4 | 15,6 | 16,6 | 16,8 | 16,7 |
| C2H4 | 23,0 | 29,9 | 29,3 | 33,3 |
| C3H6 | 13,6 | 12,7 | 12,2 | 11,7 |
| C4H6 | 2,2 | 3,8 | 4,2 | 4,8 |
| C5 | 32,8 | 29,7 | 27,8 | 23,9 |

The methodology for the study of materials pyrolysis (more precisely, their gas-making ability) is as follows. 5 g of the test PL was loaded into the working chamber of the plant for the study of thermal stability. After sealing the chamber was fixed inside the heating furnace. The temperature inside the chamber was indicated with a thermocouple. Inside the chamber the volatile products of pyrolysis created pressure, which was registered with a high-precision model manometer. To find out the actual gas-generating value of the PL, the reading of the air pressure at the given temperature was subtracted from the pressure gauge indication.

Gas-generating value of some lubricants are presented in figure 3.
From table 2 it can be seen that the composition of the medium is of critical importance for the thermal decomposition of the PL and thermal stability caused by it. Graphite enhances its gas-generating value sharply. Gas pressure reaches values comparable with the energy of deformation and can significantly distort the stress state pattern in the zones of friction and plastic deformation. Silicone oil has little gas-generating value. In some cases, the air dissolved in the lubricating film may influence the gas pressure.

| The area of pyrolysis | PL                                      | Rate of pyrolysis, kPa / g • °C |
|----------------------|----------------------------------------|-------------------------------|
| I                    | Aluminol E (concentrate)               | 16,4·10^2                   |
|                      | IHO                                    | 19,6·10^2                   |
|                      | Graphitol E-21 (concentrate)           | 24,5·10^2                   |
|                      | Aluminol E (concentrate)               | 55·10^2                     |
| II                   | IHO                                    | 98,8·10^2                   |
|                      | Graphitol E-21 (concentrate)           | 165,2·10^2                  |

Summarizing the above, we can conclude that the thermal decomposition of PL is accompanied by complex physicochemical processes. Experimental and theoretical study of the products of PL thermal decomposition helps deepen the understanding of the mechanism of contact boundary friction and affect the tribological situation radically.

**References**

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