Research on the use of coke chemical production resin and its reducing properties to obtain copper powder for cladding lubricant

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The article presents studies on the possibility of using a heavy fraction of coke-chemical resin as a macrocomponent of cladding lubricant, its reducing properties for obtaining copper powder and protecting it from oxidation under the influence of temperature and oxygen in the air. All experiments were carried out using a thermal weighing unit consisting of a vertical tubular furnace, electronic scales. To obtain the kinetic characteristics of the pyrolysis of the resin of JSC "Shubarkulkomir", the dependencies of velocity on time at different temperatures were constructed. The values of the activation energy through the rate constant of the processes for different periods of removal of fractions are calculated. Based on these calculations, mathematical models of the removal of fractions of different periods at 200 and 257 °C. are obtained. To determine the temperature onset and the interval of complete reduction of copper oxide, curves of interaction of the charge components were obtained on a derivatograph (Model: Q-1500D; Manufactured by Paulik and Erdei, Hungary). At the rate of non-isothermal heating of the charge equal to 10 °/min, complete recovery of copper is achieved in the temperature range of 100-360 °C and within 26 min. Further, the resulting copper powder was tested as a composite material. Samples for testing composite powders based on a mixture of copper were made of 45 with a hardness of HRC 40-42. dimensions l x b x h = 10 x 10 x 10 mm. All samples had surfaces of class 8 roughness according to GOST 2789. The control bodies were rollers with d = 40 mm, 15 mm thick, made of 45 steel (GOST 1050) with a hardness of HRC 35-40. Based on the results obtained, it can be assumed that the finest copper films were obtained in the friction pair node, which contributed to a significant improvement in the basic tribotechnical parameters of the tested oil after the introduction of the developed antifriction composites into it.
Keywords: copper oxide, coking resin, pyrolysis, friction, tribological properties, cladding lubricant.
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Currently, the micron powders with a natural layered structure such as a molybdenum disulfide have been widely used as solid lubricants and effective additives to oils and lubricants in order to improve their tribological properties. Advances in this field have stimulated the research development on processes and mechanisms of wear with using the new compounds. Thus, the operating conditions, requirements for the mechanical properties, reliability, durability and maintainability of machines and mechanisms have been applied [1, 2].

The need to consider the availability and low cost of raw materials and reagents has required the study in order to use some different component compositions.

The aim of this paper has been to study availability of a heavy fraction of the coke-chemical coal tar pitch as a macrocomponent of a cladding lubricant, of its reducing properties in order to produce a copper powder and to prevent its oxidation at temperature and air oxygen.

The coal tar pitch is formed in the coke-chemical production, but has not found widespread use despite the availability to obtain many compounds [3-8]. In addition, coal tar and some of its pyrolysis products (soot, pitch) could be applied as a pure reducing agent. It would make it possible to use them to obtain pure substances, powders, because the excess can be removed by increasing the temperature [9]. Thus it may be possible to use them to obtain pure substances, powders, i.e. an excess can be removed at the high temperature [9]. In this paper, a copper oxide has been studied as a initial raw material to produce a metallic powder and as a product of re-oxidation by air oxygen during the lubricant operation. A stabilizing medium has been needed to prevent oxidation of a copper powder. Thus, solidol, soap grease and heavy alcohols have been used in the practice [10-12]. Therefore, presence of soot carbon in a pitch composition and a viscous liquid state give reason to study its using as a plastic lubricating macrocomponent of the cladding lubricant.

Fig. 1. Coke-chemical coal tar

The coal tar pitch has contained hydrocarbons and other organic compounds. They had the permanent reducing properties with copper oxide. They have formed soot carbon or poorer and high evaporation temperature hydrocarbons.

The technical characteristics of coke-chemical coal tar

It is a viscous black liquid, a characteristic phenolic odor, a product of coal carbonization. The yield has been 3.5 % (wt.) of coal charge (**Fig. 1**).

It is a thermodynamically unstable dispersed system of oligomers, the individual substances, their associates and molecular crystals.

Density is 1.17-1.20 g/cm^3. A low heat value makes 35.6-39.0 MJ/kg. A self-ignition temperature is 580-630 °C. maximal permissible concentration (MPC) in air of a working zone is 15-10-4 mg/m^3. Coal tar composition includes about 10 thousand compounds, of which more 480 (up to 50 % of total weight) have been isolated and identified.

Experiments on pyrolysis of coal tar made by Shubarkulkomir JSC

All experiments have been performed on a thermobalance with a vertical tube furnace and electronic balances. A cell with vertically moving free stand has been set on balances. After setting a furnace temperature, a crucible with coal tar sample has been placed in a crucible cell. Thus, the values have been calculated from weight loss and rate of weight loss (evaporation). On this basis, the readings of balances have been recorded over time. For this experiment, a sample of pitch has been used. It has been produced at 360 °C, an evaporation rate of 0.04 mg/min from 1,500 mg sample.

In order to obtain the kinetic characteristics of pyrolysis of coal tar made by "Shubarkulkomir" JSC, the rate-time dependencies have been plotted at different temperatures (Fig. **2-5**).

Activation energy of processes has been calculated using a rate constant for different periods by the formula:

- for a middle fraction:
$E_{each} = RT_1T_2\ln(k_2/k_1)/T_2\text{-}T_1 = E =$
$= 8.314\text{-}473\text{-}432\ln(1.548/0.38)/473K\text{-}432K = 7000.29$ J/mol
- for a light fraction:
$E_{each} = 8.314 \cdot 473 \cdot 432\ln(2.29/0.666)/473K\text{-}432K =$
$= 7961.34$ J/mol
- for a heavy fraction:
$E_{each} = 8.314 \cdot 473 \cdot 432\ln(0.2675/0.151)/473K\text{-}432K=$
$= 17195.27$ J/mol

Removal of the light fraction has been accompanied by an incubation period. It has been required a significant amount of energy to heat a sample to a set point of temperature. In this case, the light fraction has been intensively removed and the solid components of coal tar pitch have been melted. If activation energy of the parallel processes (heating and melting of a sample) is subtracted, then net activation energy of the light fraction's removal would be the lowest numerically.

Removal of the heavy fraction has been accompanied by the higher energy consumption.

The activation energy of processes has been calculated using a rate constant for different periods by the formula:

- for the light and middle fractions:
$E_{each} = RT_1T_2\ln(k_2/k_1)/T_2\text{-}T_1 =$
$= 8.314 \cdot 473 \cdot 530 \cdot \ln(2.188/1.519)/530\text{-}473 = 13343.5$ J/mol
- for a heavy fraction:
$E_{each} = 8.314 \cdot 473 \cdot 530 \cdot \ln(1.035/0.65)/530\text{-}473 =$
$= 17030$ J/mol
- for the super-heavy fraction:
$E_{each} = 8.314 \cdot 473 \cdot 530 \cdot \ln(0.496/0.6)/530\text{-}473 =$
$= 6960.25$ J/mol

Thus, activation energy values with using a rate constant for different periods of the fraction removal have been calculated.

Based on these calculations, the mathematical models of the fraction removal of different periods at 200 °C and 257 °C have been obtained.

Copper oxide reduction experiment

A charge for copper reduction has been made with a pitch excess by the formal reaction equation:

$$CuO + C_nH_{2n} = Cu + C_nH_{2n-2} + H_2O \quad (1)$$

In order to determine a temperature start and an interval of the complete copper oxide reduction, the interaction curves of the charge components have been obtained on Q-1500D derivatograph (Paulik and Erdei, Hungary).

Changes in a studied charge mass (1,500 mg) have been obtained from the data of a thermogravimetric curve (TG), including a copper oxide content in a sample of 563.27g (450 g copper).

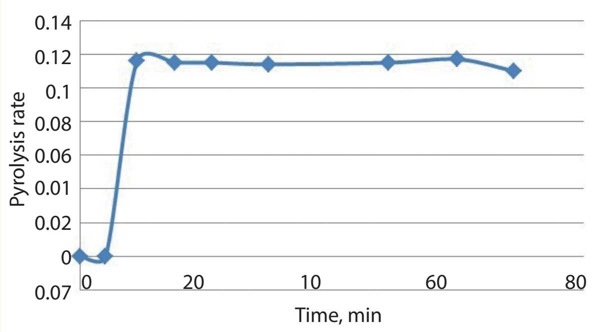

Fig. 2. Pyrolysis rate of coal tar at 95 °C

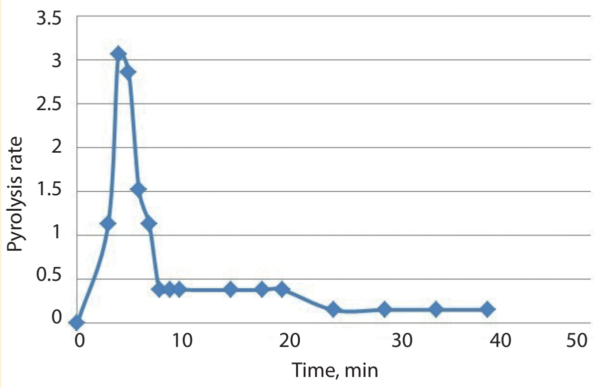

Fig. 3. Pyrolysis rate of coal tar at 159 °C

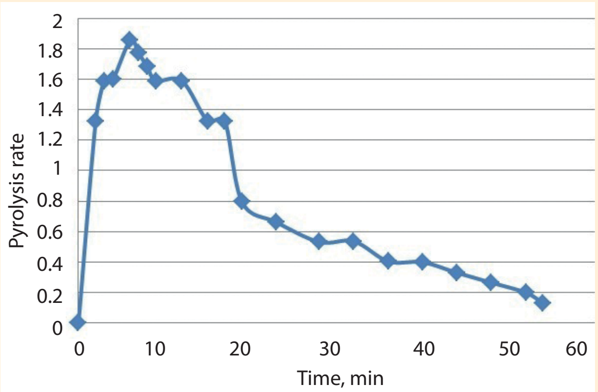

Fig. 4. Pyrolysis rate of coal tar at 200 °C

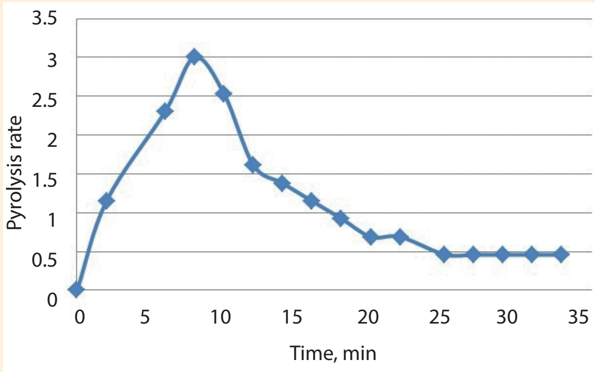

Fig. 5. Pyrolysis rate of coal tar at 257 °C

No	Non-isothermal TG curve data and calculation results			
	Temperature, °C	Δτ	Weight loss and degree of interaction	
	$T_2 - T_1$	Min	mg	α,%
1	100- 225	12.5	20	15.75
2	225- 270	4.5	15	11.81
3	270- 320	5	27	21.26
4	320- 360	4	65	51.18
Σ	100-360	26	127	100.0

The theoretical expected amount of flashed gas (water vapor) has been assumed to be 127 mg (100 %), based on the reaction equation (1). This approximate copper content in the charge has been due to the fact that a main component of the lubricant would be carbon with a residual amount of heavy hydrocarbon, then the reduced copper and a small amount of the refractory metal sulfides. A weight loss of the sample on the TG curve has begun at just higher 100 °C. TG data at 360 °C have corresponded to an expected amount of charge weight loss (127mg). Therefore TG data in the range of 100-360 ˚C have been taken for calculation. Data on the reduction of copper oxide by TG under non-isothermal heating conditions are presented in the **Table**. However, an inaccuracy due to evaporation of coal tar has been low (less 1%). In addition, vapors of coal tar have interacted with copper oxide.

At a rate of the non-isothermal heating of the charge equal to 10 °/min, the complete recovery of copper has been achieved in a temperature range of 100-360 °C during 26 min. Above 470 °C, a weight loss has increased to 265 mg, i.e. it has been related to decomposition of coal tar. In addition, 1,235 mg has remained from total weight of the charge. It has contained 450 mg of copper. As a result, it has been recommended to be used as the main component of the cladding lubricant. In this case, the pitch with a low liquefaction temperature has been able to replace the basic lubricating components such as solidol or soap, and copper has played the well-known role as a cladding additive [1].

Initial data of copper oxide reduction by TG under non-isothermal heating conditions of charge (1,500 mg)

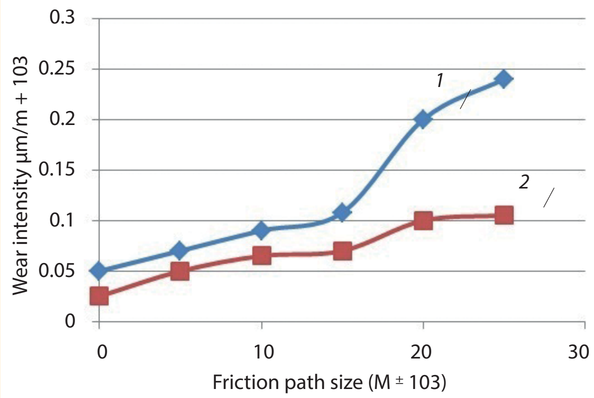

Fig. 6. Dependence of wear intensity on friction path of a complex:
1 - for base oil I-40 without additive; *2* - for oil I-40 with 1 % copper additive

containing 563.27 mg of copper oxide and the rest-coal tar pitch.

Then the obtained copper powder has been tested as a composite material.

Samples to test the composite powders based on a copper mixture have been made of steel (grade 45, hardness 40-42 HRC, units of size - l x b x h = 10 x 10 x 10 mm). All samples had the surface roughness of class 8 according to the GOST 2789. The control bodies have been rollers (d = 40 mm, thickness 15 mm, steel 45 under the GOST 1050) with hardness of 35-40 HRC.

The wear resistance of the metal liner has been investigated with oils containing the metal-cladding additives. The friction modes have been chosen as averaged. These modes have been used to the operating modes of friction units of machines and apparatuses. The dependence of the wear intensity on the friction path of the complex is shown in **Fig. 6**. In this case, the sliding speed of a metal roller has made V = 1m/s. Load on the sample has been increased stepwise from 2 MPa to the limit values. As a result, workability of the friction pair has been maintained. In some cases, the load on the sample has been increased until the scuffing appeared on the friction surfaces [4].

In order to separate a copper powder from the excess pitch, one of the known methods has been used such as distillation at a higher temperature or solvent cleaning (alcohols, esters).

Conclusions

A heavy fraction of coke-chemical resin was used as a cladding lubricant. Its reducing properties in the production of copper powder have been investigated. Based on the results, it can be assumed that the unit of the friction pair had the thinnest copper films. As a result, it has promoted the substantial improvement of the basic tribotechnical parameters of the tested oil after introduction of the developed anti-friction composites into it.

Results of this study have been obtained in laboratory of Branch "Zh. Abishev chemical-metallurgical institute" of RSE "National Center on complex processing of mineral raw materials of the Republic of Kazakhstan" of Ministry of industry and new technologies of the Republic of Kazakhstan within the framework of the scientific and technical project "Technology of producing the anti-friction composites with the high thermal and physical characteristics".

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