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OXIDATIVE STABILITY OF LUBRICATING MATERIALS WITH FULERENE NANOADDITIVES

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Abstract

Purpose: The purpose of this article is to investigate the possibility of using fullerene additives to fuels and lubricating materials for the improvement their oxidative stability and to determine the concentration of nanoadditives in hydrocarbon solutions. ***Research methods:*** Methods of increasing the oxidative stability of Castrol Magnet SAE 5w-30 oil by adding fullerene C60 and determination the content of nanoadditives in the hydrocarbon liquids were considered in the article. ***Results:*** The optimal concentrations of fullerene additives are determined, the method of photoelectrocolorimetric determination of their concentrations in lubricants is developed, the experimental data of optical properties of C_{60} solutions are obtained and the amount of fullerene in solution is calculated. ***Discussion:*** It is proposed to use fullerenes as an antioxidant additive, which significantly improves the thermal oxidative stability of oils and the method of determining of fullerene content.

Keywords: fullerene content, oil, oxidative stability, optical density, resins, photoelectrocolorimeter, fullerene additives

1. Introduction

The oxidative stability of hydrocarbons decreases when heating oil even to its operating temperature in the presence of dissolved oxygen and air oxygen. These factors cause formation the solid phase as a sediment and resins, which, deposited on the parts of the oil system, change its lubricating characteristics and cause filter contamination.

Stabilization of lubricating materials with traditional oxidation inhibitors is not effective enough. Therefore, there is a necessity to develop and implement a new generation of additives for the efficient operation of friction units, as well as the introduction of more efficient methods of oil regeneration.

The problem of determining the content of additives in fuels and lubricating materials today is no less relevant. The replacement period and the durability of the friction unit depend on their concentration [1].

2. Analysis of the research and publications

The main criterion for replacing any oil is the formation of oxidation products in addition to the depletion of the additive package.

Improvement of machines and mechanisms, their transition to more forced modes of operation, increasing the heat load of engines and their fuel and oil systems leads to a reduction of the service life of lubricants. Therefore, it is especially relevant the question of oxidative stability of oils, which means the resistance of hydrocarbons to oxidation by air oxygen and minimal susceptibility to the formation of resinous compounds, and also the possibility of regeneration for further use as intended.

Hydrocarbons of all classes are subject to oxidation, but with different speed and direction of reactions. That is why there is a difference between compositions of oxidation products, which is of great importance for the performance properties of lubricating materials [2-3].

Recently, there is a significant progress in the production and research of nanoobjects, new nanomaterials and nanotechnologies have emerged. Nanoclusters of a number of metals, fullerenes, and carbon nanotubes were synthesized. The new methods of observation and study of the properties of carbon nanostructures were created due to the development of physicochemical methods for studying their use in lubricating materials [4-6].

The discovery of a new allotropic modification of carbon has contributed to the significant development of many areas of science and techniques. This discovery is also very important for petrochemistry.

The use of nanomaterials in this field is a particularly promising area. Thus, fullerenes for petroleum products are used as a variety of additives that significantly improve physicochemical properties of lubricants.

Fullerenes have unique chemical properties. Their molecules are made up of five- and hexagonal fragments. The pentagons are absent in the layer structure of the graphite and they ensure the closure of the fullerenes structure. Fullerene C_{60} is the least stable and the most available of the fullerenes. The C_{60} molecule belongs to the icosahedron group and is a polygon which resembles a football of the type made of hexagons and pentagons, with a carbon atom at the corners of each hexagon and a bond along each edge.

Fig. 1. Fullerene molecula C_{60}

Fullerenes have high chemical inertness in relation to the process of monomolecular decomposition. Thus, the C_{60} molecule retains its thermal stability up to a temperature above 1500 °C, which cannot be said about other antiwear and antioxidant additives [7-10].

However, the oxidation of this form of carbon to CO and CO_2 is observed at significantly lower temperatures (about 250 °C) in the presence of oxygen, but such a temperature in the lubrication system of modern automobile and aircraft engines is not achieved. The process of slow oxidation leads to the formation of an amorphous structure in which one molecule of C_{60} has twelve oxygen atoms, while the molecule of fullerene almost completely loses its shape. It is necessary to take into account the fact that one molecule of antioxidant additive can contain one oxygen atom. This characterizes the high efficiency of nanoadditives in lubricating materials. An intensive formation of CO and CO_2 takes place when temperature increases above 500 °C and the final destruction of the ordered structures of fullerenes happens.

3. Problem statement

It was noted that hydrocarbons of all classes are subjected to oxidation, but with different rates and directions of reactions, and hence the composition of oxidation products.

Heating of oil to temperature above 100 °C in the presence of oxygen reduces the thermal and oxidative stability of hydrocarbons and leads to the formation of sediments and resins, which change, first of all, the color of the oil, its acid number, ash content, contaminate filters and oil supply channels to the friction units, accumulate on the parts as of varnish formations.

Therefore, there is a need to develop and study modified additives – fullerenes with the improvement of techniques to increase the oxidative stability of fuels and lubricants, as well as to determine the content of nanoadditives during the work of the friction unit.

4. Problem Solution

4.1. Methods and determination of oxidative stability of oil

The experiments were performed in accordance with GOST 11802 to evaluate the effect of fullerene C_{60} on the antioxidant properties of fuels and lubricants. The scheme of the device is shown in Fig. 2.

Fig. 2. Device for studying the oxidative stability of fuels and lubricants TCPT-2M

The method consists in the oxidation of a sample of fuel or lubricating material in the presence of copper as a catalyst at a temperature of 150 °C for 4 hours, followed by quantification of the formed precipitate.

It should be mentioned that the evaluation of oxidative stability is carried out only for gasoline, by the induction period, fuels for jet engines, diesel fuels, especially of vegetable origin (biodiesel), vegetable fats.

The same techniques and equipment can be used to assess and study the oxidative stability of oils.

The TCPT-2M device is designed to study the thermal stability of jet fuels. It is a metal electronic thermostat with four hermetically sealed stainless steel bombs. A manometer is placed to control the tightness of each bomb. The pressure must be at least 0,02 MPa. The constant temperature in the apparatus (150 °C) is maintained with an accuracy of ± 2 °C and monitored by a thermometer. The volume of one bomb is 225 – 250 cm^3, the ratio of volumes of fuel (lubricant) and air in the bomb is 1 : 3.

The device is heated to 150 ºC to perform the study, and then prepared bombs with oil samples are placed in it [3]. After 1 hour the temperature reaches 150 ºC. After 4 hours from the start of the test, the bombs are removed from the device and cooled to the room temperature. Then the bombs are opened, their contents are washed with a solvent and filtered. The precipitate is transferred to a filter from beakers, sticks, copper plates by washing them with a solvent. Then the filters are placed in cups used for drying and weighing, and the filters are dried to a constant weight.

The mass concentration of a sediment (C_{ced}), mg per 100 cm^3 is calculated by the formula:

$$C_{ced} = 2\,(m_2 - m_1),$$

where m_1 is the mass of the beaker for weighing with a clean filter, mg;

m_2 is the mass of the beaker for weighing with sediment on the filter, mg.

The change in the concentration of the precipitate was observed during the study depending on the concentration of fullerene, which was added as an additive to improve the antioxidant properties. Castrol Magnet SAE 5w-30 car engine oil was selected for the investigation. The test results are shown in Table.

4.2. Determination of fullerene concentration in solution

Fullerenes are the only soluble form of carbon, so the study of their solubility in different solvents has both fundamental and applied importance.

All known methods of analysis can be classified by the nature of the interaction of the substance with various types of external influences, and by the properties of the substance that can be determined by these methods.

Table

The results of investigation of oxidative stability of oil Castrol Magnetec SAE 5w-30

Composition	Fullerene concentration, g/kg	Precipitate concentration, mg/100 cm^3
SAE 5w-30	–	16
SAE 5w-30 + C_{60}	0.008	15.4
SAE 5w-30 + C_{60}	0.012	13.5
SAE 5w-30 + C_{60}	0.02	10.6
SAE 5w-30 + C_{60}	0.032	8.1
SAE 5w-30 + C_{60}	0,041	8.05

Photoelectrocolorimetric method is one of the most common and simplest ways to determine the amount of substance in the solution. It is more objective compared to visual colorimetry and gives more accurate results. The light flux is partially absorbed when passing through the colored liquid. The rest of the light flux falls on the photocell causing the formation of an electric current, which is registered by an ammeter. More concentrated solutions have higher optical density, higher degree of light absorption, and, accordingly, the lower strength of the resulting current.

There is a direct proportional dependence between the optical density and the concentration of the substance in the solution and further research were based on it.

A photocolorimetric measurement of solutions of fullerene C_{60} in toluene solution with different known concentrations of fullerenes was performed to establish the unknown concentration of fullerene C_{60} in toluene solution. Then a calibration graph of dependence for a certain wavelength of optical density on the fullerene concentration was built. The corresponding calculations of the unknown concentration of C_{60} fullerene in toluene solution were performed using obtained dependence.

Fig. 3 represents dependence of the optical density of fullerene solutions in toluene (with different concentrations) on the wavelength.

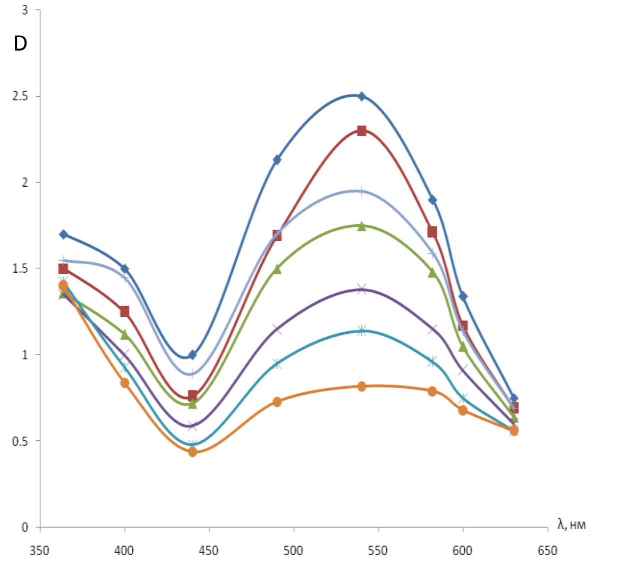

Fig. 3. Absorption spectra of fullerene solutions C_{60} in toluene. Fullerene C_{60} concentration beginning from the upper curve (1-6): 1 – 0,56 mg/ml; 2 – 0,45 mg/ml; 3 – 0,38 mg/ml; 4 – 0,28 mg/ml; 5 – 0,23 mg/ml; 6 – 1,14 mg/ml; 7 – unknown concentration C_{60}

A calibration graph for the selected wavelength (540 nm) was built to calculate the unknown concentration of C_{60} in the solution (Fig. 4).

A Trendline was added on the curve on the graph using the capabilities of Microsoft Excel.

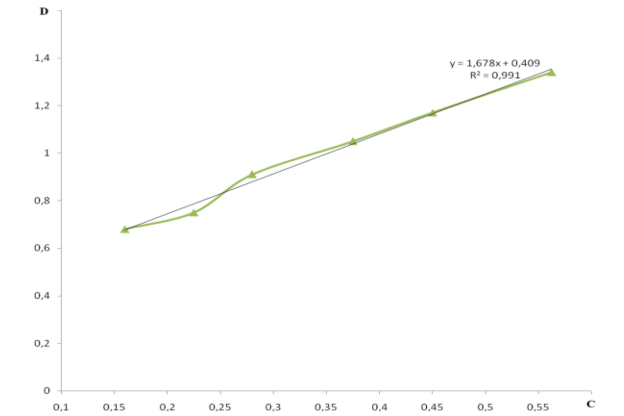

Fig. 4. The graph of dependence of optical density (D) on fullerene concentration (C) for the wavelength 540 nm

Thus we obtain a mathematical description of the Trendline in the form of an equation:

$$y = 1.678x + 0.409,$$

and calculate the concentration of C_{60} in a solution of toluene by the equation:

$$y = 1.678x + 0.409,$$
$$y = 1.95,$$

hence x = (1.95-0.409) / 1.678 = 0.92 mg/ml,

Thus, 0.92 mg/ml is the concentration of fullerene C_{60} in the solution.

This is a fairly high concentration of fullerene in solution, but it is possible to determine lower concentrations using this technique.

5. Discussion of results

The device TCPT-2M designed to determine the thermal stability of jet fuels was used to evaluate and study the oxidative stability of oils.

It was observed a change in the concentration of the precipitate during the analyzes depending on the fullerene concentration, which was added as an additive to improve the antioxidant properties. Castrol Magnet SAE 5w-30 car engine oil was selected for the investigation.

The performed investigation showed that increasing the concentration of fullerene C_{60} leads to a decrease in the content of resins in the oil, which indicates the antioxidant effect of the additive. The additive concentration of 0.03-0.04 g/kg gives a slight decrease in resin formation, which makes it possible to determine the optimal content of the additive in the oil.

An important factor is the approbation of the photocolorimetric method for determining the concentration of fullerene in oils and other hydrocarbon liquids, which is the simplest and the most accessible, and the possibility of its application in petrochemistry has been proved.

6. Conclusions

It have been determined the optimal content of fullerene additive in the oil, which is 0.003-0.004 mass %. The use of fullerenes as an antioxidant additive significantly improves the thermal oxidative stability of oils and is a promising area of research.

The efficiency of using the photocolorimetric method to establish the unknown concentration of C_{60} fullerene in solutions was confirmed. It is proved that this method is quite accurate and does not require large costs. Thus, it is possible to determine the concentration of fullerene additives in fuels and lubricating materials.

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Окисна стабільність змащувальних матеріалів з фулереновими наноприсадками

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Мета: Метою даної статті є дослідження можливості застосування фулеренових присадок до паливно-мастильних матеріалів для покращення їх окисної стабільності та визначення концентрації наноприсадок у вуглеводневих розчинах. **Методи**: У статті розглянуто метод підвищення окисної стабільності оливи Castrol Magnetec SAE 5w-30 шляхом добавки фулерену C_{60}, а також методику визначення вмісту наноприсадок у вуглеводневих рідинах. **Результати**: Визначено оптимальні концентрації фулеренових присадок та розроблено методику фотоколориметричного визначення їх концентрацій у змащувальних матеріала, отримані данні оптичних властивостей розчинів C_{60} та проведені розрахунки кількісті фулерену у розчині. **Обговорення**: Запропоновано використання фулеренів в якості антиокиснювальної присадки, що значно поліпшує термоокисну стабільність олив та методику визначення їх вмісту

Ключові слова: вміст фулеренів, олива, окисна стабільність, оптична густина, смоли, фулеренові присадки, фотоелектроколориметр

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Окислительная стабильность смазочных материалов с фуллереновыми наноприсадками

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Цель: Целью данной статьи является исследование возможности применения фуллереновых присадок к горюче-смазочных материалов для улучшения их окислительной стабильности и определения концентрации наноприсадок в углеводородных растворах. **Методы:** В статье

рассмотрен метод повышения окислительной стабильности масла Castrol Magnetec SAE 5w-30 путем добавки фуллерена C_{60}, а также методику определения содержания наноприсадок в углеводородных жидкостях. **Результаты:** Определены оптимальные концентрации фуллеренових присадок и разработана методика фотоколориметрического определения их концентрации в смазочных материала, полученные данные оптических свойств растворов C_{60} и проведены расчеты количеству фуллерена в растворе. **Обсуждение:** Предложено использование фуллеренов в качестве антиокислительной присадки, значительно улучшающую термоокислительную стабильности масел и методику определения их содержания.
Ключевые слова: содержание фуллеренов, масло, окислительная стабильность, оптическая плотность, смолы, фуллереновые присадки, фотоэлектроколориметр

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