

Features of the polyurethane study as a result of arson attacks

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ABSTRACT

Introduction. In most cases, the attackers use combustion initiators — affordable and cheap oil products (gasoline, diesel fuel, engine oils, or their mixtures) to intensify combustion. In order to establish the cause of a criminal fire, it is necessary to determine the presence of a fire initiator at the fire site. The study has been conducted in order to establish the interfering effect of decomposition products of the carrier object on the determination of the presence of diesel fuel.

Materials and methods. Polyurethane (car upholstery), which is able to adsorb liquid on its surface, was chosen as the carrier object, and diesel fuel was used as the combustion initiator, as the most common combustion initiator. The method of fluorescence spectroscopy was used in the study process.

Study results and discussion. Polyurethane samples with diesel fuel on its surface and without it were burned in a muffle furnace at temperatures from 200 to 300 °C for 5–20 min. After firing, the crushed samples were extracted, and fluorescence spectra were measured with the help of fluorimeter.

Conclusion. Analysis of the study results showed that when heating polyurethane samples covered with diesel fuel, it is possible to identify the combustion initiator as a strongly burned diesel fuel up to 250 °C inclusive for 5, 10, 15, and 20 min. When polyurethane samples are heated to temperatures above 250 °C, the identification of the combustion initiator as highly burnt diesel fuel is impossible.

Keywords: polyurethane; arson attack; combustion initiator; fluorescence analysis; monoaromatic hydrocarbons; biaromatic hydrocarbons; light oil products; luminescence; diesel fuel.

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Introduction

In Russia, the number of arson attacks is increasing at an alarming rate from year to year. Cars, real estate, documents are destroyed as a result of this criminal act. Moreover, people become victims of arson attacks [1]. Nowadays, an arson attack in Russia is one of the most accessible and simple method of settling accounts, intimidation, putting pressure on a competitor or other persona non grata. "The number of arson attacks is steadily increasing, since the probability of solving a crime after a fire, which destroys all traces, in attacker's opinion, is significantly reduced. This trend leads to a rigorous growth of undiscovered fires, as along with the growing popularity of arson attacks among criminal elements, the skill of the arsonists is growing, their methods are improved, new igniting substances are used" [2].

The bringing of an open fire source with the use of combustion initiators should be attributed to socially dangerous causes of fire. The problem of determining

the combustion initiators is becoming ever more important, and a fire-technical expert plays the key role, since the success of further investigation depends on his/her competent and quick actions.

The presence of several fire areas, the rapid spread of combustion, uncharacteristic for combustible materials, which are present at the facility, may be a consequence of the use of combustion initiators, they are typically highly flammable liquid (HFL), less often flammable liquid (FL), which are used by criminals as a mean for an arson attack [2].

Many experts believe that "the main factor that determines the frequency of use of certain highly flammable and flammable liquids as combustion initiators is their prevalence and accessibility to arsonists, the majority of whom use the first thing that is ready at hand. That is why so-called light oil products are often used — gasolines, kerosene, diesel fuels. Over the past three to four years, the arsonists use diesel fuels and motor

gasolines to commit a crime, but most often they use mixtures of HFL and FL (mixture of motor gasoline with diesel fuel and engine oil: a mixture of engine oil with diesel fuel and mixed solvent)” [2, 3].

Establishing the source and causes of any fire is a complex task and requires highly qualified specialists. One of the main tasks of the expert in identifying the combustion initiators is to detect them in the fire area, to establish their involvement in the beginning of combustion, to determine the component composition. The task is difficult to solve, since it is difficult to detect traces of combustion initiators in the conditions of a developed fire due to its fast burning out, but it is possible to identify them on carrier objects. Such objects are solid materials on the surface of which residues of HFL or FL are adsorbed [3]. One of such materials is polyurethane, which is widespread both in everyday life and in industry.

Various types of materials and products are produced on the basis of polyurethane: filled, reinforced, foamed, laminated, in the form of plates, sheets, blocks, profiles, fibers, films. Due to the variety of forms that polyurethanes can take — from soft foams to hard materials with different properties, they are used in the manufacture of products for the automotive and electronic industries, household goods, as a part of insulation materials, etc.

Polyurethane-based products and structures are widely used in all industries without exception [4–7], which causes a high probability of their use as objects for an arson attack with the use of combustion initiators.

Polyurethanes are materials on the surface of which combustion initiators can be adsorbed during an arson attack. The study of polyurethane as a carrier object, which adsorbed the remnants of flammable liquids or FL, will provide significant information about the causes of the fire.

The choice of polyurethane as a study subject, which is widely used for car upholstery, is due to the fact that cars (including car seats) are often the targets of arson attacks. The choice of diesel fuel for study is connected with its frequent use by attackers as a means of an arson attack due to its availability and low cost.

When burning, most polymeric materials decompose with the release of various decomposition products. Polyurethanes are no exception. The released combustion products can affect the results of determining the presence or type of combustion initiator.

The relevance of the study topic is that the interfering effect of polyurethane decomposition products on the identification of combustion initiators used during an arson attack has not been previously studied. In any case, materials on the interfering effect of the decomposition products of polyurethane on the results of determining the presence and type of combustion initiators has not been found.

The purpose of this work is to study the effect of polyurethane thermal decomposition products on the detection and identification of combustion initiators.

In accordance with the goal, the following tasks were solved:

- study of the properties of polyurethane and its behavior in fire conditions;
- study of research methods for combustion initiators and the selection of the most optimal one;
- study of the extractive components of carbonized polyurethane residues by fluorescence spectroscopy.

Some samples of polyurethane used for upholstery of car seats covered with the combustion initiator were used as study objects.

Materials and methods

When conducting a fire investigation, various research methods are used. Gas, gas-liquid, thin layer chromatography, infrared, fluorescence spectroscopy, field research methods, etc. are widely used to detect traces of oil and oil products [8–19].

The method of fluorescence spectroscopy is “a fast, simple and, at the same time, a very sensitive method of detecting highly flammable and flammable liquids in objects taken from fire sites” [2, 3].

The ability of oil, separate petroleum fractions and petroleum products, such as diesel fuel, to luminesce has been known for a long time. This effect is actively used not only in science, but also in engineering, medicine, and ecology [12–22], for example, in the detection of oil and oil reservoirs in geology, oil products (OP) in natural and waste waters, the study of drugs, the carrying out of analyzes in analytical environmental laboratories, etc.

At an excitation light wavelength of 255 nm in range of 270–300 nm, monoaromatic hydrocarbons (MH) luminesce — benzene homologues, mainly di- and tri-substituted alkyl benzenes; in the range of 300–330 nm — bicyclic aromatic hydrocarbons (BAH) — diphenyl, naphthalene homologues, including mono-, di-, tri- and tetrasubstituted, etc. The fluorescence wavelength of aromatic hydrocarbons and its intensity increase with increasing number of rings and conjugated double bonds [2, 3].

Aromatic hydrocarbons have the ability to fluoresce under the action of ultraviolet rays, from among the constituent components of HFL (FL): bicyclic aromatic hydrocarbons, tricyclic aromatic hydrocarbons (TAH), polycyclic aromatic hydrocarbons (PAH). Fluorescence of asphalt-resinous components is possible — products of the pyrolysis of the original HFL, as well as organic carrier objects. Such substances and materials include diesel fuel as a combustion initiator and polyurethane as a carrier object [2, 3].



Fig. 1. Polyurethane sample



Fig. 2. Muffle furnace



Fig. 3. Charred at $t = 200\text{ }^{\circ}\text{C}$ polyurethane samples: 1 — 5 min; 2 — 10 min; 3 — 15 min; 4 — 20 min

Experimental studies were conducted in accordance with the method set out in [23].

Polyurethane pre-cut into samples with dimensions of $50 \times 50\text{ mm}$ was used for the study (Fig. 1).

Polyurethane samples were prepared and tested without covering their surface with diesel fuel, there were three samples at each time point at a given temperature, as well as samples covered with 0.5 ml of diesel fuel, there were three samples at each time point at given temperature.

The samples obtained were fired in a muffle furnace (Fig. 2) at temperatures from 200 to $300\text{ }^{\circ}\text{C}$ for 5, 10, 15, and 20 min.

Charred polyurethane residues (Fig. 3) were selected for further study by fluorescence spectroscopy.

Sample preparation for the study was carried out by dissolving residues of HFLs in an organic solvent (hexane) being suitable for this purpose. Hexane is not able to fluoresce, so it is used in the study by the fluorescence analysis method.

The crushed polyurethane (without initiator and with the combustion initiator) was placed in a flat-bottomed flask with a glass stopper and poured with the minimum



Fig. 4. Shaking the crushed sample with the residues of the combustion initiator



Fig. 5. Extracts filtering

necessary amount of hexane so that the sample was covered with solvent, and then shook for about 0.5 h (Fig. 4).

The necessary stage of sample preparation is the extracts filtering prepared for the study (Fig. 5).

The spectrofluorimetric study of the analyzed samples was performed on a Fluorat-02-Panorama spectrofluorimeter (TU 4321-001-20506233-94). The analyzed samples with a volume of 5 mcl were placed in a cuvette with a capacity of 3 ml filled with $3/4$ hexane using a microsyringe and mixed. The conditions for the fluorescence spectra measurements were as follows: the spectral range of measurements is 270–450 nm, the excitation wavelength is 255 nm, the scanning step is 1 nm, the number of flares is 25, and the sensitivity is low.

Study results and discussion

In order to highlight the areas of the main maxima of the fluorescence spectrum, it is necessary to find in the Table 7 ([23], p. 51) the combination of areas of maxima of fluorescence, characteristic of the fluorescence spectrum of the object under study, and rank the analyzed object (categories) of HFLs or FLs corresponding to this combination.

Fig. 6 shows the spectrum on which an intense peak is observed in the range of 270–290 nm, in which MH is luminescent. The fluorescence intensity is 0.15 rel. units.

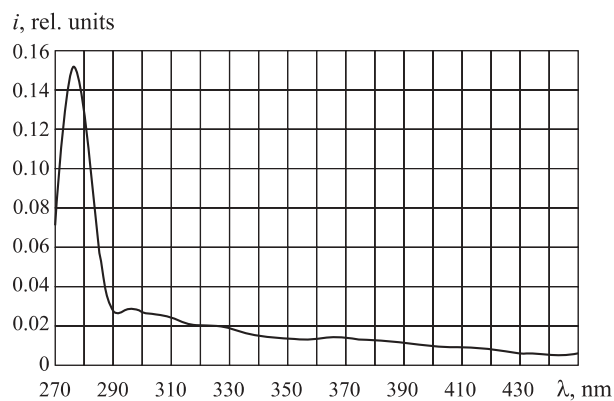


Fig. 6. Fluorescence spectrum of pure hexane: λ — wavelength, nm; i — fluorescence intensity

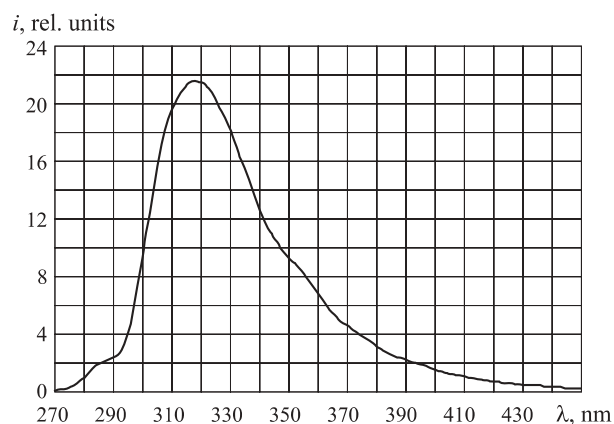


Fig. 7. Fluorescence spectrum of diesel fuel

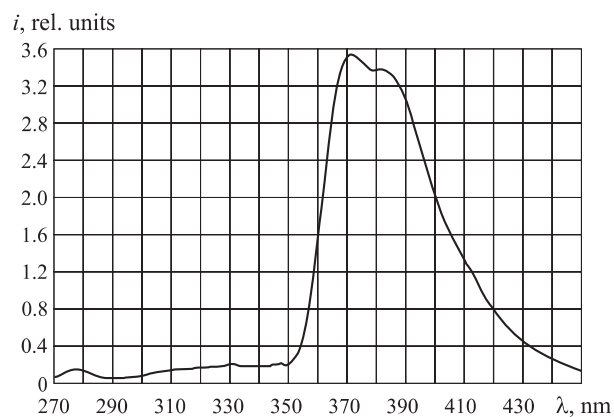


Fig. 8. Fluorescence spectrum of pure polyurethane at room temperature

This peak at a given intensity corresponds to the fluorescence spectrum of pure hexane.

Fig. 7 shows the fluorescence spectrum of diesel fuel, in which a maximum is observed in the range of 300–330 nm. The presence of this peak indicates the presence in the sample of bicyclic aromatic hydrocarbons, such as diphenyl and naphthalene homologues. The fluorescence intensity is 21 rel. units

The fluorescence spectrum of polyurethane that is not exposed to thermal effects is shown in Fig. 8.

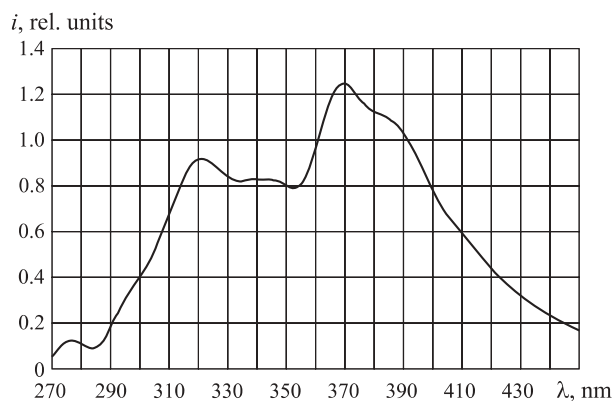


Fig. 9. Fluorescence spectrum of charred polyurethane at $t = 200\text{ }^{\circ}\text{C}$ for 5 min

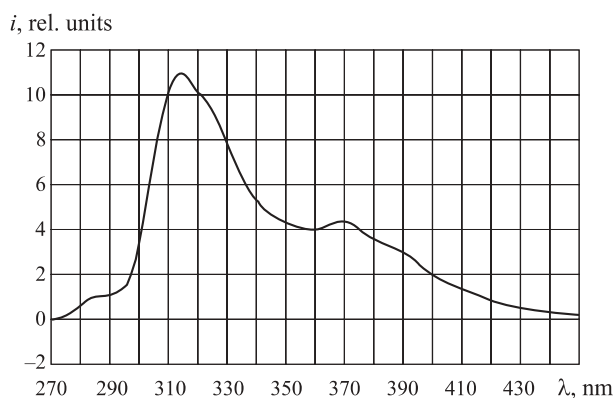


Fig. 10. Spectrum of a charred polyurethane sample with diesel fuel at $t = 200\text{ }^{\circ}\text{C}$ for 5 min

Fig. 9 shows the fluorescence spectrum of a polyurethane sample charred at $200\text{ }^{\circ}\text{C}$ for 5 min.

The study of the spectra presented in Fig. 8 and 9 showed the following facts. In the spectrum of a sample of pure polyurethane (see Fig. 8), there is a peak of maximum fluorescence in the range of 370–385 nm, in which TAH (for example, phenanthrene) is luminescent. In the spectrum of a charred polyurethane sample (see Fig. 9), there is an arm of maximum fluorescence in the range of 310–330 nm, corresponding to the BAH luminescence, and maximum fluorescence peaks in the range of 360–380 nm characteristic of TAH luminescence. The fluorescence intensity in the spectrum of pure polyurethane (see Fig. 8) is 3.6 rel. units, in the spectrum of charred polyurethane (see Fig. 9) — 1.25 rel. units. The obtained results indicate a decrease in TAH and the appearance of BAH in the spectrum of charred polyurethane (see Fig. 9).

Fig. 10 shows the fluorescence spectrum of a sample of polyurethane covered with diesel fuel charred at a temperature of $200\text{ }^{\circ}\text{C}$ for 5 min.

The spectrum of a charred polyurethane sample with diesel fuel (see Fig. 10) shows peaks of maximum fluorescence in the range of 300–330 nm corresponding to the BAH luminescence, in the range of 360–380 nm

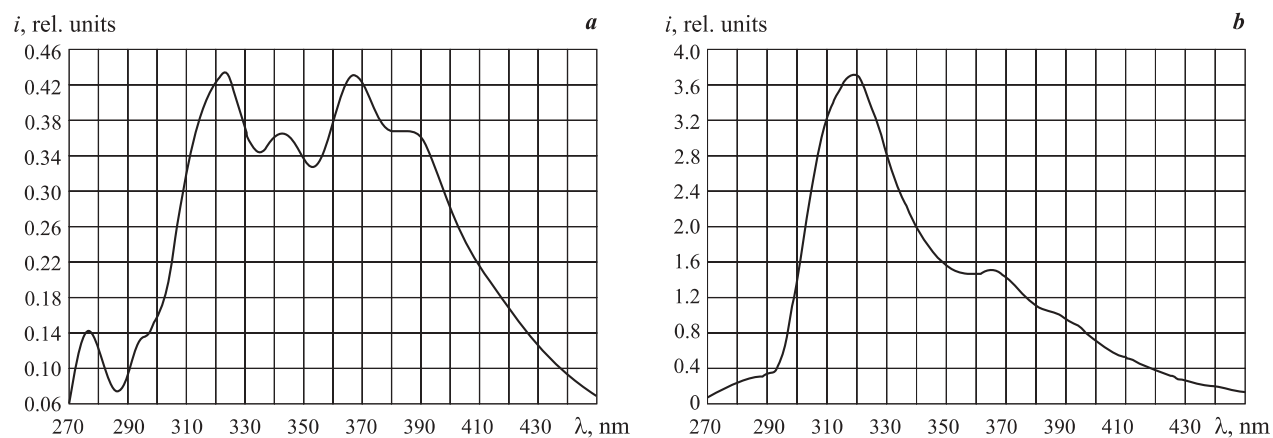


Fig. 11. Fluorescence spectrum of pure carbonized polyurethane (a) and with diesel fuel (b) at $t = 200\text{ }^{\circ}\text{C}$ for 10 min

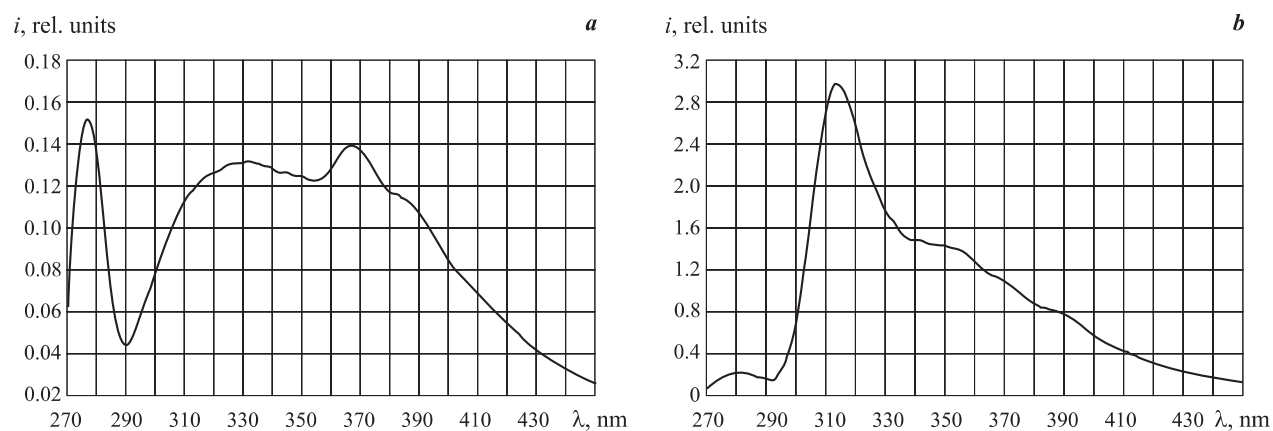


Fig. 12. Fluorescence spectrum of pure carbonized polyurethane (a) and with diesel fuel (b) at $t = 250\text{ }^{\circ}\text{C}$ for 20 min

characteristic of TAH luminescence, and a peak of low intensity in the range of 285 nm characteristic of MH luminescence. The fluorescence intensity in the spectrum in Fig. 9 is 1.25 rel. units, in the spectrum in Fig. 10 — 11 rel. units, which indicates an increase in BAH and a decrease in TAH in the spectrum in Fig. 10. According to Table 7 ([23], p. 51) fluorescence peaks found in the spectrum in Fig. 10 in the area of BAH and TAH give a possibility to identify the combustion initiator as a highly burned diesel fuel.

Fig. 11 shows the fluorescence spectra of polyurethane samples that do not contain diesel fuel and are covered with it, after heating in a muffle furnace for 10 min at a temperature of $200\text{ }^{\circ}\text{C}$.

In the spectrum of charred polyurethane (see Fig. 11,a), peaks of maximum fluorescence are observed in the range of 315–330 and 335–355 nm corresponding to the BAH luminescence, as well as in the range of 360–380 nm characteristic of TAH luminescence.

In the spectrum of charred polyurethane with diesel fuel (Fig. 11,b), there are peaks of maximum fluorescence in the range of 310–325 nm, in which BAH is luminescent, and in the range of 360–375 nm characteristic of TAH luminescence. The fluorescence intensity in the spectrum in Fig. 11,a is 0.44 rel. units, in the spectrum

in Fig. 11,b — 3.7 rel. units, indicating an increase in BAH and a decrease in TAH in the spectrum of charred polyurethane with diesel fuel. It is possible to identify the combustion initiator as intensity burned diesel fuel ([23], p. 51, Table 7) on the basis of fluorescence peaks discovered in the spectrum in Fig. 11,b in the area of BAH and TAH.

Fluorescence spectra of polyurethane samples heated to a temperature of $250\text{ }^{\circ}\text{C}$ for 20 min, which are covered and uncovered with diesel fuel are shown in Fig. 12.

In the fluorescence spectrum of charred polyurethane (Fig. 12,a), there are peaks in the range of 315–345 nm, corresponding to the BAH luminescence, and in the range of 360–375 nm characteristic of the TAH luminescence. The fluorescence intensity is 0.15 rel. units. Since the fluorescence intensity is below 0.25 rel. units, this result is considered to be related to background contamination.

In the fluorescence spectrum of charred polyurethane with diesel fuel (Fig. 12,b), there are peaks of maximum fluorescence in the range of 310–325 nm, in which BAH is luminescent, and in the range of 340–375 nm characteristic of TAH luminescence. Fluorescence intensity in the spectrum in Fig. 12,a is 0.15 rel. units,



Fig. 13. The outburst when heating polyurethane

in the spectrum in Fig. 12,*b* — 3.0 rel. units, which indicates an increase in the amount of BAH and a decrease in TAH in the spectrum in Fig. 12,*b*. According to Table 7 [22], fluorescence peaks found in the spectrum in Fig. 12,*b* in the area of BAH and TAH give a possibility to identify the combustion initiator as a highly burned diesel fuel.

When heating samples of polyurethane with diesel fuel at a temperature of 300 °C, an outburst occurred within 3 min inside the muffle furnace, which was accompanied by several claps, the temperature sharply increased up to 500 °C (Fig. 13), the fumes of diesel fuel and combustion products of polyurethane self-ignited. Polyurethane burned out with the formation of a porous black residue.

Fig. 14 shows samples of polyurethane without the addition of diesel fuel and with the addition of a combustion initiator after time-exposure in a muffle furnace at 500 °C for 3 min.

An analysis of the spectra obtained (Fig. 15) shows the following facts.

In the fluorescence spectrum of charred polyurethane (see Fig. 15,*a*), there are observed peaks in the range of 315–335 nm, in which BAH is luminescent, and in the range of 350–370 nm characteristic of TAH luminescence. The fluorescence intensity is 0.68 and 0.63 rel. units.

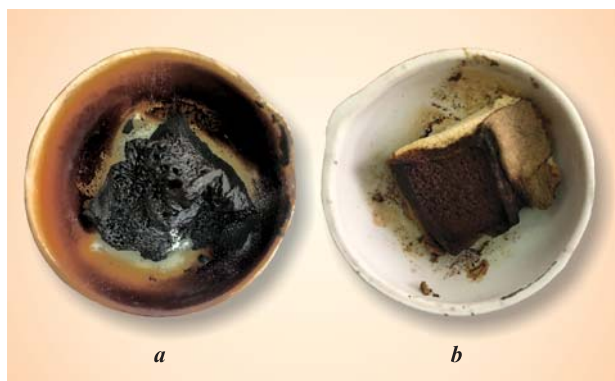


Fig. 14. Polyurethane sample after heating at 500 °C for 3 min: *a* — with diesel fuel; *b* — without diesel fuel

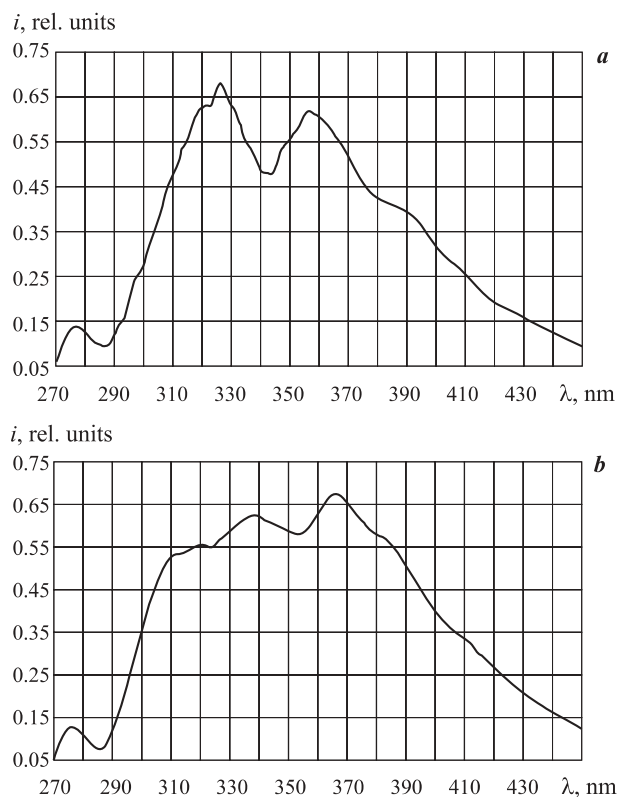


Fig. 15. Spectrum of pure charred polyurethane (*a*) and with diesel fuel (*b*) when heated at a temperature of 500 °C for 3 min

In the spectrum of charred polyurethane with diesel fuel (Fig. 15,*b*), there are observed peaks in the range of 310–340 nm, in which BAHs are luminescent, and in the range of 360–375 nm characteristic of the TAH luminescence, which are also observed in the polyurethane spectrum. The maximum fluorescence intensity is 0.6 and 0.68 rel. units in this case. Thus, when comparing the fluorescence spectra presented in Fig. 15, it can be concluded that it is not possible to identify the combustion initiator as diesel fuel in this case.

Conclusions

1. Analysis of the obtained study results has shown that when heating polyurethane samples up to 250 °C inclusive for 5, 10, 15, and 20 min, it is possible to identify the combustion initiator as a highly burned diesel fuel.

2. When polyurethane samples are heated to temperatures above 250 °C, the identification of the combustion initiator as intensely burnt diesel fuel is impossible.

3. When heating polyurethane samples with diesel fuel to a temperature up to 250 °C, the decomposition products of polyurethane do not interfere with the identification of the combustion initiator.

4. When heating polyurethane samples with diesel fuel up to 300 °C, the samples ignite with a sharp rise in temperature up to 500 °C. According to the obtained fluorescence spectra, it is impossible to establish the combustion initiator in this case.

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