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INVESTIGATION OF FIRE OCCURRENCE FROM IGNITION AND EXPLOSION OF A VAPOR-AIR MIXTURE DURING GAS WELDING OPERATIONS

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Abstract. Using the example of a real fire that occurred as a result of violations of fire safety requirements during gas welding operations, it is demonstrated how the combined use of instrumental and computational methods makes it possible to determine the cause of the fire. The nature of combustible substances has been determined by fluorescence spectroscopy, gas-liquid chromatography and infrared spectroscopy. Using mathematical calculations, the amount of combustible substances necessary for the formation of an explosive mixture was determined. It is demonstrated how a combination of physical-chemical research methods and computational methods, allows for the determining the causal relationship between gas welding operations and the aforementioned explosion.

Keywords: gas welding, instrumental research methods, gas-liquid chromatography, fluorescence spectroscopy, infrared spectroscopy, calculation methods, explosion, fire technical expertise

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Introduction

Fires that result from the formation of vapor-gas-air mixtures lead to serious consequences, thus, it is a great emphasis must be made on study the possibility of their occurrence and causes. Often the cause of such fires with are gas welding operations.

During gas welding operations at facilities containing flammable substances many fire-hazardous processes take place. They can easily cause an explosion or ignition of aforementioned mixtures. Lots of heated sparks are formed, which can directly cause a fire or an explosion. In addition, during the wielding process, the temperature of surrounding objects rises, resulting in the evaporation of flammable liquids, which can lead to the formation of vapor-gas-air mixtures.

When investigating fires, it is necessary to answer questions regarding the possibility of explosive vapor-gas-air mixtures formation, as well as to find the cause of the fire, (which is usually associated with the heated sparks). To establish the nature of combustible substance physical-chemical analysis methods (such as fluorescence spectroscopy, gas-liquid chromatography and infrared spectroscopy) are used. In addition, it is necessary to calculate the concentration of a combustible substance in order to determine whether the value of this concentration is in the range between the lower (LCLP) and the upper concentration limit (UCLP) of flame propagation. As a result of the study, it is possible to answer questions regarding the possibility of the explosive vapor-gas-air mixture formation and determine the cause of the fire.

Main part

During electric and gas welding operations in maintenance plant an ignition and explosion occurred when a worker was cutting an empty 200-liter metal barrel, which previously contained Gazprom Neft Diesel 15W-40 engine oil. During the welding process, the barrel was covered with a lid. While inspecting the scene, a barrel with residues of a dark brown oily liquid, presumably engine oil, was found (fig. 1) and later a lid from a barrel with traces of a light gray substance on its inner side was located (fig. 2).

a b

Fig. 1. **A metal barrel submitted for expertise with oily liquid residues: a – metal barrel; b – oily liquid residues**

Fig. 2. **The lid of a metal barrel received for expertise, with traces of a light gray substance**

The experts were tasked with determining the kind of residues left in metal barrel: was it fuel, lubricant or any other fire-explosive substance? Determining the possibility of ignition and explosion of a vapor-air mixture formed with an oily liquid inside that metal barrel and a light gray substance on the lid when exposed to a flame from a welding machine was also tasked.

To complete these tasks, physical-chemical studies of the oily liquid residues found in the barrel were carried out using fluorescence and infrared spectroscopy, as well as gas-liquid chromatography (GC). The study of the chemical composition of the light gray substance found on the lid was carried out by IR spectroscopy, and the acetone extract of this substance was studied by the GC method. Moreover, mathematical calculations were carried out to determine the possibility of explosive vapor-gas-air mixture formation.

The study of an oily liquid from a barrel by fluorescence spectroscopy and GC was carried out without preliminary sample preparation according to the conditions specified in the methodological manual [1]. When taking fluorescence spectra, the amount of the studied oily liquid when added to a cuvette with 3 ml of hexane of the OSCH brand was 0,02 µl. The fluorescence spectra of the studied liquid are shown in fig. 3.

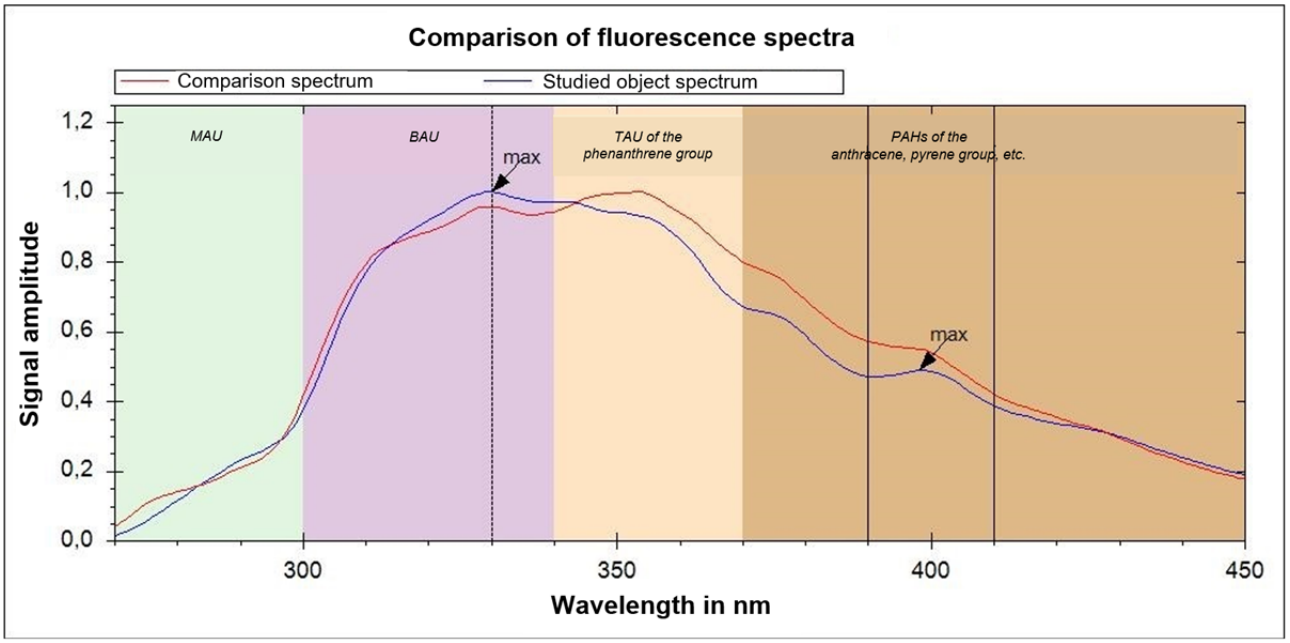

Fig. 3. **Studied liquid fluorescence spectra (blue curve) and the arbitration sample of Lukoil Avangard 10W-40 engine oil, STO 00044434-005-2005 (red curve)**

As can be seen from Fig. 3, the fluorescence spectrum of the studied liquid has a maximum in the 300–330 nm area, which indicates the presence of bicyclic aromatic hydrocarbons (diphenyl, naphthalene and their homologues) in the sample, as well as a maximum in the 340–370 nm area, which indicates the presence of tricyclic aromatic hydrocarbons (phenanthrene and its homologues) in the sample [1], these hydrocarbons are contained in products of heavy oil fractions, in particular, in engine oils, lubricants, impregnations, fuel oil, etc. [2]. When comparing the fluorescence spectrum of the oily liquid with the fluorescence spectra of arson agents from the all-Russian spectral data base (fig. 3), the similarity of the obtained spectrum in position and intensity of the fluorescence maxima with the spectrum of motor oil was revealed.

Chromatographic examination of the oily liquid from the barrel and an acetone extract of the light gray substance from the lid was carried out on a gas-liquid chromatograph device «Kristall 5000.1» manufactured by SCB Chromatek according to the conditions specified in the methodological manual [2].

Fig. 4 shows the chromatogram of the studied oily liquid (curve 1). It represents a multiplicity of peaks in the region of retention times from 19 min to 75 min. In addition, hydrocarbons from C_{12} and higher are present on the chromatogram, which is typical for components of heavy oil fractions such as motor oils. From the comparison using the «fingerprint» method, the similarity of the chromatograms of the liquid under study with the chromatogram of the arbitration sample of motor oil was revealed (fig. 4).

From the analysis of the chromatogram of the acetone extract of a light gray substance, by concurrence of retention times with the retention times of peaks of aliphatic and aromatic hydrocarbons, it was found that ethyl acetate, benzene and toluene are present in the extract, as well as a fairly intense unidentifiable asymmetric peak with a linear retention index equal to 996 (fig. 5). The asymmetry of the peak indicates that this component belongs to an oxygen-containing compound [3].

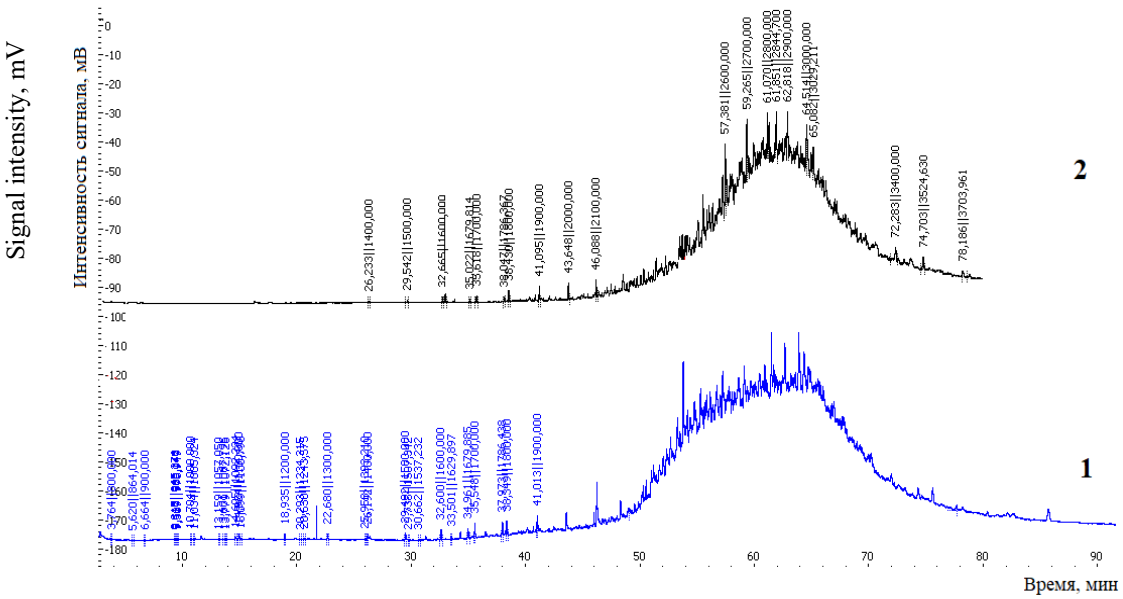

Fig. 4. **Chromatogram of the test liquid with an arbitration breakdown of the motor oil: 1 – the liquid sample; 2 – universal all-season motor oil**

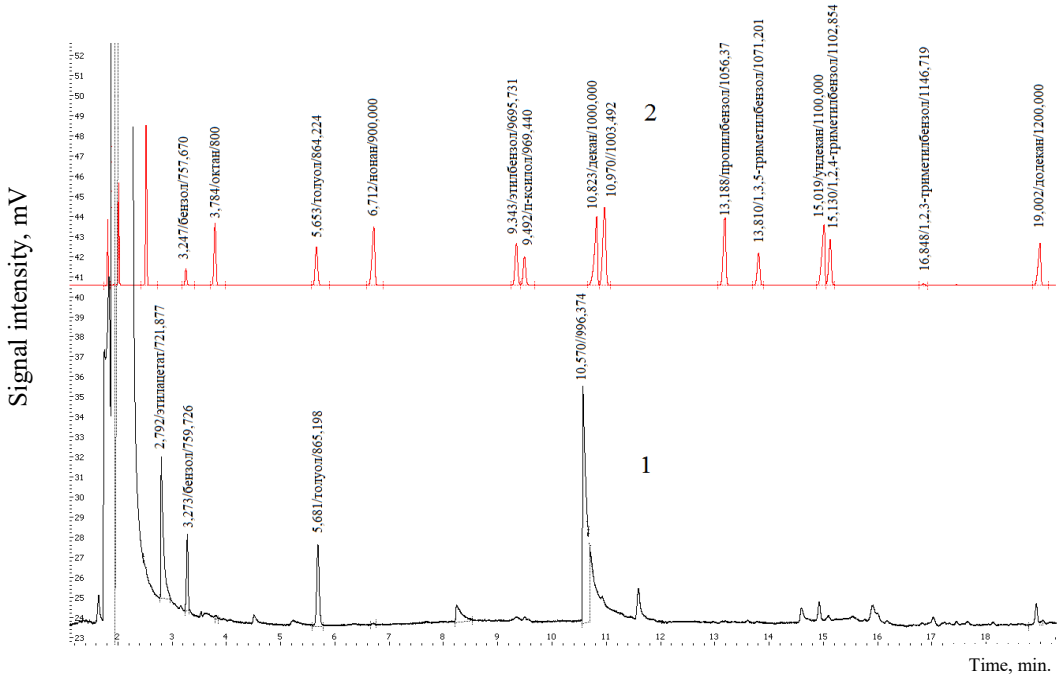

Fig. 5. **Chromatogram of acetone extract of a light gray substance and a reference mixture of aliphatic and aromatic hydrocarbons: 1 – acetone extract of a light gray substance from the barrel lid; 2 – reference mixture of aliphatic and aromatic hydrocarbons**

Next, a liquid from a metal barrel and a light gray substance from the lid were examined. In addition, an acetone extract of a light gray substance was studied by IR spectroscopy to determine the type of binder. The liquid and acetone extract of the substance were studied without preliminary sample preparation using an optical window made of KBr crystal. The study of a light gray substance was carried out using the method of tableting with potassium bromide (KBr). The spectra were taken on an IR Fourier spectrometer FSM 1201 in the range of 4000–400 cm^{-1} according to the conditions specified in the methodological manual [4]. Based on the obtained spectra, the composition of the submitted samples was determined by the «fingerprint» method. The interpretation of the IR spectra was carried out in accordance with the sources [5–7].

The IR spectrum of an oily liquid is shown in fig. 6 (curve 1), from which it can be seen that absorption bands 2955, 2924, 2855, 1462, 1377 and 723 cm^{-1} are observed on the IR spectrum.

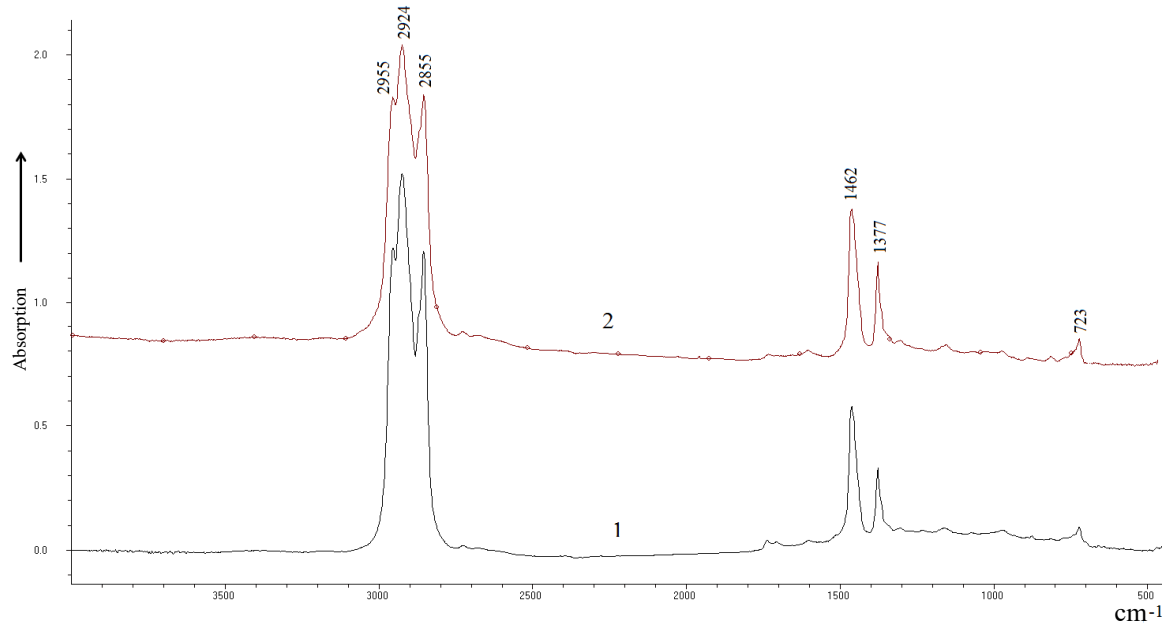

Fig. 6. **IR spectrum of the liquid under study with an arbitrage breakdown of engine oil: 1 – studied liquid; 2 – motor oil BP Visco 3000 10W-40**

The presence of absorption bands in the 3000-2800 cm^{-1} region suggests that the sample is an organic substance. The absorption bands 2955, 2924 and 2855 cm^{-1} refer to valence vibrations of C-H bonds of methyl and methylene groups, the bands 1462 and 1377 cm^{-1} refer to symmetrical and antisymmetric deformation vibrations of C–H bonds, and the absorption band 723 cm^{-1} refers to the deformation pendulum oscillation of the methylene group in paraffin hydrocarbons with an unbranched structure (fig. 6). The presence of these absorption bands on the IR spectrum of the liquid under study indicates the presence of aliphatic hydrocarbons in its composition. These hydrocarbons are included, in particular, in the composition of various petroleum products. When comparing the spectrum of the liquid under study with the arbitrage sample of engine oil (fig. 6, curve 2), a coincidence in the position of the main absorption bands is visible.

Absorption bands 2953, 2924, 2855, 1725, 1688, 1458, 1421, 1379, 1180, 1120, 1078, 1018, 875, 713, 671, 640, 611, 535 and 467 cm-1 (fig. 7, curve 1) are observed on the IR spectrum of a light gray substance from the lid. Bands 3060, 3026, 2955, 2924, 2855, 1730, 1688, 1530, 1460, 1379, 1246, 1159, 1070, 1030, 766 and 700 cm^{-1} are observed on the IR spectrum of its acetone extract (Fig. 7, curve 2). The presence of a group of intense absorption bands in the region of 3000-2840 cm^{-1} (valence vibrations of C-H bonds in methyl and methylene groups) and absorption bands of 1458 and 1379 cm^{-1} (deformation vibrations of C-H bonds) suggests that the samples contain organic substances having linear hydrocarbon fragments in their structure.

In addition, the IR spectrum shows relatively weak absorption bands of 3060 and 3026 cm^{-1}, as well as of 1600 and 1530 cm^{-1}, characteristic of valence vibrations of =C-H and C=C bonds of aromatic compounds and absorption bands of 766 and 700 cm^{-1} of out-of-plane deformation vibrations of C-H of various types of benzene ring substitution.

The presence of absorption bands 1730, 1246 and 1159 cm^{-1} on the IR spectrum is characteristic of valence vibrations of the C=O and C-O groups in the ester group. In addition to the bonds of ester groups in the infrared spectrum of the substance, there are fluctuations in the C-O and O-H bonds of alcohol functional fragments in the range of wave numbers 1070–1020 cm^{-1}.

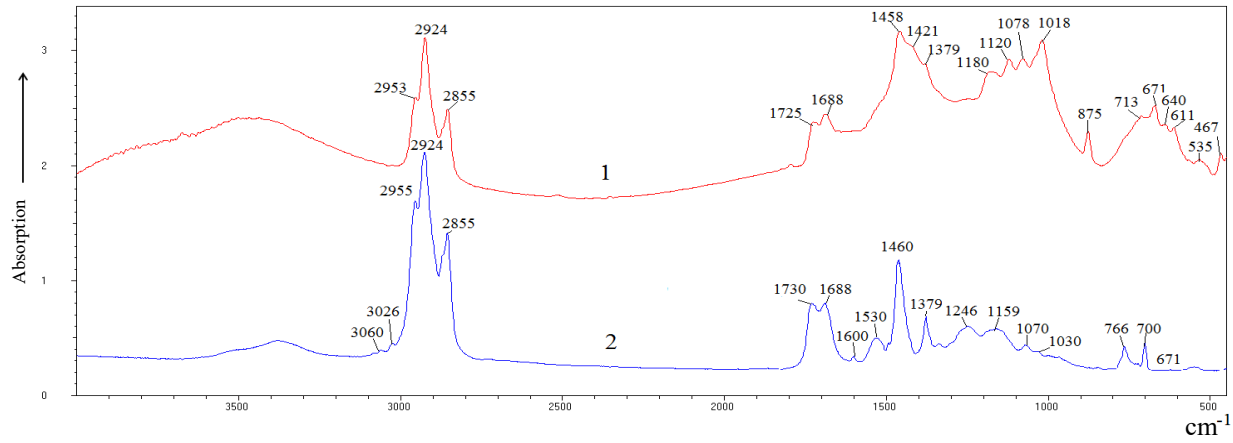

Fig. 7. **IR spectra: 1 – light gray substance;**
2 – acetone extract of a light gray substance

The presence of these absorption bands on the IR spectrum of the studied substance is characteristic of alkyd resin-based paints and varnishes (paint coatings, GF, PF, etc.).

It is known that paint and varnish materials, in addition to the film-forming agent, contain plasticizers, fillers, stabilizers, etc. Thus, the presence in the IR spectrum of the studied paint of an absorption band in the region of 1500–1400 cm^{-1} (1423 cm^{-1}), a clearly defined absorption band of 875 cm^{-1} and a band of 713 cm^{-1} indicates the presence in this a sample of the CO_3^2 (carbonate) anion, which is most likely present as a filler (chalk) in this paint coating (fig. 7). The presence of absorption bands in the region of 670-450 cm^{-1} indicates the presence of various inorganic compounds in the studied material, such as oxides, hydroxides, etc., which can be included as fillers, inorganic pigments in the composition of paint and varnish materials

Thus, using the methods of fluorescence spectroscopy, GC and IR spectroscopy, it was revealed that the residues of the submitted oily liquid are petroleum products related to engine oil, and the submitted light gray substance on the lid is a paint coating based on alkyd resins.

Further investigation consisted in determining the amount of residues found in the barrel (engine oil and paintwork), which could lead to ignition and explosion of the vapor-air mixture. To do this, two scenarios of ignition of the vapor-air mixture were considered:

1) ignition of a vapor-air mixture of motor oil and air vapors;
2) ignition of a vapor-air mixture of vapors of paint solvent components and air.

Let's consider the scenario of ignition of a vapor-air mixture of engine oil and air vapors.

The flash point of the Gazprom Neft Diesel 15W-40 engine oil in the barrel is 230 °C, which is much higher, than air temperature on the repair plant at the time of the fire.

It is known that electric and gas welding carried out in containers containing residues of combustible substances is very dangerous even if the flash point of the combustible substances is higher than the temperature of the container, which is explained by the heating and evaporation of the combustible substance occurring during welding. Thus, in [8] it was indicated that diesel fuel can ignite from welding particles at 62 °C. The warm-up time in the experimental results ranged from 15 s to 180 s, depending on the height of fuel filling.

The video footage presented for the study shows that ignition and explosion in the barrel occur almost instantly (no more than 3 seconds. after the start of work), and the temperature according to data from the archive of the actual weather of the Federal Hydrometeorological Center in the territory of the repair plant did not exceed 25 °C. In this regard, this scenario is not possible, since the engine oil could not, under these conditions, lead to ignition and explosion of the vapor-air mixture.

Let's consider the scenario of ignition of a vapor-air mixture of vapor components of paint solvents and air.

The components of paint solvents have fairly low flash points (as a rule, lower or comparable to the ambient temperature in the workshop). So, toluene has a flash point of 5 °C, benzene – 11 °C, ethyl acetate – 2 °C [9].

Since as a result of ignition and explosion of the vapor-air mixture, a significant part of the substances contained in the barrel burned out, it is not possible to accurately determine the initial composition of the mixture and the ratio of components.

Therefore, to calculate the amount of residues found in the barrel, which could lead to ignition and explosion of the vapor-air mixture, toluene was selected, which was detected by the GC method in the study of acetone extract of the paint coating. Toluene has a flash point of 5 °C and an LCLP value of 1 % [9].

To answer the question both traditional engineering calculation methods [8, 10, 11] and mathematical modeling of gas propagation in a vapor-gas-air mixture [12, 13] are used. In this case, there is no need to carry out mathematical modeling, since the vapor distribution in the volume of the barrel is uniform due to the fact that the barrel was closed and sufficient time has passed to equalize the concentration inside its volume.

The amount of toluene needed to ignite its mixture with air was calculated. The calculation used a barrel volume value of 200 liters.

The concentration of toluene vapors in the barrel, corresponding to the LCLP, was:

$$C = \frac{V_g}{V_b}.$$

where V_g – gas volume, l; $V_b = 200$ – barrel volume, l.

The LCLP of toluene was 1%. Therefore, the required volume of toluene vapors for the creation of LCLP is equal to:

$$V_g = V_b C = 200 \cdot 0{,}01 = 2\ l.$$

Thus, the required volume of toluene to create an explosive vapor mixture of 2 liters was:

$$V = \frac{V_g}{22{,}4} \cdot \frac{M}{\rho \cdot 1000} = \frac{2}{22{,}4} \cdot \frac{92{,}1}{0{,}867 \cdot 1000} = 9{,}5 ml.$$

where M = 92,1– molar mass of toluene, g/mol; ρ = 0,867– toluene density, kg/m^3.

A similar calculation for benzene and ethyl acetate resulted in values of 11,4 ml and 19,1 ml. The unidentifiable component detected by the GC method in the acetone extract of the paint coating was not taken into account when calculating the possibility of formation of an explosive mixture, since there was no data on its physical-chemical properties. In addition, the release time of this component (10,570 min) is similar to the release time of the decane (10,823 min), and, accordingly, their temperature characteristics are close, which makes the contribution of this component to the formation of an explosive mixture unlikely.

It must be remembered that in the case of mixed solvents, the amount of solvent required to create explosive concentrations will be determined by the ratio of the solvent components to each other.

Thus, from the calculations carried out, it was concluded that the presence of motor oil could not lead to ignition and explosion of the vapor-air mixture when exposed to the flame of the welding machine. The formation of an explosive concentration of a vapor-air mixture in a barrel is possible if there are components of organic solvents in it. The formation of an explosive concentration in a 200-liter barrel is possible if it contains 9,5 ml of toluene, 11,4 ml of benzene or 19,1 ml of ethyl acetate.

Conclusion

Thus, the article shows how, with a combination of physical-chemical research methods and computational methods, it is possible to determine the causal relationship between gas welding operations and the explosion.

Physical-chemical studies of the oily liquid residues found in the barrel were carried out using fluorescence and infrared spectroscopy, as well as the GC method. The nature of the combustible substance has been established by methods of fluorescence spectroscopy, GC and IR spectroscopy. Using mathematical calculations, the amount of combustible substance necessary for an explosive mixture formation of was determined. It is demonstrated how, using a combination of physical-chemical research methods and calculational methods, it is possible to determine the causal relationship between gas welding operations and an explosion.

The novelty of the study of this problem lies in the ability to solve this type of problem with the combined application of instrumental research and computational methods.

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