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Coordination compounds for rheological and physical-chemical regularity of energy consumption decrease while transporting crude oils

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Abstract

For the first time, complex compound of zinc (II) 1, 2, 4, 5-benzenetetracarboxylic acid with a porous structure was synthesized. Individuality and chemical formula of a complex compound was determined according to X-ray diffraction, elemental, IR spectroscopy and derivatographic analysis. The process of thermal decomposition of the resulting compound was also studied. It is also found that, despite the fact that the parameters of the unit cell of the crystal are significantly different from the known complex, it retains its layered polymer and porous structure. Recently, high-viscosity oil fields, where non-Newtonian crudes are met, are rapidly developed.

1. Introduction

Oil is a natural multicomponent organic liquid. It is based on a mixture of naphthenic, aromatic and paraffinic hydrocarbons. Oil is a mixture of about 1000 individual substances, of which most are liquid hydrocarbons and heteroatomic organic compounds, mainly sulfurous, nitrous and oxygen, organometallic compounds, the remaining components are dissolved hydrocarbon gases, water, mineral salts, solutions of organic acid salts, etc., mechanical impurities.

The content of all these components can vary widely and depends on the oil field. The oil consists of about 425 hydrocarbon compounds. Any oil under natural conditions consists of a mixture of methane, naphthenic and aromatic hydrocarbons.

It is also found out that formation of these types of connections is directly related to their structures, that is, when they are in contact with these acids due to their polymeric structures, acid molecules are positioned in interchain spaces. The number of included molecules depends on size and geometric forms of these molecules, that is, their clathrate formation is dependent on the size factor.

In addition to the size factor, pH medium is also of great importance. Depending on pH values, their structures change for easy clathrate formation [1-2]. We have also synthesized and decoded crystal structure of decahydrate complex of copper (II) with 1,2,4,5 – benzenetetracarboxylic (pyromellitic) acid [3].

From the crystal structure it is seen that the complex consists of polymeric nets of parallel planes [2]. The acid anion for coordination impact uses all four carboxyl groups.

The composition of the crystalline compound coordinately bound with copper atoms of water

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molecules also includes two molecules of water of crystallization, which by means of hydrogen bonds covering all oxygen atoms bind the layers into a single unit in the form of 3D crystal structure. Wherein one layer of complexes (light) is slightly shifted in the plane (011) with respect to other layer systems (black). Based on the above mentioned, it can be assumed that in the absence of water molecules of crystallization, there would not occur displacement of layers. In this case, large pores in the carcass layers would lie on top of each other and large through columns with ability to include "guest" molecules would be formed. It should be noted that in this structure the interlayer space is also available for the inclusion of appropriate molecules [4].

Thus, the aim of this work is to study the complexation of pyromellitic acid, with further receipt of its non-bonded joints on its basis [5].

2. Method

This work presents the results of the synthesis, physical and chemical and structural and chemical studies of complex compounds of zinc (II of) resulting in a weakly acidic medium (pH = 6.8).

As seen in Figure 1, the complex compound is highly crystalline and has a high symmetry. With X-ray indexing unit cell parameters were computed: a = 9,78, b = 19,7, c = 11,76Å.

Comparison of the parameters of the complex compound with parameters of the known complex compounds of copper (II) the crystal structure of which was decoded (a = 9,679 (5), b = 18,17 (2), c = 12,18 Å) showed that they differ respectively by 0.11; 1 and 0,42 Å. As it is seen, the parameters of a and b increase, whereas parameter of c decreases. These values are low, so at the first approach it would be found out that they are isostructural. But the results of the elemental, IR spectroscopy and differential thermal analyzes have not confirmed these isostructural compounds, as elemental analysis results showed that the content of the complex is very different from the complex [6].

Elemental analysis results are presented in Table 1.

Table 1. The results of elemental analysis of the complex compounds of copper and zinc (II)

Found out, %			Composition of compounds	Calculated, %		
H	C	Zn, Cu		Zn, Cu	C	H
-	-	-	$Cu_2C_{10}H_{22}O_{18}$	22,81	21,5	3,95
2,31	26,72	29,0	$Zn_2C_{10}H_{10}O_{12}$	28,877	26,5	2,20

As it is seen from the table, the compositions of the compounds are very different from each other. The composition of the newly obtained compound has the preliminary chemical formula $Zn_2(C_6H_2(COO)_4)(H_2O)_4$, whereas the chemical formula of the famous complex is $Cu_2(C_6H_2(COO)_4)(H_2O)_{10}$.

Decomposition of the complex compounds of zinc (II) begins at 90°C in the temperature range of 90–138°C and is accompanied by a shallow but clear endothermic effect at 110°C and corresponds to the removal of two molecules of water. Experimental loss value of mass is 8 % (calculated 7.95%). Thereafter, in DTA curve there occurs the second endothermic effect in the temperature range of 138 - 180°C with maximum at 150°C, which corresponds to 1.5 moles of water removal. Experimental loss value of mass is 6% (calculated 5.96%).

Then there occurs the third fuzzy and shallow endothermic effect in the temperature range of 180 – 280 °C with maximum at 240 °C which corresponds to removal of an additional 0.5 moles of water. Here, experimental weight loss of the mass is 2% (calculated 1.99%). Anhydrous intermediate complex is stable up to 400°C which is extremely rare for complex compounds. At 400°C, first slowly, then with high-speed decomposition of anhydrous complex takes place in the temperature range of 400 - 600°C with a single clear exothermic effect with the maximum 520°C. Here the experimental weight loss of the mass is 48% (calculated 48.15%). Since on the curve TG after complete decomposition is not observed weight increase, it can be concluded that oxidation of the zinc ion is due to oxygen atoms of the carboxyl groups. The final product is a ZnO. Experimental mass of the final product is 36% (calculated 35.95%). Below is a diagram of a solid phase transformation of complex compounds:

Since a weight increase is not observed on TG curve after complete decomposition, it can be concluded that oxidation of the zinc ion is due to oxygen atoms of the carboxyl groups. As the final product there remain ZnO. Mass of final experimental product is 36% (calculated 35.95%). Below is a diagram of a solid phase transformation of complex compounds:

IR spectroscopic study also indicates that the frequency at 461; 534; 553 and 590 sm^{-1} refer to liberational vibrations of water of crystallization or torsional vibrations of water molecules with limited interactions with neighboring atoms [2].

Besides it, absorption bands are observed in IR spectrum of compound at 3550 - 3200 cm-1 (symmetric and asymmetric valent vibrations of OH) and at 1630 - 1600 cm-1 (deformation vibrations of HOH), which are characteristic for water of crystallization.

Absorption bands at 1597, 1548, 1505 (νa) and 1457, 1401, 1337 cm1 (νs) refers to the carboxyl group of an acid anion [7]. Value of the difference value Δ (νa - νs) are respectively 140, 146 and 127 cm1 and it is significantly less than that of ionic compounds, but is in good agreement with the values of bidentate chelate complexes [5].

Thus, the central atom is coordinated to six. Coordination zinc (II) includes four oxygen atoms of two carbonyl groups and two oxygen atoms of water molecules. Coordination polyhedron is octahedron.

As it is seen from the figure, the structure of the complex compound $Zn_2(C_6H_2(COO)_4)(H_2O)_4$ consists of alternating layers along the axis [2]. The structure is porous and the size of pores is approximately 9 x 16 Å, as in [3]. The layers are stitched together due to hydrogen bonds formed by coordination of water molecules in different layers on the tops of octahedra. It is also possible to assume that the skeleton pores in the structure will be one above the other and, in this case, through columns for the available "guest molecules" will be generated. Thus, one can conclude that a series of non-bonded compounds having practical value can be synthesized on the basis of this compound.

3. Results

The purpose of this article is to study the effect of additives on the rheological properties of the oil field of Azerbaijan Bulla, Balakhany heavy and Surakhany. Additives of Difron 4201 and BAF-1 grades are used as additives [1]. Separation of paraffins, asphaltenes and resins from oil was carried out according to the procedures GOST 11851-85 and GOST 11858-66. The pour point, or the pour point, was determined in the S.D.M. - 530 (Germany), RK 1530-2006 supplied with three cameras for maintenance of temperatures of 0,-17 and 34 ^{o}C wasps according to ST. Effective viscosity and shear stress were measured on a rotary rheometer REOTEST-2 using a measuring system standard GOST 26581-85 [2]. The main physicochemical characteristics of oil, such as viscosity, solidification temperature, paraffin content, etc. from Bulla, Balakhany heavy and Surakhani deposits are studied in the work, which are given in Table 2.

Table 2. The main physical and chemical characteristics of oil from the Bulla, Balakhany heavy and Surakhany fields

Indicators	Bulla	Bala-khany heavy	Sura-khani
Density, at 20 °C kq/m^3	842,1	921,7	859,3
Amount of water, mass %	0,76	0,21	0,79
Chloride Salt Content, mq/l	138,6	38,4	139,5
Amount of mechanical impurities, mass %	0,007	0,009	0,008
Resins content, mass, %	9,6	16,2	14,8
Asphaltenes content, mass, %	0,22	2,8	2,94
Paraffins content, mass, %	13,1	0,31	2,73
Puor point temperature, ˚C	+12	-33	-21
Viscosity at 20°C mm^2/sec	23,2	160,3	20,2
Fractional composition: Overpoint,temperature, °C			
To 200 ^{0}C, by volume %	71,5	97,5	78
To 300 ^{0}C, by volume %	24,5	16	21
To 350 ^{0}C, by volume %	44	32,5	40,5
Final boiling point, °C	63	54	61,5
	341,5	302	328

Table 1 shows that oil from Bulla field belongs to high-paraffinic oil, compared to oil from Balakhana fields heavy and Surakhany. It should also be noted that oil from Surakhany fields has a positive freezing point, which also indicates the presence of a large number of paraffins. It is known that when pumping highly paraffinic oils, paraffin deposition is observed on the inner walls of the pipeline. In order to prevent this phenomenon, a hot pumping method is used when transporting high-paraffin oils. For this purpose, oil is further heated every 25-150 km of pipeline length. Heating oil solves the problem of pumping high-paraffinic oil, but this complicates and increases the cost of its production, transportation and processing. In terms of the dissolution efficiency of ARPS, most often these compositions differ slightly from natural solvents, and in some cases are even less effective. Natural ARPS removers associated with oil production, such as gas condensate, gas gasoline, a mixture of liquefied petroleum gases, light oil, have become the most widespread. The undeniable advantage of such solvents is their availability. They are usually produced or obtained in oil areas, have a low cost, do not affect further oil processing processes. To increase the effectiveness of ARPS removers, compositions comprising a hydrocarbon solvent and various surfactants are often provided, the addition of which increases the surface activity of the solvents and the dispersion effect of ARPS to the compositions up to 3 wt%. Such surfactants include composite additives, polyalkylbenzene resin (PABR), heavy pyrolysis resin (PR), catalytic cracking thermogasoil (TG), nitrogen-containing block copolymer (BC) of ethylene oxide and propylene oxide with molecular weight of 5000 and phenol-formaldehyde resins [4]. After the reagent was added to the asphaltene-paraffin resin compounds separated from the oil, the results of their electron microscopy were obtained (Figure 3). The results of electron microscopy are of great importance in the analysis of the structural viscosity of oils.

Our studies show that the rheological properties of oils can be improved by selecting a suitable chemical reagent for the group composition.

The results of experimental investigations have shown that reagents BAF-1 (technical conventional name reagents) reduce the viscosity of petroleum such as heavy and crude oil (Balakhany heavy), to facilitate transportation of the subterranean formation from the production site to the refinery or oil storage tanks, increased production, purified oil and oil from the sludge in the tanks.

As is known all these properties of oils (high viscosity, difficulty of transportation, the decline in production, the sludge formation in tanks, etc.) directly related to forming asphaltene-resin-paraffin sediments (ARPS).

X-ray diffraction and electron microscopic studies conducted to elucidate the mechanism of action of reagents us. To conduct the study, two samples of oil (for 300ml) from the same wells taken. To one sample of the oil added 40ml composite reactant solution, and another - left unchanged and distilled to their obtaining the fraction of tar.

As is known, tar is a dry distillate oil at 450-600 ^{0}C temperature (depending on the nature of oil) in vacuum condition and atmospheric pressure. The yield of tars depending on the oil's composition is 10-45% (wt.). Resinis a black viscous liquid and formed during the fragmentation of small glittering particles. The composition of the sludge includes paraffin, the naphthenates aromatic hydrocarbons (45-95%), asphaltenes (3-17%), petroleum resin (2-38 %) and the atoms of metals. Depending on the nature of the oil and from the entrance of the transparent fraction of the density of the sludge varies from 0.95 to 1.03 g/cm3, coking 8-26% (weight) and the melting point of the 12-55 ^{0}C.

As is known at atmospheric and vacuum distillation the chemical composition of the oils not change.

Therefore, test results obtained for dry and oil products relates directly to oils themselves.

Given the above, the dry product of oil samples subjected to X-ray diffraction and electron microscopy studies. The results are shown in Figures 1, 2, 3 and 4, respectively.

X-ray analysis and electron microscopic images obtained respectively From X-ray diffraction (Fig.1) shows that the dried product sample without reagent pronounced bright consists of three phases between planar distances 4.44, 4.22 and 3.64. On the radiograph (Fig.2) are removed from the dry product oil sample with the reagent, the third phase completely disappears in the first two phases of the maxima are shifted to the low-angle side, i.e., between planar distances increase. This suggests that after the disappearance of the third phase, the structure of 1-st and 2-nd phase changes and their crystallinity increases.

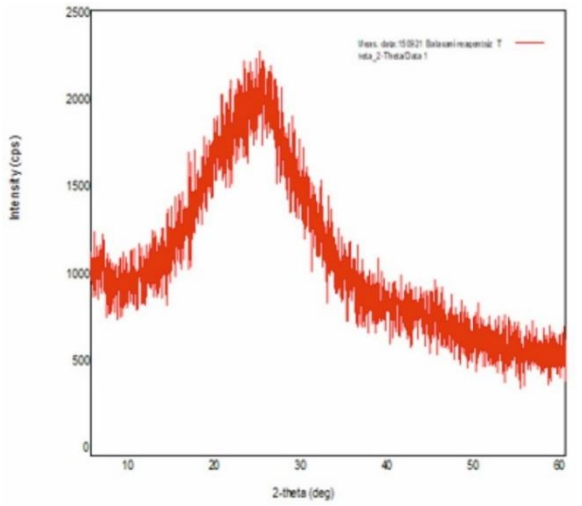

Figure 1. Radiograph of a dry oil sample without reagent

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The results of electron microscopic studies reagent less sample (Fig.3) showed that in the dry rest there is the associate consisting of asphaltenes, resins and waxes that worsen the rheological properties of crude oils.

The results of electron-microscopic investigations of the sample with the reagent (Fig.4) indicate that in this associate is fragmented and are distributed evenly in oil, which is in a dissolved state.

4. Discussion

The elemental composition of the obtained compound was defined by gas chromatography method by means of an analyzer CHN30E Carlo ERBA. The content of the metal was calculated on the basis of the weight loss curve by the quantity of oxide obtained after being heated on derivatograph up to 800° C. X-ray phase analysis was performed on the device Commander Sample ID (Coupled Two Theta/Theta) WL 1.54060. IR spectra were recorded on a device SPECORD-MBO in 400 - 4000 cm-1 area. Derivatograms recorded derivatograph on NETZSCH STA 449F3 STA449F3A-0836-M (range 21 / 10.0 (K / min) / 800).

Synthesis of the compound. The starting materials were $C_6H_2(COO)_4$, $Zn_2(CH_3COO)_2$ of qualification 4 (GOST 3759 - 75). The complex is prepared by reacting pyromellitic acid with zinc acetate at a stoichiometric ratio of 1:2. The solution was refluxed until disappearance of the odor of acetic acid, filtered while hot and cooled to room temperature.

The disappearance of the third phase with between planar distance (d = 3,60) reveals that the reactants porous (pore size is ~20A ° BAF-1 with the third phase non-valence form compounds with self-organization and self-construction, i.e., by reacting a reagent with oil arise non-valence skeking interaction between porous polymers and chromatic focal and heteroatom makroassociates third phase. liberated from the third phase of the first and second associates (ARPS) turn into small particles and dissolve in the crude oil. In this regard, and improved rheological properties of oil. An increase in the between planar spacing of the first and second phases shows that their structure changes.

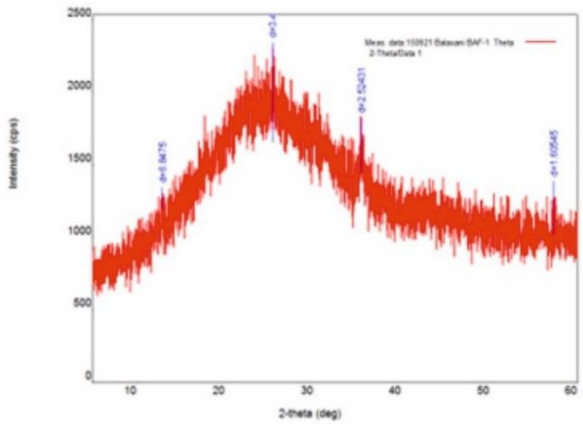

Figure 2. Radiograph of a dry sample oil with reagent

5. Conclusion

According to the results of electron microscopic analysis also clear that in the dry product without reagent paraffin oil associates are in a solid mass, which deteriorate its properties. A dry product oil with a reagent ARPS associates fragmented into small particles, i.e., they uniformly distributed in the oil and therefore improves the rheological properties of oil. This again proves that the reactants form a hetero chromatic non valence compound.

Thus, the research results show that the reagents can solve all the problems arising from paraffin formation, particularly, improve the recovery of oil wells, reducing the viscosity of heavy oils, improve the efficiency of transportation of such crudes and perform effective cleaning oil tanks of oil and petroleum deposits, then is based on the technology of said reactant is multifunctional.

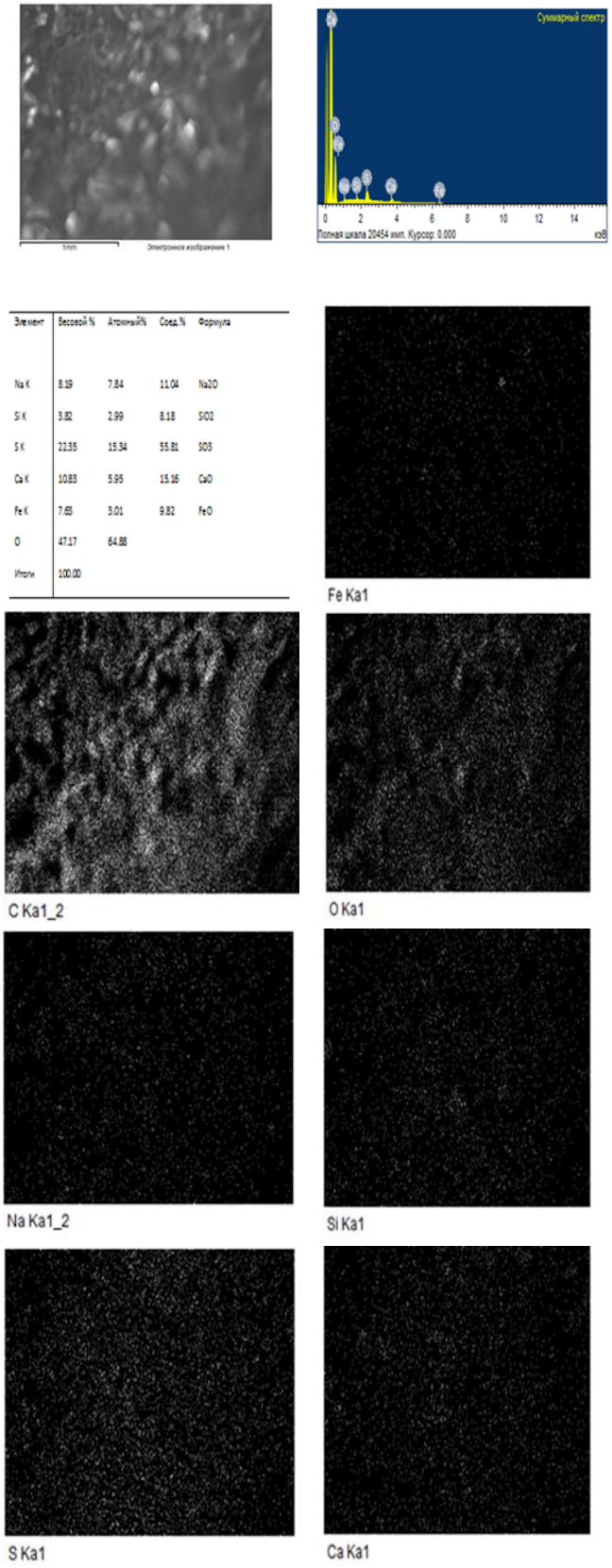

Figure 3. Electron- microscopic image of a dry oil sample without reagent

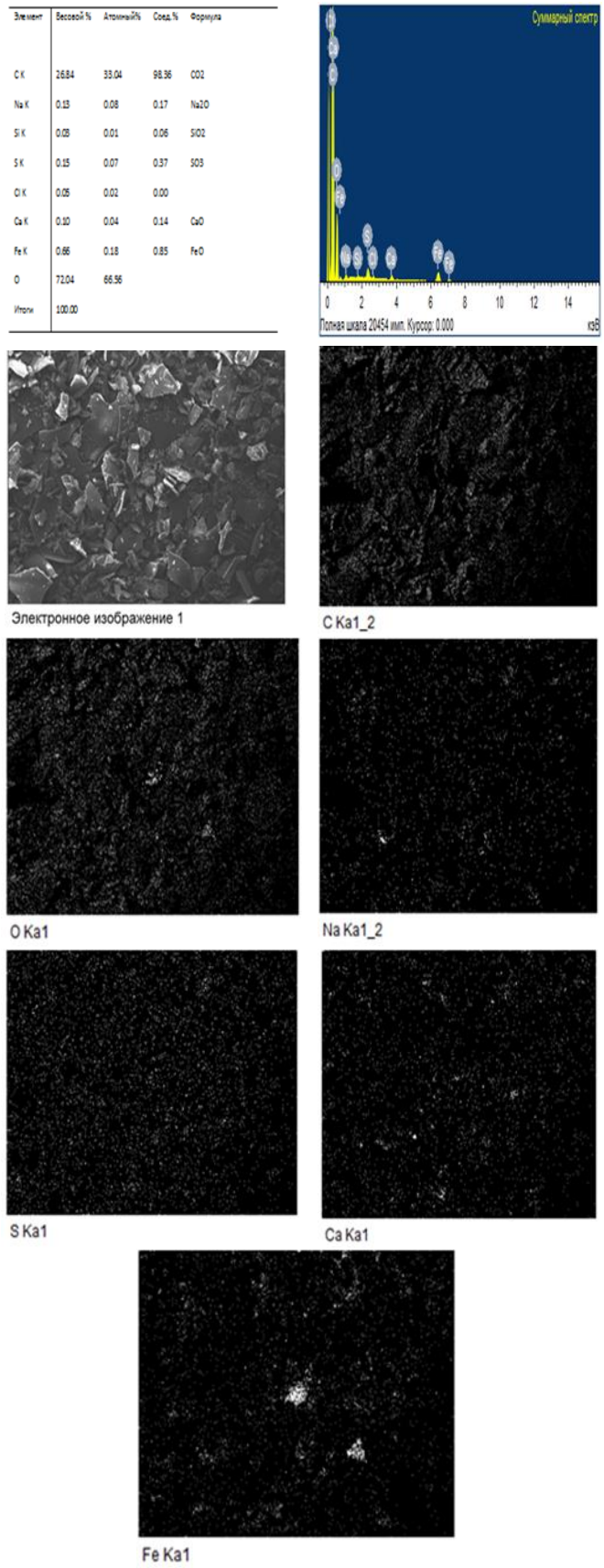

Figure 4. Electron microscopic image of a dry sample reagent free oil with reagent

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Author contributions

Nurullayev Vali Hanaqa, Usubaliyev Baybala Taci, Gurbanov Gusein Ramazan: Conceptualization, Methodology, Software **Abdullayeva Zeynab Arif, Gasimzadeh Aysel Valiyaddin:** Data curation, Writing-Original draft preparation, Software, Validation. **Hasanova Matanat Maxsud:** Visualization, Investigation, Writing-Reviewing and Editing.

Conflicts of interest

The authors declare no conflicts of interest.

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