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# SELECTION OF REAGENT COMPOSITIONS FOR MODIFYING SPECTRAL CHARACTERISTICS OF WEAKLY AND ANOMALOUSLY LUMINESCENT DIAMONDS IN THE PROCESS OF X-RAY LUMINESCENCE SEPARATION

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#### Abstract

The feasibility of targeted modification of the spectral properties of weakly and anomalously luminescent diamonds by modifying reagents containing luminophores based on sulfides and zinc orthosilicate, characterized by medium and low deviation of the luminescence signal from that of natural diamond. It was found that the hydrophobic treatment of inorganic luminophores with potassium butyl xanthate could increase the recovery of anomalous luminescent diamonds in the process of X-ray luminescence separation up to 80%. Organic collectors (optically transparent oil products with high extractability for luminophores and adhesion to diamonds) based on technical-grade diesel fuel and catalytically cracked heavy gas oil are recommended for the luminophore-containing compositions. The feasibility of reducing the fixation of luminophores on the surface of kimberlite grains using sodium hexametaphosphate, sulfonol, carboxymethylcellulose and liquid glass was demonstrated. The application of these reagents in low-salinity water provides decreasing coating of kimberlite grains with luminophores while maintaining the required concentration of luminophores on the surface of diamonds. Semi-industrial tests with an LS-D-4-03N separator proved the possibility of complete recovery of weakly and anomalously luminescent diamonds after treatment of XRS tailings with the modifying reagents.

Key words: diamonds, separation, X-ray luminescence, signal modification, luminophores, collectors.

## 1. Introduction

Increasing the extraction of weakly and anomalously luminescent diamonds is an important task, the solution of which will provide a significant increase in the performance of diamond mining enterprises [1, 2]. A promising area for solving this problem is the use of stateof-the art techniques for modifying spectral characteristics of diamonds, including the use of luminophore-containing compositions [3]. The technique of treatment of diamond-containing material is based on the use of specially selected compositions of luminophores and an organic liquid, which is selectively fixed on the surface of diamonds, and bring the spectral and kinetic characteristics of non-extractable crystals closer to those required for their extraction at the standard settings of X-ray luminescence separators [4].

Zinc and cadmium chalcogenide luminophores activated by copper and silver ions, as well as zinc

orthosilicate activated by manganese, were proposed as the main components of modifying reagents (modifiers) [5]. Successful application of modifying reagents is provided by intensive fixation of luminophore-containing compositions on the surface of diamonds, the condition of which is the formation of a stable luminophore-organic liquid-diamond aggregate [6]. This problem can be solved both by increasing the oleophilicity of luminophores and diamonds and by a rational selection of collector composition.

A requirement for achieving the efficiency of the Xray luminescence separation process is minimum fixation of luminophores on kimberlite minerals. Increasing the selectivity of the developed modifying reagents is possible through the use of reagent-dispersants and regulation of the ionic-molecular composition of the aqueous phase.

The aim of this work was to solve the above problems in order to select a rational composition of luminophore-

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containing reagents that would eventually increase the efficiency of modifying the spectral characteristics of diamonds and their extraction in the process of X-ray luminescence separation.

#### 2. Experimental methods and Materials

In the experiments, we used collections consisting of diamond crystals and kimberlite mineral grains ranging in size from 1 to 5 mm, selected from the concentrate of the gravity concentration cycle, which is the starting material for X-ray luminescence separation. The diamonds were extracted from the ore mass and the crystals with weak and anomalous luminescence were selected at individual separator settings.

The pre-selection of luminophores and organic collectors for research involved spectral analysis of luminescent emission obtained with an ultraviolet chromatograph when the samples were irradiated with ultraviolet light (v=253 and 364 nm) [5]. The resulting luminescence spectrum was practically the same as the spectrum obtained with X-rays [7].

The visiometric method adapted to the analysis of diamond-containing products was used for the assessment of the luminophore fixation on the surface of diamonds [5]. This method involved obtaining images of diamond crystals and kimberlite mineral grains with the fixed luminophores in UV spectrum and their visiometric analysis with identifying areas with the luminophore color characteristics (HSL characteristics) and determination of their areas proportion relative to the sum of all the image areas [8].

The experimental procedure included the steps of preparation of luminophore-containing water-organic emulsion, the mineral mix emulsion treatment, the emulsion removal and sample washing, the visiometric analysis of luminophore fixing efficiency on diamonds, the measurement of spectral-kinetic characteristics of minerals during their activation by X-ray radiation and Xray luminescence separation [3, 5].

The received X-ray luminescence signals of the modified crystals were compared with the averaged signal of a typical natural diamond [5]. A normalized function of the X-ray luminescence signal was used to estimate the deviation of the signals of luminophores, the compositions, and the treated minerals from the signals of natural diamonds [9].

The oleophilicity of inorganic luminophores and diamonds was estimated by heterophase extraction method based on the distribution of particles of a studied luminophore between the phases of water-organic emulsion [5, 10].

The spectral-and-kinetic characteristics of diamond crystals and kimberlite mineral grains in laboratory conditions were measured on a "Polus-M" separator of JSC "Burevestnik" [1, 2, 5, 9].

The X-ray luminescence signals of the diamonds and the minerals were identified based on the following parameters: the amplitude of slow and fast signal components ( $A_{SC}$ ,  $A_{FC}$ ), the signal attenuation time constant ( $\tau_a$ ), the normalized correlation function - signal convolution ( $S_v$ ); the ratio of amplitude of slow and fast signal components ( $K_A$ ) [5].

The parameter "component ratio"  $K_A$  was calculated according to the formula [9, 11]:

$$K_A = \frac{A_{SC} + A_{FC} - A_A}{A_{FC}} \tag{1}$$

where  $A_A$  is amplitude of air X–ray luminescence signal.

The similarity of X-ray luminescence signals of luminophores and diamantes was evaluated using the signal deviation criterion  $D_{\nu}$ , calculated as an integral function of the deviation of the studied normalized X-ray luminescence signal from a standard signal [5].

In the technological tests, the kimberlite samples with added diamond crystals s were placed into an industrial X-ray luminescent separator. The separation of diamonds and kimberlite grains was carried out in the selective regime characterized by the following parameters settings:  $A_{SC} \ge 0.2B$ ,  $S_v \ge 0.1$ ,  $\tau_a = 1.0 - 18 ms$ ,  $K_A = 1 - 12$ , used in the industrial X-ray luminescence separation. The experimental setup and test methods have been described in more detail in previous studies [4, 5, 6].

#### 3. The Findings and Discussion

## 3.1. Selection of luminophores for modifying reagents

Zinc and cadmium sulfides and arsenides are the most representative group of luminophores [7, 12]. Luminophores have a crystal lattice of sphalerite and wurtzite and are characterized by green, light blue, and blue luminescence due to the activation by copper or silver [5]. The samples under consideration also include luminophore FL-530, which is a zinc orthosilicate activated by manganese. Anthracene and luminol were considered from organic luminophores. The luminophores of zinc and cadmium sulfide group, zinc orthosilicate, antracene and luminol are

characterized by acceptable spectral characteristics and high luminescence brightness (Table 1, Figure 1).

Table 1 Spectral characteristics of the investigated luminophores (in HSL format)

No	Brand name	Composition	lonic supplement	Maximum wavelength, nm	Color parameters H(0), S(%), L(%)	Luminescence intensity, µW/cm²/nm
1	EL 570M	ZnS, ZnSe	Cu, Ag	563	97, 73.9, 56.5	0.077
2	FK-110	ZnS	Cu	465, 510, 545	149, 72.6, 71.2	0.122
3	P-530	ZnS, CdS,	Ag	534	142, 77.4, 54.9	0.308
4	FS-4	ZnS	Ag	474	229, 91.4, 86.3	0.204
5	PC-424	ZnS	Ag	563	258, 90, 39.2	0.058
6	FK-1	ZnS	Ag	484	225, 88, 45.9	0.152
7	FK-2	ZnS	Ag	527	180, 87, 59.8	0.200
8	E-455-115	ZnS	Cu	515	222, 78, 72.9	0.194
9	E-515-115	ZnS	Cu	515	163, 91.1, 51.4	0.118
10	FL-530	ZnSiO <sub>4</sub>	Mn	530, 544, 575	149, 37.6, 63.5	0.109
11	Antracene*	$C_{14}H_{10}$	-	423, 473	245, 88.4, 78.9	0,030
12	Luminol*	$C_8H_7N_3O_2$	-	476	212, 85.4, 74.2	0,048

\*0.5% solution in diesel fraction

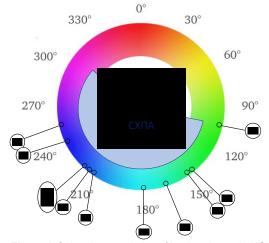


Figure 1 Color characteristics of luminophores in HSL color wheel format (H is chromaticity, deg): SCND range of spectral characteristics of natural diamonds; 1-10 - color characteristics of luminophores (see numbering in Table 1)

The selected luminophores are in the middle part of the working range of the detectors used in separators that confirms the feasibility of signal fixation by the detectors used in separators. At the same time, the maximum wavelength of the diamond signal with the initial emission in yellow and red spectral region is shifted to the region of positive detection [5]. In addition to the wavelength, the kinetic characteristics of the X-ray luminescence signal, based on the trend of the luminophore signal build-up according to the law close to the exponential one and the signal attenuation according to the law close to the second order hyperbola, are used as the parameters for diamond identification and separation from kimberlite minerals [5, 7, 11].

The spectral-and-kinetic characteristics of diamond crystals and kimberlite mineral grains in laboratory conditions were measured on a "Polus-M" device of JSC "Burevestnik" [5]. The results of the studies showed that the shape of X-ray luminescence signal of sulfide luminophores was characterized by a medium and small deviation from the shape of natural diamond signal (Dv - 3-5, Figure 2, Table 2).

The studied organic luminophores do not have the required spectral and kinetic characteristics and can only be used as additives to the luminophore FL-530, which has a strong slow component of the X-ray luminescence signal (Dv - 7, Figure 2, Table 2).

The most pronounced slow component is characteristic of luminophore FL-530 (Figure 2), and this fact does not allow using this luminophore without the addition of luminophores with a more pronounced fast component [3, 5]. The analysis of spectral-kinetic characteristics of luminophores at the "Polus-M" separator (Figure 2, Table 2) allowed carrying out a preliminary selection and choosing the most satisfactory luminophores EL-570, FK-110, P-530, FS-4, FK-1, FK-2, and E-515-115, which can be used without the addition of other luminophores. The recommended samples also included luminophore FL-530, the characteristics of which could be corrected by adding organic luminophores or organic liquids that had a significant fast component of X-ray luminescence signal [5, 6].

# 3.2. Increasing the intensity of luminophore fixation on the surface of diamonds

To increase the oleophilicity of luminophores, the process of hydrophobization of their surface was used. An important condition for the selection of hydrophobic reagents and the calculation of optimal concentrations in solution was the creation of conditions for irreversible chemisorption reactions of a heteropolar ion on the surface of a luminophores without a volumetric reaction [5]. This provided the necessary increase in the oleophilicity of the luminophore surface while maintaining its high spectral activity [5].

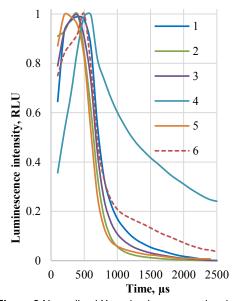


Figure 2 Normalized X-ray luminescence signals of inorganic and organic luminophores: a) 1 - FK-110; 2 - EL-570; 3 - E-515-115; 4 - FL-530; 5 – antracene; 6 - diamond

Table 2 Spectral and kinetic characteristics of inorganic luminophores in static regime at "Polus-M" separator

No.	Designation	$S_v$	$ au_z$ , ms	$A_{MK}$ , mV	$A_{FC}$ , mV	$K_A$	$D_v$	Identification result
1	EL-570	0.13	9.6	1,137	18,165	5.4	5	+
2	FK-110	0.15	4.8	1,511	10,590	6.6	3	+
3	P-530	0.19	0.6	3,815	19,774	5	4	+
4	FS-4	0.15	0.8	11,943	19,777	1.6	5	+
5	PC-424	0.08	0.2	305	17,877	≥50	5	-
6	FK-1	0.23	2	18,132	19,772	2	4	+
7	FK-2	0.12	2	19,776	19,766	2	4	+
8	E-455-115	0.17	7.6	7,250	19,764	27	5	-
9	E-515-115	0.32	0.6	1,887	19,765	8.2	3	+
10	FL-530	0.62	3.4	9,241	6,641	0.6	4	-
11	Antracene	0.10	1.7	235	5810	23.17	7	-
12	Luminol	0.02	1	245	5450	20.80	7	-

+, Recognized as a diamond; -, Not recognized as a diamond

For zinc sulfide minerals, potassium xanthates were used as the surface hydrophobizers [13,14]. The interaction of zinc sulfide with butyl xanthate at the concentrations up to  $10^{-4}$  mol/L was limited to the chemisorption reaction [5]. At the concentrations higher than  $10^{-4}$  mol/L, a zinc butyl xanthate phase could form according to the following reaction [15]:

$$ZnS + 2ButX + 0.5mO_2 = Zn(ButX)_2 + S_n O_m^{2-}$$
(2)

For better fixation of xanthate on the surface of sulfide, it is advisable to change its composition due to the course of an exchange reaction [16]:

$$ZnS + Cu^{2+} = CuS + Zn^{2+}$$
(3)

After the activation, the fixation of xanthate ions proceeded on the surface of the mineral much more intensively. In this case, the concentration of butyl xanthate for the hydrophobization of luminophores decreased significantly [15, 16].

The increased oleophilicity of inorganic luminophores after their hydrophobization caused a significant redistribution of the particles of the studied luminophore between the organic and aqueous phases of waterorganic emulsion [5] due to heterophase extraction into the organic phase [6], which determined the concentration of luminophores on drops of the applied organic collector and stable fixation on the diamond surface.

The results of the studies of anomalously luminescent diamonds using an E-515-115-based modifying reagent showed that the use of hydrophobic treatment could increase the diamond recovery from 20 to 60%. The hydrophobization of the luminophore with butyl potassium xanthate significantly enhanced the growth of  $A_{SC}$  and  $A_{FC}$  that allowed the increase of the recovery of anomalously luminescent diamonds in the X-ray luminescence separation process up to 80%.

The research results thus showed that the use of the luminophore-containing composition based on hydrophobic zinc sulfide (luminophore E-515-115) provided weakly and anomalously luminescent diamonds the required spectral properties and enabled their more complete extraction into the concentrate during X-ray luminescent separation.

# 3.3. Selection of collectors for luminophore compositions

An important prerequisite for the developed technique efficiency is the right selection of an organic collector [6]. The main function of the collector is to provide stable diamond-luminophores aggregates [17]. An equally important requirement for the organic collector to be selected is its possession of acceptable spectral characteristics [17].

The analysis of the luminescent radiation power spectral distribution curves showed that the maximum radiation of the studied organic liquids lay in the wavelength range of 470 - 600 nm and almost completely corresponded to the permitted range (350-550 nm) of the frequencies of all separators' light detectors [1, 2, 17].

The results of the measurements of spectral characteristics using a HSP-350UV UV - spectrometer showed that the signal intensity of X-ray luminescence of

the studied organic collectors per unit mass was 20-50 times lower than that of the inorganic luminophores. Considering the actual ratio of phosphors and collector in the composition (1:10-1:20). The intensity of the collector signal is comparable to the luminophore signal and the resulting signal should be calculated as the sum of the signals from the diamond, collector and luminophore [17].

The analysis of the X-ray luminescence signal buildup-attenuation curves of the studied liquid hydrocarbons showed that the signal shape was characterized by the presence of a pronounced amplitude of fast component  $(A_{FC})$ , a weakly pronounced slow component  $(A_{SC})$ , and it differed significantly from the corresponding characteristics of a natural diamond. The degree of deviation of the collectors' X-ray luminescence signal shape from that of a natural diamond was very high  $(D_v = 6 - 8$  on a scale of 1-14). Most organic liquids were characterized by low values of signal convolution  $(S_v)$ , satisfactory values of attenuation time constant  $(\tau_a)$ , and a significant excess of the ratio of amplitudes of the fast and slow components  $(K_A)$  relative to the upper limit of the working range was noted [17].

The selection of organic collectors with high extraction ability to luminophores and adhesive ability to diamonds was carried out using a special technique. which involved the treatment of luminophores in aqueous solutions and their extraction by an oil phase as a result of fixation at the interface between the oil and aqueous phases [17]. While conducting the research, a special installation included the units for supply of an organic liquid, transport water, and for collection of float fractions was used. In the installation operating zone, luminophores or diamonds were fixed on the collector droplets, then floated up, and then the floating aggregates of collector droplets with luminophores or diamonds were removed by the transport water flow to the discharge zone and unloaded into the vessel with a filtering partition. The device used in the experiments was an advanced tube for flotation monomineral fractions (Hallimond tube) [18].

To modify the spectral and kinetic characteristics of diamonds, hydrophobic potassium xanthate-containing luminophores suitable for use in luminophore compositions were investigated. As collectors, the following substances: saturated and unsaturated olefins, diesel fuel of different grades, kerosene, vacuum gas oils, etc. were studied. The analysis of the study findings showed that the best extraction ability in relation to the studied luminophores (the average recovery above 70%) was demonstrated by technical grade diesel fraction

(DF), catalytic cracking heavy gas oil (CCHGO), CCHGO and DF compound, F-5 bunker fuel oil, vacuum gas oil. The most oleophilic luminophores (the average recovery above 75%) were FK-110, E-515-115, P-530, FK-1, and FK-2 [17].

Similarly, the propensity of organic collectors to adhesive interaction with diamonds was determined. The comprehensive evaluation of the collectors' efficiency was carried out based on the value of efficiency criterion  $K_E$  calculated as the sum of natural diamond recovery ( $\varepsilon_D$ ) and the average recovery of the studied luminophores ( $\varepsilon_L$ ) minus kimberlite recovery ( $\varepsilon_K$ ), multiplied by the coefficient taking into account the effect of recoverable kimberlite on concentrate finishing costs ( $K_C = 1.5$ ) [17]:

$$K_E = \varepsilon_D + \varepsilon_L - K_C \cdot \varepsilon_K \tag{4}$$

Taking into account spectral and optical characteristics, and the ability to extract inorganic luminophores and diamonds, the following collectors were selected for further studies: DF, CCHGO, and CCHGO+DF compound ( $K_E$  above 140).

The results of the luminescence intensity measurements of luminophores in organic collectors showed that dark-colored oil products, in particular, bunker fuel oil and vacuum gas oil, reduced the luminescence of inorganic luminophores that led to a decrease in the efficiency of compositions based on them.

The tests on samples of diamonds and kimberlite using the "Polus-M" separator showed that the shape of the X-ray luminescence signal of the composition of inorganic luminophores E-515 and FL-530 with an organic collector on the basis of catalytic cracking heavy gas oil was close to the shape of the signal of natural diamond (Figure 3). The degree of deviation of the collectors' X-ray luminescence signal shape from that of a natural diamond is small ( $D_v = 2 - 4$  on a scale of 1-14) [17].

In further studies, the modifier of spectral-kinetic characteristics of diamonds was used in the form of an emulsion of a luminophore-containing composition (luminophores in an organic collector) in an aqueous solution of reagent-regulators (surfactants and dispersants). Inorganic luminophores based on zinc orthosilicate and sulfide E-515-115-G4 and FL-530-G3 with increased oleophilicity achieved by their

hydrophobization were used in the luminophorecontaining composition [17].

The measurements results showed that applying the modifiers with the recommended luminophores and organic collectors modified spectral characteristics of weakly and anomalously luminescent diamonds so that they were readily extracted into concentrate by X-ray luminescence separation (Table 3).

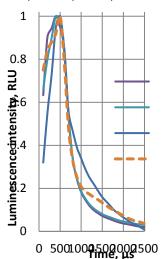


Figure 3 Normalized X-ray luminescence signals of inorganic luminophores in CCHGO: 1 - FK-110; 2 - E-515; 3 - FL-530; 4 - natural diamond)

The selected modifiers were tested for treating different types of hard-to-recover natural diamonds (sample collections of 20 crystals each) mixed with kimberlite. The studies were conducted on colored diamonds with weak luminescence, as well as on crystals with low amplitude of slow component. The performed tests' findings enabled proposing the compositions of modifiers designed to improve the spectral and kinetic characteristics of different types of diamonds. MLA-1 and MLA-2 modifiers based on hydrophobic luminophore FL-530-G3 (Table 3) were designed to modify the characteristics of anomalously-luminescent diamonds by significant enhancing the slow component of their X-ray luminescence signal [17]. MLA-3 modifier based on hydrophobic luminophore E-515-115-G5 was effective for weakly luminescent diamonds. When processing ore material with approximately similar proportions of both types of diamonds, the selection of a modifier brand could be carried out based on the results of additional technological research.

diamond	S								
Brand	Luminophores composition	Collector composition	Mineral	$S_v$	$ au_a,$ ms	A <sub>SC</sub> , mV	$A_{FC} - A_{AFC}$ , mV	K <sub>A</sub>	Recovery, %
		-	Diamond (w)	0.15	4.3	120	564	5.7	40
	Without Iuminophore		Diamond (a)	-	0.1	not measured	1,022	≥50	20
-			Kimberlite	-	-	not measured	<50	-	0.5
			Kimberlite	-	-	not measured	156	-	0.6
	FL-530-G3	CCHGO - 85% DF – 15%	Diamond (w)	0.22	1.6	329	1,216	4.7	80
MLA-1			Diamond (a)	0.17	0.6	275	1,469	6.3	90
			Kimberlite	-	-	not measured	<50	-	0.9
	FL-530-G3 + anthracene	DF	Diamond (w)	0.22	1.6	296	1,336	5.5	60
MLA-2			Diamond (a)	0.11	0.4	209	1,332	7.4	85
			Kimberlite	-	-	not measured	<50	-	0.7
	E-515-115-G5	CCHGO -85% DF-15%	Diamond (w)	0.25	2.4	275	1122	5.1	90
MLA-3			Diamond (a)	0.17	0.6	167	1,499	10.0	85
			Kimberlite	-	-	not measured	<50	-	0.7

Table 3 Testing of luminophore-containing reagents for modifying of weakly (w) and anomalously (a) luminescent diamonds

A<sub>AFC</sub> is the amplitude of fast component of air X-ray luminescent signal (background)

## 3.4. Improvement of selectivity of fixation of luminophore emulsion on diamonds and minerals of kimberlite

To assess the selectivity of the process, a combination of methods of the visiometric analysis of coating the surface of minerals with luminophores and the analysis of diamond and kimberlite recoverability on the laboratory X-ray luminescent separator "Polus-M" was used. The covering of luminophores on the diamond surface were measured using visiometric method in ultraviolet light [19] with subsequent image processing by a specialized software program, which calculated the proportion of the image areas with the specified color characteristics [20].

The visiometric analysis showed that increasing the concentration of a dispersant in the aqueous phase of a luminophore-containing emulsion (for example, sodium polyphosphate) resulted in decreasing the amount of luminophore fixed on the surface of diamond and kimberlite grains (Table 5).

The comparison carried out in study [21] allowed us to establish that with an increase in the concentration of polyphosphate in the range of 0-1.5 mg/l, a sufficiently high level of coating of the diamond surface with luminophores and almost complete diamond extraction was maintained. In the same range of the concentrations, a noticeable decrease in coating of kimberlite grains with luminophores and a decrease in the recovery of kimberlite into diamond concentrate to a technologically acceptable level (less than 1.5%) was observed [21]. A further increase in the concentration of polyphosphate led to a decrease in the luminophore fixation on the surface of both diamonds and kimberlite, which correspondingly led to a decrease in diamond recovery and kimberlite recovery into XRS concentrate [21].

The analysis of the research findings showed that high selectivity of the X-ray luminescent separation process will be achieved when the surface concentration of a luminophore on diamonds is not less than 15%, and the surface concentration of the luminophore on kimberlite minerals does not exceed 3% [21]. Under these conditions, weakly luminescent diamonds and kimberlite minerals effectively separated with high diamond recovery.

The use of polyphosphates was tested in earlier studies of selecting optimal modifiers [4, 6]. In addition to polyphosphates, organic polymers (carboxy methyl cellulose), polysaccharides (starch), water-soluble silicates (liquid glass), alkyl phosphates and alkyl sulfonates (OEDP, sulfonol) can be used to hydrophilize non-sulfide minerals [21]. These reagents are used in flotation processes to gidrophilization of rock-forming minerals [22-23]. When choosing regulatory reagents, it was necessary to take into account the influence of the degree of mineralization of the aqueous phase [6, 24].

Dispersants were selected based on their ability to prevent fixing luminophores on the surface of kimberlite grains [21]. To evaluate the effectiveness of luminophore fixation on minerals, an isometric analysis in ultraviolet light was used to determine the degree of its coating of the surface of minerals. The research method consisted in calculating the proportion of the area occupied by phosphors to the surface of mineral grains (Figure 4). A luminophore-containing composition included an organic liquid (collector) with a sulphide luminophore E-515-115 (100 mg/L) and an aqueous solutions of dispersants (99-99.5%). Low- and high-salinity process water from ALROSA's diamond producing enterprises was used as the aqueous phase of the emulsion. In all tests, 0.5 g/L of secondary alkylsulfonates was added to the aqueous phase, which provided a stable emulsion of the luminophore-containing composition [21].

It follows from the research findings [21] that sodium hexametaphosphate, sulfonol, carboxymethylcellulose and liquid glass had the greatest propensity to prevent fixation of luminophores on the surface of kimberlite grains in low-salinity aqueous solution (Figure 5).

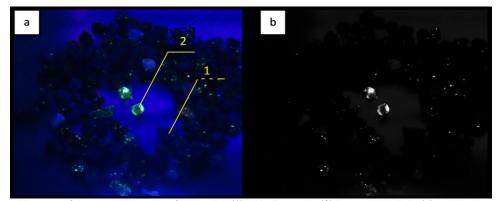


Figure 4 Images of the treated sample of kimberlite (1) with diamonds (2) in ultraviolet light (a) and in the case of visiometric analysis (b)

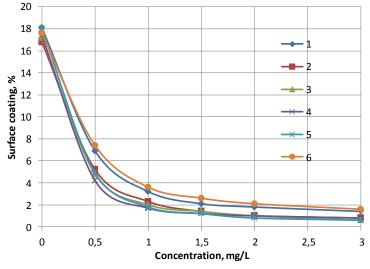


Figure 5. The results of a visiometric analysis of the effect of reagents in slightly mineralized water on the fixation of luminophores on the surface of kimberlite: 1 - tripolyphosphate, 2 - hexamethate, 3 - CMC, 4 - sulfonol, 5 - sodium metasilicate, 6 - lignosulfonate

The application of these reagents in low-salinity water enabled decreasing coating of kimberlite grains with luminophores from 18 to 0.5%. An acceptable level of the covering of luminophores on kimberlite grain surface (3%) was achieved at the concentration of reagents above 1 g/L.

When using high-salinity water, the results of applying dispersants noticeably changed. High-salinity

water itself is a factor that reduces the fixation of luminophores on the surface of kimberlite from 18 to 7%. The efficiency of dispersants in high-salinity water decreases, and the required level of kimberlite coating with luminophores (not more than 3%) is achieved at the concentration of reagents 1.5 g/L [21]. Tripolyphosphate, hexametaphosphate, Alkyl sulfate on this system have relatively higher dispersing ability.

When comparing the efficiency of fixation of luminophores on the surface of kimberlite, one can conclude that preference should be using of low-salinity water. The reagent-dispersants providing a decrease in the surface concentration of luminophores on kimberlite to 3% on average, which allowed limiting the recovery of kimberlite grains into the diamant concentrate to 1-1.5%, which, in turn, corresponded to a typical XRS process performance, were selected as the most promising. These dispersants were hexametaphosphate, sodium metasilicate, and alkyl sulfate. The selected reagent composition decreased luminophore fixation` on a diamond crystal to a lesser extent that was confirmed by maintaining the concentration of luminophores on at 16.5 - 33.0% [21].

# 4. Testing the technique for modifying diamond characteristics by luminophorecontaining compositions on industrial X-ray luminescent separators

A diamond-containing material entering X-ray luminescence separation (XRS) process contained diamonds with different luminescence intensities, spectral and kinetic properties which, in most cases, differred significantly (contrast) from those of kimberlite minerals. The selected boundary values of separation features, such as the amplitude of slow component in the "collective" regime, enabled extracting the bulk ofdiamond crystals. In the tailings of the main XRS operation (separation), which were fed as feed to the check XRS operation, the spectral-and-kinetic characteristics of diamonds (not extracted in the main XRS) and kimberlite minerals differred to a significantly lesser extent. This explains low performance of the check separation.

After the treatment of a diamond-containing product with a luminophore emulsion, the value of the diamond distribution separative feature (ASC in the "collective" regime or the set of spectral and kinetic characteristics in the "selective" regime) changes, and the objective of diamond extraction with a minimum recovery of kimberlite minerals becomes achievable again.

Testing of the selected regime of diamond-containing material preparation with the use of luminophorecontaining emulsions was carried out using natural diamonds and kimberlite product of the main XRS production stage (Figure 6a,b) on a LS-D-4-03N separator (Figure 6c). In the tests, the samples of diamonds and kimberlite were treated with the organicwater emulsion containing a mixture of FL-530 luminophore with an organic collector (MLA-1 sodium composition) with additives of hexametaphosphate in aqueous phase. After the initial feed treatment, the excess of the luminophore-containing emulsion was separated, and the diamonds and kimberlite were sent to the X-ray luminescence separator. The applied separator settings and recorded parameters (the values of the main spectral-and-kinetic characteristics) corresponded to those used in operating industrial separators.

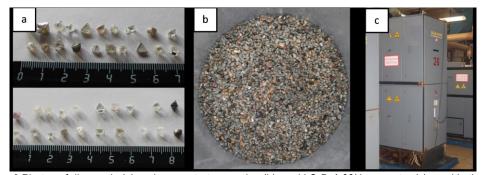


Figure 6 Photos of diamonds (a) and concentrate samples (b), and LS-D-4-03N separator (c) used in the tests

The analysis of the spectral-and-kinetic characteristics showed that diamonds treated with luminophore-containing emulsion demonstrated an average increase of ASC and AFC by 24-32%, which

provided the improvement of their spectral-and-kinetic characteristics and extraction into the concentrate.

Counting of diamond crystals in the concentrate showed that, after the treatment with the luminophore emulsion, all diamonds of the sample were extracted, including the crystals previously not detected by the LS-D-4-03N separator detecting system when processing the same sample in the check test. The increase in diamond recovery was 5% in the first series and 4.7% in the second series. This increase corresponded well to the fraction of weakly and anomalously luminescent diamonds in the initial feed, so one can conclude that these diamonds were successfully recovered.

An important result was also the complete recovery of normally luminescent diamond crystals, i.e., the absence of negative effects of the treatment on natural diamonds with normal luminescence was confirmed. Thus, the study results confirmed the effectiveness of the developed technique as a whole and the proposed methods for improving and intensifying luminophore fixation on the surface of diamonds.

## 5. Conclusions

The performed research enabled selecting effective luminophore-containing reagent compositions for modifying spectral characteristics of weakly and anomalously luminescent diamonds for their extraction in the process of X-ray luminescence separation.

The application of hydrophobic luminophores based on zinc sulfides and orthosilicate, characterized by medium and small deviation of the luminescence signal from that of a natural diamond, and organic collectors (optically transparent oil products with high extraction ability to luminophores and adhesive ability to diamonds) was substantiated.

The use of reagent-dispersants to increase the selectivity of luminophore fixation on the surface of diamonds was proposed. Semi-industrial tests demonstrated the feasibility of extracting weakly and anomalously luminescent diamonds after treatment of XRS tailings with modifying reagents of the selected composition.

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# IZBOR REAGENSA ZA MODIFIKACIJU SPEKTRALNIH KARAKTERISTIKA SLABO I ANOMALNO LUMINESCENTNIH DIJAMANATA U PROCESU RENDGENSKE SEPARACIJE

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#### lzvod

U ovom radu je istraživana mogućnost modifikacije spektralnih osobina slabo i anomalno luminescentnih dijamanata različitim modifikatorima koji sadrže luminofore na bazi sulfida i cink ortosilikata, karakterišući se srednjim i niskim odstupanjem luminescentnog signala od prirodnog dijamanta. Utvrđeno je da hidrofobna obrada neorganskih luminofora pomoću kalijum butilksantata može povećati iskorišćenje anomalno luminescentnih dijamanata u procesu rendgenske separacije do 80%. Preporučuje se korišćenje organskih kolektora (optički transparentnih naftnih proizvoda sa visokom ekstraktivnošću za luminofore i adhezijom za dijamante) na bazi tehničkog dizel goriva i kataltički krakovanog teškog gasnog ulja koje sadrže luminofore. Pokazana je mogućnost smanjenja fiksacije luminofora na površini kimberlitskih zrna primenom natrijum heksametaphosphate, sulfonola, karboksimetilceluloze i tečnog stakla. Primena ovih reagenasa u vodi niskog saliniteta omogućava smanjenje oblaganja kimberlitskih zrna luminoforima, uz održavanje potrebne koncentracije luminofora na površini dijamanata. Poluindustrijski testovi sa separatorom LS-D-4-03N dokazali su mogućnost potpunog iskorišćavanja slabo i anomalno luminescentnih dijamanata nakon tretmana XRS jalovine sa modifikatorima.

Ključne reči: dijamanti, separacija, rendgenska luminescencija, modifikacija signala, luminofori, kolektori.