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# Synthesis and Thermal Conversions of Unsaturated Nickel(II) Monocarboxylates—Precursors of Metal-Containing Nanocomposites

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**Abstract**—Nickel(II) salts with unsaturated monocarboxylic acids (acrylic, methacrylic, sorbic, 4-pentynoic, propiolic, crotonic, linoleic, and oleic acids) have been synthesized. The compounds have been studied by thermogravimetry, differential scanning calorimetry, elemental analysis, and IR spectroscopy. Controlled thermolysis of the obtained carboxylates afforded nickel-containing nanocomposites, which were studied by elemental analysis, IR spectroscopy, scanning and transmission electron microscopy, energy dispersive X-ray spectroscopy, and X-ray powder diffraction analysis. The enthalpies of the reaction  $\Delta H_r^{\circ}$  for the formation of unsaturated nickel(II) monocarboxylates have been calculated by the semi-empirical quantum-chemical PM3 method. A positive correlation has been found between the average nanoparticle diameter ( $d_{av}$ ) of nano-

composites and  $\Delta H_{\rm r}^{\circ}$ . The magnetic properties of the obtained nanocomposites have been studied.

*Keywords:* unsaturated monocarboxylic acids, nickel, synthesis, carboxylates, thermolysis, nanocomposites **DOI:** 10.1134/S0036023620080136

Salts of unsaturated monocarboxylic acids constitute a class of compounds having not only carboxylate, but also unsaturated function, which makes them typical representatives of metal-containing monomers [1]. Interest in the chemistry of these compounds is determined by the flexibility of their properties, largescale industrial use, and the possibility of using these materials as precursors in the preparation of metal polymer nanocomposites [2–5].

Acrylates and acrylic acid derivatives are widely used in the production of acrylic emulsions in the paint industry, for impregnation of leather and fabrics, as feedstock for the production of adhesives and building mixtures, acrylate rubbers and polyacrylonitrile fibers. A significant proportion of acrylic acid is spent on the production of superabsorbents and structural materials. Oleates and linoleates of various metals are used as thickeners and desiccants in the paint industry [6], as well as in the preparation of nanoparticles [7]. Sodium and potassium sorbates are used as preservatives [4]. Conjugated linoleic acid is a dietary supplement and is widely used by athletes [8].

Interest in transition metal complexes containing a carboxylate monomer with an unsaturated double or triple bond as a ligand is growing due to the ability of these bonds to open at high temperatures in an inert atmosphere and to produce nanocomposites [9, 10].

Similar materials containing nanosized particles are widely used in various fields of science, such as chemistry, physics, and biology, which, in turn, stimulates further studies of theoretical and practically significant problems associated with their preparation and analysis [10, 11]. Studying nanoparticles, efficient stabilization techniques, and methods for controlling their composition is by far the most urgent task, despite an extensive number of scientific papers devoted to the study of these compounds. Physicochemical characteristics and properties of nanocomposites are mainly contributed by the quantum size effect. Significant interest in *d*-metal nanoparticles is due to the peculiarities of their magnetic properties [12], as well as the possibility of creating magnetic carriers with a high information density based on cobalt, nickel, and iron nanoparticles [13]. Magnetic nanoparticles are widely used in biomedicine [14]. One of the most promising methods for the synthesis of nanocomposites is controlled thermolysis of metalcontaining monomers in an inert atmosphere. It simultaneously combines the synthesis of a finely dispersed metal phase, presented in the form of a core consisting of metal/metal oxide or a mixture thereof, and the formation of a stabilizing polymer matrix that prevents agglomeration of particles of the resulting nanocomposites [9, 15].

Previously, cobalt and nickel acrylates, methacrylates [16, 17], and oleates [18] have been synthesized. In the present work, we report the synthesis of unsaturated nickel monocarboxylates of acrylic acid  $CH_2=CH-COOH$  (AcrA), crotonic acid  $CH_3$ -CH=CH-COOH (CrotA), linoleic acid  $CH_3(CH_2)_3 - (CH_2CH = CH)_2(CH_2)_7COOH$  (LinA), methacrylic acid CH<sub>2</sub>=C(CH<sub>3</sub>)-COOH (MethAcrA), oleic acid CH<sub>3</sub>(CH<sub>2</sub>)<sub>7</sub>CH=CH(CH<sub>2</sub>)<sub>7</sub>COOH acid  $CH \equiv C - CH_3 - CH_2 - CH_3 -$ (OleicA), 4-pentynoic COOH (PentA), sorbic acid CH<sub>3</sub>CH=CH-CH=CH-COOH (SorbA), and propiolic acid CH≡C-COOH (PropiolA) and their thermal properties and the production of nickel-containing nanocomposites through controlled thermolysis and their properties.

# **EXPERIMENTAL**

The following reagents were used: nickel acetate tetrahydrate Ni(CH<sub>3</sub>COO)<sub>2</sub> · 4H<sub>2</sub>O (pure grade), nickel chloride hexahydrate NiCl<sub>2</sub> · 6H<sub>2</sub>O (State Standard GOST 4038-79), nickel nitrate nonahydrate Ni(NO<sub>3</sub>)<sub>2</sub> · 9H<sub>2</sub>O (pure for analysis grade), acrylic acid (99.5%, Sigma-Aldrich), crotonic acid (99%, Sigma-Aldrich), linoleic acid (99%, Sigma-Aldrich), methacrylic acid (99.5%, Sigma-Aldrich), oleic acid (97.4%, Technical conditions TU 9145-1724731297-94), 4-pentynoic acid (99%, Sigma-Aldrich), propiolic acid (99%, Sigma-Aldrich), and sorbic acid (99%, Sigma-Aldrich).

Nickel carboxylates were synthesized by different procedures depending on the properties of acids and available procedures for various compounds.

Nickel crotonate, sorbate, acrylate, propiolate, and methacrylate were produced by the reaction of aqueous solutions of the acids with a solution of nickel acetate tetrahydrate (combined in a 2 : 1 molar ratio). The synthesis was carried out at room temperature, except that with sorbic acid carried out at 90°C because of its poor solubility. Then the solution was evaporated, and the resulting precipitate was heat-treated at 120°C until constant weight was achieved to remove acetic acid forming in the course of reaction.

Nickel linoleate was prepared as follows: 0.018 mol of sodium hydroxide was added to 3.8 mol of water and stirred until complete dissolution, and then 0.018 mol of linoleic acid was added. The mixture was heated to  $60-70^{\circ}$ C with stirring until the resulting precipitate was completely dissolved, and 0.009 mol of nickel chloride hexahydrate was added, which led to deposition of a light green precipitate. The resulting precipitates were dried to constant weight in air, then ground and washed several times with acetone to remove the acid residue and allowed to dry in air. Then, nickel linoleate washed from acid was washed several times

with water to remove sodium chloride and allowed to dry in air to constant weight, and then it was dried in a vacuum oven at 45°C to constant weight. The total yield of the product was 33.14%.

Nickel oleate was prepared by the following procedure: an equimolar amount of sodium hydroxide was mixed with oleic acid and 70 mL of water, 70 mL of hexane, and 70 mL of methyl alcohol were successively added, then a stoichiometric amount of nickel nitrate nonahydrate was introduced. The resulting ternary mixture with layering was heated to  $70^{\circ}$ C on a magnetic stirrer under constant stirring and kept at this temperature for 3 h. Then, the upper organic layer was separated in a separatory funnel, washing it several times with distilled water. Evaporation of the solution until complete removal of hexane gave a green nickel oleate powder.

The IR spectra of samples were recorded as discs with KBr in the range 4000–500 cm<sup>-1</sup> on a Bruker Equinox 55 IR FT spectrophotometer. Elemental analysis was carried out on a Thermo Finnigan automatic CHNS elemental analyzer. The nickel content was determined by direct titration with EDTA in the presence of Murexide [19]. Thermal analysis of nickel carboxylates was carried out on an MOM Q-1500 D Paulik-Paulik-Erdey derivatograph on heating in air (powders, m = 0.03-0.04 g) at a rate of 10 K/min in the range 20–500°C.

Nickel nanocomposites were synthesized under isothermal conditions at 335  $\pm$  1°C using an ET-MGK electric crucible 0.7 × 1.5/12 with a Delta digital temperature controller of a DTA series for 9 h in an argon atmosphere.

The composites synthesized by thermolysis were studied by transmission electron microscopy (TEM) on a Jeol JEM 100CX electron microscope at a accelerating voltage of 80 kV (Shared Facility Center "UNIQEM collection," Federal Research Center of Biotechnology, RAS) and scanning electron microscope (SEM) on a Jeol JSM-6700F electron microsscope equipped with an Oxford INCA system for energy-dispersive spectrometry. X-ray powder diffraction analysis was performed on a DRON-4.0 diffractometer using  $CoK_{\alpha}$  radiation. The diffraction spectrum was interpreted using the PHAN% quantitative phase analysis program [20].

For automatic processing of electronic images, the LabVIEW 8.5.1 software was used [21]. The magnetic properties of the nanocomposites were measured at room temperature by means of an M4500 EG&G PARC vibrating sample magnetometer (VSM) calibrated using a standard 90-mg nickel sample. During measurements, the magnetic field varied from 0 to 800 kA/m. The weight of the test sample was ~50 mg.

Quantum-chemical calculations of the enthalpy of the formation reaction of unsaturated nickel monocarboxylates were performed with the HyperChem 8.0.8 software (Hypercube, Inc.) by the semi-empiri-

Compound	$v_{OH}(H_2O)$	v(COOH)	v(mult. bond)	ν <sub>s</sub> (COO <sup>-</sup> )	v <sub>as</sub> (COO <sup>-</sup> )
Nickel acrylate	3535 (m)	_	1640 (w)	1354 (w), 1437 (s)	1559 (s)
Acrylic acid	-	1705 (s)	1635 (w)	_	—
Nickel crotonate	3581 (m)	1700 (w)	1659 (m)	1408 (s)	1539 (s)
Crotonic acid	_	1705 (s)	1643 (m)	1395 (m)	1530 (w)
Nickel linoleate	3430 (br)	1710 (w)	_	1409 (br)	1572 (br)
Linoleic acid	_	1712 (s)	_	1375 (m)	_
Nickel methacrylate	3437 (m)	_	_	1413 (s)	1559 (s)
Methacrylic acid	_	1708 (s)	1638 (m)	1389 (w), 1425 (w)	_
Nickel oleate	3419 (br)	1708 (w)	_	1411 (s)	1573 (s)
Oleic acid	_	1712 (s)	_	1375 (m)	_
Nickel 4-pentynoate	3252 (br)	1714 (m)	1571 (s)	1415 (br)	1537 (br)
Nickel sorbate	3400 (br)	1698 (m)	1643 (m)	1410 (br)	1558 (br)
Sorbic acid	—	1690 (br)	1640 (m)	1378 (m)	_
Nickel propiolate	3277 (br)	2106 (s)	_	1379 (s)	1587 (m)

**Table 1.** Characteristic frequencies  $(v, cm^{-1})$  in IR spectra of unsaturated nickel carboxylates

cal PM3 method. The calculation was carried out taking into account the effect of an aqueous medium, for which a  $10 \times 12 \times 19$  Å cell was used where the calculated molecules were placed. For this aspect ratio and with taking into account the minimum distance between the atoms of the compound and solvent of 2.3 Å, the cell accommodated 72 water molecules. The calculation was carried out to a gradient value of 0.03 kcal/mol.

# **RESULTS AND DISCUSSION**

To confirm the preparation of nickel carboxylates, elemental analysis and IR spectroscopy were used. The IR spectra allow us to draw a qualitative conclusion about the presence of carboxylate ions in the obtained compounds and indicate the presence of coordination water. Based on the data obtained, it is seen (Table 1) that oleic and linoleic acids, as well as nickel carboxylates based on them, do not have a pronounced characteristic vibration frequency of a multiple bond. This does not indicate the absence of the latter in the obtained compounds, but the symmetric or closely symmetric structure of the studied compounds with respect to this bond. The conclusions made are quantitatively confirmed by the results of elemental analysis (Table 2). It was established that all synthesized compounds have water in their composition, as evidenced by broad absorption bands in the IR spectrum ( $v_{OH}(H_2O) = 3277-3581 \text{ cm}^{-1}$ ). All the salts obtained, with the exception of oleate and linoleate, are water-soluble; a similar situation was observed for the corresponding cobalt carboxylates [22].

Thermolysis of the studied compounds is accompanied by gas evolution and weight loss of the samples, which is due to the occurrence of endothermic reactions accompanied by the loss of water molecules during heating (Table 3). Then, exothermic decarboxylation reactions occur with the loss of an organic ligand (Fig. 1). The major product of thermolysis, according to X-ray powder diffraction, is NiO.

The observed weight loss for these processes coincides with the theoretical values. The decomposition of anhydrous complexes immediately follows the dehydration process, and the residual weight is in good agreement with the values corresponding to NiO (Table 4).

The composites obtained as a result of thermal decomposition of unsaturated nickel monocarboxylates in an argon flow are black powders consisting of two structural elements: an amorphous carbon matrix into which nanoparticles are implanted as follows from electron microscopy data. As can be seen from the data obtained, the thermolysis of nickel acrylate and linoleate leads mainly to cubic Ni metal (cF4/1) with an admixture of cubic Ni oxide (cF8/2). In the case of thermolysis of nickel crotonate, methacrylate, and propiolate, cubic Ni oxide (cF8/2) predominates

# PRONIN et al.

Salt	Ni, %	C, %	Н, %
Ni $(C_3H_3O_2)_2 \cdot 3H_2O$ Nickel acrylate	20.85/23.70	28.30/28.28	3.49/4.25
$Ni(C_4H_5O_2)_2 \cdot 3H_2O$ Nickel crotonate	23.89/22.20	34.39/34.01	4.51/5.10
Ni $(C_{18}H_{31}O_2)_2 \cdot 7H_2O$ Nickel linoleate	9.12/7.73	58.53/58.12	8.93/9.30
$Ni(C_4H_5O_2)_2 \cdot 6H_2O$ Nickel methacrylate	15.97/17.40	28.18/28.50	4.20/5.25
$Ni(C_{18}H_{33}O_2)_2 \cdot 9H_2O$ Nickel oleate	7.89/7.49	54.88/55.18	8.31/9.20
Ni $(C_5H_5O_2)_2 \cdot 2H_2O$ Nickel 4-pentynoate	19.37/20.32	36.79/41.57	4.73/4.88
$Ni(C_3HO_2)_2 \cdot 2H_2O$ Nickel propiolate	23.23/25.19	31.37/30.92	3.02/2.60
Ni $(C_6H_7O_2)_2 \cdot 4H_2O$ Nickel sorbate	18.82/16.63	41.25/40.90	4.44/5.25

Table 3.	Dehydration	of nickel	carboxylates	(transformatio	on is endot	hermal)
				<b>`</b>		,

Compound	T °C	Weight loss, %			
Compound	1, C	calcd. found			
$Ni(C_4H_5O_2)_2 \cdot 3H_2O \rightarrow Ni(C_4H_5O_2)_2$ Nickel crotonate	138	19.08	17.26		
$Ni(C_{18}H_{31}O_2)_2 \cdot 7H_2O \rightarrow Ni(C_{18}H_{31}O_2)_2$ Nickel linoleate	148	16.94	16.62		
$Ni(C_6H_7O_2)_2 \cdot 4H_2O \rightarrow Ni(C_6H_7O_2)_2$ Nickel sorbate	108	20.40	20.59		

Table 4.	Decomposition of	nickel carboxylates	(transformation	is exothermal)
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Drogoss	T °C	Residue, %		
1100055	1, C	calcd.	found	
$Ni(C_4H_5O_2)_2 \rightarrow NiO$ Nickel crotonate	355-412	32.66	33.29	
$Ni(C_{18}H_{31}O_2)_2 \rightarrow NiO + Ni$ Nickel linoleate	425-465	10.82	9.01	
$Ni(C_6H_7O_2)_2 \rightarrow NiO$ Nickel sorbate	253-350	26.61	32.44	



**Fig. 1.** TG/DTA curves for thermolysis of unsaturated nickel carboxylates: (a) nickel crotonate Ni( $C_4H_5O_2$ )<sub>2</sub> · 3H<sub>2</sub>O, (b) nickel sorbate Ni( $C_6H_7O_2$ )<sub>2</sub> · 4H<sub>2</sub>O, and (c) nickel linoleate Ni( $C_{18}H_{31}O_2$ )<sub>2</sub> · 7H<sub>2</sub>O.

with an admixture of Ni metal (cF4/1). In the case of nickel oleate, 4-pentynoate, and sorbate, a mixture of these phases is observed (Table 5). The composite obtained by thermolysis of nickel crotonate also contains graphite (structure type hP4/1). The diffraction patterns of the obtained samples are shown in Fig. 2.

The black color of the composites is explained by the presence of amorphous carbon [23]. Based on the data of elemental and EDX analysis of the thermolysis products (Table 6), it has been suggested that an amorphous carbon matrix is formed. According to SEM, the studied composites are aggregates ranging from 1 to  $100 \,\mu\text{m}$  in size (Fig. 3).

The stages of processing the TEM image of the composite obtained by the decomposition of nickel crotonate are presented in Fig. 4.

Table 7 presents the results of processing TEM images of composites obtained by the decomposition of nickel carboxylates, and Fig. 5 shows the particle size distribution.

The growth and size of nanoparticles depend on a number of factors: temperature, time, environment,

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Phase	Structure type	volume, %	<i>a</i> , A	
Thermolysate of nickel acrylate				
FCC-Ni	<i>cF</i> 4/1	71.4	3.526	
FCC-NiO	<i>cF</i> 8/2	28.6	4.217	
Т	hermolysate of n	ickel crotona	te	
FCC-Ni	<i>cF</i> 4/1	12.2	3.520	
FCC-NiO	<i>cF</i> 8/2	78.6	4.187	
Graphite	<i>hP</i> 4/1	9.2	—	
Т	hermolysate of r	nickel linoleat	e	
FCC-Ni	<i>cF</i> 4/1	68.7	3.526	
FCC-NiO	<i>cF</i> 8/2	31.3	4.191	
The	ermolysate of nic	kel methacry	late	
FCC-Ni	<i>cF</i> 4/1	3.4	3.523	
FCC-NiO	<i>cF</i> 8/2	96.6	4.219	
	Thermolysate of	nickel oleate		
FCC-Ni	<i>cF</i> 4/1	51.9	3.522	
FCC-NiO	<i>cF</i> 8/2	48.2	4.208	
The	ermolysate of nic	kel 4-pentyno	oate	
FCC-Ni	<i>cF</i> 4/1	48.5	3.519	
FCC-NiO	<i>cF</i> 8/2	51.5	4.217	
Thermolysate of nickel propiolate				
FCC-Ni	<i>cF</i> 4/1	7.7	3.523	
FCC-NiO	<i>cF</i> 8/2	92.3	4.214	
Thermolysate of nickel sorbate				
FCC-Ni	<i>cF</i> 4/1	29.1	3.527	
FCC-NiO	<i>cF</i> 8/2	70.9	4.205	

 Table 5. XRD data for thermolysis products of nickel monocarboxylates

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and a number of other characteristics. Factors affecting these characteristics of nanoparticles can also include the Gibbs energy of the formation of nanoparticle precursors (in this case, nickel carboxylates). We have previously suggested that there is a relationship between the energy characteristics of metal carboxylates (complementarity, preorganization energy, formation energy) and nanoparticles (sizes, size distribution, magnetic properties) obtained by thermolysis [24]. In [22, 25, 26], the existence of a dependence of

**Table 6.** Elemental composition of thermolysis products ofnickel carboxylates, at %

Carboxylate thermolysis product	С	Н	0	Ni
Acrylate	37.07	0.67	10.93	51.33
Crotonate	23.40	0.57	16.80	59.23
Linoleate	58.85	2.19	4.96	34.00
Methacrylate	28.86	0.23	22.38	48.53
Oleate	53.30	2.04	5.04	39.62
Propiolate	27.74	0.93	6.94	64.39
4-Pentynoate	33.62	1.77	9.75	54.86
Sorbate	34.24	2.05	8.15	55.56

the average nanoparticle diameter on the enthalpy of formation reaction of metal carboxylates, which are the precursors of nanocomposites, has been proved by the example of unsaturated cobalt and nickel dicarboxylates.

The experimental energy characteristics of carboxylates are not always known, since their determination is often associated with difficulties. One of the possible ways to determine these characteristics is quantumchemical calculations, which are often performed for vacuum. However, it is known that the effect of the medium has a significant effect on the course of chemical reactions. Since the entropy component often makes a small contribution to the Gibbs energy, and the latter is usually proportional to enthalpy [27], one of the aims of this work was to calculate the enthalpy of the formation of unsaturated nickel monocarboxylates taking into account an aqueous medium, since the synthesis of all compounds carried out in an aqueous medium or at the interface with water. According to Eq. (1), the calculation was carried out under the condition that there were two acid molecules in the cell.

The reaction of formation of unsaturated nickel monocarboxylates is

$$2HA + Ni^{2+} = NiA_2 + 2H^+,$$
(1)

where HA is an unsaturated monocarboxylic acid.

The enthalpy of this reaction  $\Delta H_r^{\circ}$  can be calculated as

$$\Delta H_{\rm r}^{\circ} = \Delta H_{\rm f(s)}^{\circ} - 2\Delta H_{\rm f(fa)}^{\circ}, \qquad (2)$$

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Fig. 2. X-ray powder diffraction patterns of composites synthesized from nickel carboxylates: (a) nickel acrylate, (b) nickel sorbate, and (c) nickel linoleate.

where  $\Delta H_{f(s)}^{\circ}$  is the enthalpy of formation of a salt, and  $2\Delta H_{f(fa)}^{\circ}$  is the enthalpy of formation of two molecules of free acid. The calculation results are presented in Table 8.

Figure 6 shows a correlation between the average diameter of nanoparticles formed in the course of thermolysis of nickel carboxylates and enthalpy of reaction of carboxylates formation.

The observed dependence of the average nanoparticle diameter on the enthalpy of the reaction of nickel carboxylate formation can be interpreted as follows. The enthalpy of the reaction of formation of nickel carboxylates characterizes their stability, which, in turn, determines the onset and rate of thermal decomposition of these carboxylates: the higher the stability of the carboxylate, the later it begins to decompose and, accordingly, to form an amorphous carbon



Fig. 3. SEM images of the products of nickel carboxylate thermolysis: (a) nickel sorbate, (b) nickel crotonate, and (c) nickel 4-pentynoate.

matrix with the phase of nanoparticles distributed in it. The nucleation process is apparently associated with an inhomogeneous distribution of nickel atoms in the solid-phase structure of its carboxylates, which may be due to the peculiarity of the crystalline structure or its defects.

The magnetic characteristics of the obtained nanocomposites are given in Table 9.

To create high-density magnetic information storage media, magnetic nanoparticles should have a large coercive force, which helps prevent self-demagnetization due to thermal fluctuations [12, 28].

It has been noted in [29, 30] that nanoparticles 11-26 nm in size containing  $\beta$ -Ni have a face-centered cubic (FCC) crystal lattice and are ferromagnetic.

A massive NiO sample has antiferromagnetic properties [31]. With a decrease in the grain size of the magnetic material to the nanoscale, it transforms into superparamagnetic [32]; therefore, NiO nanoparticles exhibit a superparamagnetic nature [31, 33] and have zero coercive force [12]. Taking into account that, in all the composites obtained, the nanoparticles consist of FCC-Ni and FCC-NiO in different ratios (Table 5), and considering that a nanoparticle has a core—shell structure [34], i.e. consists of a ferromagnetic core surrounded by a superparamagnetic NiO shell, we calculated the size of the ferromagnetic core and constructed the dependence of the coercive force on the average diameter of the ferromagnetic core (Fig. 7), described by the linear equation:



Fig. 4. Stages of processing of the TEM image of the composite obtained by decomposition of nickel crotonate using the Lab-VIEW 8.5.1 software.

$$H_{\rm c} = 3.65 + 4.09 d_{\rm npFCC-Ni}$$

with the approximation reliability  $R^2 = 0.976$  and the correlation coefficient r = 0.988. Checking the significance of the correlation coefficient by the *t*-criterion showed that with a confidence probability of 0.999, the correlation coefficient is significant. The obtained dependence is the left branch of the dependence of the coercive force on the diameter of ferromagnetic particles, which has the form of a curve with a maximum [12, 35]. Literature data [36] show that the critical diameter for nickel is about 79 nm, i.e. at a signifi-

cantly larger particle diameter. The established dependence allows one

(i) to calculate the coercive force of a sample if the volume fraction of the ferromagnetic phase and the average particle diameter are known;

(ii) to determine the volume fraction of the ferromagnetic phase if the coercive force of samples and the average particle diameter are known;

(iii) to determine the average particle diameter if the coercive force of samples and the fraction of the ferromagnetic phase are known.

Nanocomposite precursor	Number of particles in a studied fragment	Average particle diameter, nm*
Nickel linoleate	348	$4.3 \pm 0.2$
Nickel methacrylate	565	$3.5\pm0.2$
Nickel sorbate	415	$2.6 \pm 0.4$
Nickel oleate	397	$3.6 \pm 0.1$
Nickel 4-pentynoate	735	$2.2\pm0.2$
Nickel propiolate	621	$2.2 \pm 0.3$
Nickel acrylate	978	$2.9 \pm 0.3$
Nickel crotonate	325	$5.3 \pm 0.2$

Table 7. Processing of the TEM images of thermolysis products of nickel carboxylates

\*Average of two values; the confidence interval was calculated at the significance level  $\alpha = 0.1$ .



Fig. 5. Size distribution of particles in nickel nanocomposites synthesized from precursors: (a) nickel 4-pentynoate, (b) nickel propiolate, and (c) nickel crotonate.

It follows from Table 9 that the highest coercive force (21.3 kA/m) is observed for the nanocomposite obtained by thermolysis of nickel oleate. The average diameter of the metal-containing nanoparticles of this nanocomposite is 3.6 nm, and the diameter of the fer-

romagnetic core consisting of FCC-Ni is 2.9 nm. With a decrease in the average diameter of the ferromagnetic core of nanoparticles from 3.8 nm (nanocomposite obtained by thermolysis of nickel linoleate) to 0.9 nm (nanocomposite obtained by thermolysis of



Fig. 6. Average particle diameter vs. the enthalpy of the reaction of formation of unsaturated nickel monocarboxylates.

nickel propiolate), the coercive force decreases from 19.1 to 7.2 kA/m, which is associated with an increase in the role of thermal fluctuations [36, 37]. The maximum saturation magnetization ( $18.0 \text{ A m}^2/\text{kg}$ ) and the

Table 8. Enthalpy of formation reaction of unsaturated nickel monocarboxylates

Carboxylate	$\Delta H_{ m r}^{\circ},$ kJ/mol	Nanoparticle diameter, nm
Nickel 4-pentinoate	-1441	2.2
Nickel propiolate	-1410	2.2
Nickel methacrylate	-605	3.5
Nickel sorbate	-445	2.6
Nickel acrylate	-342	2.9
Nickel oleate	-188	3.6
Nickel linoleate	21	4.3
Nickel crotonate	493	5.3

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Carboxylate	$\Delta H_{ m r}^{\circ},$ kJ/mol	Nanoparticle diameter, nm	
Nickel 4-pentinoate	-1441	2.2	
Nickel propiolate	-1410	2.2	
Nickel methacrylate	-605	3.5	
Nickel sorbate	-445	2.6	
Nickel acrylate	-342	2.9	
Nickel oleate	-188	3.6	
Nickel linoleate	21	4.3	
Nickel crotonate	493	5.3	



Fig. 7. Coercive force  $H_c$  vs. the average diameter of the ferromagnetic core of nanoparticles.

remanent magnetization (6.90 A m<sup>2</sup>/kg) were also recorded for the nanocomposite obtained by thermolysis of nickel oleate.

It should be noted that, in the case of a nanocomposite obtained by frontal polymerization of a cobalt acrylamide complex with subsequent thermolysis, the coercive force was 7.96 kA/m [28].

The scatter of points in Fig. 7 is associated with the difficulties of a theoretical study of magnetic hysteresis in nanoparticles because of the fact that this nonlinear, nonequilibrium, and nonlocal phenomenon caused by the existence of energy minima and the barriers separating them depends in a complex way on the external magnetic field [12, 37].

Figures 8 and 9 show the dependences of the magnetization of composites obtained from nickel carboxvlates on the magnitude of the magnetic field.

Nanocomposite precursor	Core diameter of FCC-Ni nanoparticles, nm	Saturation magnetization, A m <sup>2</sup> /kg	Remanent magnetization, A m <sup>2</sup> /kg	Coercive force, kA/m
Nickel 4-pentinoate	1.7	16.5	4.69	11.4
Nickel propiolate	0.9	6.77	0.38	7.24
Nickel methacrylate	1.1	5.66	1.21	8.84
Nickel sorbate	1.7	12.2	3.02	9.47
Nickel acrylate	1.6	17.4	5.73	14.6
Nickel oleate	2.9	18.0	6.9	21.3
Nickel linoleate	3.8	15.6	4.28	19.1
Nickel crotonate	2.6	9.75	3.44	14.4

 Table 9. Magnetic characteristics of nanocomposites



Fig. 8. Magnetization of composites obtained from nickel carboxylates as a function of the magnetic field magnitude: (1) nickel linoleate, (2) nickel sorbate, (3) nickel crotonate, and (4) nickel propiolate.



**Fig. 9.** Magnetization of composites obtained from nickel carboxylates as a function of the magnetic field magnitude: (1) nickel oleate, (2) nickel acrylate, (3) nickel 4-pentynoate, and (4) nickel methacrylate.

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# CONFLICT OF INTEREST

The authors declare no conflict of interest.

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