Nail polish, in particular gel polish, is the most commonly used cosmetic product. A component of the gel polish, which determines the consumer color characteristics of the gel polish. Layered double hydroxides (LDH) are promising pigments. To expand the range of colors and shades of pigments, the use of LDH with colored host and guest cations is promising. The parameters of synthesis and color characteristics of samples of Zn-Co and Cu-Co hydroxide pigments were studied. To obtain LDH with Co as a guest cation in the synthesis, the conversion of cobalt to the trivalent state was carried out at a temperature of 80 °C using oxidation with atmospheric oxygen or sodium hypochlorite. The oxidation efficiency was evaluated by X-ray phase analysis by the presence or absence of cobalt-containing phases. The color characteristics of the synthesized pigment samples were studied by spectroscopic measurement and calculation in RGB, CIELab, and LCH color models.

The low efficiency of cobalt oxidation at the moment of Zn-Co LDH synthesis with atmospheric oxygen at an elevated synthesis temperature of 80 °C was shown, while cobalt was released as a separate Co_3O_4 phase. A higher efficiency of cobalt oxidation at the moment of synthesis using sodium hypochlorite with the formation of Zn-Co LDH was revealed. It is recommended to use the hypochlorite oxidation of Co^{2+} to Co^{3+} in the LDH synthesis with Co in the form of a guest cation. The formation of a separate phase of zinc oxide was found in both types of oxidation due to the thermal decomposition of zinc hydroxide.

Comparative analysis of color characteristics showed that all samples have a brown color of different saturation. It was revealed that during the formation of Co-containing LDH, the lightness of the color decreases. Color saturation increases in the case of a colored host cation, such as Cu

Keywords: Zn-Co layered double hydroxide, pigment, Cu-Co layered double hydroxide, oxidation, hypochlorite

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THE DETERMINATION OF SYNTHESIS CONDITIONS AND COLOR PROPERTIES OF PIGMENTS BASED ON LAYERED DOUBLE HYDROXIDES WITH Co AS A GUEST CATION

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1. Introduction

Since ancient times, people have widely used cosmetics for health, decorative or sacred purposes. One of the most commonly used cosmetics is nail polish. Nowadays, various nail polishes are used for manicure and pedicure, both for decorative and therapeutic as well as prophylactic purposes.

Common decorative nail polish consists of a polymer (usually nitrocellulose [1]), solvents, plasticizers, and pigments. However, at present, the most promising is a gel polish, the curing of which occurs under the influence of ultraviolet radiation. It is the pigments that give the polish its color. Cosmetic pigments of gel polish can be both natural and synthetic. The most common mineral pigments are salt and oxide materials, for example, cobalt-chromium oxide [2], as well as spinel [3–5] pigments and pigments with the structure of various silicates [6, 7]. Pigments of inorganic nature are characterized by high color stability, but at the same time, they have a limited range of colors. Organic pigments have a wide range of colors but are characterized by low light stability.

Materials of organic-inorganic nature combine the advantages of both organic and inorganic pigments. Among the pigments of this type, the most promising are layered double hydroxides (LDH) [8] intercalated with anionic dyes [9, 10].

The use of various metal cations and anionic dyes of various colors in the composition of LDH will significantly expand the color palette of cosmetic pigments. For example, Zn-Al and Acid Yellow 17 [11], Mg-Al and o-Methylene Red [12], Ni-Fe and o-Methylene Red [13], Zn-Al and Mordant Yellow 3 [14, 15], Zn-Al and Acid Yellow 3 [16], Zn-Al and Acid Green bianion 28 [17].

Also, LDH was used to purify wastewater from anionic dyes by ion exchange to obtain dye-intercalated LDH. In particular, Evans Blue was extracted using Zn-Al LDH [18], and Orange-type dyes – using Zn-Al LDH [19]. Various azo dyes [20], including Remazol Brilliant Violet [21], were extracted using Ni-Al LDH, blue dyes (including Maya Blue) [22] – using Zn-Al LDHS, Methyl Orange [23] – using Zn-Al LDH. Amaranth [24] was removed from wastewater using Mg-Al LDH, Acid Yellow 42 [25] –

using Mg-Al LDH, Congo Red [26] – using Ni-Al LDH, and Indigocarmine [27] – using Mg-Fe LDH.

However, the color of the LDH pigment can be changed not only due to the intercalated dye anion, but also due to the colored cations of the host metal and the guest metal. It should be noted that this approach is relevant for the targeted production of pigments of the required color range.

2. Literature review and problem statement

Polymorphism was revealed for hydroxides of divalent metals (except for alkaline earth metals). Two modifications are characteristic of them: β-modification (chemical formula $Me(OH)_2$, brucite structure) and α-modification (chemical formula $3Me(OH)_2{\cdot}2H_2O$, hydrotalcite structure). For nickel hydroxide, structures intermediate between the α- and β-form were described. [28]. The article [29] showed the formation of nickel hydroxide with a mixed layered (α+β)-structure.

Layered double hydroxide (LDH) is the α-modification of the host metal hydroxide, in the crystal lattice of which part of the host metal cations are replaced by the guest metal cations: for example, Zn^{2+} (a host) is replaced by Al^{3+} (a guest). Because of this, an excess positive charge is formed in the crystal lattice, which can be compensated by the introduction of additional anions into the interlayer space. The anions of the salts from which the synthesis was carried out can act as such anions. However, most often, anions with special functional properties are purposefully intercalated into the LDH structure. Stabilizing [30] or activating anions [31, 32] are most often added to the LDH composition. It is promising to use LDH as a nano container for special anions, for example, drugs [33, 34], dye anions [35], anions for sensors [36], corrosion inhibitors [37], biologically active additives [38], food additives [39, 40] and others.

In this case, the LDH structure includes the following main components [41]: cations of the host metal, cations of the guest metal, and intercalated anions. With a purposeful choice of all three components, it becomes possible to design an LDH with the required characteristics [37].

For the synthesis of a pigment on the LDH basis, the most promising is the use of Mg^{2+} and Zn^{2+} as the host metal cation. Zn and Mg hydroxides are white, therefore Mg or Zn LDH represent a good basis for the clear development of the color of the intercalated dye. LDH as a pigment base must be health-friendly for use in cosmetics. A review article [42] showed the minimum toxicity of Zn-Al and Mg-Al LDH, as well as the low toxicity of other LDHs due to their very low solubility.

Al^{3+} is most often used as the guest metal cation. This choice is based on high structure-forming and stabilizing properties to the α-modification of LDH.

Sometimes in the literature, pigments obtained by intercalation are called nanocomposites. It should be noted that composite materials (organic-organic [43] or inorganic-inorganic [44]) contain a matrix and a filler, between which there is always an interface. However, pigments intercalated with LDH are mainly monophasic substances. Therefore, it is incorrect to call them nanocomposites.

The method of synthesis and the conditions for its implementation directly determine the micro- and macrostructure of LDH particles. Hydroxides can be obtained by chemical precipitation by direct synthesis (adding an alkaline solution to a solution of a metal salt) [45, 46], synthesis with high supersaturation (adding a solution of a metal salt to an alkali solution) [47, 48], and a sol-gel method [49]. Moreover, two-stage high-temperature synthesis [50, 51], and homogeneous precipitation can be used for the synthesis [52]. To obtain hydroxides, electrochemical methods are used: cathode template synthesis [53] and synthesis in a slit diaphragm electrolyzer [20]. However, not all of the listed methods can be used to synthesize a dye-intercalated LDH pigment. To obtain such materials, two types of methods can be distinguished. The first of these is a two-stage type. It includes:

1) the LDH synthesis with inorganic anions (mainly anions of precursor salts) by the methods of precipitation with high supersaturation [11, 16], precipitation at constant pH [9, 41], homogeneous precipitation [37], etc.;

2) intercalation of the dye anion by ion exchange [16, 17].

One of the variants of the two-stage type is the method of LDH reduction from LDO (layered double oxide obtained by LDH calcining) in the presence of a dye anion [12]. The disadvantages of the two-stage methods are the duration of the ion exchange, as well as the need to synthesize LDH with anions that can be easily exchanged for dye anions. It should be pointed out that the two-stage methods of preparation make it possible to synthesize pure dye-intercalated LDH. However, such methods are technologically poorly applicable in production due to the complexity, high duration, and high cost.

The second variant is a one-stage type of preparation. In this case, the formation of dye-intercalated LDH occurs directly during the synthesis. For this purpose, the method of coprecipitation by synthesis at constant pH [54, 55] or synthesis with high supersaturation [25, 56] is used. Direct synthesis is the most promising.

To expand the color variability of pigments based on LDH, it is promising to use colored cations of the guest metal and the host metal. This will make it possible to use dyed LDHs both for intercalation with dye anions and as independent pigments. It should be noted that the choice of colored host and guest metal cations is very limited: host – Ni^{2+}, Co^{2+}, Fe^{2+}, Mn^{2+}, Cu^{2+}, guest – Fe^{3+}, Cr^{3+}, Co^{3+}.

From the above list of colored host metal cations, Ni^{2+} and Cu^{2+} are the most promising. LDHs based on nickel hydroxide (both intercalated with various dyes [35, 52, 56] and without dyes in their composition [45–47]) have been well studied. At the same time, data on the LDH characteristics based on copper hydroxide are practically absent, despite the promising blue color of possible pigments.

When considering the list of colored guest metal cations, it should be noted that all colored cations have a yellow-brown color. Among them, the most promising is Co^{3+}. Cobalt is interesting because Co^{2+} can be a host cation, and Co^{3+} can be a guest cation. The disadvantage of this cation is that it is impossible to use aqueous solutions of cationic salts for synthesis since there are no water-soluble Co^{3+} salts. For the synthesis, Co^{2+} salts are used, and for the conversion of the cobalt cation to the trivalent state, oxidation is necessary directly during the LDH formation. It should be pointed out that the methods for the LDH synthesis with Co^{3+} have not been sufficiently studied, as well as the color characteristics of similar LDH.

3. The aim and objectives of research

The study aims to identify effective conditions for the synthesis of Zn-Co and Cu-Co LDH and to study the characteristics, including color characteristics, of the obtained substances. This will reveal the conditions for the LDH synthesis with Co^{3+} as a guest, as a result, it will be possible to obtain pigments with new colors and shades. It will also allow studying the color characteristics of Co-containing LDH as pigments that do not contain dyes.

To achieve the aim, the following tasks were set:

– to obtain samples of Zn-Co and Cu-Co layered double hydroxides by the method of chemical synthesis using various methods of chemical oxidation of cobalt, with the determination of the most effective oxidation method;

– to carry out a comparative analysis of the color characteristics of the obtained Zn-Co and Cu-Co LDH samples.

4. Materials and methods of research

4. 1. Method for obtaining pigment samples

For the study, analytical grade qualification substances were used except for NaOH, which was used as a granular alkali of high analytical grade qualification. The synthesis was carried out using Zn, Cu(II), and Co(II) sulfates.

For the synthesis of Zn-Co and Cu-Co LDH samples, the chemical method of synthesis with high supersaturation described in [35] was used. LDH was obtained by feeding a solution of metal salts (with the ratio of cations host:guest=4:1) with a peristaltic pump into a reaction beaker containing an alkali solution. The synthesis was carried out at a temperature of 80 °C and continuous stirring. After the end of the synthesis, the reaction mixture was kept for an hour at the same temperature and stirred to undergo the crystallization process [57]. After that, the LDH precipitate was separated from the mother liquor on a vacuum filter. The resulting hydroxide, like polymer composites [43], is a composite material. In this case, the role of the matrix former was played by the hydroxide and the filler – by the mother liquor. Due to the closed-cell composite structure and highly active sorption characteristics [58], it was extremely difficult to rinse the wet LDH precipitate from the soluble salts (mainly sodium nitrate). For effective rinsing, a two-stage method was used: drying (70 °C, 24 hours), grinding, soaking in distilled water (24 hours), filtering and re-drying under the same conditions. Before studying the characteristics, the samples were additionally ground in a mortar and sieved through a 71 μm sieve.

The general research scheme consisted of three stages:

Stage 1. Determination of an effective method for the oxidation of Co^{2+} to Co^{3+}. Two oxidation methods were used as oxidation methods. The first one was oxidation by atmospheric oxygen at the moment of LDH synthesis. To supply oxygen through the reaction mixture at the time of synthesis, the air was bubbled with a flow rate of 0.5 L/min. The second method was oxidation with sodium hypochlorite. To implement the method, an alkali solution with sodium hypochlorite (with an active chlorine content of 1 g/L) was used for the synthesis. Zn-Co LDH (type colorless host-colored guest) was chosen as a synthesized sample for the first stage. Sample markings: during oxygen cobalt oxidation – Zn-Co, during hypochlorite oxidation – Zn-Co+NaClO. X-ray phase analysis was used to control the LDH formation.

Stage 2. Obtaining of Cu-Co LDH of the colored host-colored guest type using an efficient method of cobalt oxidation. The sample will be marked with Cu-Co based on an efficient oxidation method.

Stage 3. Comparative study of the color characteristics of the obtained LDH samples in different color models (RGB, CIE Lab, LCV).

4. 2. Methods for studying the characteristics of pigment samples

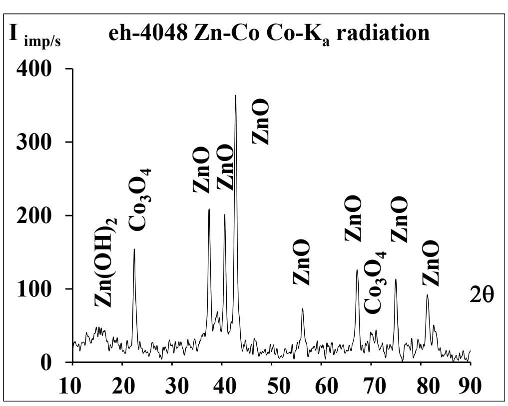
The crystal structure of the samples was studied by X-ray phase analysis (XPA) using a DRON-3 diffractometer (Russia) (Co-Kα radiation, angular range 10–90°2θ, scanning rate 0.1°/s).

The color characteristics of LDH samples were studied using a spectrophotometer. For this, an LDH sample was placed in a uniform thin layer in a polyethylene ZIP bag, which was placed on an even solid base. As a result of the measurement, color characteristics were obtained in the coordinates of the international color model CIE 1976 L*a*b*. Recalculations of color characteristics into other color models were carried out: LCH (L – Lightness, C – Chroma, H – Hue) and RGB (119,119,119). In the last model, H – Hue, V – Value, and S – Saturation were also calculated.

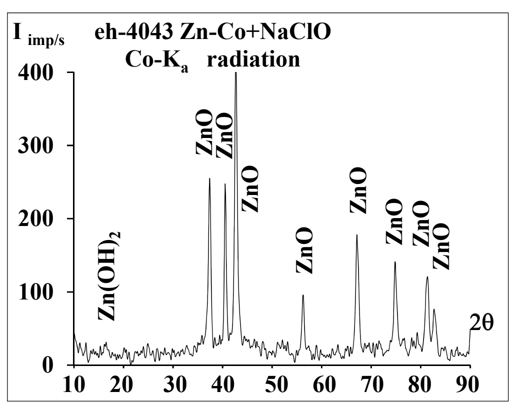
5. Results of studying synthesis methods and characteristics of Co-containing layered double hydroxides samples

5. 1. Results of determining the efficiency of cobalt oxidation methods in the synthesis of Zn-Co LDH

The results of X-ray phase analysis are shown in Fig. 1.



a



b

Fig. 1. Diffractograms of pigment samples: *a* – **Zn-Co**; *b* – **Zn-Co+NaClO**

Both samples, according to diffractograms (Fig. 1), contain both Zn-Al LDH (with a $Zn(OH)_2$ lattice) and ZnO (peaks at 2Θ=37°, 41°, 42°). At the same time, in the diffractogram of the **Zn-Co** sample (Fig. 1, *a*), obtained by Co oxidation with atmospheric oxygen, there are pronounced peaks at 2Θ=24.5° and 71°. These peaks correspond to mixed cobalt oxide Co_3O_4. At the same time, in the diffractogram of the **Zn-Co+NaClO** sample (Fig. 1, *b*), the peaks of individual cobalt-containing phases (including Co_3O_4) are absent. This indicates a higher efficiency of the oxidation of Co^{2+} to Co^{3+} by sodium hypochlorite than by atmospheric oxygen. Therefore, the synthesis of the Cu-Co LDH sample was carried out in the presence of sodium hypochlorite (the sample marking was **Cu-Co+NaClO**).

5. 2. Study of the color characteristics of pigments

Visual observation showed that the samples **Zn-Co, Zn-Co+NaClO,** and **Cu-Co+NaClO** have brown colors from light brown to brown (Fig. 2). The color characteristics of pigment samples in RGB and CIE 1976 L*a*b color models are given in Table 1. Fig. 3 shows the color characteristics of samples in the LCH color model.

a *b* *c*

Fig. 2. Samples of pigments: *a* — **Zn-Co**; *b* — **Zn-Co+NaClO**; *c* — **Cu-Co+NaClO**

Table 1

Color characteristics of pigment samples in RGB and CIE L*a*b models

Sample	RGB model						CIE L*a*b model		
	R	G	B	RGB model	CIE L*a*b model	RGB model	CIE L*a*b model	A	b
Zn-Co	172	156	110	45	67	36	64.91	0.99	26.4
Zn-Co+NaClO	113	103	75	44	44	34	43.98	0.65	17.4
Cu-Co+NaClO	93	80	48	43	36	48	34.73	1.96	20.9

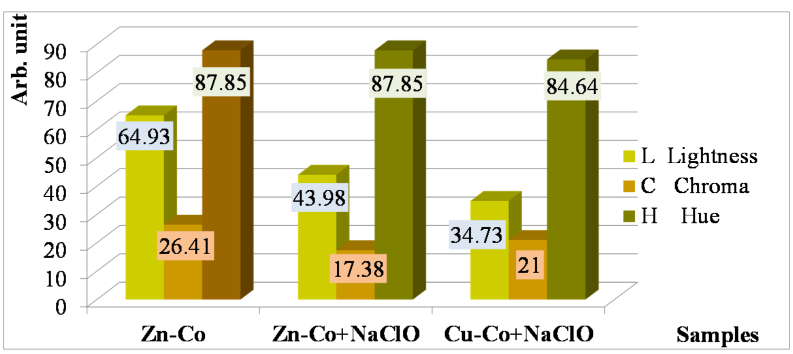


Fig. 3. Color characteristics of pigment samples in the LCH color model

Hue (H) (Table 1, Fig. 3) and Lightness (L) correspond to the visually determined color and the lightness of the pigments. The Lightness of the pigments in the Lab and LCH models, as well as the Value (V) parameter in the RGB model, which is the highest for the **Zn-Co** sample, increases for the **Zn-Co+NaClO** sample, and increases even more for the **Cu-Co+NaClO** sample. The color Saturation is maximum for the **Cu-Co+NaClO** sample – 48, for the **Zn-Co** and **Zn-Co+NaClO** samples it practically does not differ (36 and 34, respectively).

6. Discussion of the results of studying the methods of synthesis and characteristics of Co-containing layered double hydroxides samples

Determination of the efficiency of cobalt oxidation methods in the synthesis of Zn-Co LDH.

The diffractogram of the Zn-Co sample (Fig. 1, *a*), obtained by oxidizing cobalt with atmospheric oxygen, shows peaks of zinc oxide and zinc hydroxide phases, as well as distinct peaks of the Co_3O_4 phase. A separate mixed cobalt oxide phase can be formed by the partial oxidation of a separate cobalt hydroxide phase. In this case, it should be concluded that the oxidation efficiency of cobalt with atmospheric oxygen at elevated temperatures is low. The Zn-Co sample is a three-phase system containing ZnO, $Zn(OH)_2$, and Co_3O_4. In this case, the **Zn-Co** sample does not contain Zn-Co LDH. The reason for this composition can be explained based on the two-stage mechanism of the LDH formation:

Stage 1. Precipitation of the guest metal cation hydroxide.

Stage 2. The reaction of freshly precipitated guest metal hydroxide with host metal cations and excess hydroxyl anions to form LDH.

To implement this mechanism, the pH of the beginning of hydrate formation of the guest hydroxide must be lower than the pH of the beginning of the hydrate formation of the host hydroxide. However, the pH of the beginning of hydrate formation (for a 0.01 M solution) is:

– host $Zn(OH)_2 pH_{init.\ hydr}$=6.4;

– guest $Co(OH)_2 pH_{init.\ hydr}$=7.6.

In this case, in the absence of oxidation of $Co^{2+} \rightarrow Co^{3+}$ or its insufficient efficiency, the hydroxide of the host metal falls out earlier, and then the hydroxide of the guest metal falls out. And these two hydroxides practically do not interact, and LDH is not formed. It is known that the pH of the beginning of hydrate formation of CoOOH is much less – 1.5. Therefore, in the case of effective oxidation of cobalt to the trivalent state, a two-stage mechanism for the LDH formation is possible.

Based on the data presented, it should be noted that the efficiency of oxidation of cobalt with atmospheric oxygen is insufficient for the formation of Zn-Co LDH. The efficiency of cobalt oxidation by hypochlorite is significantly higher, which leads to the formation of Zn-Co LDH, which is confirmed by the absence of peaks of individual cobalt-containing phases in the diffractogram of the **Zn-Co+NaClO** sample (Fig. 1, *b*).

It should be noted that the **Zn-Co+NaClO** sample is biphasic and contains ZnO and Zn-Co LDH phases. ZnO is formed by the partial thermal decomposition of zinc hydroxide. This phenomenon was described earlier in [54, 55] during synthesis in an alkaline medium at elevated temperatures. The high synthesis temperature was used to increase the rate of cobalt oxidation. Due to the high efficiency of the oxidation of cobalt with hypochlorite, it is recommended to lower the synthesis temperature, as a result of which the amount of zinc oxide will decrease.

Pigment characteristics of the samples.

The analysis of the color characteristics of the samples given in Table 1, Fig. 2, 3, made it possible to draw the following conclusions. Cobalt trivalent oxyhydroxide (CoOOH) is dark brown in the color. As a result, all synthesized samples have brown colors. The **Zn-Co** sample, which is a three-phase system of zinc oxide, zinc hydroxide, and mixed cobalt oxide, has the highest Lightness (L=65) and the lowest Saturation (S=36), which is the result of bleaching with zinc oxide. The **Zn-Co+NaClO** sample containing Zn-Co LDH (colorless host-colored guest system) has a lower Lightness (L=44) and comparable color Saturation (S=34). The **Cu-Co+NaClO** sample containing Cu-Co LDH (the system colored host-colored guest), due to the introduction of a colored cation of the host metal, has a darker and more saturated brown color – Lightness L=35 and Saturation S=48. In general, it should be noted that when LDH is formed with Co as a guest cation, the pigment color becomes darker and the color Saturation increases. These characteristics are also enhanced by the use of a colored host cation.

This study revealed an effective method for the oxidation of cobalt with sodium hypochlorite for the LDH formation with Co in the form of a guest cation. These results can be used to develop industrial technologies for the production of cobalt-containing LDH for use as pigments, electrochemically or catalytically active substances. However, it was revealed that the synthesis at high temperatures (80 °C) leads to partial thermal decomposition of zinc hydroxide to zinc oxide and the formation of a biphasic system, which also changes the color characteristics of pigments. To prevent the formation of zinc oxide and obtain pigments with higher color saturation, it is necessary to research the synthesis of such LDHs with hypochlorite oxidation at low temperatures.

7. Conclusions

1. It has been shown that in the production of Zn-Co LDH, oxidation of cobalt at the moment of synthesis with atmospheric oxygen at an elevated synthesis temperature of 80 °C is ineffective, cobalt is released as a separate phase of Co_3O_4. A higher efficiency of cobalt oxidation at the moment of synthesis using sodium hypochlorite with the formation of Zn-Co LDH has been revealed. It is recommended to use the hypochlorite oxidation of Co^{2+} to Co^{3+} in the LDH synthesis with Co in the form of a guest cation. The formation of a separate phase of zinc oxide has been found in both types of oxidation due to the thermal decomposition of zinc hydroxide.

2. Color characteristics of Zn-Co and Cu-Co hydroxide pigments have been obtained in RGB, CIE L*a*b, and LCH color systems. It has been shown that all samples have a brown color of different saturation. It has been revealed that the lightness of the color decreases during the formation of Co-containing layered double hydroxides. Color saturation also increases in the case of a colored host cation, such as Cu.

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