

Синтезовані мурексид-інтеркальований та мурексид-інтеркальовано-хемосорбований Ni-Al ПШГ пігменти, виготовлені зразки лака для нігтів. Вивчені характеристики зразків пігментів та лаку. Показано позитивний вплив хемосорбції на властивості пігменту. Мурексид-інтеркальовано-хемосорбований пігмент легко легко подрібнювався, при приготуванні лаку для нігтів добре диспергувався з отриманням стабільного зразку жовтого кольору з високою чистотою кольору 43 %. Показана висока укривна здатність пігменту

Ключові слова: косметичний пігмент, мурексид, Ni-Al ПШГ, хемосорбція, інтеркалювання, лак для нігтів

Синтезированы мурексид-интеркальированный и мурексид-интеркальированно-хемосорбированный Ni-Al СДГ пигменты, изготовлены образцы лака для ногтей. Изучены характеристики образцов пигментов и лака. Показано положительное влияние хемосорбции на свойства пигмента. Мурексид-интеркальированно-хемосорбированный пигмент легко измельчался, при приготовлении лака для ногтей хорошо диспергировался с получением стабильного образца желтого цвета с высокой чистотой цвета 43 %. Показана высокая укрывистость пигмента

Ключевые слова: косметический пигмент, мурексид, Ni-Al СДГ, хемосорбция, интеркальирование, лак для ногтей

SYNTHESIS AND CHARACTERISATION OF DYE-INTERCALATED NICKEL-ALUMINIUM LAYERED-DOUBLE HYDROXIDE AS A COSMETIC PIGMENT

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1. Introduction

Decorative cosmetic had been widely used by mankind since ancient times. One of such cosmetic substances is nail polish. It can be used for decorative and medical purposes. In ancient China during the Ming dynasty, long fingernails were a sign of elite. Painted nails are also encountered among some ancient Egypt statues. In the modern world, the majority of women use nail polish.

A decorative nail polish consists of a polymeric base (usually nitrocellulose [1]), solvents, plasticizers and pigments. Pigments are responsible for the color of nail polish. Pigments used for nail polish production can be of natural or synthetic origin. Among mineral pigments, the most common materials are of salt and oxide nature, such as iron oxide pigments [2], also spinel-type [3–5] and pigments of various silicate structures [6, 7]. Inorganic pigments are character-

ized by high color stability, but have a limited color range. Organic pigments have a very wide color range, but are more expensive and less stable.

Advantages of organic and inorganic pigments can be combined by synthesis of organic-inorganic materials. The most promising materials of such type are layered double hydroxides (LDH) with various anions [8], including anionic dyes, intercalated into the interlayer space [9, 10].

Polymorphism is characteristic for divalent metal hydroxides with two polymorphs being described. β -form (chemical formula $\text{Me}(\text{OH})_2$, brucite structure) and α -form (chemical formula $3\text{Me}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$, hydrotalcite structure). Layered double hydroxide (LDH) is an α -form of the “host” metal hydroxide with a part of “host” metal ions in the crystal lattice substituted with “guest” metal ions. For instance, the Ni^{2+} cation is substituted with Al^{3+} cation. This leads to the formation of an excessive positive charge

in the crystal lattice, which can be compensated by the inclusion of additional anions. A general formula for divalent metal-based LDH is $\text{Me}_1\text{Me}_2^{n+}(\text{OH})_2\text{A}_{(n-2)/m}^{m-}$ $0.66\text{H}_2\text{O}$, where $\text{Me}_1=\text{Ca}^{2+}$, Mg^{2+} , Ni^{2+} , Zn^{2+} etc., $\text{Me}_2=\text{Al}^{3+}$, Fe^{3+} , Cr^{3+} , Ti^{4+} , etc. A – various-purpose anions, including drugs, anti-corrosion agents, dyes, vitamins, etc.

Use of LDH with various cation compositions and different organic anionic dyes would allow broadening the color range of pigments, especially for cosmetic applications. For instance, Zn-Al and Acid Yellow 17 [11], Mg-Al and o-Methyl Red [12], Ni-Fe and o-Methyl Red [13], Zn-Al and Mordant Yellow 3 [14, 15], Zn-Al and Acid Yellow 3 [16], Zn-Al and bi-anion Acid Green 28 [17]. Therefore, the synthesis of dye-intercalated LDH is of relevance.

The development of synthesis method of dye-intercalated LDH for pigment application should include three stages:

- 1) selection of LDH type, including selection of “host” and “guest” metal cations;
- 2) selection of anionic dye for intercalation;
- 3) selection of synthesis method.

When preparing LDH for pigment application, the most common “host” metal cations are Mg^{2+} , Zn^{2+} and Ni^{2+} . Additionally, Zn and Mg-based LDH are white. These hydroxides are a good base for the color of the intercalated dye to manifest. At the same type, Ni hydroxide-based LDH has different light-green shades, which allows obtaining pigments with a different color range using the same intercalated dyes. As a “guest” metal cation, Al^{3+} is most commonly used, because of its high ability to stabilize the α -form of hydroxides, in particular, LDH. Thus, the Ni-Al LDH is rather promising.

2. Literature review and problem statement

The choice of dye for the synthesis of LDH-based organic-inorganic pigments is based on the nature of the compound. In order to obtain the pigment of the desired color, a dye with the corresponding color should be chosen. However, to be intercalated into LDH, the dye must be anionic in nature. Monovalent anionic dyes, such as Acid Yellow 17 [11], Methyl Red [12, 13], Mordant Yellow 3 [15], Acid Yellow 49 [16], and also bi-anionic Acid Green 28 are mentioned in literature [17]. It should be noted that all anionic dyes can be used. Some authors call the obtained pigments nanocomposites. However, composite materials contain a matrix and a filler, for instance, organic-organic [18] and inorganic-inorganic [19] materials, and there is always a boundary between a filler and a matrix (or a binder). The intercalated LDH pigments are mainly monophase compounds, so calling them nanocomposites is incorrect.

It should be mentioned; that there is a significant number of works, which describe the use of LDH for treatment of dye-containing wastewater. In particular, it is proposed to extract Evans Blue using Zn-Al LDH [20], Orange-type dyes – using Zn-Al LDH [21], Perylenediimide – using Zn-Al, Co-Al, Ni-Al LDH [22]. Various azo-dyes [23], including Remazol Brilliant Violet [24], had been extracted using Ni-Al LDH, blue dyes (including Maya Blue) [25] – using Zn-Al LDH, Methyl Orange [26] – using Zn-Al LDH, Amaranth [27] – using Mg-Al LDH, Acid Yellow 42 [28] – using Mg-Al LDH, Congo Red [29] – using Ni-Al LDH, and Indigo carmine [30] – using Mg-Fe LDH. The main mechanism of dye removal is adsorption, including chemisorption

[20, 26] and intercalation [24]. However, the pigment preparation was not the aim of the study. Thus, it can be concluded that adsorption, including chemisorption, of anionic dyes is a known effect that must be considered during synthesis of dye-intercalated LDH pigments. It should also be mentioned that anionic dyes with affinity to LDH can be chosen. However, both of these aspects are not reviewed in the published papers.

Synthesis method and conditions determine the micro- and macrostructure of LDH particles. There are various methods for synthesis of nickel hydroxide and nickel-based layered double hydroxides. Hydroxide preparation can be achieved by means of chemical precipitation using titration method (addition of basic solution to the solution of nickel salt) [31], coprecipitation at high supersaturation (addition of nickel salt solution to a basic solution) [32, 33], two-stage high temperature synthesis [34], sol-gel method [35], homogeneous precipitation [36, 37]. Electrochemical methods, including cathodic template synthesis [38, 39] and slit diaphragm electrolyzer synthesis [33, 40] are also used. However, not all listed methods can be used for dye-intercalated LDH pigments. For the preparation of such materials, two fundamental methods can be outlined. The first method is composed of two stages:

- 1) synthesis of LDH with inorganic anions, using coprecipitation at high supersaturation [11, 16, 17], coprecipitation at constant pH [9, 24], homogeneous coprecipitation [37], etc.;
- 2) intercalation of anionic dye by means of anion exchange [16, 17, 37].

A variation of such two-stage method is a reconstruction of LDH from LDO (layered double oxide prepared by calcination of LDH) in the presence of anionic dye [12]. The disadvantages of the two-stage method are implementation difficulties, duration of the anion exchange process and necessity to prepare LDH with anions that can easily be replaced with anion dyes.

The second method is a one-stage direct synthesis. In this case, the formation of dye-intercalated LDH takes place directly during the synthesis. Coprecipitation at high supersaturation with constant pH [13, 14, 15] is used for this method. The direct synthesis is the most promising.

Unfortunately, based on available information it is difficult to predict the possibility synthesis, color and other properties of a specific dye-intercalated LDH pigment. Additionally, the influence of chemisorption and formation of coordination complexes of anionic dye and LDH on pigment properties is not studied in detail. Synthesis of dye-intercalated LDH with consideration of the chemical interaction of dye with LDH and determination of its usability in nail polish almost has not been conducted.

3. The aim and objectives of the study

The aim of the work is to determine the properties of the nail polish pigment based on Ni-Al LDH, synthesized under conditions of intercalation or simultaneous intercalation and chemisorption. This would enable to synthesize a new type of pigment and evaluate the influence of chemisorption on the properties of this pigment.

In order to achieve the set-out aim, the following objectives were set:

- to conduct targeted selection of anionic dye for the synthesis of a new type of pigment;
- to conduct the synthesis of pigment samples based on Ni-Al LDH, intercalated or intercalated-chemisorbed with the chosen dye using coprecipitation at high supersaturation method;
- to study physicochemical and color properties of the prepared samples;
- to evaluate the possibility of using synthesized pigment samples for preparation of nail polish by preparing samples of nail polish, applying it and studying the resulting coat.

4. Materials and method for the preparation of dye-intercalated Ni-Al LDH pigment samples and study of their properties

4.1. Rationale behind the dye choice for the synthesis of dye-intercalated Ni-Al LDH pigment

The dye for the synthesis of such pigment from aqueous solution must meet several requirements. First, the dye must be water-soluble with the colored form being an anion. Second, the dye must have a chemical affinity toward nickel cation, in particular, the complex formation with nickel cation is desirable. In this case, not only the intercalation of anionic dye in the LDH structure, but also chemisorption of the dye on the LDH surface is possible.

4.2. Synthesis method for the preparation of dye-intercalated Ni-Al LDH pigment

For the synthesis of dye-intercalated Ni-Al LDH samples, the coprecipitation at high supersaturation was used. The synthesis procedure is based on the method for preparation of Ni-Al-CO₃²⁻, described in literature [33]. A solution of nickel and aluminum nitrates (molar ratio of Ni²⁺:Al³⁺=4:1) was slowly introduced at constant stirring to a solution containing NaOH (120 % of the stoichiometric amount necessary to precipitate LDH) and anionic dye. The feeding rate of the metal salt solution was 0.1 ml/s, with a synthesis temperature of 60 °C. After the metal salt solution was added, the obtained pigment suspension was stirred at a synthesis temperature for 30 min. After that, the obtained samples were filtered, dried, ground, sifted through a nickel mesh (70 μm), washed with distilled water from soluble salts and dried again.

In order to evaluate the possible influence of chemisorption, two pigment samples were prepared:

1) The amount of anionic dye was calculated based on the excessive positive charge of LDH according to the formula:

$$v_{\text{dye}} = v_{\text{Ni}^{2+}} \times (z_{\text{Al}^{3+}} - z_{\text{Ni}^{2+}}) / z_{\text{dye}} = v_{\text{Ni}^{2+}} \times (3 - 2) / z_{\text{dye}} = v_{\text{Ni}^{2+}} / z_{\text{dye}}$$

where v_{dye} is the number of dye moles; $v_{\text{Ni}^{2+}}$ is the number of nickel cations moles; $z_{\text{Al}^{3+}} = +3$ is the charge of aluminum cation; $z_{\text{Ni}^{2+}} = +2$ is the charge of nickel cation; z_{dye} is the charge of dye anion. Sample label – Intercalated.

2) The amount of anionic dye was calculated based on the number of nickel cations in LDH, according to the composition of Ni²⁺ with dye. Sample label – Intercalated+Chemisorb.

4.3. Method for the preparation of decorative nail polish with synthesized pigment samples

In order to evaluate the applicability of synthesized pigments for production of nail polish, the decorative nail polish samples were prepared. The samples were prepared by grinding of dry pigment, followed by grinding with the colorless commercial base, with the gradual addition of the remaining base.

4.4. Characterization of pigment and nail polish samples

Characterization of synthesized pigment samples.

Phase composition of the samples was studied by means of X-ray diffraction analysis (XRD) using DRON-3 diffractometer (USSR) (Cu-Kα radiation, scan range 10–90° 2θ, scan rate 0.1°/s).

Color parameters of the pigments (x , y , chromaticity values) were recorded using color comparator CC-3. The values of dominating wavelength (λ) and color purity (P) were determined by finding the crossing point of the curve passing through the point of light source A and the point with measured chromaticity coordinates x and y with lines corresponding to spectral tones and color purity on the XYZ chromaticity diagram.

Characterization of nail polish samples with synthesized pigments.

The prepared nail polish samples were studied organoleptically by the parameters of nail polish homogeneity and stability (no layering) for 7 days.

Color parameters of the dried nail polish were studied using color comparator CC-3. For characterization, a thin uniform layer of nail polish samples was applied in-between two glass covers and dried. Values of dominating wavelength and color purity of nail polish samples were determined using the previously described method.

The covering ability of the pigment was evaluated visually. For this purpose, the nail polish samples with different pigment contents were applied as a uniform layer and the coat opacity was evaluated by visual observation by putting on a white sheet of paper with printed text. In order to evaluate the covering ability, nail polish samples with pigment contents of 45, 30 and 15 % (wt.) were prepared.

5. Results of synthesized pigment and nail polish samples characterization

Selection of anionic dye. Based on the formulated requirements, it was proposed to use Murexide (Ammonium 2,6-dioxo-5-[(2,4,6-trioxo-5-hexahydropyrimidinylidene)amino]-3H-pyrimidin-4-olate). Thus, the colored form is purpurate anion. Additionally, Murexide is used as a metal indicator for trilonometric quantity analysis, including determination of nickel cation. Murexide and nickel form a weak yellow-colored complex. The charge of the dye anion is -1 .

XRD analysis of synthesized pigments. The Intercalated sample (Fig. 1, *a*) is single-phase – Ni-Al LDH with the crystal lattice of α -Ni(OH)₂. The sample crystallinity is not high. The samples Intercalated+Chemisorb (Fig. 1, *b*) has even lower crystallinity, which renders the determination of phase composition difficult.

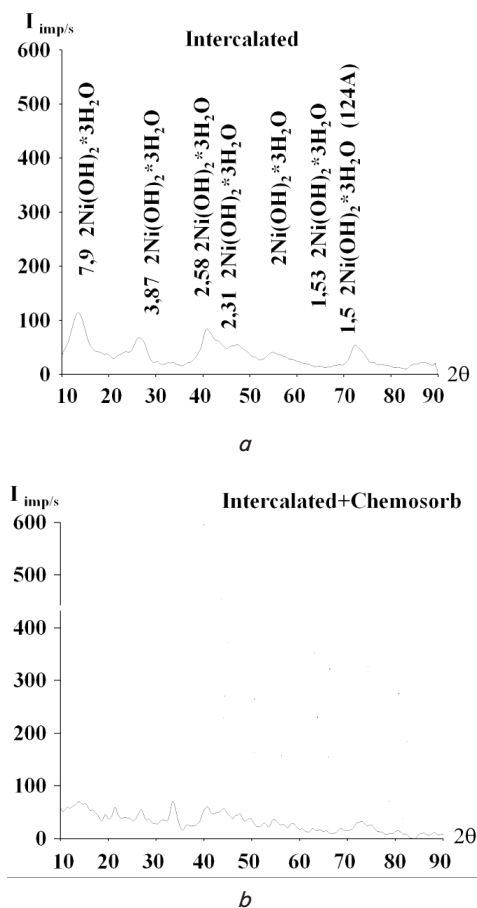


Fig. 1. XRD patterns of Murexide-intercalated Ni-Al LDH pigment samples: *a* – Intercalated; *b* – Intercalated+Chemosorb

Organoleptic parameters of synthesized samples and prepared nail polish samples. Fig. 2 shows digital images of synthesized pigment samples. It should be mentioned that the sample Intercalated has a green color and the sample Intercalated+Chemosorb – light-yellow.

Organoleptic parameters of pigments. The sample Intercalated is green, weakly susceptible to grinding, the ground powder has a coarse structure and is composed of shiny hard particles. The sample Intercalated+Chemosorb is light-yellow, very susceptible to grinding, the ground powder has a soft, powder-like structure.

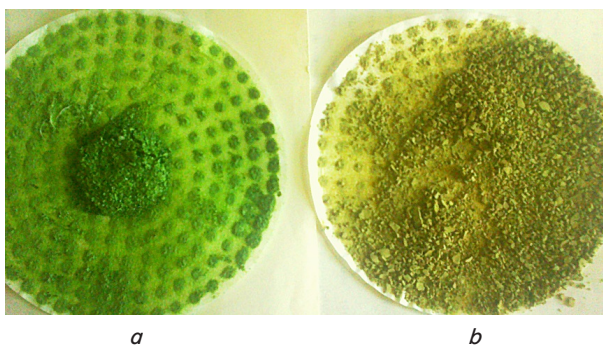


Fig. 2. Digital images of Murexide-intercalated Ni-Al LDH pigment: *a* – Intercalated; *b* – Intercalated+Chemosorb

Organoleptic parameters of nail polish samples prepared with synthesized pigments. Initially, nail polish samples with

a pigment content of 45 % wt. were prepared. Nail polish with the pigment Intercalated showed poor pigment dispersion, murkiness and low stability – after 24 hours the nail polish sample had layered with partial pigment precipitation. The samples with the pigment Intercalated turned out to be practically unusable as decorative nail polish, so further studies of covering ability and color parameters of this nail polish sample were discontinued. During the preparation of nail polish with the pigment Intercalated+Chemosorb, it had been discovered that the pigment Intercalated+Chemosorb had good dispersibility. The prepared nail polish sample has saturated color and high stability: during 14 days no layering of nail polish or pigment precipitation was not observed.

Covering ability of nail polish samples prepared with synthesized pigments. Covering ability was only evaluated for nail polish with the Intercalated+Chemosorb pigment by preparing samples with a pigment content of 45 %, 30 % and 15 % (wt.). Upon one-time application and drying, all samples produced a high-quality, opaque layer of nail polish with saturated color. This indicates high covering ability of nail polish with the Intercalated+Chemosorb pigment.

Color parameters of prepared pigments and nail polish prepared with them. Coordinates of color, chromaticity and dominant wavelength of the Intercalated and Intercalated+Chemosorb pigment samples, and the nail polish sample with 45 % (wt.) of the pigment Intercalated+Chemosorb are listed in Table 1. The results reveal that the sample Intercalated is a pigment of the green color spectrum and the Intercalated+Chemosorb – a pigment of the yellow color spectrum.

Fig. 3 shows the color purity of samples of Intercalated and Intercalated+Chemosorb pigments, and also of nail polish samples with 45 % (wt.) content of the pigment Intercalated+Chemosorb.

Table 1

Color parameters of pigments and nail polish samples prepared with synthesized pigments

Sample	Color coordinates			Chromaticity coordinates		<i>l</i> , nm
	<i>X</i>	<i>Y</i>	<i>Z</i>	<i>x</i>	<i>Y</i>	
Pigment Intercalated	48.27	48.47	13.95	0.4360	0.4378	555
Pigment Intercalated+Chemosorb	61.80	56.31	15.37	0.4629	0.4218	583
Nail polish with pigment Intercalated+Chemosorb	31.49	28.91	6.20	0.4728	0.4340	582

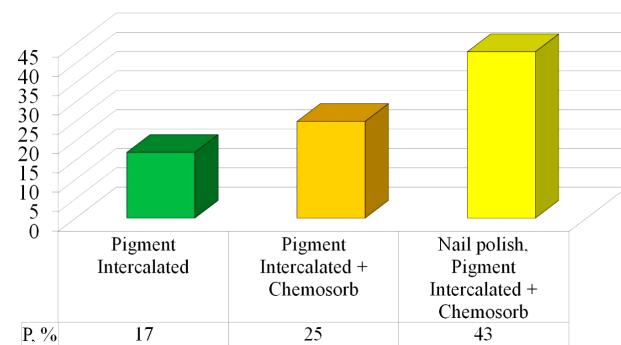


Fig. 3. Color purity of pigment igments, %

The high color purity of the pigment Intercalated+Chemosorb, and, especially, the sample of nail polish with the pigment Intercalated+Chemosorb should be noted.

6. Discussion of characterization results of Murexide-intercalated Ni-Al LDH pigments and nail polish

For the synthesis of dye-intercalated Ni-Al LDH, the Murexide (ammonium purpurate), which is capable of forming coordination bonds with nickel cations was chosen. Because of that, when a large amount of Murexide is present, it would be chemisorbed on the surface of forming Ni-Al LDH particles and would prevent the aggregation and growth of particles. Accordingly, the following discussion will be conducted taking into account this effect.

Phase composition and crystallinity of synthesized pigments. The XRD pattern presented in Fig. 1, *a* clearly shows that the sample Intercalated contains only a single phase with the crystal lattice of α -Ni(OH)₂, which is characteristic for Ni-Al-LDH. The absence of reflection of other phases proves that the sample Intercalated is murexide-intercalated Ni-Al LDH. The XRD pattern (Fig. 1, *b*) indicates that Intercalated+Chemosorb is X-ray amorphous. This is likely because during the formation, the nickel ions are bound into a complex with murexide. Additionally, the purpurate ion is adsorbed on primary particles and hinders their growth and aggregation. Thus, this shows a significant influence of chemisorption and, possibly, complex formation on crystallinity of the dye-intercalated Ni-Al LDH pigment.

Organoleptic and color properties of synthesized pigments and nail polish samples with them. Upon the analysis of pigment properties, it should be clarified that synthesis and treatment conditions of pigments were unfavorable for pigment samples, for which only Murexide intercalation (pigment Intercalated) was assumed. Low aluminum content in relation to nickel (molar ratio Ni²⁺:Al³⁺=4:1) results in low excessive positive charge leading to the low amount of intercalated murexide. Therefore, the color of the pigment Intercalated doesn't differ much from that of pure Ni-Al LDH. It should also be mentioned that in the study, pigment samples were dried at 25 °C. At such temperature, the water evaporation rate doesn't exceed the diffusion rate within the solid particle of the sample and doesn't cause the pigment cake pressed during vacuum filtering to crack and fall apart. As a result, the pigment sample Intercalated consisted of glass-like, poorly grindable particles. After grinding, the powder had a coarse consistency, so the large-sized particles were probably predominant. During the preparation of the nail polish sample, the pigment Intercalated had poor dispersibility, and the prepared nail polish had low stability and layered within 24 hours. This also indicates; that even after grinding the pigment powder had large particles with low specific surface area. At the same time, the pigment Intercalated+Chemosorb, prepared under conditions of possible intercalation and chemisorption of murexide and dried at the same temperature, was easy to grind with the formation of fine powder. During the preparation of nail polish, the

ground pigment Intercalated+Chemosorb was easily dispersed with the formation of highly stable nail polish. This indicated that during the synthesis, the murexide was partially chemisorbed onto forming particles, which prevented aggregation during synthesis, caking during vacuum filtering and drying at low temperature. As a result, the pigment powder was easily separated into small particles with high specific surface area. The chemisorption is also supported by the color of the pigment Intercalated+Chemosorb – light-yellow (dominant wavelength 582 nm). This color corresponds to that of murexide complex with Ni²⁺. High color purity values should also be noted: for the powder like pigment Intercalated+Chemosorb 25 %, nail polish with the pigment Intercalated+Chemosorb 3 %. This indicates a high quality of this pigment and the nail polish with it.

7. Conclusions

1. It was proposed to use murexide (Ammonium 2,6-dioxo-5-[(2,4,6-trioxo-5-hexahydropyrimidinylidene)amino]-3H-pyrimidin-4-olate) as an anionic dye that is capable of forming a complex with nickel cations for the synthesis of dye-intercalated Ni-Al LDH. A direct synthesis of two types of pigments had been conducted: intercalated (with the amount of murexide required for intercalation into LDH) and intercalated-chemisorbed (with the murexide amount for Ni²⁺). Structural, organoleptic and color properties of pigment samples were studied. It was discovered that the intercalated pigment is single-phase Ni-Al LDH, and intercalated-chemisorbed is X-ray amorphous. The analysis of organoleptic and color properties of synthesized pigments had revealed that the intercalated-chemisorbed pigment even in suboptimal conditions is easily ground, producing a fine powder, has a yellow color (dominant wavelength 583 nm) and color purity of 25 %. The intercalated pigment prepared under the same conditions was poorly grindable, producing a coarse powder and had a green color (dominant wavelength 555 nm) that didn't differ significantly from pure Ni-Al LDH.

2. Using intercalated and intercalated-chemisorbed pigments, the nail polish samples had been prepared. It had been demonstrated; that during the preparation of nail polish, the intercalated-chemisorbed pigment is easily dispersed and produces nail polish with saturated color and high stability. High covering ability of the intercalated-chemisorbed pigment, which produces high-quality, uniform coat at the pigment content in the nail polish of 45 %, 30 % and 15 % (wt.) was demonstrated qualitatively. Color properties of the nail polish were determined: dominant wavelength 582 nm, color purity 43 %.

3. The positive influence of chemisorption on the properties of dye-intercalated pigments had been demonstrated. It was discovered, that due to sorption during the synthesis, the chemisorbed-intercalated pigment is fine, and is easily dispersed during the preparation of nail polish and is characterized by high covering ability. For the synthesis of such pigments, it is recommended to choose anionic dyes that can form coordination bonds with LDH cations.

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