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X-RAY DIFFRACTION AND THERMAL STUDIES ON SOME FOOD AND COSMETIC BENTONITE CLAYS

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Due to the peculiarities of the layered structure and cationic composition of the interlayer space of the smectite (montmorillonite) minerals present in bentonite clays, it is possible to use such clays in the food industry, medicine, pharmaceuticals, and cosmetics. In order to line up bentonite clays with the high content of smectite group mineral for the development of new functional fillers of hygienic cosmetics, a study of the phase composition of a number of bentonite clays of Ukrainian and foreign origin has been carried out.Using powder diffraction (CuK$_\alpha$ radiation) and thermal analysis (a derivatograph Q-1500D) methods, the phase composition of commercial bentonite clays for food and cosmetic purposes has been analyzed. Food clays were represented by clay of the south of Ukraine, such as bentonite, blue and green clay and Minerol. Cosmetic clays were represented by South-Ukrainian yellow and pink clay, as well as French Russoul and Indian Multani-mitti. To identify smectite group mineral, an analysis of the basal reflections of XRD patterns of the clays saturated with water and dehydrated at 400 °C was performed. The shift of the first basal reflection (001) with an interplanar distance of 1.5 nm in the initial clay samples was accompanied by an increase to 1.8–2 nm or a decrease to 0.9 nm interplanar distance in water-saturated or dehydrated clay samples, which confirmed the assignment of the clay mineral to the smectite group. Thermal analysis was carried out to determine the temperatures of thermal effects corresponding to the phase transformations and clarification of phase composition of the samples. Thus, smectite group mineral was found in all clays. Associated minerals, such as kaolinite, calcite, quartz, mica, gypsum were detected in these clays as well. It has been found that the Ukrainian blue clay and Minerol, the foreign Ghassoul and Multani-mitti contain a significant amount of smectite group mineral and can be used to modify them with various compounds to give desired properties to cosmetic compositions.

Keywords: *X-ray diffraction, thermal analysis, bentonite food and cosmetic clays, montmorillonite, phase composition, concomitant minerals*

INTRODUCTION

Bentonite clays are known and used by man since the ancient times. They were first described at the end of the 19th century and received the real name in the 20s of the 20th century with the discovery and development of large clay deposit in Fort Benton (Wyoming, USA) [1]. These clays have unique adsorption and ion-exchange properties due to the presence in them of minerals of the smectite group from the subclass of layered silicates. Montmorillonite is the most famous mineral from this group. It was extracted and described in the middle of 19th century near the town of Montmorillon (France), from which it received its name [2]. Currently, bentonite clays are used in such areas as filtration of oil, water, drilling of the wells, ion exchange, production of building materials, ceramics, textile, paper, food industries, agriculture, medicine, pharmacology, cosmetics, nutritional supplements [3–7)]. The recent interest in bentonite clays is explained by their mineral, that is natural origin, ecological purity, dispersion of particles and possibility of modifying the external and inter-package surface of montmorillonite group mineral particles with compounds of different nature [8–11].

The natural character, ecological purity and dispersion of particles of natural bentonite clays are of practical interest for the development of new nanomaterials in areas related to nutrition, health and human hygiene.

The structure and properties of clay minerals have been studied by many researchers [12–17]. Ukrainian school scientists F.D. Ovcharenko and Yu.I. Tarasevich were among them also [18, 19]. According to these data, the layered structure of clay minerals is formed by a certain alternation of layers of silicon-oxygen tetrahedra and aluminum-hydroxyl octahedra. The thickness of one layer averages 0.33 nm. Silicon atoms in tetrahedral layers can be partially replaced by aluminum atoms, and aluminum atoms in octahedral layers can be replaced by magnesium, iron and others atoms. The interacting layers form two-layer and three-layer packages. The number of layers in the package, the chemical composition and the nature of interpackage interaction determine the type of clay mineral and its adsorption and ion-exchange properties. Thus, layered minerals of the kaolinite group with the structural formula $Al_2(Si_2O_5)(OH)_4$ are formed by two-layered packages consisting of one layer of silicon-oxygen tetrahedra and one layer of aluminum-hydroxyl octahedra. Layered minerals of the muscovite group with the structural formula $KAl_2[AlSi_3O_{10}]\cdot[OH]_2$ are formed by three-layered packages consisting of two layers of silicon-oxygen tetrahedra with one layer of aluminum-hydroxyl octahedra between them. Strong interpackage interaction is characteristic of these minerals. In the minerals of the smectite group (montmorillonite) with the structural formula $(Na,Ca)_{033}(Al,Mg)_2(Si_4O_{10})\ (OH)_2\cdot nH_2O$ three-layered packages composed as in muscovite are separated by a layer of water containing metal cations. Thus, the periodicity of the motif of the layered structure in montmorillonite is larger than that of muscovite (~1 nm) and is ~1.5 nm. When mineral is wetted with water, this period increases to 2 nm or more. Therefore, the adsorption of water and ion exchange occurs not only on the surface of the particles, but also within the crystalline structure of the mineral, in contrast to the minerals of kaolinite and muscovite groups.

The X-ray diffraction [20, 21] and thermal analysis [22, 23] are the main methods for identifying the phase composition of clays. The powder diffraction method is highly effective in determining the clay mineral group. Mainly clay minerals crystallize in monoclinic syngony, for which a large number of diffraction reflections are characteristic. The weak crystallinity of clay minerals leads to broadening, superposition, and smearing of the diffraction peaks. However, the parallel arrangement of the layers in the direction of the crystallographic axis ***c*** creates a series of intense basal reflections with indices (00*l*), that is (001), (002), (003), *etc*. The difference in the angular position of the family of reflections (00*l*) for basic clay minerals is clearly visible from Fig. 1 with the image of diffractograms of these minerals, recorded by the authors.

The interplanar distance of the first basal reflection (001) practically corresponds to the thicknesses of the initial package of the layered structure. For kaolinite, muscovite and montmorillonite it is 0.714, 0.99 and 1.5 nm, respectively.

At a weak intensity of the first basal reflection, various techniques are applied to identify the minerals of the montmorillonite group. One of them is the study of diffraction of clay samples swollen in water or other organic liquids, such as glycerol, diethylene glycol, in the angular range of the first basal reflection. For minerals of the montmorillonite group, this reflection shifts to smaller angles, and the interplanar distance increases to 1.8–2.2 nm [24]. Another method is the study of the diffraction by clay samples after the complete removal of water from the inter-package space at a temperature of ~400 °C. The position of the first basal reflection shifts to a large angles, approaches to the position of the first basal reflection of the minerals of the muscovite group and decreases in intensity. Each clay mineral has certain thermal properties, such as dehydration, dehydroxylation, chemical destruction temperatures and corresponding thermal effects. The heating of minerals to such temperatures leads to characteristic phase changes as well [25].

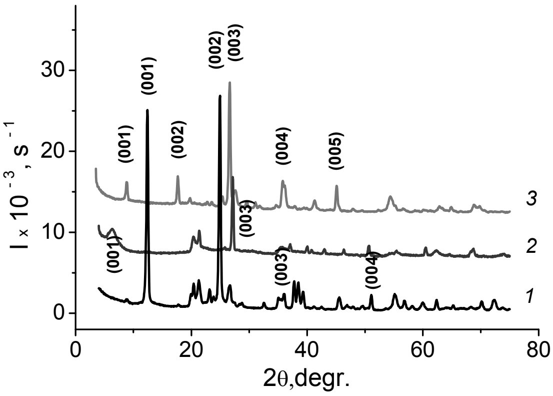

Fig. 1. XRD patterns of kaolinite (*1*), montmorillonite (*2*), muscovite (*3*)

Ukraine is rich in deposits of bentonite clays, formed mainly of sedimentary rocks. The main regions of their occurrence are western Ukraine, Transcarpathia, Dnieper area, Donbass, Southern Ukraine. Bentonite clays are multi-mineral and heterogeneous materials depending on the deposit and geological conditions of their formation. Different batches of clays from the same deposit can have different composition as well [27]. Western Ukraine, Dnieper, Donbass clays are the most studied. Our choice was on the bentonite clays from Southern Ukraine. In order to optimize the selection of certain types on bentonite clays for the subsequent development of new functional fillers for hygienic cosmetics, a study on the phase composition of a series of commercial bentonite clays of Ukrainian and foreign origin, denoted as food and cosmetic and sold through a network of cosmetics ingredient stores, has been carried out. Food and cosmetic clays are clays that have obtained sanitary-epidemiological conclusions or certificates of conformity, or manufacturer's specifications (MS) for their use as food additives and cosmetics by Ukrainian certification agencies, in accordance with the law [27, 28].

EXPERIMENTAL

In this work six clays from deposits of the south of Ukraine, classified as food and cosmetic, such as bentonite, blue, green, Minerol (trade mark for bentonite clay product MS 21540172-1-2001), yellow, pink, and two foreign cosmetic clays, such as Multani Mitti of Indian origin and Ghassoul of French (Moroccan) origin, were taken as objects of the study. Two geological samples such as beidellite (Khmelnitsky) and montmorillonite (Cherkasy) with the structure of smectite group mineral were used for comparison. The clays were divided into three groups according to their assignment: geological samples, food clays and cosmetic clays.

X-ray diffractograms were recordered using a diffractometer DRON-4-07 (Burevestnik, Russia) in filtered copper radiation ($\lambda = 1.5418$ Å) with Bragg-Brentano geometry in the angular interval 2θ of 1–80 degrees. Identification of crystalline phases in the samples was performed using the X-ray database of ICDD PDF-2. Semi-quantitative phase analysis was executed using the program of phase identification from powder diffraction Match! V.1.9. The measurement error of the intensity of diffraction reflections ranged from 1 to 3 % according to the formula $1/\sqrt{N}$, where N – reflection intensity.

Thermal studies were carried out on a derivatograph Q-1500D (Firm MOM, Hungary) with linear heating rate of 10 deg/min in the temperature range from 20 to 1000 °C. Heating of the samples at intermediate temperatures was carried out in a muffle furnace.

RESULTS AND DISCUSSION

Our results on the application described in paper [22] several techniques for treating the clay materials in order to identify the minerals of the montmorillonite group are presented for geological samples consisting mainly of this type of mineral.

XRD patterns of geological samples beidellite and montmorillonite are shown in Fig. 2. The data are similar to those given in [29, 30] for clays of Khmelnitsky and Cherkassky deposits. The diffraction peaks related to the mineral of the montmorillonite group are observed on them excluding the peaks of quartz and insignificant amount of impurity phases, being in the geological sample of montmorillonite. The first basal reflection (001) of these samples corresponds to an interplanar distance d or parameter c of montmorillonite crystal lattice of 1.5 nm. When the samples are wetted with water, the reflection (001) shifts towards smaller angles so that its interplanar distance d increases to 2.1 nm. At the same time, heating the samples to 400 °C, based on thermal analysis data, results in the removal of water from the inter-package space in the structure of montmorillonite and consequently shift of the reflection (001) towards larger angles and decrease in its interplanar distance d to 1.0 nm, as it is illustrated in Fig. 3. The interplanar distance d is calculated from Wulff-Bragg's formula $2d \sin\theta = \lambda$, where θ – half diffraction angle, λ – radiation wavelength.

Thus, the swelling nature of the crystal structure and the presence of a water-containing inter-package layers in minerals of these samples, as the main criteria, confirm their belonging to the minerals of the montmorillonite group.

According to thermal data, the weight loss (TG), differential weight loss (DTG) and differential thermal analysis (DTA) curves have a similar character for both samples. As example in Fig. 4, the derivatogram of montmorillonite sample is given.

As seen, the destruction of the layered structure of minerals occurs, in general, in two stages. At the beginning, at the temperatures of

100–180 °C, the adsorbed and interlayer water removes from the sample. Above 500 °C, dehydroxylation of aluminum-hydroxyl octahedral layers occurs. For beidellite, dehydration and dehydroxylation temperatures are higher than those for montmorillonite. So, they are 140–200 °C and 670 °C, respectively. Apparently, this is due to a stronger interaction of the layers in the beidellite, in which the partial substitution of silicon in the tetrahedral layers by aluminum takes place. This is consistent with the data given in the literature [23, 24].

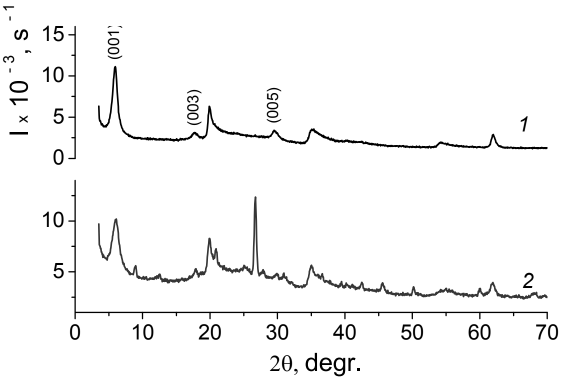

Fig. 2. XRD patterns of beidellite (*1*), montmorillonite (*2*)

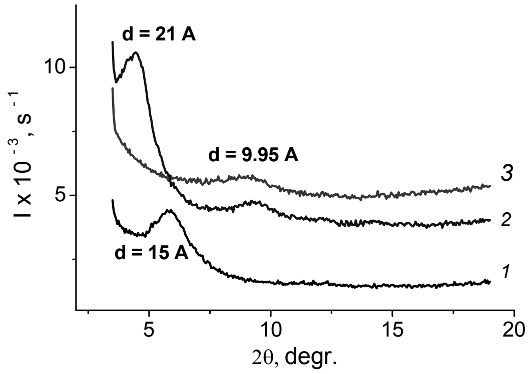

Fig. 3. Small-angle part of diffractogram of montmorillonite: initial (*1*), impregnated with water (*2*), heated to 400 °C (*3*)

X-ray diffraction patterns of commercial products: bentonite, blue, green, Minerol, designated as food clays are presented in Fig. 5.

Diffraction peaks corresponding to the weakly crystalline structure of the mineral of the montmorillonite group are observed on all diffractograms. The most intense peaks of this phase are observed for the Minerol sample and blue clay. High-crystalline quartz is present in all samples as well. For the samples, except for Minerol, calcium carbonate (calcite) is found with a different content. Kaolinite and mica are present in small amounts, about a few weight percent. In Table 1, crystalline phases and the relative content of calcite and quartz without taking into account the slightly crystalline montmorillonite and low content of kaolinite and mica are given.

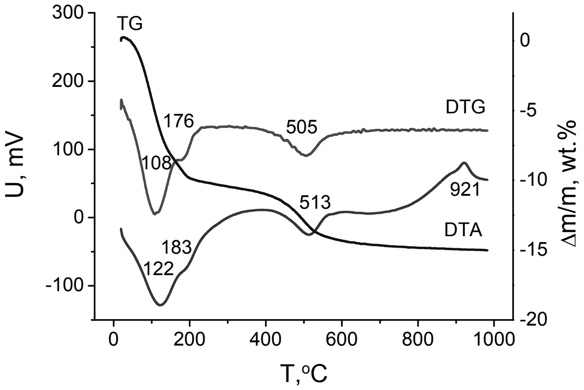

Fig. 4. Derivatogram of montmorillonite sample

The samples are listed on the decrease of calcite content and increase of quantity in montmorillonite also. Thus, these food bentonite clays have a different content of montmorillonite, calcite and quartz.

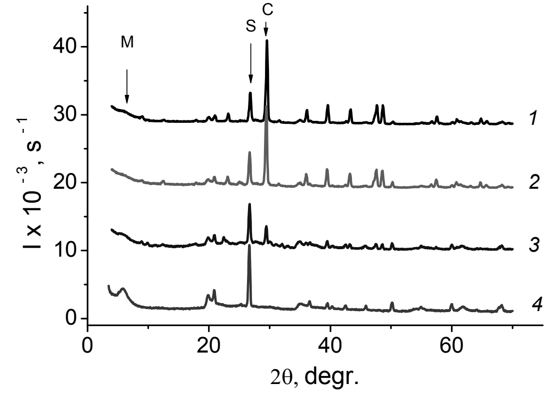

Fig. 5. XRD patterns of food clays: bentonite (*1*), green (*2*), blue (*3*), Minerol (*4*). Signs: M – montmorillonite, S – SiO_2 quartz, C – $CaCO_3$ calcite

Experimental data of thermal studies of two clays with a significant difference in the content of montmorillonite and calcite (bentonite and blue clay) are presented on Fig. 6 and 7.

Table 1. Phase composition of food clays

Sample No	Clay	Phase composition	Relative content of calcite and α-quartz, wt.%
1	Bentonite	Calcite α-quartz Montmorillonite	74 ± 2 26 ± 2
2	Green	Calcite α-quartz Montmorillonite	72 ± 2 28 ± 2
3	Blue	Calcite α-quartz Montmorillonite	34 ± 2 66 ± 2
4	Minerol	α-quartz Montmorillonite	100 ± 2

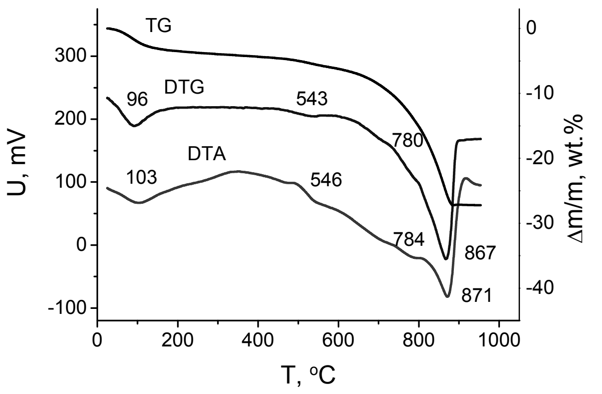

Fig. 6. Derivatogram of bentonite

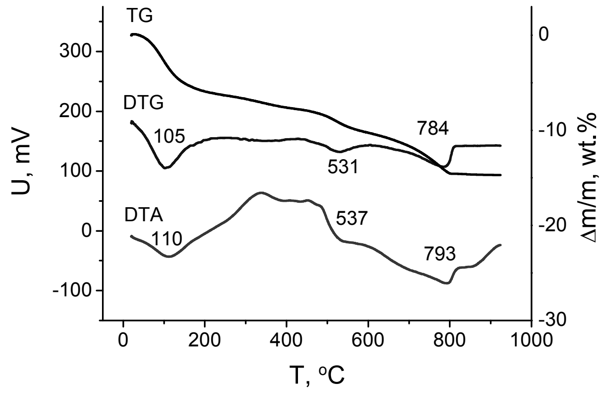

Fig. 7. Derivatogram of blue clay

Such thermal phenomena as mass loss and endothermic effects in the temperature range of 780–870 °C indicate the decomposition of calcite. These effects are expressed more for a sample of bentonite. The presence of montmorillonite is confirmed by thermal effects in the temperature range of ~100–150 and 500 °C, which correspond to the removal of water and hydroxyls, respectively. That is the data of the two methods confirm the multi-mineral character of food bentonite clays.

X-ray diffraction data of cosmetic bentonite clays are presented on Fig. 8.

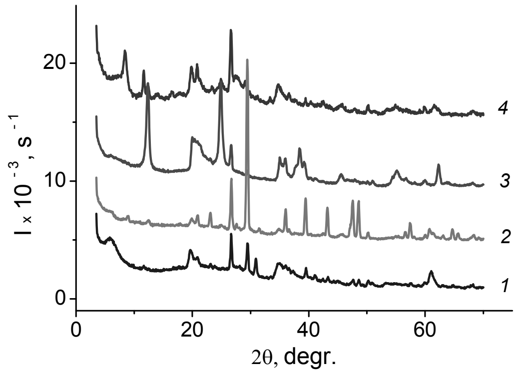

Fig. 8. XRD patterns of cosmetic clays: Ghassoul (*1*), Yellow bentonite (*2*), Pink montmorillonite (*3*), Multani-mitti (*4*)

As seen, cosmetic clays are also multiphase, as food clays. Montmorillonite minerals are weakly crystalline also. The greatest amount of montmorillonite mineral is found in the clays Ghassoul and Multani mitti. The phase composition of cosmetic clays is collected in Table 2. So, clays with N 1–3 consist of two phases, significantly different in the crystallinity. Clay Multani-mitti (N 4) contains at least four phases with different crystallinity. Therefore, quantitative phase analysis within the framework of the Match! program is not quite correct.

So, in the clays of Ukrainian origin, kaolinite and calcite accompany the montmorillonite. French clay Ghassoul contains mainly stevensite – a mineral of the montmorillonite group with a structural formula $(Ca,Na)_xMg_{3-x}(Si_4O_{10})(OH)_2$, as claimed by the manufacturer. As shown by thermal analysis data (Fig. 9), destruction of stevensite occurs stepwise in the temperature range of 630–850 °C and confirms its complex composition.

Table 2. Phase composition of cosmetic clays

Sample No	Clay	Phase composition
1	Ghassoul	Stevensite Magnesium silicate
2	Yellow bentonite	Montmorillonite Calcite
3	Pink montmorillonite	Montmorillonite Kaolinite
4	Multani-mitti	Montmorillonite Mica, Gypsum, Kaolinite

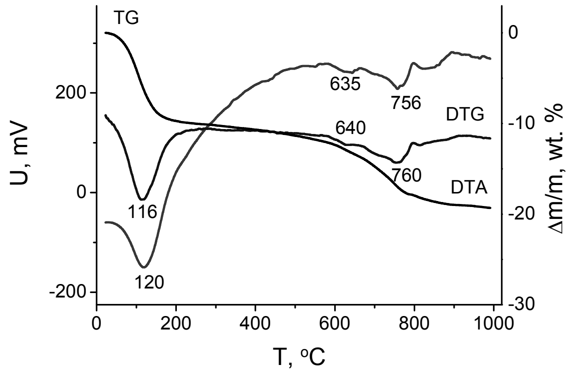

Fig. 9. Derivatogram of Ghassoul clay

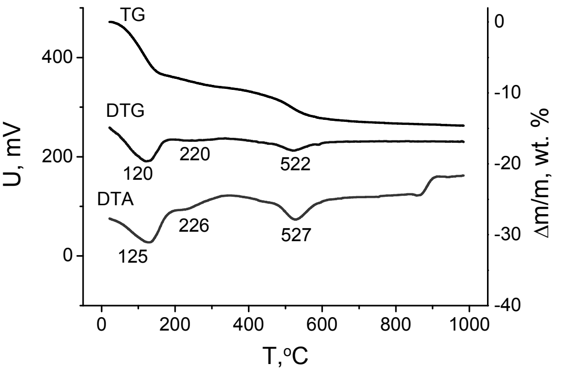

Fig. 10. Derivatogram of Multani-mitti clay

The phase composition of the Indian clay Multani-mitti is a good example of the multi-minerality of a clays. In addition to main montmorillonite mineral, it contains kaolinite, mica, gypsum, quartz. However, only the effects of decomposition of montmorillonite mineral are observed on the derivatogram of this clay (Fig. 10). It is known that the destruction of gypsum and kaolinite occurs at 180 and 500 °C, respectively, which, apparently, leads to the imposition of the thermal effects. Further, the successive heating of Multani-mitti clay to 200 and 500 °C is accompanied with the disappearance of diffraction peaks of gypsum and then kaolinite on the corresponding diffractograms.

CONCLUSION

The data on the phase composition of a number of studied food and cosmetic clays, obtained using X-ray diffraction and thermal analysis methods, allows us to optimize, in the first approximation, the choice of clays by the criterion of the highest content of the smectite group mineral in them in order to develop new functional fillers of hygienic cosmetics. So, it has been shown that the mineral of the montmorillonite group is present in all samples. Its content is greatest in the clays such as Ukrainian blue clay, Minerol, French Ghassoul clay and Indian Multani-mitti clay. At the same time, the presence and content of concomitant minerals, such as kaolinite, quartz, mica, gypsum, which can affect physical, chemical properties of cosmetic compositions and human skin, should be taken into account.

Рентгенодифракційне та термічне дослідження деяких харчових та косметичних бентонітових глин

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Завдяки особливостям шаруватої структури і катіонного складу міжшарового простору мінералів групи смектиту (монтмориллоніту), присутніх в бентонітових глинах, можливе застосування таких глин в харчовій промисловості, медицині, фармацевтиці, косметиці. З метою відбору бентонітових глин з високим вмістом мінералу з групи смектиту для розробки нових функціональних наповнювачів гігієнічної косметики вивчено фазовий склад ряду бентонітових глин українського та іноземного походження. З використанням методів порошкової дифракції (CuK_α випромінювання) та термічного аналізу (дериватограф Q-1500D) проаналізовано фазовий склад комерційних бентонітових глин харчового і косметичного призначення. Харчові глини були представлені глинами півдня України - бентонітом, блакитною і зеленою глиною та Мінеролом. Косметичні - південно-українськими жовтою і рожевою глиною, а також французькою Рассул та індійською Мултані-мітті. Для ідентифікації мінералу групи смектитів проведено аналіз базальних рефлексів рентгенограм глин, насичених водою і зневоднених при 400 °С. Зсув першого базального рефлексу (001) з міжплощинною відстанню 1.5 нм в вихідних зразках глин відповідав збільшенню до 1.8–2 нм або зменшенню до 0.9 нм його міжплощинної відстані в насичених водою або зневоднених зразках глин, що підтвердило віднесення глинистого мінералу до групи смектитів. Термічний аналіз використано для визначення температур теплових ефектів, пов'язаних з фазовими перетвореннями та уточнення фазового складу зразків. Таким чином, у всіх глинах було виявлено мінерал з групи смектитів. Виявлені також супутні мінерали, такі як каолініт, кальцит, кварц, слюда, гіпс. Було встановлено, що українські блакитна глина і Мінерол, іноземні глини Рассул і Мултані-мітті містять значну кількість мінералу з групи смектитів і можуть бути використані для модифікування різними сполуками з метою надання косметичним композиціям бажаних властивостей.

Ключові слова: *рентгенівська дифракція, термічний аналіз, бентонітові харчові та косметичні глини, монтмориллоніт, фазовий склад, супутні мінерали*

Рентгенодифракционное и термическое исследование некоторых пищевых и косметических бентонитовых глин

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Благодаря особенностям слоистой структуры и катионного состава межслоевого пространства минералов группы смектита (монтмориллонита), присутствующих в бентонитовых глинах, возможно применение таких глин в пищевой промышленности, медицине, фармацевтике, косметике. С целью отбора бентонитовых глин с высоким содержанием минерала из группы смектитов для разработки новых функциональных наполнителей гигиенической косметики изучен фазовый состав ряда бентонитовых глин украинского и зарубежного происхождения. С использованием методов порошковой дифракции (CuK_α излучение) и термического анализа (дериватограф Q-1500D) проанализирован фазовый состав коммерческих бентонитовых глин пищевого и косметического назначения. Пищевые глины были представлены глинами юга Украины - бентонитом, голубой и зеленой глиной и Минеролом. Косметические – южно-украинскими желтой и розовой глиной, а также французской Рассул и индийской Мултани-митти. Для идентификации минерала смектитовой группы проведен анализ базальных отражений рентгенограмм глин, насыщенных водой и обезвоженных при 400 °С. Сдвиг первого базального отражения (001) с межплоскостным расстоянием 1.5 нм в исходных образцах глин соответствовал увеличению до 1.8–2 нм *или уменьшению до 0.9 нм его межплоскостного расстояния в насыщенных водой или обезвоженных образцах глин, что подтвердило отнесение глинистого минерала к группе смектита. Термический анализ был использован для определения температур тепловых эффектов, соответствующих фазовым превращениям и уточнения фазового состава образцов. Таким образом, во всех глинах был обнаружен минерал из группы смектитов. Выявлены также сопутствующие минералы, такие как каолинит, кальцит, кварц, слюда, гипс. Было установлено, что украинские голубая глина и Минерол, зарубежные глины Рассул и Мултани-митти содержат значительное количество минерала из группы смектитов и могут быть использованы для модифицирования различными соединениями с целью придания косметическим композициям желаемых свойств.*

Ключевые слова: *рентгеновская дифракция, термический анализ, бентонитовые пищевые и косметические глины, монтмориллонит, фазовый состав, сопутствующие минералы*

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