CHEMISTRY & CHEMICAL TECHNOLOGY

Vol. 7, No. 2, 2013 Chemical Technology

***Valentyn Sviderskyi*[1] *and Taras Karavayev*[2]**

# COMPOSITION AND PHYSICO-CHEMICAL PROPERTIES OF UKRAINIAN KAOLINS SURFACE

*[1]National Technical University of Ukraine "Kyiv Polytechnic Institute"*
*37, Peremogy Ave., 03056 Kyiv, Ukraine*
*[2]Kyiv National University of Trade and Economics*
*19, Kioto str., 02156 Kyiv, Ukraine; karavayev@meta.ua*

*Received: October 05, 2012 / Revised: November 17, 2012 / Accepted: January 25, 2013*

**Abstract.** The results of comprehensive researches of the physico-chemical properties of kaolins as extenders of water-dispersion paints are shown in the article. The results of RF-analysis, energy state estimation of researched kaolins surface with different content of nonclay components and index ordering of the crystal structure are analyzed. Quantitative IR-analysis of basic functional groups of kaolins surface has been conducted to estimate their reactivity.

**Keywords:** water-dispersion paint, extender, kaolin, RF-analysis, IR-analysis, properties of surface.

## 1. Introduction

Due to permanent increase of harsh ecological requirements to the paint materials in the world, which are introduced by the respective legislative acts [1, 2], the content of organic solvents in paint materials shall be reduced 2–13 times (depending on their kind and application domain), which will compel the producers to pass to production of water-based compositions.

Today, environmentally friendly water-dispersion paints rightfully occupy a leading position on the market in the repair and finishing works in the industrialized countries. In Ukraine we have also a tendency to increase production and use of water-dispersion paints, however their part in the overall structure remains low [3, 4].

The extenders have significant influence on the quality of water-dispersion paints and coatings and can be active components of water-dispersion paints and carry out a number of positive functions, the main of which are the impact on the distribution of pigment particles, structure and rheological properties of paints, increase of strength, hardness, and weather resistance of coatings, *etc*. [5]. The main mineral extenders whose reserves are sufficient in Ukraine are carbonates (mainly natural precipitate chalk) and primary kaolin. Despite this, nowadays the majority of extenders are imported to Ukraine from abroad [6].

However, comprehensive researches in this direction have not been conducted in Ukraine till now. To solve this problem, we undertook the research of the properties of carbonates and kaolins of Ukrainian deposits, the results of which are presented in the publications [7-11].

Kaolins are used in the paint industry as extenders for specific functions in different compositions and coatings, including water-dispersion paints. Composition of kaolin by major chemical elements and their surface properties are important in shaping the interaction with the polymer film forming in the water-dispersion paints, and thereby in providing the quality of paints and coatings.

### 1.1. Formulation of the Problem and its Relationship with the Most Important Scientific and Practical Tasks

Kaolin is a mineral rock that is fully or partially composed of kaolinite. Minerals of kaolinite are characterized by such theoretical chemical composition (%): $SiO_2$ – 46.5; $Al_2O_3$ – 39.6; $H_2O^+$ – 13.9, which is expressed by the formula $Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$ with the theoretical ratio of 1: 2: 2 [12].

Kaolins are widely used in industry in the manufacture of various products. Kaolins are used as extenders in the manufacture of paints, plastics, rubber, and other products. The composition of the basic chemical elements, the presence and activity of functional groups of kaolins when used in water-dispersion paints are equally important. These properties allow predict their adsorption ability and interaction with polymers in aqueous dispersions to obtain optimal composition.

Kaolins of various deposits and the degrees of enrichment have different chemical composition, content nonclay components, index ordering of the crystal structure and other characteristics. One of the most important characteristic of kaolin as mineral extender is physic-chemical properties of the surface. This causes different effects of kaolin as extender on the properties of water-dispersion paints and coatings based on them.

A lot of works are devoted to the study of chemical and mineralogical composition of kaolin. However, almost no work has been conducted, which would present the results of the elemental composition and integrated analysis of physical and chemical properties of the surface, as well as the presence and activity of the functional groups of Ukrainian kaolin deposits as mineral extenders of water-dispersion paints. In view of the above mentioned, the researches conducted by the authors and their results presented in the article are very topical.

The aim of the article is to determine the composition of Ukrainian deposit kaolins by major chemical elements and presence on their surface of the structural or functional groups of atoms and their relative content as well as to determine the prospects of their use in aqueous polymer systems.

## 2. Experimental

The kaolins of the following major industrial deposits, brands and manufacturers were selected as the objects of the study: Glukhovetske deposit, KC-1 and KCCK brands (company manufacturer JSC "Glukhivtsi kaolin plant", Glukhivtsi, Vinnytsia region); Prosianivske deposit, KC-1 brand (LLC "Prosko Resources", Prosiana, Dnipropetrovsk region); Turbivske deposit, raw kaolin brand (Turbiv, Vinnytsia region); Katerynivske deposit, alkaline kaolin E2013 brand (LLC "UkrRosKaolin", Katerynivka, Donetsk region); Oboznivske deposit, secondary kaolin KO-1 brand (Public JSC "Kirovogradske Mine", Katerynivka, Kirovograd region). Prosianivskyi and Glukhovetskyi kaolins KC-1 brand is enriched, the others are unenriched.

Determination of kaolin composition by major chemical elements has been carried out by roentgen fluorescent analysis (RFA). This method relates to spectroscopic studies of matter in order to obtain its elemental composition. RFA is a modern method that allows to obtain the data on material composition for basic chemical elements.

RFA method is widely used in industry and research laboratories because of its simplicity, the possibility of rapid analysis, accuracy, and absence of complex sample preparation. The research was carried out on elemental composition analyzer Expert 02 L in helium atmosphere, which allows getting more accurate data and exploring content of light elements.

An infrared (IR) spectroscopy method was used to determine the presence and activity in the kaolin separate structural or functional groups of atoms and their relative content. IR method is based on the radiation absorption of the substance in the infrared region of the spectrum associated with the excitation of valence and deformation vibrations of molecules [13, 14].

IR absorption spectra of materials were taken on IR-10 and Specord-75IR automatic spectrometers on the area of 400–4000 cm$^{-1}$. The samples were prepared by vacuum pressing of finely divided powder (1–3 micron) with spectrally pure KBr (3700 mg) under pressure of 1000 MPa.

X-ray analysis was carried out by powder method on X-ray DRON-1,5 and DRON-3 with SuK$\alpha_1$ radiation [15, 16]. Radiograms recording was performed in the range of angles 2θ that equal to 6–60$^{o}$ at speed counter 1 deg/min. The phases were identified by the values of interplanar distances using the data given in [15].

Wetting by soakage of kaolins ($B_н$) was determined by nonpolar fluid (benzol) and polar fluid (water). The method is based on the thermodynamic theory of capillary dripping. Determination was carried out on the Deriagin device [17].

Liophilic coefficient was calculated using the equation [18]:

$$\beta = B_H/B'_H, \tag{1}$$

where $B_н$ – wetting by polar liquid soakage; $B'_н$ – wetting by nonpolar liquid soakage.

The effective specific surface area was determined on the same device, using the known equation for calculations [18]. Determination of the critical surface tension of kaolin was carried out using experimental data of relation between wetting and surface tension of the liquid.

Conditional dielectric loss tangent (tg$\delta$) is an important characteristic of the extenders surface. Measurements of tg$\delta$ were conducted by direct method after previous exposure of kaolins in 45 % humidity condition using a cylindrical capacitor with nickel plate with copper screen on alternating current bridges R-5004 and R-5010 types at 1000 Hz frequency [18, 19]. The measures were recorded directly from the device scale.

## 3. Results and Discussion

### 3.1. Kaolins Chemical Elemental Composition

Research of chemical composition of Ukrainian kaolins conducted by RFA method, which results are indicated in Table 1 allows to make a conclusion that the content of aluminum, which indicates the content of its oxide and kaolinite, has minimum value in Glukhovetskyi kaolin brands KCCK and KC-1 – 28.2 and 28.4 % respectively, and maximum value in Oboznivskyi kaolin brand KC-1 – 36.3 %. The aluminum content in other kaolins is within the range of 30.6 % in Katerynivskyi kaolin to 34.7 % in Prosianivskyi.

*Table 1*

**Chemical composition (elemental) of Ukrainian kaolins by the results of RFA method**

| Name of kaolin by deposit, kaolin brand | Elemental chemical composition, mas % | | | | | |
|---|---|---|---|---|---|---|
| | Al | Si | K | Ca | Ti | Fe |
| Glukhovetskyi, KC-1 | 28.4 | 55.7 | 2.4 | 4.5 | 4.2 | 4.8 |
| Prosianivskyi, KC-1 | 34.7 | 56.0 | 1.1 | 3.2 | 2.2 | 2.9 |
| Oboznivskyi, KO-1 | 36.3 | 57.4 | 0.2 | 0.7 | 2.8 | 2.5 |
| Turbivskyi, raw kaolin | 31.7 | 61.6 | 1.0 | 0.8 | 3.1 | 1.8 |
| Glukhovetskyi, KCCK | 28.2 | 58.2 | 6.4 | 0.7 | 3.0 | 3.5 |
| Katerynivskyi, E2013 | 30.6 | 56.9 | 5.9 | 1.6 | 1.3 | 3.8 |

*Note: Na, Mg, S, P, Mn, Zn, Sn, V, Zr – dirt.

The content of solid silicium oxide is important for kaolins. The results of conducted research presented in Table 1 allow to make a conclusion that silicium content ranged from 55.7 % in kaolin Glukhovetskyi KC-1 to 61.6 % in kaolin Turbivskyi.

The ratio of alumina oxide to silicium oxide is a measure of the ordering kaolinite structure. The ideal ratio $Al_2O_3$:$SiO_2$ is 1:2 [12]. The real ratio can be determined by the ratio between the content of aluminum to the content of silicium, respectively. The calculations according to Table 1 data allow to make a conclusion that the most ordered kaolinite structure has kaolin Glukhovetskyi brands KC-1 (Al:Si ratio is 1:1.96), KCCK (ratio 1:2.06) and Turbivskyi raw kaolin (1: 1.94).

The data of kaolin chemical element composition presented in Table 1 gives an idea of the real deviation content from the theoretical content of the main components (silicium and alumina). These deviations, as well as the presence of a number of elements that are not included in the formula of kaolinite (K, Na, Ca, Fe, Mg, Ti), can be attributed to inadequate cleaning kaolin mineral contamination or isomorphic substitution of exchange complex.

## 3.2. IR Analysis of Basic Functional Groups of the Kaolins Surface

Quantitative IR analysis of basic functional groups of kaolin surface that have been selected for use as extenders in the aqueous polymer systems was conducted to assess their reactivity.

Absorption bands responsible for the fluctuation of the surface and structural hydroxyl groups associated with the silicium and aluminum atoms and water were selected for this purpose. It is well known that these functional groups and compounds together with the chemical composition and crystal structural construction determine basic physico-chemical properties of kaolin surface.

Studied bands attributing was carried out as follows, compared to the basic kaolin (Glukhovetskyi KC-1):

- bands at 3680 and band at 3640 $cm^{-1}$ relating to the internal vibrations of surface structural hydroxyl groups (*i.e.* groups that are on the kaolinit packages surface);
- maximum at 3613 $cm^{-1}$ in the kaolin spectrum related mainly with stretching vibrations of internal OH groups of kaolinit package placed in the plane common to tetrahedral and octahedral layers;
- maxima at 926 $cm^{-1}$ and at 900 $cm^{-1}$ related to structural deformation vibrations of the hydroxyl groups of kaolinite associated with octahedral $A1^{+3}$ cations;
- band at 3440 $cm^{-1}$ and band at 1605 $cm^{-1}$ related to the valence and deformation vibrations of adsorbed water.

The intensity and position assessment of IR absorption spectra bands which are characteristic of OH groups valence vibrations on the kaolinit surface packages (3680 and 3640 $cm^{-1}$), showed the presence of a certain dependence on the composition and structure of kaolin. It should be noted that these bands shift toward lower frequencies by 20–25 $cm^{-1}$ (for the classic kaolinit they are recorded at 3700 and 3665 $cm^{-1}$, respectively) as compared to base kaolin (Glukhovetskyi KC-1) (Table 2).

The absorption band offset at 3680 $cm^{-1}$ toward higher wave numbers for all other studied kaolin ranges from 20 to 33 $cm^{-1}$. The offset maximum values were recorded for kaolin with minimal content of nonclay compound. The intensity of this absorption band for the same kaolins and also for Prosianivskyi is 78–92 % compared with the base band. These figures make 60–68 % for other unenriched kaolins.

Similar patterns are observed in the change of other absorption bands intensity responsible for stretching vibrations of surface OH groups (3640 $cm^{-1}$). However, they are different in quantitative terms. This quantitative difference for kaolin Glukhovetskyi KCCK and kaolin Katerynivskyi E2013 makes from 49 to 58 %, and for all others – from 76 to 101 %. Specified bands offset makes 0 and 20–27 $cm^{-1}$, respectively.

Regarding the absorption band at 3613 $cm^{-1}$ (in kaolinit 3625 $cm^{-1}$) it should be noted that it occupies an intermediate position between the bands at 3680 and 3640 $cm^{-1}$ by the intensity and degree offset, if the laws of their change are similar to the mentioned above.

*Table 2*

**Change in position and intensity of the IR absorption bands characteristic of vibrations of OH-groups and adsorbed water in kaolins**

| Name of kaolin by deposit, kaolin brand | Characteristic absorption band, cm$^{-1}$ | | | | | | |
|---|---|---|---|---|---|---|---|
| Glukhovetskyi, KC-1 | 3680 | 3640 | 3613 | 3440 | 1605 | 926 | 900 |
| Prosianivskyi, KC-1 | 33 (78.2) | 27 (76.1) | 27 (80.0) | 13 (85.4) | 35 (63.2) | 14 (69.8 ) | 27 (74.4) |
| Oboznivskyi, KO-1 | 33 (92.0) | 20 (101.5) | 27 (98.7) | 13 (126.1) | 21 (110.5) | 14 (73.8) | 13 (75.2) |
| Turbivskyiskyi, raw kaolin | 20 (90.8) | 26 (86.6) | 13 (86.7) | 27 (100.0) | 35 (89.5) | 0 (81.7) | 13 (85.0) |
| Glukhovetskyi, KCCK | 20 (59.8) | 0 (49.2) | 7 (57.3) | 0 (78.0 ) | 35 (105.3) | 31 (69.8) | 27 (76.7) |
| Katerynivskyi, E2013 | 33 (67.8) | 0 (58.2) | 13 (66.7) | 0 (97.6) | 35 (89.5) | 27 (77.0) | 27 (82.7 ) |

Note: In parentheses the intensity of the absorption bands in % relative to 100 % for kaolin Glukhovetskyi KC-1 is indicated.

Thus, on the basis of the analysis of IR absorption bands spectra, which are characteristic of OH-groups vibrations, bound to the kaolinit surface package it can be concluded that the OH-groups number is reduced to at least 8 % in Oboznivskyi and to the maximum of 14 % in Prosianivskyi KC-1 among the kaolin with ordering index more than 0.8. In unenriched kaolins their contents makes 49–68 % compared with Glukhovetskyi KC-1.

Regarding communication energy of OH-groups with the kaolinit surface it should be noted that by offset bands degree which are characteristic of their valence vibration they are placed in the following line by reduction: 3680 > 3613 > 3640 cm$^{-1}$. Moreover displacement was not recorded for the finish band in case of kaolin Glukhovetskyi KCCK and kaolin Katerynivskyi. The lowest bonding energy of OH-groups with the matrix by these criteria is observed in kaolin Prosianivskyi and kaolin Oboznivskyi.

Slightly different patterns were observed in the appropriate structural hydroxyl groups of kaolinite associated with the octahedral $A1^{+3}$ cations. In the case of kaolin Glukhovetskyi KC-1 absorption bands, which are responsible for their deformation vibrations, are shifted from 940 and 915 cm$^{-1}$ to 922 and 900 cm$^{-1}$, respectively.

In its turn, the maximum and minimum offset was observed in the direction of higher frequencies of indicated peaks relative to the baseline in unenriched kaolins (Glukhovetskyi KCCK and Katerynivskyi – from 27 to 31 cm$^{-1}$ and Turbivskyi – up to 13 cm$^{-1}$). In other kaolins magnitude of this offset varies from 13 to 27 cm$^{-1}$.

Their absorption intensity is 70–81 % for $\upsilon$ equal to 926 cm$^{-1}$ and 74–85 % for $\upsilon$ equal to 900 cm$^{-1}$. The most intense peaks are characteristic of Turbivskyi kaolin raw. Hydroxyl group associated with $A1^{+3}$ cations in this material are characterized by the highest binding energy after kaolin Glukhovetskyi KC-1 by the offset criterion of absorption bands. Minimum binding energy was observed in other unenriched kaolins.

Taking into account the data obtained by IR spectroscopy it can be assumed that the contribution of this type of hydroxyl groups will have an overriding effect on the properties of the surface in the case of unenriched kaolins.

## 3.3. Research of Adsorbed Water on the Kaolins Surface

State and amount of adsorbed water on the kaolin surface were determined by IR spectroscopy (absorption bands are characteristic of valence vibrations (3440 cm$^{-1}$) and deformation vibrations (1605 cm$^{-1}$) of adsorbed water molecules) in combination with the data of complex thermal analysis.

Analysis of valence and deformation vibrations shows that there are significant differences in the infrared kaolin spectra. The maximum band offset is observed in Turbivskyi kaolin at 3440 cm$^{-1}$ (27 cm$^{-1}$ in the direction of higher wave number values). The offsets are absent in unenriched kaolins as compared with Glukhovetskyi KC-1. The offset volume makes 13 cm$^{-1}$ for Prosianivskyi and Oboznivskyi kaolins.

The intensity of this band is greatest for kaolin KO-1 (126.1 %). For all others it ranges from 78 % (for kaolin Glukhovetskyi KCCK) to 100 % (for kaolin Turbivskyi).

The intensity of the absorption band that is responsible for the deformation vibrations of water molecules adsorbed on the surface of kaolin ranges depending on the kaolin composition in a narrow diapason (from 89.5 % (for kaolin Turbivskyi) to 110.5 % (for kaolin KO-1)). Kaolin Prosianivskyi, for which this value is 63.2 % is an exception.

The absorption band offset at 1605 cm$^{-1}$ reaches 35 cm$^{-1}$ with a minimum value of 21 cm$^{-1}$ for kaolin KO-1. Thus the composition and structure of kaolin to a greater extend have an effect on the deformation vibrations of adsorbed water (Table 2).

The data of IR spectroscopy on the evaluation of adsorbed water in kaolin were confirmed using the method of complex thermal analysis (Table 3). The maximum weight loss is observed in kaolin KO-1 during dehydration of kaolins (11.7 %). This index has lower value for kaolin Glukhovetskyi and Prosianivskyi KC-1 (11.5 and 11.4 %, respectively). Evaluation of relative inside effect area (compared with kaolin E2013) allows further differentiation of this difference. It is 496.7, 408.7 and 387.0 %, respectively.

*Table 3*

**Parameters of kaolin process dehydration**

| Name of kaolin by deposit, kaolin brand | Relative thermal effect area, % | Loss of mass $\Delta m$, % |
|---|---|---|
| Glukhovetskyi, KC-1 | 408.7 | 11.5 |
| Prosianivskyi, KC-1 | 387.0 | 11.4 |
| Oboznivskyi, KO-1 | 496.7 | 11.7 |
| Turbivskyi, raw kaolin | 294.6 | 9.1 |
| Glukhovetskyi, KCCK | 258.7 | 6.5 |
| Katerynivskyi, E 2013 | 100.0 | 4.4 |

The increase of nonclay components eliminates the relationship between the intensity of the peaks at 3440 and 1605 cm$^{-1}$ and the number of dehydrated water in the rest of the kaolins. Quantity of dehydrated water ranges from 9.1 to 4.4 %, and the relative area of endoeffects (inside effect) ranges from 294.6 to 100.0 % for unenriched kaolins. This phenomenon may be explained by the presence of the effect of "dilution", when the quantitative parameters of the absorption bands in the IR spectra are associated only with kaolinite. At the same time, the content of kaolinite decreases relative to increasing of nonclay components in unenriched kaolins.

It is relatively difficult to evaluate binding energy of adsorbed water on the surface of kaolins by the methods of complete thermal analysis. The thermal range of water removal has certain limitations in contrast with the existing wide range of displacements characteristic absorption bands at 3440 and 1605 cm$^{-1}$ in the IR spectra of kaolins. A small endothermic effect is fixed at 408 K in Glukhovetskyi KC-1, at 423 K in Prosianivskyi KC-1 and E2013, at 373 K in KO-1, and at 393 K in Turbivskyi raw kaolin and Glukhovetskyi KCCK. At the same time the mass loss is quite low and practically not recorded on thermogravimetric (TG) and derivative thermogravimetric (DTG) curves.

A start of more intense endothermic effect is observed at 698 K, that is associated with the removal of water in kaolins with minimal content of nonclay components. Its displacement is recorded in Turbivskyi raw kaolin up to 683 K, while in Katerynivskyi E2013 and Glukhovetskyi KCCK up to 723 and 713 K, respectively. Maximum endothermic effect is observed at 793 in the first group of kaolins and KCCK brand, and at 773 K – in Turbivskyi and Katerynivskyi kaolins.

Completion of dehydration occurs at the temperatures of 893 K in KC brand kaolins, at 883 K in brand KO-1 and KCCK kaolins, at 873 K in Turbivskyi raw kaolin, and at 843 K in Katerynivskyi kaolin E2013 brand.

Thus, the adsorbed water is most closely associated in the case of kaolin KCCK and E2013 brands (dehydration begins at 713–723 K and zero bands offset of $H_2O$ valence vibrations). However, the quantity of this water is relatively small (1.5–2.5 times less than in the enriched kaolins due to the "dilution") and dehydration process ends at lower temperatures (843–883 K).

In contrast, in enriched kaolins adsorbed water removal process begins at 698 K and ends at 883–893 K. A special case is Turbivskyi kaolin, in which the adsorbed water binds most weakly. This fact is also confirmed by the maximum displacement of valence band and deformation vibrations of $H_2O$.

Presence of specific features in the composition and structure according to the researched kaolins (chemical and mineralogical composition, crystal chemical structure, concentration and energy state of the functional groups (OH) and adsorbed water, macrostructure parameters and other factors) greatly complicates the interpretation of quantitative parameters obtained by different methods in evaluation of the state surface energy. This parameter together with the above mentioned characteristics determines the processes of structure formation in water dispersions of polymers during formation of water-dispersion paints compositions.

## 3.4. Evaluation of Surface Kaolins Energy State

Methods of energy state evaluation of dispersed materials surface at soakage were used in the researches taking into account the specifics of kaolin usage in the production of water-dispersion paints and their aggregate state. A characteristic feature of the indicated method is the opportunity to evaluate both the degree of kaolin wetting by polar and nonpolar solvents (benzol and water respectively) and the kaolin dispersion degree (filtration rate and effective specific surface).

As previously noted, kaolins are characterized by relatively low quantitative indicators of water wetting due to their crystal chemical structure and composition. The values of $B_H$ for enriched kaolins range from 0.024 (Glukhovetskyi KC-1) to 0.058 (Prosianivskyi KC-1). The values of $B_H$ are almost in the same range for other kaolins.

Kaolins wet much better by nonpolar liquids (benzol). The values of $B_H'$ increase 4–8 times for kaolin grades KO and KC and 2.4–6.4 times for unenriched kaolins, as compared to water (Table 4).

The effect of maximum wetting by test liquids is fixed for Prosianivskyi kaolin while minimum wetting is fixed for Katerynivskyi kaolin. The least differentiation in wetting by water and benzol is for kaolin KCCK, and the highest – for kaolin Glukhovetskyi KC-1.

*Table 4*

**Surface properties of dispersed kaolin**

| Name of kaolin by deposit, kaolin brand | Wetting by soakage / filtration coefficient, $K \cdot 10^{-6}$ | | Liophilic coefficient | Effective specific surface, $m^2/g$ | | Conditional dielectric loss tangent (tg$\delta$) |
|---|---|---|---|---|---|---|
| | Water | Benzol | | Water | Benzol | |
| Glukhovetskyi, КС-1 | 0.024/0.95 | 0.194/1.03 | 0.123 | 36.0 | 17.0 | 0.114 |
| Prosianivskyi, КС-1 | 0.058/1.51 | 0.236/4.39 | 0.247 | 49.6 | 18.7 | 0.193 |
| Oboznivskyi, КО-1 | 0.039/1.99 | 0.170/2.06 | 0.228 | 44.6 | 34.7 | 0.114 |
| Glukhovetskyi, КССК | 0.061/4.16 | 0.145/5.27 | 0.418 | 20.0 | 14.3 | 0.088 |
| Katerynivskyi, E2013 | 0.022/0.19 | 0.141/1.69 | 0.153 | 18.0 | 14.6 | 0.116 |
| Turbivskyi, raw kaolin | 0.043/2.08 | 0.151/6.27 | 0.283 | 47.3 | 13.5 | 0.217 |

The explanation of the found patterns in wetting may be given by the analysis of IR spectroscopy data. The best wetting is achieved in kaolins with the lowest intensity of the absorption bands characteristic of OH groups and water (Prosianivskyi KC-1) among kaolins KC and KO. A similar pattern is observed for unenriched kaolins (Glukhovetskyi KCCK).

The fact of kaolin E2031 slight wetting can be explained by the significant difference between its mineralogical composition compared with other kaolins (kaolinite content is only 31.6 wt % compared with 53.5–68.1 wt % in other clays at the ratio of kaolinite : $\beta$-quartz 0.7 and 1.5–4.6, respectively). The possibility of microcline influence (~ 16.5 wt %) is not excluded either.

Except chemical and mineralogical composition the wetting process of kaolins is also significantly influenced by the macrostructural parameters of particles, *i.e.* shape, size and degree of compaction. The impact of these factors may be evaluated taking into account such indicator as filtration coefficient of dispersion systems. Quantitative indicators of filtration coefficient, unlike wetting, vary over a wide range. Filtration coefficient ranges from 0.19 to $4.16 \cdot 10^{-6}$ for water, and from 1.03 to $6.27 \cdot 10^{-6}$ for benzol.

It is should be noted that the value of filtration coefficient is not always essential for the development of the surface kaolin wetting process. This pattern is observed both for water and for benzol. Kaolin Prosianivskyi KC-1 brand is a typical example of such pattern.

Effective specific surface of the researched kaolins is a marker that uniquely allows us to estimate the contribution of the wetting kaolins factor and their macrostructure and degree of compaction. It should be noted that the value of the effective surface area ranges from 49.6 $m^2/g$ (Prosianivskyi KC-1 brand) to 18.0 $m^2/g$ (Katerynivskyi E2031 brand) for water, and from 34.7 $m^2/g$ (Oboznivskyi KO-1 brand) to 13.5 $m^2/g$ (Turbivskyi raw kaolin) for benzol. A significant excess of specific effective surface by water in kaolin KC-1 and KO-1 brands over similar figures for unenriched kaolins (approximately 2 times except Turbivskyi kaolin) should be noted. These parameters were not significantly different when using benzol as the wetting liquid. Kaolin Oboznivskyi KO-1 brand is an exception.

Oboznivskyi and Prosianivskyi kaolins have the most developed specific effective surface (in absolute values) while Katerynivskyi kaolin has the smallest one. It should also be noted that the surface by water is 1–2.5 times higher in materials with high content of kaolinite (nonclay components should be less than ~ 25 wt %) as compared with less enriched kaolins.

A significant content of the basic natural origin material without using physical and chemical methods of enrichment can be one of explanations for the presence of high specific effective surface in kaolin KO-1 brand wetted by benzol (2 times higher than in all others).

Direct dependence of the bond strength of adsorbed water in assessing the effective surface of kaolins by their dielectric properties should be noted. The minimum value of conventional dielectric loss tangent (0.088) is marked for kaolin KCCK brand, which has the dehydration initial temperature of 723 K.

Among the researched kaolins Turbivskyi kaolin has the maximum value of tg$\delta$ (0.217), which may be explained by much lower initial temperature of adsorbed water (683 K) removal from its content. This agrees well with the known facts regarding the direct dependence of dielectric losses contingent on the amount of adsorbed water.

Relatively high values of conventional dielectric loss tangent in Prosianivskyi kaolin KC-1 brand (0.193) may be due to high activity of its surface to the interaction (wetting) with both polar and nonpolar liquids. The values of tg$\delta$ are within the range 0.114–0.116 for all other kaolins, which corresponds to a correlation between the degree of surface wettability and bond strength and the quantity of adsorbed water in their structure.

## 4. Conclusions

Results of complex physico-chemical research of kaolins (using the methods of IR spectroscopy, complete thermal, X-ray and chemical analyses, evaluations of wetting by soakage, effective specific surface and conventional dielectric loss tangent analyzes) with different content of nonclay components and ordering index of the crystal structure allowed to establish the followings:

- quantitative assessment of the binding energy of the hydroxyl groups and adsorbed water on the surface of kaolins was made by the degree of displacement of the characteristic bands in the IR spectra compared with kaolin Glukhovetskyi KC-1 brand. For all kaolins except for some varieties of OH groups (Turbivskyi kaolin, kaolin KCCK brand, E2013 brand) and the forms of adsorbed water (kaolin KCCK and E2013 brands) it was shown that their binding energy is less than in the base kaolin (Glukhovetskyi KC-1);
- using the methods of quantitative IR-spectrometry the relative content of different types of OH groups and adsorbed water (compared with kaolin Glukhovetskyi KC-1) was determined. Clear correlation with the data of complete thermal analysis of adsorbed water (by mass loss on the TG curves and endoeffect area on the DTG curves) was determined. It should be noted that the number of OH-groups of different species is up to 50 % smaller in almost all of the researched kaolins as compared with Glukhovetskyi KC-1;
- kaolins surface energy condition assessment was conducted using the data on their wettability by water and benzol soakage and its dependence on the content of OH groups of various structural origin, adsorbed water, crystal structure and chemical composition of the material, and geometric parameters of the particles was established;
- effective area of kaolin surface was determined by water and benzol wetting. The influence of liquid wetting nature and composition of kaolins on quantitative indicators of effective surface area was shown;
- estimation of the researched kaolins surface energy condition was conducted by dielectric index of kaolin-air (conventional dielectric loss tangent tg$\delta$). It was shown that tg$\delta$ is determined by the amount of adsorbed water and water binding strength with the kaolins surface and its ability to soakage;
- the correlation effects patterns determined according to the chemical composition, crystal structure, content and strength of major structural links, various forms of hydroxyl groups and adsorbed water in the structure of kaolin on the physico-chemical properties of its surface can be implemented at targeting management process of structure formation in compositions of kaolins with water polymer dispersions.

## References

[1] Council Directive 1999/13/EC. Official J. Eur. Commun., 1999, **L085**, 0001.

[2] Directive 2004/42/CE of the European Parliament and of the Council. Official J. Eur. Commun., 2004, **L143**, 0087.

[3] Sviderskyi V. and Karavayev T.: Lakokrosochnie Materialy ich Primenenie, 2010, **9**, 8.

[4] Karavayev T.: Farbe und Lack, 2012.

[5] Ermylov P., Indeykin E. and Tolmachev I.: Pyhmenty i Pyhmentyrovannye Lakokrasochnye Materialy. Khimiya, Lviv 1987.

[6] Karavayev T. and Sviderskyi V.: Commodities and Markets, 2011, **2,** 18.

[7] Karavayev T. and Sviderskyi V.: Commodities and Markets, 2010, **2**, 164.

[8] Karavayev T. and Sviderskyi V.: Keramika: Nauka and Zhizn, 2012, **1-2**, 4.

[9] Karavayev T. and Sviderskyi V.: Visnyk Nats. Tehn. Univ. "Kharkiv Politehnichnyi Instytut", 2012, **32**, 116.

[10] Sviderskyi V. and Karavayev T.: Proceed. 17th IGWT Symposium, "Facing the Challenges of the Future: Excellence in Business and in Commodity Science", Romania, Bucharest 2010, **II**, 1004.

[11] Karavayev T. and Sviderskyi V.: 18th IGWT Symposium "Technology and Innovation for a Sustainable Future: a Commodity Science Perspective", Italy, Rome 2012.

[12] Ovcharenko F., Kruhlytskiy N. *et al.*: Kaoliny Ukrainy : Spravochnik. Naukova dumka, Kyiv, 1982.

[13] Kondal D. (Ed.): Prykladnaya Infrakrasnaya Spektroskopiya. Mir, Moskwa 1970.

[14] Plyusnyna I.: Infrakrasnye Spektry Sylykatov. Mosk. Hos. Univ., Moskwa 1967.

[15] Pochynok K.: Metody Biokhimicheskogo Analiza Rasteniy. Naukova Dumka, Kyiv 1976.

[16] Horshkov V., Tymashev V. and Savel'ev V.: Metody Fiziko-Khimicheskogo Analiza Viazhushchykh Veshchestv. Vysshaya shkola, Moskwa 1981.

[17] Deryahyn B., Zakhaev M. *et al.*: Novye Metody Fiziko-Khimicheskykh Issledovaniy. Izd. Akad. Nauk SSSR, Moskwa 1957.

[18] Pashchenko A., Voronkov M. *et al.*: Hidrofobnyi Vspuchennyi Perlit. Naukova Dumka, Kyiv 1977.

[19] Éme F.: Dielektricheskie Izmereniya. Khimiya, Moskwa 1974.

## СКЛАД ТА ФІЗИКО-ХІМІЧНІ ВЛАСТИВОСТІ ПОВЕРХНІ УКРАЇНСЬКИХ КАОЛІНІВ

***Анотація.*** *У статті висвітлено результати комплексних досліджень складу та фізико-хімічних властивостей каолінів як наповнювачів водно-дисперсійних фарб. Проаналізовано результати РФА, оцінки енергетичного стану поверхні досліджуваних каолінів з різним вмістом неглинистих складових та індексом впорядкованості кристалічної структури. Виконано кількісний ІЧ аналіз основних функціональних груп поверхні каолінів з метою оцінювання їх реакційної здатності.*

***Ключові слова:*** *водно-дисперсійна фарба, наповнювач, каолін, РФА, ІЧ-аналіз, властивості поверхні.*