RIGA TECHNICAL UNIVERSITY

Faculty of Materials Science and Applied Chemistry
Institute of General Chemical Engineering

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DEVELOPMENT OF PREPARATION TECHNOLOGY AND INVESTIGATION OF PROPERTIES OF LATVIAN CLAYS FOR APPLICATION IN COSMETIC PRODUCTS

Summary of Doctoral Thesis

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The Thesis for the doctoral degree in engineering sciences is to be publicly defended on the 5th February 2015, at the Riga Technical University, in room 272 at 15.00 in the afternoon.

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CONFIRMATION

I confirm that I have developed the present Doctoral Thesis, which is submitted for consideration at Riga Technical University for scientific degree of the doctor of engineering sciences. The Doctoral Thesis has not been submitted at any other university for the acquisition of a scientific degree.

Inga Dušenkova …………………………….

Date: ………………………

The Doctoral Thesis is written in Latvian language, it contains Introduction, 3 chapters - Review of Literature, Methods, Discussion of Experiments, Conclusions, list of References, as well as 49 illustrations, 14 tables, 1 annex, together 106 pages. 162 references are used for this Doctoral thesis.

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CONTENTS

OVERVIEW OF THE DOCTORAL THESIS 6
State of the art and novelty 6
The aim of the Doctoral Thesis 6
Tasks set to realize the aim of the Doctoral Thesis................................. 6
Scientific significance of the Doctoral Thesis... 7
Practical significance of the Doctoral Thesis 7
Approbation of the Doctoral Thesis... 7
REVIEW OF THE LITERATURE.. 8
EXPERIMENTAL METHODS... 10
Preparation and evaluation of clay samples 10
Determination of clay sample properties before and after the treatment 11
DISCUSSION OF EXPERIMENTS... 13
1. Mineralogical and chemical composition of clay samples before and after chemical treatment... 13
2. Mineral phase composition of clay fractions under 2 μm 15
3. Adsorption of squalene and oleic acid 16
4. Viscosity of clay/water suspensions 18
5. Viscosity and stability of clay fraction/glycerol solution suspensions 19
6. Stabilization of oil-in-water emulsions 23
7. UV protection ability 23
8. Antibacterial properties.. 25
9. Technological shemes of clays preparation for application in cosmetic products 26
REFERENCES 30
LIST OF PUBLICATIONS... 31
SCIENTIFIC CONFERENCES.. 31
Participation in the conferences with reviewed conference proceedings 31

OVERVIEW OF THE DOCTORAL THESIS

State of the art and novelty

Based on the latest research about harmful effects on human health and allergic reactions of various chemical compounds found in cosmetic products, demands for cosmetics made from natural ingredients are increasing. Clays are one of such natural materials. They are used in various cosmetic and medical products as active ingredients, thickeners and stabilizers in creams, lotions and pastes. The application of clays in these fields is based on their sorption and rheological properties, which are provided by the presence of clay minerals. The application of certain clays depends on their mineralogical composition, because the occurrence of pure clay minerals deposits is rare. The purification of clays with physical and chemical methods affects their further application.

Clays are one of the largest mineral deposits in Latvia and their reserves are among the largest in Northern Europe. The application and research of Latvian clays are mostly connected with the production of building and ceramic materials. Latest research [1] show that the most part of commercially available cosmetic clay masks in Latvia contain illite – the most abundant clay mineral in Latvia, but from 125 analyzed commercial clay containing products only 3 % are produced in Latvia. Until now there is no scientific research on application of Latvian clays in cosmetic products for certain functions. By applying appropriate purification methods it would be possible to use them in development on cosmetic products.

The aim of the Doctoral Thesis is to investigate and evaluate properties of illite containing Latvian clays from various deposits for application in cosmetic products and to develop possible clay preparation technologies for certain functions in cosmetic products.

Tasks set to realize the aim of the Doctoral Thesis:

- to perform chemical and physical treatment of illite containing Latvian clays;
- to investigate and evaluate the influence of used treatment methods on the viscosity and stability of clay suspensions, adsorption of organic compounds, transmittance of UV radiation and antibacterial properties;
- to evaluate the effect of illite containing clay mineral addition on the stability of emulsion oil-in-water;
- to develop possible technological schemes of clay preparation for application in cosmetic products for certain functions.

Scientific significance of the Doctoral Thesis:

- for the first time physicochemical properties of Latvian clays for application purpose in cosmetic products are investigated;
- for the first time adsorption of organic compounds found in human sebum on clays and viscosity of illite suspensions in glycerol solutions are investgated.

Practical significance of the Doctoral Thesis:

Possible technological schemes for preparation of illite containing Latvian clays for application in cosmetic products as active ingredients and additives are developed.

Approbation of the Doctoral Thesis:

The scientific achievements and main results of the scientific research of this Thesis have been presented in 6 international conferences, summarized in 5 full text scientific manuscripts and 8 peer-reviewed conference proceeding abstracts.

REVIEW OF THE LITERATURE

Clays and clay minerals are widely used in various cosmetic products, therapeutic and SPA procedures. The application of clay minerals in cosmetics is based mainly on their rheological properties and ability to adsorb organic compounds. These properties are provided by the net negative charge on the surface of clay mineral particles, plate-shaped particles and high specific surface area. The most commonly used are smectites (montmorillonite), bentonite, kaolinite and synthetic hectorite, but paligorskite, sepiolite and the most abundant clay mineral in Latvia illite - slightly less. Clays and clay minerals are used as active ingredients – sorbents and UV filters, and as additives – thickeners, stabilizers and emulsifiers.

- *Sorbents in facial masks.* Clay application on face is used in treatment of some skin diseases and inflammations and for skin purification from toxins and excess sebum. Sebum is an oily substance, secreted by the sebaceous glands, and consists of various organic compounds. Based on research, increased amount of oleic acid in sebum causes inflammatory skin disorder seborrhoeic dermatitis, but patients with acne have increased levels of squalene in their sebum. Until now in literature there are no scientific researches about the effect of clay mineralogical composition on adsorption of organic compounds found in human sebum. Cosmetic facial masks contain mostly montmorillonite, illite and kaolinite.
- *UV filters in sunscreens.* Clay minerals can be used as alternative to organic and synthetic UV filters, which may induce photocatalytic effect and cause skin damage, as well as penetrate into the skin and cause allergic reaction. Research show that the addition of Fe (III) compounds improves UV protection ability of clay minerals. At this moment bentonite and kaolinite are used in commercial sunscreens, but research show that also illite containing clays have a potential to be used as UV filters.
- *Thickeners.* The addition of clays and clay minerals to water containing dispersions and emulsions improves their consistency and viscosity, which is important for semi-solid product (creams, lotions, pastes, gels) application to skin. Mostly used are high purity montmorillonite, based on its high swelling ability. The most abundant clay mineral in Latvia is illite, therefore it is essential to evaluate the possibility of illite containing clay mineral application in cosmetics as thickener.

- *Stabilizing agents of suspensions and emulsions.* The addition of clay minerals to suspensions and emulsions improve their stability – retards sedimentation of solid particles in suspensions and they are easily resuspended, but in emulsions prevent the breakdown by phases and ensure homogeneity. Clay mineral particles could act as emulsifying agent in oil-in-water emulsions. Bentonite, kaolinte and paligorskite are mostly used, but research show, that illite containing clay minerals also can stabilize oil-in-water emulsion.

The application of clays in cosmetic products for certain functions depends on the type of clay minerals and the presence of non-clay minerals. From non-clay minerals clays usually contain quartz, feldspar, carbonates (calcite and dolomite), iron compounds (hematite, goethite, magnetite and others) and organic matter - humic substances. The presence of these compounds affects the physicochemical properties of clays. The presence of carbonates, iron compounds and organic matter affects mostly the stability of clay mineral particles – they can promote aggregation, thereby reducing the efficiency of obtaining pure clay minerals. The presence of carbonates forms alkaline condition in water media, therefore decreasing the viscosity of suspensions. There are several researches about the influence of addition and removal of iron compounds and organic matter on the interaction of clay mineral particles – stability and viscosity. These research shows that the removal of positively charged iron compound particles reduces the viscosity of dispersions, because the net negative charge on clay mineral particles increases. At the same time the stability and adsorption properties of clay mineral particles increases. At this point it would be important to investigate the influence of iron compound removal from clays on the application in cosmetic products for certain functions. The removal of organic matter reduce not just the viscosity of suspensions, but also the net negative charge and adsorption properties, therefore the oxidation of organic matter was not performed. The removal of quartz and feldspar was combined with fractionation, therefore obtaining clay fraction under 2 µm.

Clay reserves in Latvia are among the largest in Northern Europe and they are mainly used as building materials and ceramics. In recent years, the studies regarding the expansion of application possibilities of Latvian clays and development of innovative products are about novel and improved ceramic materials for application in environmental technologies. Therefore the research, done in the framework of this Doctoral Thesis, provides the possibilities to evaluate the application of Latvian illite containing clays in cosmetic products as active ingredients and additives.

EXPERIMENTAL METHODS

The experimental process scheme of Doctoral thesis and determined parameters are shown in Figure 1.

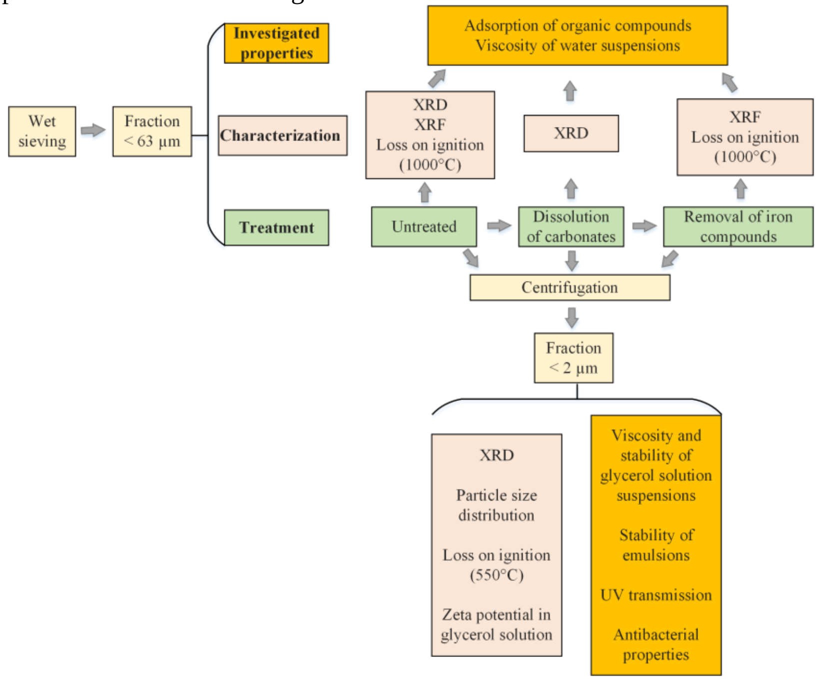


Fig.1. Clay preparation and investigated properties

Clays from 4 sites in Latvia were used. Carbonate containing Laza and Prometejs clays are from Quarternary period deposits, non-carbonated Pavari clays are from Devonian period deposit, but Iecava clays are from dolomite deposit, where clays are by-product from dolomite purification process.

Preparation and evaluation of clay samples

Fractions under 63 and 2 µm of all untreated clays were obtained by wet sieving and centrifugation, respectively. For further purification fractions under 63 µm were used. The removal of carbonates was conducted with 1 M hydrochloric and citric acid solutions. During the dissolution the pH of suspensions was kept above 4.5, until it was approximately 5 and did not change for 24 hours. To remove the excess acid, Ca^{2+}, Mg^{2+} and corresponding acid ions, all suspensions were centrifuged and the clay sediments were washed with distilled water for several times, until the electrical conductivity of the supernatant liquid was 100 µS/cm. One part of the sediments was used to obtain fraction under 2 µm, but the other part was dryed in 105°C temperature and used in removal of iron compounds. The removal of iron compounds was conducted for untreated Pavari clays and Laza, Prometejs and Iecava clays after removal of carbonates. Dithionite-citrate method was used, where insoluble Fe(III) compounds are reduced, stable Fe(II) citrate complex are developed at temperatures 75-80°C and the colour of suspenion changes to blue. The clay sediments are washed with 1 M NaCl solution and distilled water for several times, until the electrical conductivity of the supernatant liquid was 100 µS/cm. One part of the sediments was used to obtain fraction under 2 µm, but the other part was dryed in 105°C temperature.

Mineralogy and chemical composition of obtained powders was evaluated using X-ray powder diffraction (XRD, PANalytical X-Pert Pro) and X-ray fluorescence spectrometry (XRF, Bruker Pioneer S4) analysis, respectively. The presence of organic matter in clay fractions under 2 µm were detemined by loss on ignition at temperatue 550°C. Zeta potential was determined for clay fractions under 2 µm in 50% (w/w) glycerol/water solution. Particle size distribution was detemined with laser diffraction particle sizer Analysette 22.

Determination of clay sample properties before and after the treatment

The sorption properties were determined with oleic acid and squalene solutions in squalane media on dry clay samples. Solutions of oleic acid and squalene with concentration 25 mg/ml were used. 1.5 ml of oleic acid or squalene solution was added to 0.2 g of dry sample in closed container, mixed and left still for 20 minutes. Then the clays were separated by centrifugation and the concentration of oleic acid and squalene was determined with UV-VIS spectrophotometer at 247 and 288 nm, respectively. The adsorption properties were compared with two commercial cosmetic clays.

The viscosity was measured for clay sample suspensions in water and water/glycerol solution (further in text – glycerol solutions) media. Clay/water suspensions were prepared from fractions under 63 µm with mass concentration 50 wt%. Clay/glycerol solution suspensions were prepared from clay fractions under 2 µm with mass concentration 20 wt% in 50% glycerol solution and 5 wt% in 90% glycerol solution. For samples Iecava and Laza additional suspensions were prepared in 50% glycerol solution with concentration 15 and 10 wt%. The measerment were taken at room temperature 20 ± 1ºC by increasing the shear rate in this order - 1; 2;

3; 4; 5; 8; 10; 20 and 50 rpm. At each shear rate the viscosity was measured for 1 minute, except for shear rate 1 rpm it was for 3 minutes.

The stability of all glycerol suspenisons was determined by visual observation and by measuring the reduction of clay sediment volume during three weeks.

The influence of clay fraction under 2 μm on the stability of oil-in-water emulsion was determined in system safflor oil-in-water. 20 g of clay fraction suspension with solid concentration 5 and 10 wt%, homogenized for 24 hours, was added to 10 g of safflor oil and homogenized for 24 hours. The stability was determined visually by observing the separatin of oil and water phases at rest state.

The transmittance of UV radiation was determined for all suspensions in 50% glycerol solution, for untreated samples with concentration 30 wt% in 50% glycerol solution and commercial sunscreens with SPF 15, 30 and 50. A small drop was applied on 2 mm thick quartz glass and spread evenly on the whole glass surface (3.14 cm^2) with finger, until the sample mass is 0.45 mg. After 20 minutes the UV transmittance is measured in 5 different places. Three parallel measurements are made for each sample. The SPF values are calculated from the obtained data.

The antibacterial properties were determinated against three types of bacteria – gram negative *Ps.aeruginosa* and *C.alibacans* and *gram* positive *S.aureus* with concentration $0.5 \cdot 10^8$ CFU/mL. Untreated Iecava and Laza clay fractions under 2 μm were used. For better evaluation of the antibacterial properties silver doped hydroxilapatite (HAp/Ag) was used (see table 1), which possess antibacterial properties. 0.50 ± 0.05 g of paste was mixed with 1 mL of bacteria and incubated at temperature 37ºC for 30 minutes, 1, 2, and 24 hours.

Table 1

Composition of pastes

Clays	**Sample No.**	**Clay conc., wt%**	**HAp/Ag conc., wt%**	**Pure glycerol conc., wt%**	**Water conc., wt%**
Iecava	1.	30	0	10	60
	2.	30	5	10	55
	3.	30	15	10	45
Laza	4.	30	0	10	60
	5.	30	5	10	55
	6.	30	15	10	45

DISCUSSION OF EXPERIMENTS

1. Mineralogical and chemical composition of clay samples before and after chemical treatment

Table 2 shows that all untreated clays contained 50-60 wt% of clay minerals and Prometejs clays contained the higest amount. All clays, except for Pavari, contained carbonates - Prometejs and Laza 15-16 wt%, but Iecava clays just 4 wt%.

Table 2

Mineralogical composition of untreated clays with fraction < 63 μm, wt%

Clays	Illite	Kaolinite	Chlorite	Quartz	Feldspar	Dolomte	Calcite	Muscovite
Iecava	51 ± 3	-	-	11 ± 1	26 ± 2	4 ± 1	-	8 ± 2
Prometejs	51 ± 2	9 ± 1	-	14 ± 1	10 ± 1	9 ± 1	7 ± 1	-
Laza	34 ± 2	11 ± 1	8 ± 2	13 ± 1	16 ± 1	5 ± 1	8 ± 1	5 ± 2
Pavari	35 ± 3	4 ± 2	-	54 ± 2	7 ± 2	-	-	-

XRD patterns showed that after the treatment with acids the carbonates were dissolved, because the most intensive peaks of calcite and dolomite at 2θ 29.55° and 31.05°, respectively, were not seen (see Figure 2). Further in the text the clay samples after dissolution of carbonates are labeled as follows:

- Iecava clays after the treatment with hydrochloric acid - Ie-HCl;
- Iecava clays after the treatment with citric acid - Ie-C;
- Laza clays after treatment with hydrochloric acid - L-HCl;
- Laza clays after the treatment with citric acid - L-C;
- Prometejs clays after treatment with hydrochloric acid- Pr-HCl;
- Prometejs clays after the treatment with citric acid - Pr-C.

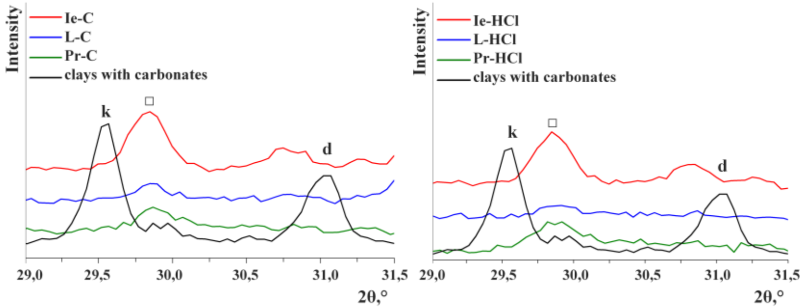


Fig.2. XRD pattern of clay samples before and after the removal of carbonates
k – calcite; d – dolomite; □ – feldspar

The changes in clay colour indicated the removal of iron compounds (see Table 3). The brown colour of untreated Laza and Prometejs clays indicated the presence of goethite and hematite [2], the light gray colour of

Iecava clays – small amounts of pyrite [3], but the light beige colour (pinkish white in Munsell scale) of Pavari clays indicated low content of iron compounds and organic matter [4]. After the removal of iron compounds Laza and Prometejs clays became light gray, Iecava clays – greenish gray, but Pavari clays – grayish white (white in Munsell scale). Because Iecava and Pavari clays were not brown, the removal of iron compounds was proved by the changes in chemical composition, as shown in Table 4. Further in text the sample after removal of iron compounds are labeled as shown in Table 3.

Table 3

Colour after Munsell scale before and after the removal of iron compounds

Samples	Colour	Colour code
Pavari	Pinkish white	7.5YR 8/2
Pa-D[1]	White	7.5YR 8/1
Iecava	Light gray	5Y 7/1
Ie-D[1]	Light greenish gray	10BG 7/1
Laza	Light brown	7.5YR 6/4
L-D[1]	Light gray	2.5Y 7/1
Prometejs	Light reddish brown	5YR 6/4
Pr-D[1]	Light gray	2.5Y 7/1

[1]Clay samples after the removal of iron compounds

After the removal of iron compounds the amount of iron in Iecava clays decreased for 20%, in Laza clays for 27%, in Prometejs clays for 25% and in Pavari clays for 13% (see Table 3). Since Fe (II) and Fe (III) ions can be found in the octahedral sheet of clay mineral structure [5], the rest of iron can be from the structure of clay minerals. The iron compounds were removed after the dissolution of carbonates, therefore the amount of calcium ions have significantly decreased.

Table 4

Chemical composition of fraction < 63 μm for untreated clays and after removal of iron compounds, wt%

Oxide ± uncertainty	Iecava	Ie-D[1]	Laza	L-D[1]	Prometejs	Pr-D[1]	Pavari	Pa-D[1]
SiO_2 ± 0.6	50,2	54.2	43.8	51.9	38.8	46.9	64.6	66.4
Al_2O_3 ± 0.7	19.9	21.2	16.8	18.8	14.7	19.1	13.2	13.6
Fe_2O_3± 0.2	7.2	5.8	8.6	6.3	8.2	6.1	7.6	7.4
CaO ± 0.2	1.4	0.5	7.3	1.1	8.3	0.9	0.7	0.4
MgO ± 0.2	3.5	2.4	3.2	2.8	6.2	3.9	1.5	1.3
K_2O ± 0.2	8.7	9.7	4.7	5.3	7.2	8.1	5.6	5.5
TiO_2 ± 0.1	1.0	1.1	0.9	1.0	1.0	1.0	1.2	1.4
Na_2O ± 0.1	0.5	0.5	0.7	0.6	0.3	0.3	0.3	0.2
P_2O_5 ± 0.1	0.2	0.1	0.1	0.1	0.1	0.03	0.2	0
LOI[1]± 0.1	7.0	4.0	13.8	11.6	15.1	13.4	3.1	2.8

[1]Loss on ignition at temperatue 1000 ℃

2. Mineral phase composition of clay fractions under 2 µm

Iecava clay fraction contained mostly illite and small amounts of dolomite and feldspar (see Figure 3). The presence of quartz was difficult to evaluate, because the illite peak at 2θ 26.67º was covered with the highest quartz peak at 2θ 26.65º. Laza and Prometejs clay fractions contained illite and kaolinite and from non-clay minerals – quartz, feldspar, dolomite and calcite. Mineral phase composition of Pavari clay fraction was similar to Laza and Prometejs clays, except of the absence of calcite and dolomite phases.

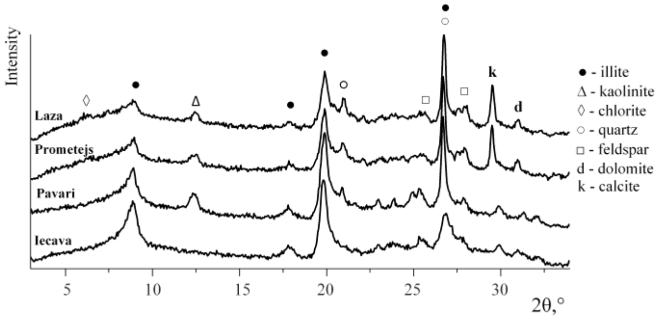


Fig.3. XRD pattern of untreated clay fractions

The typical XRD peaks of calcite and dolomite at 2θ 29.55º and 31.05º, respectively, disappeared after the dissolution of carbonates with hydrochloric acid, as shown in Figure 4. The other mineral phases were the same as for untreated clay fractions.

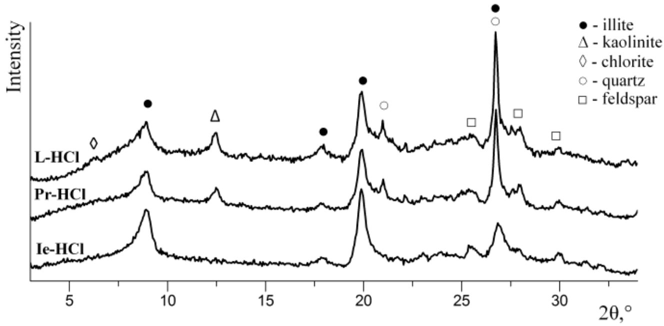


Fig.4. XRD pattern of clay samples after dissolution of carbonates with HCl

Figure 5 shows that samples L-C and Pr-C contained small amount of tricalcium citrate, which was formed in the dissolution process. Tricalcium citrate is used as food additive, therefore it’s presence in cosmetic products is not harmful.

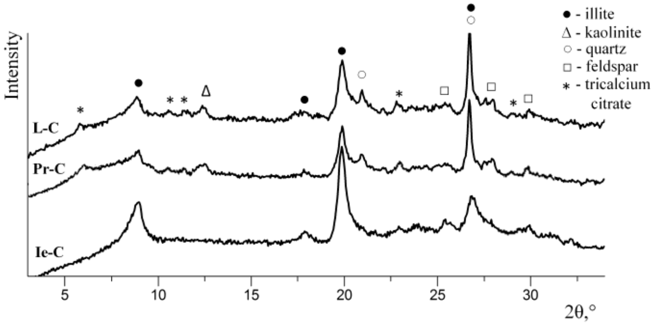


Fig.5. XRD pattern of clay samples after dissolution of carbonates with citric acid

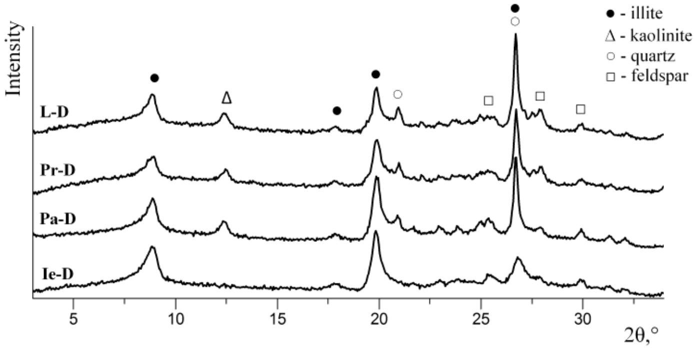


Fig.6. XRD pattern of clay samples after removal of iron compounds

After the removal of iron compounds additional phases were not formed (see Figure 6). Ie-D, L-D and Pr-D samples contained the same mineral phases as after dissolution of carbonates with hydrochloric acid, except of the absence of chlorite peak at 2θ 6.30º in sample L-D. Sample Pa-D contained the same mineral phases as untreated Pavari clays.

3. Adsorption of squalene and oleic acid

To evaluate the adsorption properties of clay samples, two commercial cosmetic clays (used as facial masks) Cosm-1 and Cosm-2 with various mineralogical compositions were used (see Table 5).

Table 5

Mineralogical composition of commercial cosmetic clays, wt%

Sample	Illite	Kaolinite	Chlorite	Quartz	Feldspar	Muscovite
Cosm-1	13 ± 2	-	48 ± 3	21 ± 1	9 ± 1	9 ± 2
Cosm-2	63 ± 3	3 ± 1	-	18 ± 1	10 ± 2	6 ± 2

The particle size distribution determines the interface between clay particles and the adsorbed substance. Figure 7 shows that untreated Laza and Prometejs clays had almost identical particle size distribution and in general they were finer than other clay samples. Both cosmetic clays had similar particle size distribution – ~ 62-68% of particles were finer than 10 μm, but particles of Iecava clays - only 53%. At the same time Iecava clays contained much finer particles under 1 μm than other clays samples.

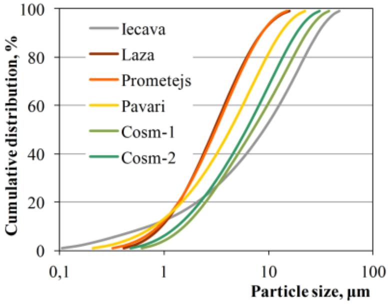


Fig.7. Particle size distribution of untreated and cosmetic clays

Figures 8 and 9 show that adsorption of squalene and oleic acid on clay samples after removal of iron compounds had increased. It could be explained with the increase of net negative charge on clay mineral particles, because the adsorption of organic compounds is based on the negative charge on clay mineral particles. Adsorption of squalene on sample Ie-D increased approximately by 27%, on sample L-D – by 69% and on sample Pr-D - by 46%. The adsorbed amount of squalene on sample Pa-D increased only by 14%, because the amount of iron oxide after the treatment with dithionite decreased only by 0.3 wt% (see Table 4). The adsorbed amount of oleic acid on Pa-D increased approximately by 6%, but on other clay samples after the removal of iron compounds - by 22-27%.

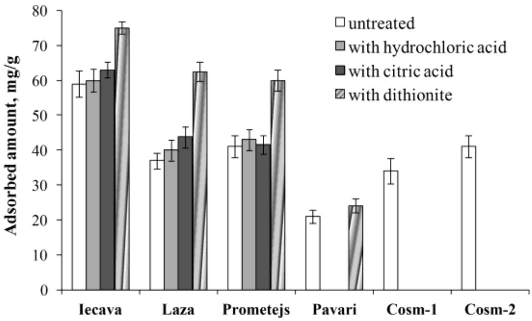


Fig.8. Adsorbed amount of squalene, mg/g

The changes in adsorption after dissolution of carbonates were insignificant and within the error limits. Both cosmetic clays showed lower adsorption than Iecava, Laza and Prometejs clay samples, although they contained similar amount of clay minerals. The lower adsorption of cosmetic clays can be connected with particle size distribution. Pavari clays showed lower adsorption than other clay samples, because they contained lower amount of clay minerals.

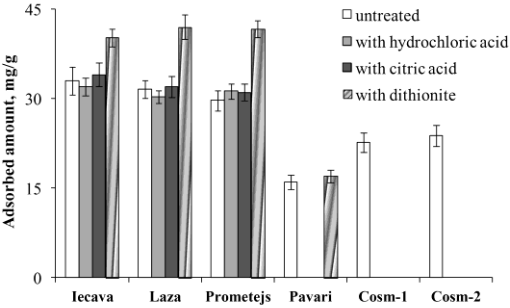


Fig.9. Adsorbed amount of oleic acid, mg/g

4. Viscosity of clay/water suspensions

The suspensions were prepared from clay sample fraction 63 μm. In comparison with untreated clays, viscosity of Iecava clays is approximately 30-40% lower than Laza clays and 40-50% lower than Prometejs clays, as shown in Figure 10. The viscosity of untreated Pavari clays was many times lower than other clay samples, due to the lowest amount of clay minerals and the higest amount of quartz.

The viscosity of Laza and Prometejs clay suspensions slightly increased after the removal of carbonates, but the viscosity of Iecava clays stayed almost constant. It could be explained with the decrease of suspension pH (see Table 6), which increases the viscosity, and with the increase of clay mineral amount in samples, due to the removal of carbonates. There was no significant increase in the viscosity of Iecava clays, because the changes in suspension pH were negligible.

Table 6

pH values of untreated and treated clay/water suspensions, stdev ± 0.1

Clays	**Type of treatment**			
	untreated	-HCl	-C	-D
Iecava (Ie)	7.3	6.8	6.7	6.8
Laza (L)	7.7	6.4	6.4	7.1
Prometejs (Pr)	7.8	6.5	6.6	7.0
Pavari (Pa)	6.7	-	-	6.9

The viscosity of suspensions rapidly decreased after removal of iron compounds. The removal of iron oxides increases the net negative charge. This leads to the destruction of the card-of-house aggregation mode because the amount of positive edge charges becomes too small to stabilize the edge-to-face contact, therefore the viscosity decreases [6].

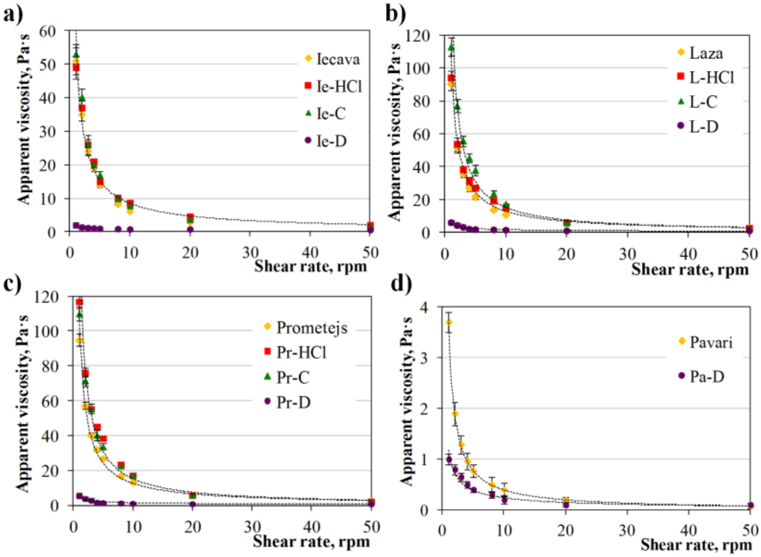


Fig.10. Influence of the used treatment on apparent viscosity of 50 wt% clay/water suspensions a) Iecava, b) Laza, c) Prometejs and d) Pavari clays

Since the viscosities of Laza and Prometejs clay suspensions were very similar, for viscosity research of glycerol suspensions Prometejs clays were not used.

5. Viscosity and stability of clay fraction/glycerol solution suspensions

Most studies about viscosity of clay minerals have been carried out in aqueous media, but in cosmetic products compounds with higher viscosities are usually used. Therefore it is important to determine the influence of clay mineral addition on the viscosity of solutions with higer viscosity than water and to evaluate the colloidal stability of obtained ssuspensions. Glycerol is one of these compounds, which is widely used in cosmetic products as moisturizing component [7].

50 and 90% glycerol solutions are Newtonian fluids with viscosities 0.006 and 0.219 Pa·s at temperature 20°C. Figure 11 shows that the addition of clay fraction to both glycerol solutions increased their viscosity several times. The obtained suspensions were Non-Newtonian fluids, in particular,

pseudoplastic fluids, where the viscosity decreases with increasing the shear rate.

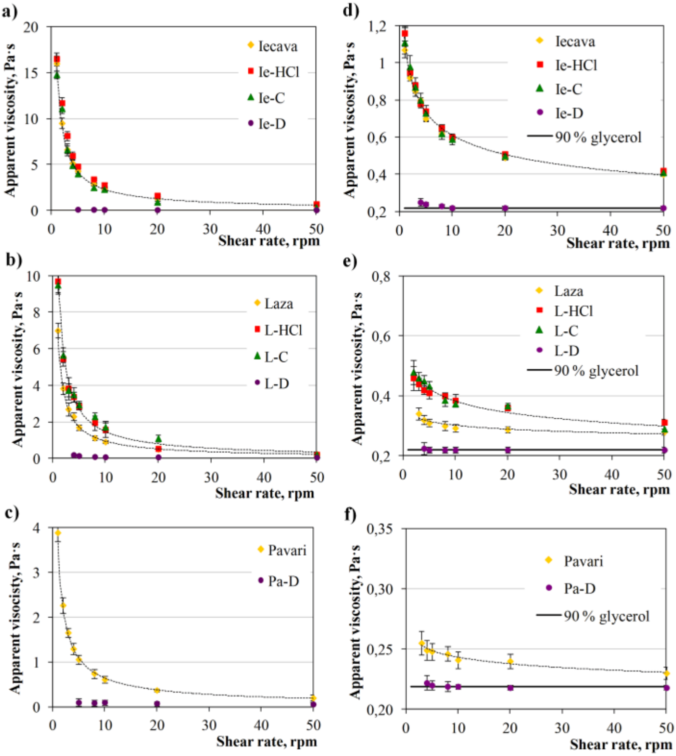


Fig.11 Influence of the used treatment on apparent viscosity of clay suspensions in 50% glycerol solution with 20 wt% of clay fraction (a, b, c) and in 90% glycerol solution with 5 wt% of clay fraction (d, e, f)

The viscosity of suspensions rapidly decreased for samples with removed iron compounds, similar to water suspensions, because of the increased net negative charge on clay mineral particles, as shown in Figure 12.

Table 7

d_{10}, d_{50} un d_{90} of particle size distribution in 50% glycerol solution suspensions, µm

	Iecava			Laza			Pavari
	untreated	-HCl	-C	untreated	-HCl	-C	untreated
d_{10}	0.09±0.01	0.02±0.01	0.02±0.01	0.40±0.03	0.20±0.04	0.22±0.06	0.24±0.03
d_{50}	0.46±0.04	0.28±0.03	0.27±0.05	1.09±0.05	0.64±0.08	0.70±0.07	0.91±0.10
d_{90}	1.97±0.30	0.94±0.09	0.87±0.10	2.68±0.20	1.88±0.20	1.95±0.20	2.72±0.40

Viscosity of sample Iecava in 50% glycerol was two times higher than viscosity of sample Laza and four times higher than of sample Pavari. It is based on the mineralogical composition and particles size distribution, where Iecava clay fraction contained the highest amount of illite and particles under size of 0.1 μm (see Table 7). After the removal of carbonates, the viscosity of Iecava clays basically did not change, but of Laza clays it increased approximately 1.4-1.7 times (depending on the shear rate) due to the decrease of suspenion's pH (see Table 8). The addition of samples Iecava, Ie-HCl and Ie-C increased the viscosity of 50% glycerol solution 700-2700 times in the range of shear rates 1-5 rpm. The addition of samples L-HCl and L-C increased the viscosity 500-1600 times, but sample Pavari – just 200-650 times.

Table 8

pH values of 50% glycerol solution suspensions, stdev ± 0.1

Clays	Type of treatment			
	untreated	-HCl	-C	-D
Iecava (Ie)	7.4	6.9	6.7	7.1
Laza (L)	7.8	6.9	7.1	7.2
Pavari (Pa)	6.9	-	-	7.0

The addition of untreated Iecava, Ie-HCl and Ie-C samples to 90% glycerol solution increased it's viscosity approximately 3-5 times in the range of shear rates 1-5 rpm. At the same time the addition of L-HCl and L-C samples increased the viscosity approximately twice, but the addition of Pavari clays - only 1.2 times in the range of shear rates 2-5 rpm.

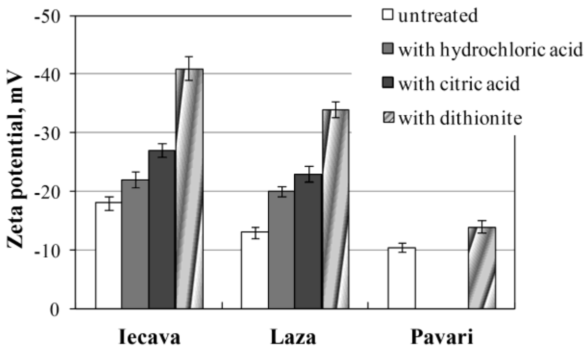


Fig.12. Zeta potential of clay fraction particles in 50 wt% glycerol

The viscosity of samples Ie-HCl and L-HCl decreased 3-5 times by decreasing the concentration of clay fraction from 20 to 15 wt% (see Figure

13). If we compare 15 and 10 wt% suspensions, viscosity of sample Ie-HCl has decreased 3-4 times, but of sample L-HCl ~ 3-5 times.

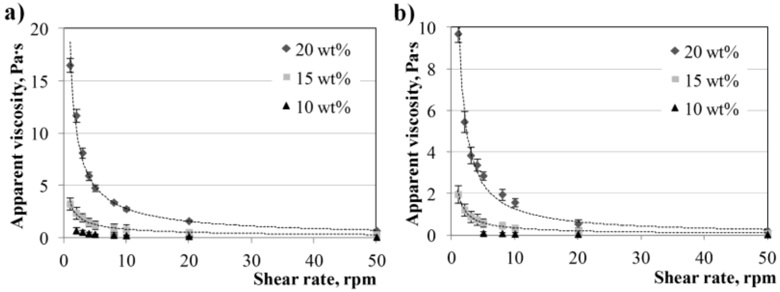


Fig.13. Influence of sample a) Ie-HCl and b) L-HCl concentration on the apparent viscosity of suspensions in 50% glycerol solution

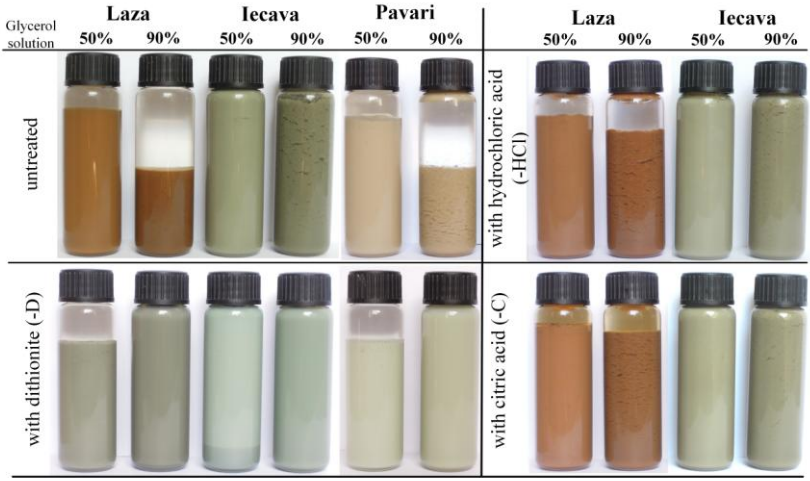


Fig.14. Stability of clay mineral/glycerol solution suspensions after 21 days

Suspensions of Iecava samples were more stabile than Laza and Pavari samples (see Figure 14). All suspensions of Iecava clay fractions in 50% glycerol were homogeneous, except for sample Ie-D, where sediments were observed. Suspension of untreated Iecava clay fraction in 90% glycerol flocculated, but other samples (treated) stayed homogeneous.

Suspensions of Laza and Pavari samples were less stabile than Iecava sample suspensions. All suspensions in 50% glycerol showed structural sedimentation, but their stability disagreed with zeta potential results, where, theoretically, samples L-D and Pa-D should be the most stabile. The stability of these dispersions (in 50% glycerol solution) is influenced by their viscosity, respectively, the stability of dispersion increased with increase of viscosity. Whereas stability of suspensions in 90% glycerol correlates with zeta potential results, where zeta potential increased in this order: Laza or Pavari < L-HCl < L-C < L-D or Pa-D.

6. Stabilization of oil-in-water emulsions

The stability of safflor oil-in-water emulsions was affected by the mineralogical composition, used treatment and the added concentration of clay fraction (see Figure 15). The addition of samples Iecava, Ie-HCl and Ie-C formed the most stable emulsions. It is explained with the relatively high viscosity, because the formation of three-dimensional network is important in the stabilization of oil droplets, where they are trapped in the 3D network and reduces the mobility of the droplets [8].

The stability of emulsions is affected by the net negative charge on clay mineral particles due to the electrostatic repulsion, where the particles cannot form a dense film around the oil droplets and prevent their coalescence [8]. The lowest stability of emulsions containing clay fraction after removal of iron compounds can be explained by the low viscosity and high net negative charge.

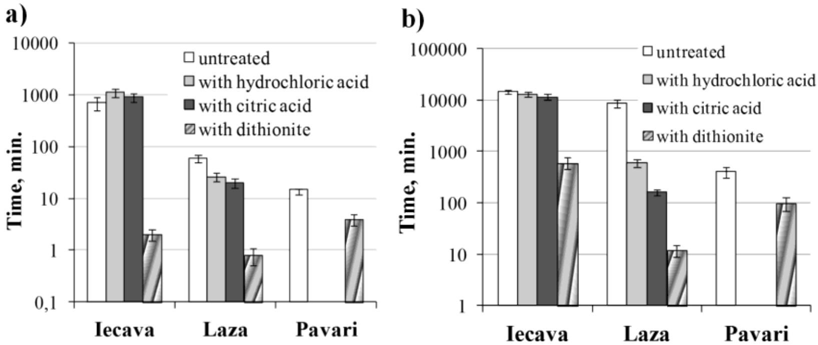


Fig.15. Stability of emulsions by addition of clay fractions with concentrations a) 5 wt% and b) 10 wt%

7. UV protection ability

UV transmission measurements were performed in the range 290-400 nm, which is based on the classification of UV radiation: UV-C (200 – 280 nm), UV-B (280 – 320 nm) and UV-A (320 – 400 nm). UV-A produces skin burn, UV-B can promote skin cancer, UV-C is the most dangerous, but it is generally adsorbed by the ozone layer [9]. Untreated clay samples showed the lowest UV trasmission (see Figure 16), therefore the removal of carbonates and iron compounds decreases the sun protection factor (SPF), as shown in Table 9. Hoang-Minh et al. research [9] obtained similar results, where UV transmission of clays decreased after the removal of iron compounds with sodium dithionite. It can be concluded, that it is useful to use clay minerals with high content of iron compounds in sunscreens.

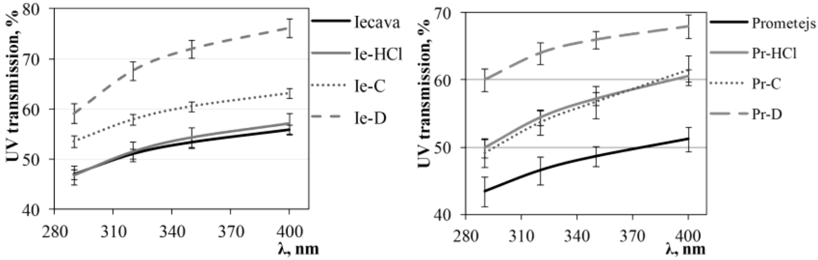


Fig.16. Influence of the used treatment on UV transmission of Iecava and Prometejs clays in 50% glycerol with soild concentration 20 wt%

With increasing the clay concentration by 10 wt% (from 20 to 30 wt%), UV transmission decreased - 26-27% for Iecava clays, 21-23% for Laza clays, 24-26% for Prometejs clays and 18-21% for Pavari clays. Thus the SPF values also increased: for Iecava clays – 2.6 ± 0.1, Laza clays – 2.7 ± 0.1, Prometejs clays – 2.8 ± 0.1 and Pavari clays – 1.9 ± 0.1. Pavari clays showed the higest UV transmission due to the lowest content of iron compounds.

Table 9

SPF values for untreated and treated clays with 20 wt% concentration in suspension

Clays	**Type of treatment**			
	untreated	-HCl	-C	-D
Iecava (Ie)	2.03 ± 0.06	1.97 ± 0.08	1.67 ± 0.04	1.53 ± 0.04
Laza (L)	2.15 ± 0.09	1.84 ± 0.10	1.88 ± 0.06	1.40 ± 0.08
Prometejs (Pr)	2.18 ± 0.07	1.82 ± 0.06	1.80 ± 0.07	1.51 ± 0.06
Pavari (Pa)	1.64 ± 0.08	-	-	0.60 ± 0.06

The commercial sunscreens showed more intensive UV protection abilities in all UV-B and the beginning of UV-A range (see Figure 17), therefore they also have much higher SPF values. Despite the relatively low SFP values of clay samples, illite containing clay minerals can be used in sunscreens with low SPF values as one of the UV filters, at the same time improving the viscosity of the product and giving a brown shade.

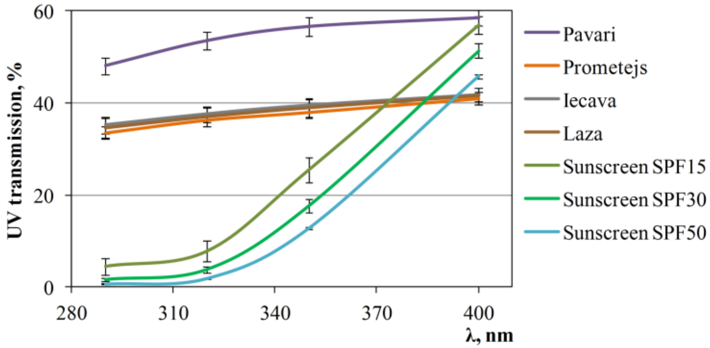


Fig.17. UV transmission of untreated clays with 30 wt% concentration and commercial sunscreens

8. Antibacterial properties

Antibacterial properties of clay pastes with various HAp/Ag concentrations were determined (see Table 10). The results showed that after 30 minutes, 1 and 2 hours there were no differences in growth nature and intensity of all bacteria between the control plate and all samples, except for sample 3, where the amount of bacteria *S.aureus* was approximately 33% lower than in the control plate.

Table 10

Concentration of HAp/Ag in clay pastes, wt%

Clays	Iecava			Laza		
Sample No.	1	2	3	4	5	6
HAp/Ag conc., wt%	0	5	15	0	5	15

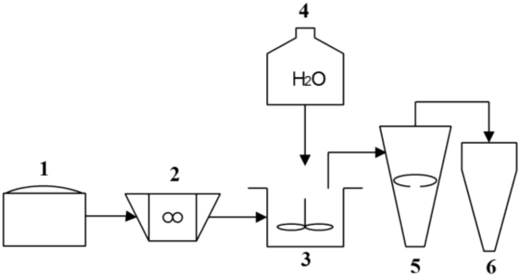
After 24 hours there were no differences in growth nature and intensity of bacteria *Ps.aeruginosa* between the control plate and samples 1, 2 and 4. Few colonies were observed on sample 3, but no growing of *Ps.aeruginosa* was observed on samples 5 and 6. For bacteria *C.albicans* there were no differences in the nature and intensity of growing between the control plate and samples 1 and 2, but few colonies were observed on samples 3, 4, 5 and 6. In the growth of bacteria *S.aureus* there were no differences between the control plate and samples 1, 4 and 5. Rare growth was observed on samples 2 and 3, but on samples 6 the growth of *S.aureus* was reduced by 50%.

Based on obtained results, Laza and Iecava clays do not have antibacterial properties.

9. Technological shemes of clays preparation for application in cosmetic products

Based on obtained results, clay preparation technologies depending on their intended use in cosmetic products were developed. Since the properties of clays depend on their mineralogical composition, the developed technological shemes are attributed only on clays with similar mineralogical composition as here investigated.

Figure 18 shows technological sheme of clay preparation for application in cosmetic products as UV filters with low SPF values.

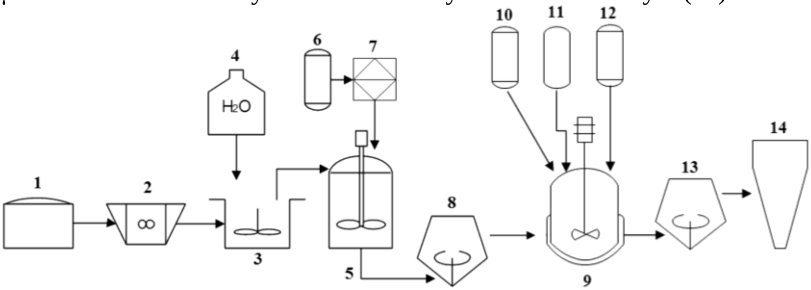


1 – untreated clays, 2 - chrushing, 3 – mixing and settling tank, 4 – distilled water, 5 – hydrocyclone or centrifuge, 6 – spray or fluid bed dryer

Fig.18. Technological sheme of clay preparation for application as UV filters

After obtaining the clays they are stored in a shed (1), dryed to certain moisture content for easier chrushing process (2). Afterwards the chrushed clays are moved to mixing and settling tank (3) and mixed with water (4) for deaggregation of clay mineral particles. The heaviest particles are allowed to settle, where the required sedimentation time can be calculated from Stokes equation. To obtain clay fraction under 2 μm, hydrocyclone or centrifuge (6) can be used. The obtained clay fraction is dryed in spray or fluid bed dryer (7).

Iecava, Laza and Prometejs clay samples after the removal of iron compounds showed the highest adsorption properties. Figure 19 shows technological sheme of clay preparation for application as sorbents in purifying masks. Description of the sheme from the beginning to the mixing (including) is the same as for Figure 18. Then the suspension is settled to obtain particles with size under 63 μm, where the required sedimentation time can be calculated from Stokes equation. The obtained fraction is moved to vessel with gas drain and pH sensor (5) for dissolution of carbonates. 1 M HCl (6) is added with the dispenser (7). The pH of the suspension is controlled not to be lower than 4.5. When the pH of suspension is ~ 5 and constant for several hours, it is moved to tube filter or rotary vacuumfilter (8) for filtration and washing, until the pH of filtrate is ~ 7. The washed clay sediments are moved to thermostatically controled reactor (9) and 3 M sodium citrate (10) and 1 M $NaHCO_3$ (11) solutions are added. The suspensions are heated to 75-80°C temperature and solid sodium dithionite (12) is added. If the colour does not change to blue, more dithionite is added. The suspension is filtered with tube filter or rotaty vacuumfilter (13) ans washed with NaCl for few times and then with distilled water, until the electric conductivity of the filtrate is under 100 μS/cm. The washed clay sediments are dryed in fluid bed dryer (14).

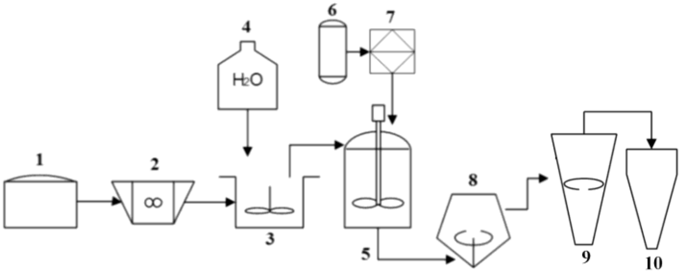


1 – untreated clays, 2 - chrushing, 3 – mixing and settling tank, 4 – distilled water, 5 – vessel with mechanical mixer, gas drain and pH sensor, 6 – 1 M HCl, 7 – dispenser, 8, 13 – tube filter or rotary vacuumfilter, 9 – thermostatically controlled reactor with mechanical mixer, 10 – 3 M sodium citrate, 11 – 1 M $NaHCO_3$, 12 – sodium dithionite, 14 – fluid bed dryer

Fig.19. Technological sheme of clay preparation for application as sorbents in purifying masks

From the investigated clays, the addition of samples Iecava, Ie-HCl and Ie-C to glycerol solutions showed the highest viscosities. The addition of samples L-HCl and L-C increased the viscosity of glycerol solutions 1.5-2 times less than Iecava clays, but the addition of sample Pavari – 3-4 times less than Iecava clays. From this point of view, the most convenient is to use Iecava clays, but at the same time cosmetic products have various viscosities (thicker and thinner) and colour is an essential factor. The white Pavari clays can be used in products with low viscosity, for example, in shampoos. The brown Laza and Prometejs clays could be used in decorative cosmetics (cream eye shadows, skin tone creams) and also in sunscreens, at the same time being also one of the UV filters. The gray Iecava clays can be used in cream eye shadows, shampoos and soaps.

The possible technological sheme of Pavari clays (without carbontes) preparation as thickeners is the same as shown in Figure 18. Figure 20 show technological sheme of carbonate containing clays. Description of the sheme from the beginning to the filtration and washing (including) is the same as for Figure 18. Then clay fraction under 2 μm ir obtained by hydrocyclone of centrifuge (9) and dryed in fluid bed dryer (10).



1 – untreated clays, 2 - chrushing, 3 – mixing and settling tank, 4 – distilled water, 5 – vessel with mechanical mixer, gas drain and pH sensor, 6 – 1 M HCl, 7 – dispenser, 8 – tube filter or rotary vacuumfilter, 9 – hydrocyclone or cenfrifuge , 10 – fluid bed dryer

Fig.20. Technological sheme of clay preparation for application as thickeners

Considering the stabilization results of oil-in-water emulsions, clay fractions that form viscous suspensions can be used as emulsifiers. By increasing the viscosity of suspension, the stabilizing effect of emulsions also increases. From the investigated clays, untreated Iecava clay fraction can be used as the most effective emulsifier, which can be obtained as showed in Figure 18.

CONCLUSIONS

1. Properties of Latvian illite clays for application in cosmetics depend on the amount of clay minerals, the presence of other non-clay minerals and particle size distribution.
2. Illite containing clay fractions, obtained from untreated clays and after dissolution of carbonates, can be used as thickeners in glycerol containing products, because their addition improves rheological properties of glycerol/water solution – the viscosity increases several times and the flow becomes pseudoplastic.
3. Illite containing Latvian clays with fraction under 63 μm before and after the treatment can be used as sorbents in purifying facial masks, because their adsorption of oleic acid and squalene is comparable with commercial illite and chlorite containing facial masks. Adsorption properties of clays depend on the amount of clay minerals and particle size composition. The highest increase in adsorption is after removal of iron compounds.
4. Illite containing clay fractions, obtained from untreated clays, can be used as UV filters in sunscreens and other cosmetic products with low SPF factors, at the same time giving a light brown colour. The presence of iron compunds improves UV protection ability of clays.
5. The influence of illite containing clay fraction addition on the stability of oil-in-water emulsions depend on the net negative charge on clay mineral particles and clay fraction suspension viscosity. The stability decreases when the net negative charge on clay mineral particles increases, but the stability increases when viscosity of clay fraction suspension increases.
6. The investigated clays do not posses antibacterial properties, but it is possible to improve the antibacterial properties of clay containing products by addition of silver doped hydroxilapatite.

REFERENCES

1. Vecstaudža J., Stunda-Zujeva A., Irbe Z., et al. Composition of commercial cosmetic clays and suitability of Latvian clays for cosmetic purposes (in Latvian)// Scientific Journal of RTU: Material Science and Applied Chemistry. – 2012. – No.26. – 42.-49. p.
2. Reeves G.M., Sims I., Cripps J.C. Clay Materials Used in Construction.– London: The Geological Society, 2006. – 580. p.
3. Merriman R.J., Highley D.E., Cameron D.G. Definition and characteristics of very-fined grained sedimentary rocks: clay, mudstone, shale and slate. – Nottingham: British Geology Survey, 2003. – 22. p.
4. The Cooperative Soil Survey: Soils Tutorial/ Internets. - http://soils.missouri.edu/tutorial/#
5. Brigatti M.F., Galan E., Theng B.K.G. Structures and mineralogy of clay minerals// Handbook of Clay Science. – Amsterdam: Elsevier Ltd., 2006. – 19.-86. p.
6. Lagaly G. Colloid clay science// Handbook of Clay Science. – Amsterdam: Elsevier Ltd., 2006. – 141.-245. p.
7. Mitsui T. New Cosmetic Science. – Amsterdam: Elsevier Science, 1997. – 499. p.
8. Lagaly G., Reese M., Abend S. Smectites as colloidal stabilizesr of emulsions I. Preparation and properties of emulsions with smectites and nonionic surfactants// Appl. Clay Sci. – 1999. – Vol.14. – 83.–103. p.
9. Hoang-Minh T., Le T.L., Kasbohm J., et al. UV-protection characteristics of some clays// Appl. Clay Sci. – 2010. – Vol.48. – 349.–357. p.

LIST OF PUBLICATIONS

1. I.Dusenkova, V.Stepanova, J.Vecstaudza, V.Lakevics, J.Malers, L.Berzina-Cimdina. Viscosity and plasticity of Latvian illite clays// Acta Geodynamica et Geomaterialia. – 2013. - Vol.10. - No.4. – 449. – 454. p. (in SCOPUS data base)
2. V.Lakevics, V.Stepanova, S.Niedra, I.Dusenkova, A.Ruplis. Thixotropic properties of Latvian illite containing clays// Proceedings of the 9th International Scientific and Practical Conference "Environment. Technology. Resources." – 2013. – Nr.1. – 133.-137. p. (in SCOPUS data base)
3. V.Lakevičs, V.Stepanova, I.Skuja, I.Dušenkova, A.Ruplis. Influence of alkali and acidic treatment on sorption properties of Latvian illite clays// Key Engineering Materials. – 2014. - Vol.604 – 71.-74. p. (in SCOPUS data base)
4. A.Pura, I.Dusenkova, J.Malers. Adsorption of organic compounds found in human sebum on Latvian illitic, kaolinitic and chloritic clays// Clays and Clay Minerals. – 2014. - accepted.
5. I.Dusenkova, J.Malers, L.Berzina-Cimdina. Effect of impurities on the viscosity and stability of illite/glycerol solution dispersions// Clays and Clay Minerals. – 2014. - accepted.

SCIENTIFIC CONFERENCES

Participation in the conferences with reviewed conference proceedings:

1. I.Dušenkova, A.Stunda-Zujeva, V.Stepanova, J.Mālers. Viscosity studies of Latvian illite clays (in Latvian). *Latvijas Universitātes 70. zinātniskā konference: Ģeogrāfija. Ģeoloģija. Vides zinātne*, **2012**, February 3, Riga, Latvia. Book of abstracts, p. 162 – 163. Oral presentation.
2. I.Dusenkova, J.Vecstaudža, V.Stepanova, J.Malers, L.Berzina-Cimdina. Viscosity and plasticity of Latvian illite clays. *14th International Meeting on Experimental Mineralogy, Petrology and Geochemistry*, **2012**, March 4 -7, Kiel, Germany. Book of Abstracts, p. 56. Oral presentation.
3. I.Dusenkova, J.Vecstaudža, V.Lakevics, J.Malers, L.Berzina-Cimdina. Treatment of illitic clays with organic acids. *6th Mid-European Clay Conference*, **2012**, September 4 -9, Pruhonice, Czech Republic. Book of Abstracts, p. 53. Oral presentation.
4. I.Dusenkova, J.Vecstaudža, V.Lakevics, J.Malers, L.Berzina-Cimdina. Influence of complete dissolution of carbonates on the aggregation of clay particles. *RTU 53rd International Scientific Conference*, **2012**,

October 11 -12, Riga, Latvia. Book of Abstracts, p. 87. Oral presentation.

5. I.Dusenkova, J.Malers, L.Berzina-Cimdina. Rheological properties and stability of Latvian illite clay-glycerol suspensions. *1st International Conference on Rheology and Modeling of Materials*, **2013**, October 7 - 11, Miskolc, Hungary. Book of Abstracts, p. 26. Oral presentation.
6. I.Dušenkova, J.Mālers, V.Lakevičs, L.Bērziņa-Cimdiņa. Changes of Fatty Acid and Squalene Sorption on Latvian Clays after Removal of Calcium and Magnesium Carbonates. *RTU 54th International Scientific Conference*, **2013**, October 14 -16, Riga, Latvia. Book of Abstracts, p. 40. Oral presentation.
7. I.Dusenkova, J.Malers, L.Berzina-Cimdina. Adsorption of squalene and oleic acid on Latvian clays before and after dissolution of carbonates. *22nd International Baltic Conference of Engineering Materials & Tribology - BALTMATTRIB 2013*, **2013**, November 14 -15, Riga, Latvia. Book of Abstracts, p. 44. Oral and poster presentation.
8. V.Lakevičs, V.Stepanova, I.Skuja, I.Dušenkova, A.Ruplis. Influence of Alkali and Acidic Treatment on Sorption Properties of Latvian Illite Clays. *22nd International Baltic Conference of Engineering Materials & Tribology - BALTMATTRIB 2013*, **2013**, November 14 -15, Riga, Latvia. Book of Abstracts, p. 92. Poster presentation