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EFFECT OF SURFACE MODIFICATION AS WELL AS TYPE AND IONIC STRENGTH OF ELECTROLYTE ON ELECTROKINETIC PROPERTIES OF TiO_2 AND TiO_2-SiO_2

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Abstract. Electrokinetic properties of the commercial titanium white (Tytanpol® RS) and precipitated TiO_2-SiO_2 composite were studied. As they depend mainly on the character of the surface of materials studied, the effect of the amount and type of surface modifying agents on the electrokinetic potential was analysed. The study was performed on the commercial titania and TiO_2-SiO_2 composite precipitated from an emulsion system, both either unmodified or modified with three organofunctional silanes applied in three different concentrations. The effect of ionic strength of the electrolyte used (KCl, $NaNO_3$ or $AlCl_3$) on the electrokinetic potential of the two systems studied was established. Stability of the dispersive systems studied was evaluated.

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keywords: zeta potential, electrophoretic mobility, TiO_2 and TiO_2-SiO_2 oxide composite, electrokinetic stability, surface modification

1. Introduction

Electrokinetic phenomena belongs to the oldest and the most important area of surface and colloid science. Discovery of such electrokinetic phenomena as electrophoresis, electroosmosis and streaming potential, permitted a description of the electric double layer, which has been of great importance for understanding of the stability of colloids. Results collected from investigation of electrokinetic phenomena have permitted prediction of specific aspects of colloidal systems behaviour (Wall 2010).

The notion of colloidal or dispersive systems, has been for the first time used by Graham and since that time its meaning has evolved. At present the colloidal systems are defined as those having two phases: a dispersed phase (internal phase) and a continuous phase (dispersion medium).

Colloidal systems belong to unstable systems. Their stability depends e.g. on electric charge and surface charge density. Colloidal particles dispersed in the solution are surrounded by ions bearing the opposite charge, which leads to formation of an adsorbed layer. In the neighbourhood of this layer there is formed another one known as diffuse layer. The electrical double layer (e.d.l.) is formed at the interface between the solid and liquid phases (Otterstedt 1998). Between the adsorbed and diffuse layers the electrokinetic (zeta) potential appears.

This potential denoted as ζ, is one of the most important parameters characterising particles of solid suspended in polar and non-polar solutions (Alkan 2005). It permits the calculation of strength and energy of interaction between the two colloidal particles which brings information on stability of the system (resistance to coagulation), dispersion viscosity, floating properties and can help choosing appropriate reagents for their modification (Hunter 1981). Low value of ζ close to zero is characteristic of instable systems, while a high value (either positive or negative) informs about a stable colloidal state (Kosmulski 2001). Strongly charged particles repel one another, which delays or prevents the ageing processes and implies that the fastest coagulation takes place at the isoelectric point (i.e.p.).

In 1941, Derjaguin and Landau explained the phenomena taking place in stable aggregations on the basis of the interplay between the attractive van der Waals forces and electrostatic repulsion force. In 1948, Verwey and Overbeek formulated a theory of liophobic colloids, which was practically identical to that proposed by Derjaguin and Landau and that is why it has been referred to as the DLVO theory (Yoon 1996; Wu 1999; Bergua 2006). Unfortunately, the theory does not work for the interactions between closely neighbouring particles. The extended XDLVO theory also takes into account the acid-base interactions according to the Lewis theory. The XDLVO theory claims the total energy of interactions between particles is a sum of the energies of van der Waals interactions, electrical double layer and Lewis acid-base interactions.

The knowledge of ζ potential brings information on several properties of dispersed systems. The potential depends to a significant degree on the type of particles, type of the medium in which they are dispersed and the type of ions present in the medium. The zeta potential responds to changes in pH, temperature and concentration of particular components (Jayaweera 1993; Leong 2005; Erdemoglu 2006) as well as in the ionic strength of the electrolyte used. Increase in the ionic strength leads to a compression of the diffuse layer and reduction in the zeta potential. High ionic strength leads to a decrease in the zeta potential values at a constant pH at all types of surfaces. It has been proved that at low concentrations of electrolyte (0.001M) the zeta potential takes values close to that of the surface potential. There are exceptions to the rule, when the electrophoretic mobility and zeta potential are independent of the ionic strength in a certain pH range, e.g. the electrokinetic curve is insensitive to ionic strength in an acidic medium. With increasing ionic strength the zeta potential of silica in an acidic environment decreases (Kosmulski 2010).

Zeta potential measurements have been widely used in advanced industrial technologies, like in water treatment, purification of building walls, biomedicine or in paper production. Determination of the potential has been used for evaluation of the effect of each substrate in colloidal phase which is of particular importance in pharmaceutical, cosmetic and food industries to get stable colloidal systems. Values of zeta potential are also used for prediction of long-term stability of paints or lacquers (Vane 1997; Hunter 2001).

Many papers on TiO_2 zeta potential evaluations have been published (Kosmulski 2009a, 2009b, 2010), but this data are commonly investigated for ungrafted titania, e.g. TiO_2 P25.

The aim of study is to establish the effect of surface modification, type and ionic strength of the electrolyte used on the electrokinetic properties of commercial titanium white and TiO_2-SiO_2 hybrid systems.

2. Experimental

2.1. Materials

The study was performed on the commercial titanium white produced by the sulphate method by the Chemical Works “POLICE” SA, Poland, Tytanpol® RS and TiO_2-SiO_2 hybrid systems precipitated from emulsion according to the method described previously (Siwinska-Stefanska 2010, 2011; Walkowiak 2010).

Changes in the surface morphology of Tytanpol® RS and TiO_2-SiO_2 systems and their hydrophilic properties (into hydrophobic ones) were achieved by addition of silane proadhesive compounds (purchased from Unisil) in the amounts of 0.5, 1 or 3 weight parts in relation to powder (Table 1). The effect of varied amount of the silane introduced on the zeta potential was also of interest in this study.

Table 1. Proadhesive silane compounds used for surface modification of the systems studied

Name	Formula
N-2-(aminoethyl)-3-aminopropyltrimethoxysilane (U-15D)	$H_2N(CH_2)_2NH(CH_2)_3Si(OCH_3)_3$
3-methacryloxypropyltrimethoxysilane (U-511)	$CH_2=C(CH_3)COO(CH_2)_3Si(OCH_3)_3$
vinyltrimethoxysilane (U-611)	$CH_2=CHSi(OCH_3)_3$

2.2. Methods

The colloidal systems studied were characterised by determination of their electrokinetic properties (zeta potential and electrophoretic mobility) influence of modification of TiO_2 and TiO_2-SiO_2 oxide composite with proadhesive silanes in different amounts and that of ionic strength (0.001–0.1M) and type of electrolyte (KCl, $NaNO_3$, $AlCl_3$) on the electrokinetic properties.

Measurements were made by Zetasizer Nano ZS equipped with an autotitrator (Malvern Instruments Ltd.). At first a certain amount of a sample to be studied was dispersed in a given electrolyte solution. Then, pH was measured by the autotitrator using a glass electrode and a desired pH value was adjusted by introducing a solution of 0.2 M HCl or 0.2 M NaOH. A fraction of the sample was then pumped by a peristaltic pump to a measuring cell in which electrophoretic mobility was measured. Finally, on the basis of the results the zeta potential was calculated from the Henry equation.

3. Results and discussion

The first stage of the study was devoted to determination of the influence of modification of the commercial titanium white and TiO_2-SiO_2 system with selected alkoxysilanes (U-15D, U-511, U-611) on the zeta potential. Figure 1a presents the zeta potential as a function of pH for unmodified TiO_2 RS and TiO_2 RS modified with 0.5, 1 or 3 wt./wt. of *N*-2-(aminoethyl)-3-aminopropyl-trimethoxysilane (U-15D). Measurements were performed in a 0.001M KCl solution for pH in the range from 1.7 to 11.

The zeta potential of unmodified TiO_2 RS, took almost exclusively negative values varied from 7 to (-43) mV for the above pH range. The isoelectric point was reached at pH close to 2.4. After modification with U-15D in the amount of 0.5 wt./wt. and for pH in the range 1.7–8.5, the zeta potential assumed positive values. The sample was stable at pH from 1.7 to 5.3. An increase in *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane content to 1 wt./wt. caused a small shift of the electrokinetic curve towards more basic pH relative to those modified with 0.5 wt./wt. of this silane. The isoelectric point was reached at pH close to 8.9. The zeta potential of this system varied from 49 to -24 mV for pH varying from 1.7 to 11 and was stable for pH from 1.7 to 6.5. When the TiO_2 RS system was modified with 3 wt./wt. of U-15D, the shift of the electrokinetic curve towards higher pH was the most pronounced and the zeta potential took almost only positive values, varying from 54 to -11 mV and reaching i.e.p. at pH close to 10.

Modification of TiO_2 RS system surface with *N*-2-(aminoethyl)-3aminopropyl-trimethoxysilane resulted in a significant shift of the electrokinetic curve towards higher pH, relative to the curve for the unmodified sample. An important process for this sample is the ionisation of $-NH_2$ groups. High density of H^+ ions induces formation of NH_3^+ groups, so that the modified surface has positive sign. With increasing H^+ ions concentration the ionisation becomes limited and the surface charge is reduced (Jesionowski 2010). The following reactions take place: $–NH_2 + H^+ = –NH_3^+$ and $–NH_3^+ + OH^– = –NH_2 + H_2O$.

Surface modification with amine compounds leads to high values of the isoelectric point, which is related to basic character of the surface. The TiO_2 or TiO_2-SiO_2 oxide composite surface treatment with aminosilane is illustrated in Fig. 1.

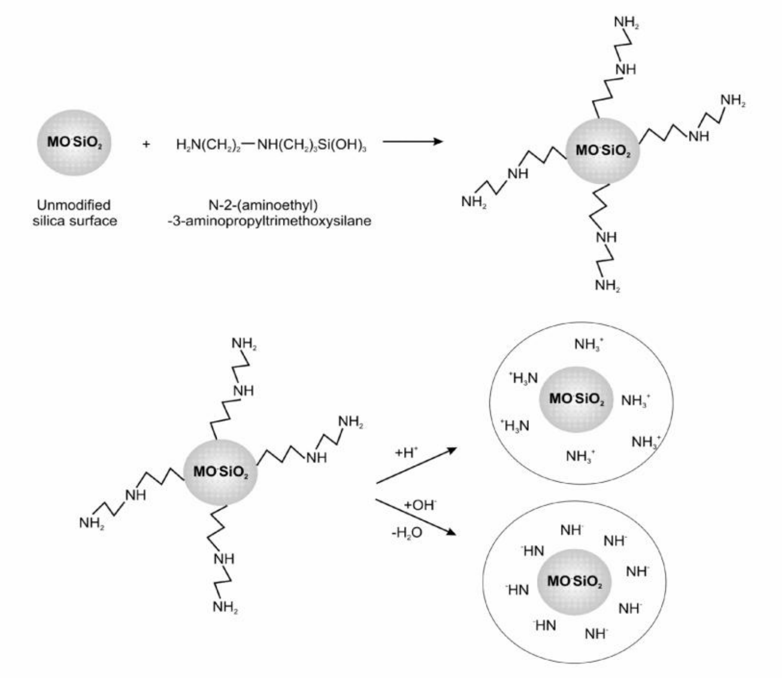
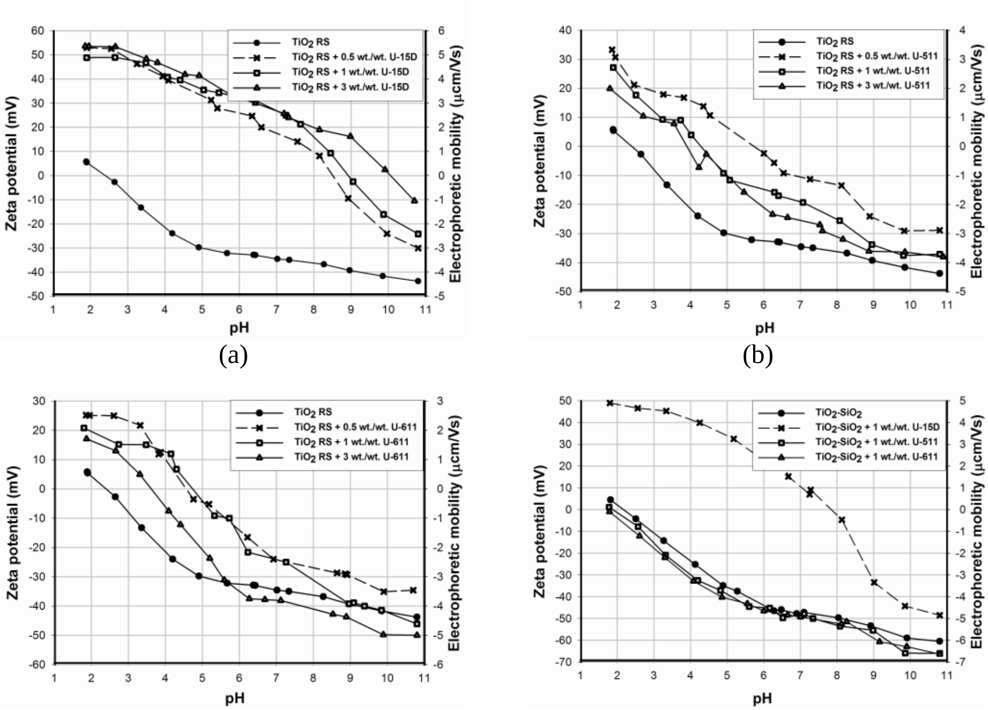


Fig. 1. Scheme of inorganic support modification with
N-2-(aminoethyl)-3aminopropyltrimethoxysilane

Plots of zeta potential measured in a 0.001M KCl solution versus pH for the TiO_2 RS unmodified and modified with 0.5, 1 and 3 wt./wt. of 3-methacryloxypropyltrimethoxysilane (U-511) are presented in Fig. 2b. The electrokinetic curve obtained for the TiO_2 RS sample modified with 0.5 wt./wt. of U-511 reaches the isoelectric point at pH close to 5.8. The zeta potential varied from 33 to -29 mV over pH from 1.7 to 11. Modification of titanium white with 1 and 3 wt./wt. of U-511 leads to a small shift of the electrokinetic curves towards lower pH values with respect to the curve for the sample modified with 0.5 wt./wt. of 3-methacryloxypropyltrimethoxysilane. Both former curves reach i.e.p. at pH close to 4.3 and the potential values vary between 28 and -38 mV. The sample modified with 1 wt./wt. of U-511 shows high stability for pH 8.5 to 11, while that modified with 3 wt./wt. for pH range of 7.7–11.

Changes in the zeta potential as a function of pH for TiO_2 RS unmodified and modified with 0.5, 1 and 3 wt./wt. of vinyltrimethoxysilane (U-611), measured in a 0.001M solution of KCl, are presented in Fig. 2c. The sample modified with 0.5 wt./wt. of U-611 is characterised by the electrokinetic curve shifted towards basic pH values with respect to that recorded for the unmodified sample, reaching i.e.p. at pH close to 4.6. This sample is stable at pH from the 9 to 11 and its zeta potential values vary from 25 to -33 mV over the pH range analysed. For the sample of

TiO_2 RS modified with 1 wt./wt. of U-611 the isoelectric point is reached at pH close to 4.8. The zeta potential of this sample varies from 21 to -46 mV and the sample is stable for pH from 7.9 to 11. For the sample modified with 3 wt./wt. of vinyltrimethoxysilane the zeta potential varies from 18 to -50 mV and i.e.p. is reached at pH near 3.6.



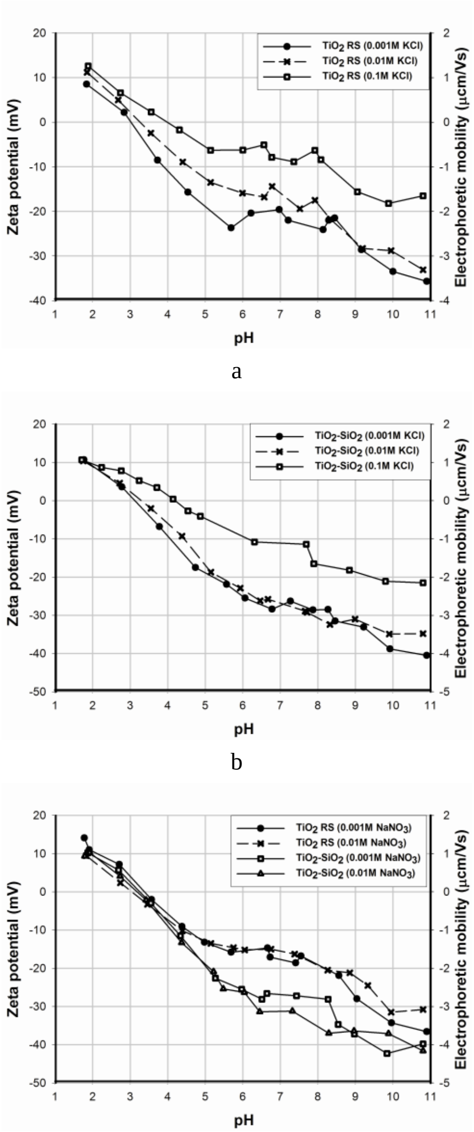
(a) (b)

(c) (d)

Fig. 2. Zeta potential and electrophoretic mobility versus pH for TiO_2 RS unmodified and modified with 0.5, 1 or 3 wt./wt. of (a) U-15D, (b) U-511, (c) U-611 and (d) for TiO_2-SiO_2 oxide composite

The electrokinetic curves estimated for TiO_2-SiO_2 composite modified with 1 wt./wt. of the silanes U-15D, U-511 and U-611 are shown in Fig. 2d. Relations between the curves are similar to those observed for the analogously modified surface of TiO_2 RS. The most pronounced changes in the electrokinetic properties were noted as a result of modification of 1 wt./wt. of U-15D, while the changes caused by modification with 1 wt./wt. of U-511 and U-611 with respect to the curve obtained for the unmodified TiO_2-SiO_2 sample were insignificant.

In the next stage of the study the subject of concern was the influence of ionic strength and type of the electrolyte on the zeta potential of TiO_2 and TiO_2-SiO_2 hybrid systems. The plots of zeta potential as a function of pH for solutions of different ionic strength obtained for TiO_2 RS and TiO_2-SiO_2 are presented in Fig. 3 a, b. The increase in concentration of the electrolyte used in the study (from 0.001 to 0.1M KCl), resulted in a shift of the electrokinetic curve towards lower values of zeta potential. When 0.001M solution was used, then over the whole pH range, the zeta potential changed from 7 to -37 mV for TiO_2 RS and from 11 to -40 mV for TiO_2-SiO_2. The zeta potential values obtained in the KCl solution of 0.1 M varied from 12 to -17 mV for TiO_2 RS and from 11 to -21 mV for TiO_2-SiO_2.



a

b

c

Fig. 3. Zeta potential versus pH for TiO_2 RS and TiO_2-SiO_2 for different ionic strengths of the electrolyte (KCl, $NaNO_3$)

Figure 3c presents the zeta potential measured versus pH for TiO_2 RS and TiO_2-SiO_2 for different ionic strengths of the $NaNO_3$ solution used as an electrolyte. Changes in the ionic strength of the electrolyte were found to have a significant effect on the zeta potential values, especially in the alkaline pH range. Results confirmed the literature reports describing the influence of the ionic strength on the zeta potential (Kosmulski 2010).

Aqueous solutions of electrolytes are divided into neutral (e.g. KNO_3) and those containing specifically adsorbing ions (e.g. $Ca(NO_3)_2$ or $Pb(NO_3)_2$). The monovalent counterions (Na^+) cause a compression of the electrical double layer and that is why they reduce the zeta potential, but they do not change the charge on the particle of a given material. The multivalent cations or their hydrated forms reverse the sign of the charge by adsorption in the Stern layer. Adsorption of $Al(OH)_3$ in the Stern layer is favoured because of hydrogen bonds formation between the OH groups and oxygen ions and hydroxyl groups on the particles of a given material (Lyklema 1984; Hiemenz 1997).

The plots of zeta potential versus pH for TiO_2-SiO_2 measured in a solution of $AlCl_3$ are presented in Fig. 4. The use of $AlCl_3$ as an electrolyte resulted in increased zeta potential values which reached a maximum value at pH close to 4.5, irrespectively of the ionic strength. For higher pH (from 4.5 to 11) the zeta potential values decrease.

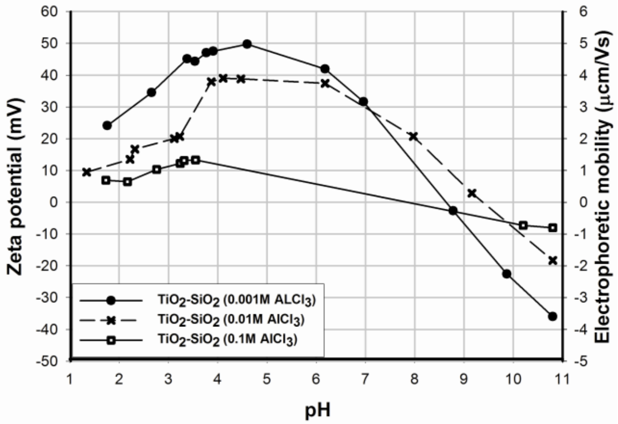


Fig. 4. Zeta potential versus pH of TiO_2-SiO_2 for different ionic strength of $AlCl_3$

4. Conclusions

The above presented and discussed results have shown that the electrokinetic behaviour of the commercial titanium white differed from that of the synthesised TiO_2-SiO_2 hybrid system. The most pronounced affect on the zeta potential values had the modification with U-15D silane. With increasing amount of this modifier used, the electrokinetic curves were shifted towards higher pH and the zeta potential took mostly positive values in the pH range studied. The modification with U-511 and

U-611 silanes did not cause significant changes in the character of electrokinetic curves. The type of electrolyte used (KCl, $NaNO_3$ or $AlCl_3$) and changes in its ionic strength also had important effect on the values of zeta potential.

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References

ALKAN M., DEMIRBAŞ Ö., 2005, Electrokinetic properties of kaolinite in mono- and multivalent electrolyte solutions, Micropor. Mesopor. Mat. 83, 51–59.

BERGUA U., ROBERTS W., 2006, Colloidal silica: fundamentals and applications, CRC Press, New York.

ERDEMOGLU M., SARIKAYA M., 2006, Effects of heavy metals and oxalate on the zeta potential of magnetite, J. Colloid Interface Sci. 300, 795–804.

HIEMENZ P.C., RAJAGOPALAN R., 1997, Principles of colloid and surface chemistry, Marcel Dekker, New York.

HUNTER R., 1981, Zeta potential in colloid science, Academic Press, Sydney.

HUNTER R., 2001, Measuring zeta potential in concentrated industrial slurries, Colloids Surf. A 195, 205–214.

JAYAWEERA P., HETTIARACHCHI S., 1993, Determination of zeta-potential and pH of zero charge of oxides at high-temperatures, Rev. Sci. Instrum. 64, 524–528.

JESIONOWSKI T., CIESIELCZYK F., KRYSZTAFKIEWICZ A., Influence of selected alkoxysilanes on dispersive properties and surface chemistry of spherical silica precipitated in emulsion media, Mat. Chem. Phys. 119, 65–74.

KOSMULSKI M., 2001, Chemical properties of material surfaces, Marcel Dekker, New York.

KOSMULSKI M., PROCHNIAK P., ROSENHOLM J.B., 2009a, Electroacoustic study of titania at high concentrations of 1-2, 2-1 and 2-2 electrolytes, Colloids Surf. B 1-3, 106–111.

KOSMULSKI M., PROCHNIAK P., ROSENHOLM J.B., 2009b, Electrokinetic study of adsorption of ionic surfactants on titania from organic solvents, Colloids Surf. A 1-3, 298–300.

KOSMULSKI M., 2010, Surface charging and points of zero charge, CRC Press, New York.

LEONG Y. K., 2005, Yield stress and zeta potential of nanoparticulate silica dispersions under the influence of adsorbed hydrolysis products of metal ions - Cu(II), Al(III) and Th(IV), J. Colloid Interface Sci. 292, 557–566.

LYKLEMA J., 1984, Points of zero charge in the presence of the specific adsorption, J. Colloid Interface Sci. 99, 109–117.

OTTERSTEDT J.E., BRANDRETH D.A., 1998, Small particles technology, Plenum Press, NewYork.

SIWINSKA-STEFANSKA K., PRZYBYLSKA A., JESIONOWSKI T., SOJKA-LEDAKOWICZ J., OLCZYK J., WALAWSKA A., 2010, Wpływ kompozytu tlenkowego TiO_2-SiO_2 na właściwości barierowe wyrobów włókienniczych, Przem. Chem. 89, 1661–1666.

SIWINSKA-STEFANSKA K., PAUKSZTA D., JESIONOWSKI T., 2011, Właściwości fizykochemiczne kompozytów TiO_2/SiO_2 otrzymanych w wyniku nukleacji układu reakcyjnego, Przem. Chem. 90, 1–11.

VANE L.M., ZANG G.M., Effect of aqueous phase properties on clay particle zeta potential and electroosmotic permeability for electrokinetic soil remediation processes, J. Hazard. Mater. 55, 1–22.

WALKOWIAK M., OSINSKA M., JESIONOWSKI T., SIWINSKA-STEFANSKA K., 2010, Synthesis and characterization of a new hybrid TiO_2-SiO_2 filler for lithium conducting gel electrolytes, Cent. Eur. J. Chem. 8 (6), 1311–1317.

WALL S., 2010, The history of electrokinetic phenomena, J. Colloid Interface Sci. 15, 119–124.

WU W., GIESE R.F., van OSS C.J., 1999, Stability versus flocculation of particle suspensions in water – correlation with the extendend DLVO approach for aqueous system, compared with classical DLVO theory, Colloids Surf. B 14, 47–55.

YOON R., MAO L., 1996, Application of extandend DLVO theory, J. Colloid Interface Sci. 181, 613–26.