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APPLICATION OF TITANYL SULPHATE FOR MANUFACTURING PAPER CONTAINING TiO₂ FILLER

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The aim of research was first, to study the interactions between components for finding out how pH effects on ζ -potential, dewatering rate and retention of TiO₂/MCC mixtures with/without titanyl sulphate in order to find a way to titanyl sulphate hydrolysis in a papermaking process. The maximum heterocoagulation interactions between TiO₂, MCC and TiOSO₄ were revealed in the pH range 4.4–5.6. Second, handsheets made from refined chemical pulp, titanyl sulphate and TiO₂ at pH 4.4 were investigated. The handsheets were formed and studied conventionally and with scanning electron microscopy (SEM). It was shown that titanyl sulphate hydrolysis leads to formation of translucent polymer film covering the fibres and TiO₂ particles. The maximum first-pass ash retention reached is lower than its values usually obtained with an organic polymer. Addition of titanyl sulphate led to higher strength, but lowered opacity and brightness compared to a reference sample. The use of low dosage of titanyl sulphate together with a filler improved air permeability. As there exist certain advantages/disadvantages of titanyl sulphate application, extended research is needed to find suitable conditions for its applying to mass paper and board grades production.

Keywords: Titanyl sulphate, titanium dioxide, polynuclear hydrolysis compounds, microelectrophoresis, microcrystalline cellulose, handsheets.

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Introduction

Uniqueness of cellulose fibres provide well recognized features to the paper products. However, their natural properties do not always meet demands for the whole range of paper grades and not fully comply with all aspects of the paper production process. Albeit the impressive results achieved by the modern paper technology there is still a room for improvement both the production process and paper properties. One of the ways to continue is finding suitable chemical additives and fillers. Addition of them can compensate insufficient fibre natural properties or even give specific unusual properties to cellulose paper, like higher wet strength, longer water-repellency, flame retardant etc. Additives are important for specialties, like decorative base paper or sack paper, and for handmade papers. To meet the desired properties to cellulose fibre materials, various components are typically added to the stock like fillers, retention aids, sizing agents, resins, specific mineral components etc [1].

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When a filler is applied to the stock, its retention and performance are critical issues. It is quite important for paper containing TiO₂ filler, because it is, first, among the most expensive ones, and second, it is used to produce high performance paper specialties. Instead of purely mechanical retention, which is not economically feasible due to the low first-pass ash retention and lower mechanical properties compared

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to the similar filled paper obtained with the aid of chemical retention [2]. Therefore, the chemical additive is improved to be used for retention. Nowadays the paper technology for the most popular grades relies on the use of polyelectrolytes. When they are used, the high retention is achieved [3]; however, the formation and dewatering may suffer, felts and wires could be plugged, and the brightness may decrease either due to diffusion of the light on the polyelectrolyte/filler interface or by the chemical reaction between cationic polyelectrolytes and optical brighteners. As an alternative, there are available some salts of polyvalent metals, hydrolysis of them may lead to the formation of inorganic polymer-like polynuclear compounds, acting like synthetic polymers. Titanyl sulphate one of those was selected for our study. Titanyl sulphate is the famous for being an intermediate product in the commercial production of TiO_2 pigments by conventional sulphate route [4]. It is also one of the strongest complexing agents, its hydrolysis compounds have a large sorption capacity and react with almost all classes of organic matters to form insoluble complexes [5]. If addition of titanyl sulphate leads to the formation of stable floccules during wastewater clarification and a well-filtered precipitate is formed, we have assumed that it can be used as a remedy for improvement of papermaking processes. Hydrolysis of titanium ions in diluted sulphuric acid is a complex physicochemical process, when the concentration of titanyl sulphate is low; the titanyl ions are present mainly in the monomeric form [4]. The chemistry of titanyl sulphate hydrolytic transition at the room temperature and low concentration can be represented as a chain of transformations leading to the formation of polynuclear hydrolysis compounds of amphoteric and hydrated hydroxide oxotitanium of a variable composition [5]. At the higher temperature, the hydrolysis chain leads to the formation of $\text{TiO}(\text{OH})_2$ [6].

There are some publications concerning titanyl sulphate mostly on obtaining of an ultrafine TiO_2 powder by high-temperature hydrolysis of diluted titanyl sulphate solution in a weak acidic medium [7]. Nevertheless, there are only few publications about the possible application of titanyl sulphate hydrolysis compounds in papermaking. For example, it was proposed to obtain a new mineral phase of finely dispersed TiO_2 particles during reaction of titanyl sulphate with chemical pulp by controlled hydrolysis at the temperature of 70 °C and the concentration of sulphuric acid up to 0.25 M [8]. Another suggestion was to use titanyl sulphate hydrolysis to generate a TiO_2 filler with mineral talc powder carrier with subsequent filtration, drying and incineration [9]. However, it has not been reported any proposals to use titanyl sulphate as a papermaking additive. To study the application of titanyl sulphate for manufacturing of paper containing TiO_2 filler our research has been divided into two parts:

1. Studies of TiO_2 /MCC/Titanyl sulphate mixtures to understand the interactions between the components;
2. Production and evaluation of handsheets to observe the effect gained in process and paper properties.

Materials and Methods

Materials. Titanium dioxide (CAS 13463-67-7) was a synthetic inorganic white powder of the anatase crystal form having a particle size range from 200 to 500 nm (GOST 9808). For the preparation of TiO_2 suspension, the powder (0.025 g) was placed in 500 cm^3 of distilled water and treated for 10 min in an ultrasound bath. Titanyl sulphate (CAS 13825-74-6) corresponded to a pure grade by TU 6-09-01-279-75 supplied by Reachim (Saint Petersburg, Russia). It was delivered in the form of a white powder. To prepare a titanyl sulphate solution with the concentration of 0.1 M, 1.96 g of $\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$ was placed into 100 cm^3 of 1 N sulphuric acid and treated for 30 min in the ultrasound bath. The solution was used within 24 h. It should be noted that the prepared solution was cloudy.

Microcrystalline cellulose (MCC, CAS 9004-34-6) was used as a cellulose model for the microelectrophoretic measurement and filtration analysis. Early in the literature, MCC was proposed as a good cellulose model [10] to study electrokinetic phenomena by this visual technique. The measurement is based on a direct microscopic observation of the particle movement. It has been used for MCC since seventies [11] and it is still used for this kind of objects because of simplicity, low operational costs and the well-recognised set-up of the method [12]. MCC was a fraction of cotton origin of industrial P grade produced by Polyeks Company (Biisk, Russia), having a particle size range from 1 to 100 μm as measured by optical microscopy and proofed by scanning electron microscopy (SEM). Fig. 1 shows an image of the unscreened MCC. Prior to use, the larger particles were eliminated by sedimentation. For the preparation of MCC suspensions 2 g of the powder was placed in 1000 cm^3 of distilled water.

The chemical pulp used for production of handsheets was obtained from Arkhangelsk pulp and paper mill. The final pulp stock consisted of northern bleached hardwood (80%) and softwood (20%) kraft. Prior to use they were disintegrated in a LC pulper of horizontal design with a top loading. Cellulose fibres afterwards were refined separately at a consistency of 1.5% in a LC refiner. The refiner used by the principle of operation was close to a homogenizer with a pair of stator and rotor rings equipped with bar blades. The rings were mounted in the centre of a metal cylin-

drical housing equipped with vanes welded around the wall. The rotor ring was rotating at 1470 rpm. The pulp suspension was continuously circulated during the process under the action of centrifugal and hydraulic forces in a turbulent flow. A refining time and clearance between the blades were used as controlled variables to monitor refining output. The clearance was 0.4 mm and the time was 1 min for hardwood pulp and 0.6 mm and 3 min for softwood pulp respectively. The refined pulp stock was mixed and poured in a proportioner container where continuously being stirred at 200 rpm. The fibre consistency was 0.4%. The degree of beating was measured according to ISO 5267/1 and maintained at 24 ± 1 °SR. The paper samples were formed according to ISO 5269/2. Addition of the titanyl sulphate solution was calculated based on the 40% dried TiO_2 equivalent content.

Zeta-potential measurement. The electrokinetic potential was determined by microelectrophoresis, in which the velocity of the studied particles was observed upon application of DC. Microelectrophoresis as a means to measure zeta potential was chosen to make a judgment for all components. In this study, a conventional modified Abramson cell was used [13], consisting of two cylindrical glass vessels connected to the bottom of a plane-parallel capillary. As reversible electrodes, copper plates immersed in a saturated solution of copper (II) sulphate were used. To isolate the electrode space, an agar jelly was used. The electrokinetic potential of the particles was calculated based on the data obtained on the electrophoretic mobility by the Helmholtz–Smoluchowski equation (written in a SI form):

$$\zeta = \frac{\eta \cdot U}{\varepsilon \cdot \varepsilon_0 \cdot E} = \frac{\eta}{\varepsilon \cdot \varepsilon_0} \cdot v, \quad (1)$$

$$E = \frac{I}{\chi \cdot S}, \quad (2)$$

$$v = \frac{l}{\bar{\tau} \cdot E}, \quad (3)$$

symbols: U –particle velocity, m/s; E – gradient of the potential of the external electric field, V/m; v –electrophoretic mobility, (m/s)/(V/m); ε –dielectric constant of the medium, $\varepsilon = 81$; ε_0 –permittivity of free space, $\varepsilon_0 = 8.85 \times 10^{-12}$ F/m; η –viscosity of the medium, $\eta = 10^{-3}$ Pa·s; I –current, A; χ –conductivity of the dispersion, S/m; S –cross-sectional area of the capillary cell, m^2 ; l –the particle path during the time τ , m; $\bar{\tau}$ –the average time of passage of the particles through l , s.

The measurements were carried out at a stationary layer. At least 10 particles of each sample were timed.

Filtration analysis. The filtration analysis of $\text{TiO}_2/\text{MCC}/\text{Titanyl sulphate}$ mixtures were performed using filter paper circles of 12.5 cm with a pore size range from 4 to 12 μm according to specification. TiO_2/MCC mixtures were prepared first and the titanyl sulphate solution was added afterwards. The final concentration of titanyl sulphate in the mixture was $0.1 \cdot 10^{-3}$ M. The measurements were carried out over a wide pH range from 3.2 to 6.7 following stirring the components for about 1 min. The rate of dewatering (V) of the mixtures through the filter circle was calculated based on the time of dewatering of 100 ml. A retention was estimated through the calculation of light transmittance based on intensities of light absorbance of the mixture (A_0) and a filtrate (A_f) at 540 nm. The measurements were performed by using of a Leki spectrophotometer with 1 cm glass cells as an average of three-five tests. The visible turbidity was low enough to use the intensity of light absorbance as a method to estimate the retention. The light transmittance (T) of the components by filter-paper method was calculated by the following formula:

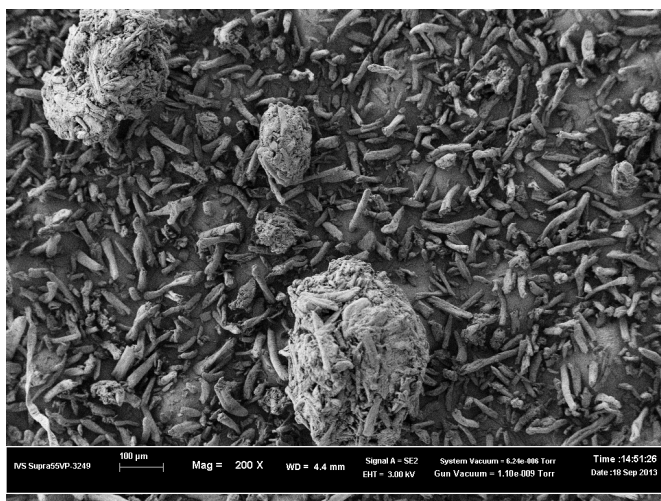


Fig. 1.–SEM image of unscreened microcrystalline cellulose (magnification $\times 200$)

$$T = 100 - \frac{A_f}{A_o} 100, (\%) \quad (4)$$

In all tests, when the pH value was needed to adjust, the desired level was set by addition of either 1 N sodium hydroxide or sulphuric acid. The pH measurements were performed with a glass electrode attached to a Hanna HI 2213 pH meter.

Design of handsheets preparation, testing and characterization. The main purpose of handsheets production was to demonstrate the effect of TiO₂/Titanyl sulphate ratios on the properties. The pH of handsheets preparation was chosen based on filtration analysis result. Two batches of the handsheets of 140±5 g/m² to resemble thick paper grades were prepared with a normal tap water used in a forming column of a sheet former. The first batch was formed with altered dosages of TiO₂/Titanyl sulphate accordingly to the design shown in Table 1. To manufacture a reference “free of any additives” sample it was required 4.4 g. of oven-dried mass of the pulp stock. The necessary volume of the suspension was being corrected for each produced sample as based on the mass of square meter of test handsheets obtained. The ash content was determined by incinerating the dried samples in a muffle furnace at 900 °C following the procedure given in ISO 2144. The first-pass ash retention (*FPR*) was calculated by the following formula:

$$FPR = (1 - \frac{C_o - C_1}{C_o}) 100, \quad (5)$$

symbols: C_o – ash content of pulp stock, %; C₁ – ash content of handsheets, %.

It should be noted that only estimation of the filler retention of the TiO₂/Titanyl sulphate mixtures is possible. It is not entirely correct to calculate the ash content based on the residue mass on ignition expressed in TiO₂, because during the dilution with water and pH raise of the mixture containing titanil sulphate first the polynuclear hydrolysis titanil sulphate compounds of variable composition are formed and only then, they are retained. Actually, the TiO₂ particles from the titanil sulphate solution are generated only during incineration.

The second batch was formed with altered dosages of titanil sulphate at fixed dosage of TiO₂ (2,0 g) and fibre (oven-dried 4.4 g.) to study the general dependence of tensile strength against ash content. This dependence was studied in the range of 1 to 10% titanil sulphate dosages at 1% spacing. The TiO₂ filled handsheets were stored away from sunlight because of possible chemical decomposition of TiO₂.

The tensile index was taken as a mechanical property due to fluctuations in handsheets properties. At least five samples were prepared for each point to calculate mean values. Prior to testing, the samples were conditioned for several hours at a standard controlled temperature (23 °C) and humidity (50% RH). The samples of each batch were tested during one day. Tensile strength was measured and the tensile index was calculated by a PC-controlled vertical Tinius Olsen tensile testing machine with 250 N load cell according to ISO 1924-1. Optical properties (brightness and opacity) were measured by Elrepho L&W Spectrophotometer according to ISO 2470, ISO 2471. The air permeability was measured by a manually operated Bendtsen tester according to ISO 5636-3 at a nominal air pressure of 1.47 kPa.

SEM images were obtained using a Carl Zeiss Supra 55 VP microscope operating at 10 kV. The spectra of chemical elements were analysed by using an Oxford Instruments INCA Energy SEM NanoAnalysis Energy Dispersive X-Ray Spectrometer (EDX) built into the Supra microscope. The Silicon Drift Detector X-Max has an active surface of 80 mm² (it could be measured elements from Be to U).

Table 1. The design of handsheets with different dosages of TiO₂/TiOSO₄. All figures are given in grams, Ref. – the reference zero point sample.

Samples	Ref.	No 1	No 2	No 3	No 4	No 5
TiO ₂	–	2.00	1.00	2.00	0.20	0.20
Titanil sulphate*	–	–	1.00	0.20	0.02	2.00

* The weight of titanil sulphate was calculated based on dried TiO₂ (2/5 of its weight).

Results and Discussions

Effect of pH on ζ -potential, retention and dewatering

The retention of a mineral filler in cellulose suspensions mainly depends on following interrelated parameters: the particle size (shape), surface charge properties, steric effects and conditions of measurement [3]. When particles have opposite charges or zero charge it helps to achieve maximum heterocoagulation interactions between them [14]. Fig. 2 shows the effect of pH on ζ -potential of TiO_2 , MCC and titanyl sulphate hydrolysis compounds. The MCC particles carried a positive charge above pH 2.0 and the TiO_2 particles were positively charged above pH 4.0. At pH greater than 5.5 all studied particles were negatively charged causes difficulties for the application of such systems at neutral papermaking. As far as TiO_2 particles are tiny enough and electrostatic forces govern its interaction with other components of the suspension [15], in order to achieve the highest possible ash retention of a paper it is necessary to run the whole dependence of electrokinetic potential on a pH. In the range of pH 4.0-5.0 it is observed the optimum conditions for heterocoagulation while maintaining the positive charge of titanyl sulphate and the negative charge for studied particles of MCC and TiO_2 .

The electrokinetic data were confirmed by the calculation of light transmittance and dewatering rate for the mixtures reported in Table 2. By increasing pH from 3.2 to 6.7 it was observed a decrease in transmittance of filtrate and in dewatering rate of TiO_2/MCC mixtures. It can be explained by the mutual negative charge rise. The reduction in dewatering rate for these mixtures indicates a suppressed attachment of TiO_2 to MCC and plugging a filtration layer by the TiO_2 particles during the filtration process. When titanyl sulphate was introduced into the TiO_2/MCC mixture, the highest light transmittance of filtrate was observed in the range of pH 4.5–5.6, which corresponds the retention on a filter paper of practically 99%. The dewatering rate practically was not affected by titanyl sulphate addition until pH 5.6, when it was decreased more than twice. Only at pH around 4.5 it was noted still rapid drainage and almost transparent filtrate. At this pH the TiO_2 particles are only negatively charged only slightly and titanyl sulphate compounds are yet positive. There were not observed any effects of titanyl sulphate at pH 3.2, probably, because of strong positive charge and no affiliations of all titanium based compounds at these conditions. By increasing pH up to 6.2 ruined the titanyl sulphate effectiveness in the studied mixtures, only the dewatering rate was still high. The increase in dewatering rate at this pH is probably related to the aggregated TiO_2 particles.

Table 2. The results of filtration analysis

Mixture	pH	A_o	A_f	$T, \%$	$V, \text{ ml/s}$
TiO_2/MCC	3.2	0.432	0.021	95.1	0.142
$\text{TiO}_2/\text{MCC}/ \text{TiOSO}_4$	3.2	0.440	0.018	96.0	0.132
TiO_2/MCC	4.3	0.430	0.089	79.3	0.140
$\text{TiO}_2/\text{MCC}/ \text{TiOSO}_4$	4.5	0.272	0.001	99.6	0.136
TiO_2/MCC	5.3	0.446	0.128	71.4	0.158
$\text{TiO}_2/\text{MCC}/ \text{TiOSO}_4$	5.6	0.342	0.007	98.0	0.051
TiO_2/MCC	6.7	0.417	0.125	70.0	0.198
$\text{TiO}_2/\text{MCC}/ \text{TiOSO}_4$	6.2	0.424	0.130	69.3	0.081

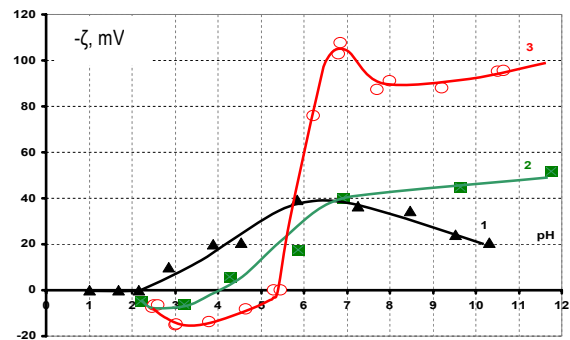


Fig. 2. Effect of pH on ζ -potential of the particles: 1. MCC; 2. TiO_2 ; 3. Titanyl sulphate hydroxyls compounds

Considering of all studied aspects the best interaction of the components should be in the range of pH 4.0–5.0. Because it was too laborious to study the whole pH range, during handsheets making the pH range was maintained at $\text{pH } 4.4 \pm 0.1$.

Properties of handsheets

It is expected that all properties of handsheets obtained with titanyl sulphate ought to be governed by the result of its hydrolytic transition, when the polynuclear hydrolysis compounds are formed and fixed among the fibres. The data depicted in Table 3 show, when only TiO_2 filler was added to the handsheets, it was observed a moderate retention and decreased tensile properties. It is commonly caused by termination of fibre-fibre bonding. At the same time, the higher opacity and brightness have been achieved comparing to a reference sample contain-

ing no TiO_2 . It should be noted that the TiO_2 retention is highly dependent on a pH, a trial sample made of the same furnish at a neutral pH had shown the TiO_2 retention as low as 20%. Addition of titanyl sulphate more than doubled the ash content due to increased retention. Nevertheless, the retention with conventional polyelectrolytes is usually a bit higher as known [16]. Besides the increased retention that is quite beneficial for any additive, it was observed a contradictory effect in terms of optical properties. The brightness and opacity of the handsheets were both decreased in all instances whereas titanyl sulphate was added. This result could be a consequence of densification, coagulation and flocculation of all particles and ions in the aqueous medium. Such behaviour of the additives usually is undesirable for filled grades, such as printing and writing, but could be a specific advantage for the others. At pH 4.4 the addition of titanyl sulphate led to an improvement of physical properties. This phenomenon is beneficial for packaging grades. The more titanyl sulphate was added, the higher strength was. It was observed a typical tendency towards decrease in the air permeability whereas the tensile strength was increased. It is likely due to the more closed pore structure was being formed. As it well known that the intensive fibre bonding leads to porosity increase. When titanyl sulphate and TiO_2 were added together in minor dosages, the strength of the handsheets remained unchanged, whilst the air permeability was greatly improved. This effect belongs to the titanyl sulphate hydrolysis reaction, which cause preflocculation of TiO_2 particles and fibre fines. This phenomenon usually deteriorates drainage. As far as the highest dosages of titanyl sulphate were applied, the tensile strength was much higher comparing to the reference sample. The samples formed could be characterized as having the lowest air permeability and the highest transparency. It took several minutes to form them in a sheet forming column. The handsheets looked yellow and transparent. Hydrolysis of titanyl sulphate apparently causes the forming of new bonds that helps to prevent the normal decrease in tensile properties due to a breakage of fibre-fibre H-bonds, whereas the ash content is increased. It should be taken into account that interactions between the components in the mixture took place in an acidic medium that helps the action of attractive forces. However, the increase in pH as a fact of dilution of pulp stock with a tap water in a sheet former caused the formation of polynuclear oxotitanium compounds. The bond links of them contribute to the paper strength.

As it is seen at Fig. 3 in the titanyl sulphate dosage range from 1 to 10% the ash content of the handsheets was increased from 22 to 34%. The more titanyl sulphate was added the more ash content was. It is worth saying that quite effective dosage of titanyl sulphate was at the beginning, just 1 % caused a growth in the ash content from 15% (see No 1 table 3) up to 22% (see 1% X-axis fig. 3). Such behaviour could be explained by the initial binding of the smallest fraction of TiO_2 particles thus the hiding power decreased that leads to transparency raise. This increase was observed while maintaining the equal tensile properties. Further growth in the ash content resulted in decreased paper strength. Although it is known, i.e. an increase in 5% of the ground calcium carbonate filler cause a reduction of more than 10% of the paper strength [1, P. 34]. Usually the tendency of the tensile strength decrease due to the ash content increase is associated with a reduction in the total number of total fibre-fibre bondings. The curve shape shows that the major changes in paper properties happened between 2 and 4%, and after 6%. Certain changes could be explained by an increase in the degree of fibre involvement in active bonding with the polynuclear oxotitanium compounds.

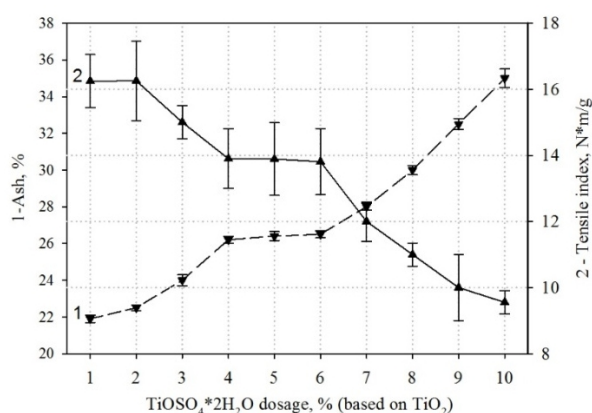


Fig. 3. The influence of titanyl sulphate dosage, calculated in % of dried TiO_2 (2/5 of its weight), on the ash content (1) and tensile strength index (2) of handsheets. Fixed amount of TiO_2 was added (2.0 g)

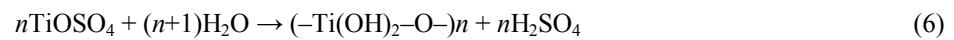
Table 3. Ash content, first-pass retention, Bendtsen air permeability, Tensile index, Opacity (O), Brightness (B) of $140 \pm 7 \text{ g/m}^2$ handsheets being prepared with different ratios of $\text{TiO}_2/\text{TiOSO}_4$ (at pH 4.4 ± 0.1)

No.	Ash, %	FPR, %	Air, ml/min	TI, N*m/g	O, %	B, %
Ref	—	—	1450	25.4	89.7	84.8
1	15.2	33	1500	16.3	99.2	95.0
2	27.0	61	1300	20.4	78.5	77.2
3	36.6	73	1400	11.0	92.5	93.4
4	2.5	50	1800	25.3	88.1	83.4
5	21.1	42	1150	28.8	65.5	73.3

SEM analysis of handsheets

SEM image (Fig. 4) of the handsheets when only TiO₂ filler was added shows that these particles are unevenly placed mainly in the pores of a paper sheet, no spreading between fibres is observed. There are practically no TiO₂ particles being attached to the surface of cellulose fibres. It could be concluded that retention of TiO₂ takes place mainly due to mechanical means, and deteriorates with an increase in a pH value due to increased surface charge and the action of repulsion forces. Certainly, the filler retention also depends on the specific surface, i.e. the degree of refining, it is related to the steric effect of microfibrils. The dependence on refining is explained by the preferential adsorption of TiO₂ on fibrils and small filaments rather than on fibres [15]. The presence of fibrils makes cellulose fibres different from the MCC particles taken as a cellulose model.

Fig. 5 shows the agglomerated particles of TiO₂ in the net of a translucent film of titanyl sulphate hydrolysis compounds which was formed between the fibres and the TiO₂ particles. The presence of these compounds containing titanium was confirmed by EDX microanalysis. The results being measured in different locations show this film consists of 42 to 45 mass% titanium as a chemical element. This titanium content range demonstrates the polymeric character of the film. This range corresponds the polymer chain structure of polynuclear oxotitanium compounds with a formula of $(-\text{Ti}(\text{OH})_2-\text{O}-)_n$. We assume for our concentration and pH ranges, the following reaction of titanyl sulphate hydrolysis may take place:



Thus, the introduction of titanyl sulphate greatly improves the retention of TiO₂ in the handsheets while a decreased tensile strength was compensated by forming of polynuclear oxotitanium compounds bonds of polymer character between fibres and TiO₂ particles.

It is not recommended to use a high dosage of titanyl sulphate because of the suffering of dewatering rate during the sheet forming, the poor optical properties are also issue to consider the titanyl sulphate efficiency of application.

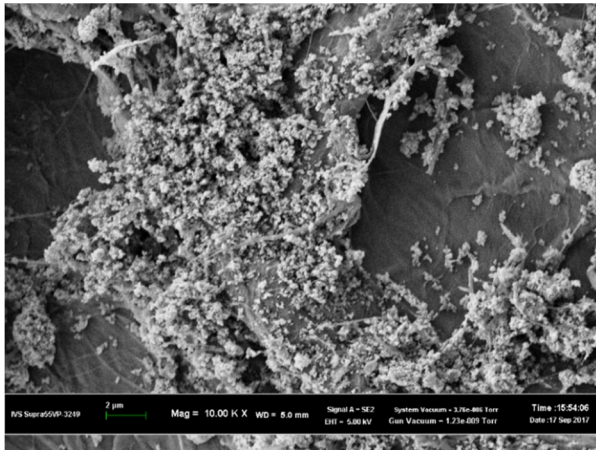


Fig. 4. SEM image of the handsheets where only TiO₂ filler was added (magnification 10K)

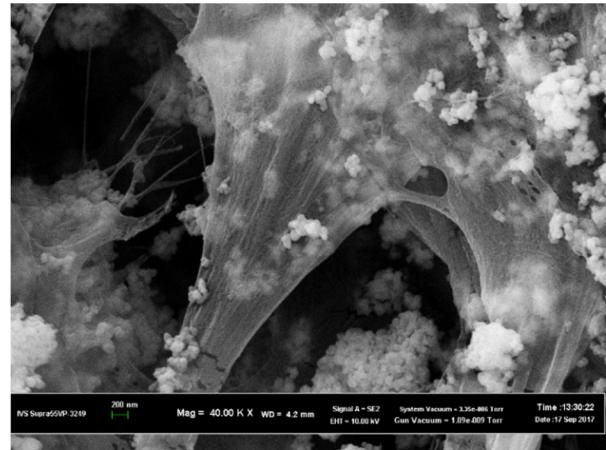


Fig. 5. SEM image of handsheet with 37% of TiO₂ and 5% of titanyl sulphate based on TiO₂ content (magnification 40K)

Conclusions

The application of titanyl sulphate for manufacturing of TiO₂-containing paper was studied. The effects of pH on ζ -potential and light transmittance of the filtrate for different mixtures of TiO₂/MCC/Titanyl sulphate were shown. It is revealed that the maximum heterocoagulation interaction between the components occurs to the range pH 4.4–5.6 due to the opposite charges between TiO₂ and titanyl sulphate, that leads to maximum retention and other process benefits. The handsheets were analysed conventionally and using SEM. It was shown that titanyl sulphate hydrolysis resulted in the formation of a translucent polymer film within the fibres and TiO₂ particles. A small dosage of titanyl sulphate enhanced the strength and the air permeability of the handsheets. A high dosage of

titanyl sulphate increased the filler retention and the strength of comparative handsheets formed without titanyl sulphate, but in this application of titanyl sulphate is difficult to compete with synthetic polymers in terms of the ash retention. Titanyl sulphate does not help to maintain or to increase the optical properties. It seems prospective the application of low dosages of titanyl sulphate in combination with some fillers to obtain the high air permeability, it could be as advantage for instance for a brown sack paper. Apart from white papers, for this kind of a paper grade the optical properties are less important.

The data obtained shows the difference between additives applied in wastewater treatment and for a paper manufacturing. Conventional flocculants and coagulants that are used to decrease a turbidity level are different to papermaking retention aids because the main idea of manufacturing process is obtaining the end product properties.

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