Fabrication of Hydrophobic Coating on Filter Paper from Self-emulsifying Carnauba Wax-alcohol Emulsions with Nano-TiO_2 Particles for Water/Diesel Separation

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Carnauba wax is a natural material with high hydrophobicity. In this study, molten carnauba wax was stably self-emulsified in ethanol without using additional emulsifiers. Hydrophobic titanium dioxide (TiO_2) nanoparticles were dispersed into carnauba wax-ethanol emulsion to form a composite coating on filter paper. The results showed that immersion in the composite coating that contained wax and hydrophobic TiO_2 conveyed to filter paper good hydrophobicity (water contact angle over 140°) and stability against acid or alkali solution. The scanning electron microscopy (SEM) images indicated the presence of micro bead/flake structures on the surface of filter paper. These obtained filter papers could effectively expel water from a water/diesel mixture. The water content in the water/diesel mixture decreased from 10% to 0.01% through the separation from the filter paper.

Keywords: Carnauba wax; Nano TiO_2; Hydrophobic; Water/oil separation

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INTRODUCTION

Carnauba wax is an ester wax of natural origin that is extracted from the leaves of the carnauba palm in Brazil (Mohd 2010). It contains components including aliphatic esters, uncombined alcohols, v-hydroxy esters, and p-methoxycinnamic aliphatic and p-hydroxycinnamic aliphatic diesters having several chain lengths, in which C26 acids and C32 alcohols predominate (Basson and Reynhardt 1988). Carnauba wax is used for food additives, cosmetics, leatherware, and paper agents due to its properties of a high melting point, its lustrousness, and good humidity resistance.

Usually, carnauba wax is emulsified in water for use (Zhang *et al.* 2007). The emulsions are prepared through mixing melting wax, suitable emulsifiers (span-80, cetyltrimethyl ammonium bromide, or lauryl sodium sulfate), and hot water while stirring intensely (Hagenmaier and Baker 1997; Li *et al.* 2010). There is a lot of research on the application of wax-emulsions in paper sizing and coating to enhance its water-resistance (Wu and Wang 2006; Gong *et al.* 2009; Yang *et al.* 2014). In Zhang *et al.*'s research (2014), the wax mixture (beeswax/carnauba wax) was emulsified by cetyl trimethyl ammonium bromide in hot water and then the emulsion was coated on the paper surface. The further heat treatment (60 °C to 70 °C) made the coated paper from hydrophobic or superhydrophobic to "Lotus" state with a water contact angle of 150° to 160°, because a submicrometer structure appeared on the base of the micrometer spherical wax particles (Huang 2012). Zhang *et al.* (2016) added a surfactant material (dodecyl dimethyl amine ethyl ester) into the mixture of carnauba wax and water to form a wax-water emulsion with stirring by a homogenizer, and then the paper coated with the emulsion could resist water with a water contact angle of 125°.

To obtain a stable wax-in-water emulsion, emulsifiers need to be added according to the literature cited above. The waterproof property of wax is considerably reduced with the increase of emulsifier quantity, which may result in failure to attain the preconceived hydrophobicity. In some recent studies, vegetable/animal oil could be emulsified in hot alcohol or other organic solvent without adding emulsifiers. The emulsions are not only evaluated as effective clean fuel substitutes for diesel engines but also for reducing the cost of the emulsification process (Bayer *et al.* 2011). Some researchers (Paul *et al.* 2016) prepared surface-treated filter papers with dipping in hydrophobic paraffin wax/toluene solution and poly(dimethylsiloxane)-b-poly(ethylene oxide) diblock copolymer/methanol solution, respectively. The treated filter papers were superoleophobic underwater and possessed excellent oil–water separation efficiency up to 99% and a rate of uptake about 77 $L \cdot m^{-2} d^{-1}$.

Inorganic nanoparticles, such as TiO_2, SiO_2, and Al_2O_3, coupled with low surface energy chemicals, such as silanes or some kinds of organic acid with long carbon chain, gave high hydrophobicity to materials through coating over them. Xu fabricated superhydrophobic coatings that were prepared from a mixture of nano-SiO_2 and TiO_2 modified by decanoic acid. Cotton fabric coated by this mixture became superhydrophobic and permeable to oil in air (Xu *et al.* 2016).

In this experiment, molten carnauba wax was self-emulsified in ethanol without using any emulsifiers to form a stable emulsion. Furthermore, nano-hydrophobic TiO_2 particles were added into the wax-emulsion to fabricate a rough microstructure on the filter paper. With immersion steps and thermal annealing, the obtained filter papers displayed superior resistance to water and acid/alkali solution, as well as performed well in emulsified water/diesel mixture separation. These filter papers with high hydrophobicity and air permeability removed the emulsified water from the water/diesel mixture effectively.

EXPERIMENTAL

Materials

Nano TiO_2 latex with a primary particle size of 5 nm and a 20% solid content was purchased from Taitang Nanotech Co., Ltd. (Hunan Province, China). Hexadecyl-trimethoxysilane (HDTMS) was from Aladdin Industrial Corporation (Shanghai, China). Ethyl alcohol was purchased from Fuyu Fine Chemical Co., Ltd. (Tianjin, China). The deionized water was made in the lab. Carnauba wax was obtained from Usolf Chemical Technology Co., Ltd. (Qingdao, China).

Preparation of the hydrophobic TiO_2 particles

First, 1.5 g HDTMS, 45 g ethanol, 5 g deionized water, and 0.1 mL acetic acid were mixed in a beaker under magnetic stirring at 30 °C for 1 h. Then, 15 g commercial nano-TiO_2 latex was dropped into this beaker with temperature transferring to 80 °C. After 3 h, the obtained milky mixture in the beaker was centrifuged at 8000 rpm for 5 min and the precipitate was washed by ethanol and water three times.

Next, the white HDTMS-TiO_2 was dried at 60 °C in a vacuum oven for 24 h and ground into powder. The prepared HDTMS-TiO_2 particles were spherical and 38 nm in size.

Preparation of composite coating

Thirty mL ethyl alcohol was brought to boiling in a constant temperature water-bath at 85 °C. Then, 0.3 g of carnauba wax flakes were slowly added within 3 min and the mixture turned into a pale yellow clear solution after the complete melting of the wax. This solution was then put in an ultrasonic instrument with hot water, sonicated for 20 min, and then cooled to room temperature.

Hydrophobic HDTMS-TiO_2 particles were added into the wax/ethanol mixture to form a HDTMS-TiO_2/wax composite coating. Varying the amounts of HDTMS-TiO_2 with mass fractions ranging from 0 to 5/3, the mixtures were then sonicated for 20 min at room temperature.

Fabrication of hydrophobic thin films on filter paper surface

Filter papers without any pre-treatment were immersed into HDTMS-TiO_2/wax composite emulsions for 10 min. Then, the papers were dipped in the HDTMS solution (The concentration of HDTMS solution was 1.5%) for 4 h. Finally, thermal annealing at 100 °C for 30 min was conducted for all of the filter paper samples. As a comparison, we prepared filter papers with immersion into HDTMS-TiO_2 (without carnauba wax) solution then HDTMS solution (The concentration of HDTMS solution was also 1.5%), the thermal annealing was performed, too.

To test the stability against acid and alkali, the obtained hydrophobic paper was immersed in the solution of acid (pH = 1) and alkali (pH = 13) for 5 h, respectively.

Separation of water/oil mixture

The water/diesel mixture was sonicated and stirred for 15 min, respectively, with a mass ratio of 1:9. The separation and filtration process by filter paper was with the help of a water circulating pump under a vacuum degree of 0.005 MPa.

Methods

Characterization

Air permeability of filter paper was tested with a pore size analyzer (100 FM, Porolux, Gent, Belgium). The size of wax and HDTMS-TiO_2 HDTMS-TiO_2 was detected by a particle size analyzer (SZ-100, Horiba, Japan).

The surface morphology and element analysis of the filter paper before and after the treatment was observed with a scanning electron microscope (SEM; Merlin, Zeiss, Germany) operating at 5.0 kV, the surfaces of paper samples were coated with gold in an ion sputtering coating instrument (108auto, Cressington, Watford, England).

Water contact angles (WCA) were measured with a 5 μL deionized water droplet at ambient temperature by using an optical contact angle meter (OCA20, Dataphysics, Filderstadt, Germany). The values of the water contact angle were obtained as an average of five measurements; the diesel water content was determined by a moisture tester (KF870, Metrohm, Herisau, Switzerland).

RESULTS AND DISCUSSION

Chemical Composition Analysis of Filter Paper Surface

The elemental compositions of the paper surface before and after dip-coating were determined by energy dispersive x-ray spectroscopy (EDX). Figure 1a shows the EDX spectrum of blank filter paper. Only carbon (C), oxygen (O), and gold (Au) elements were detected. The C and O were derived from the fibers that formed the original filter paper, and Au was from the spraying of Au on the paper sample during preparation. In Fig. 1b, besides Au, C, and O, titanium (Ti), silicon (Si), and sulfur (S) elements were also detected. The C and O elements came from the carnauba wax, the surface modifier HDTMS, and the filter paper. The Si was from HDTMS and the Ti was from TiO_2. Moreover, S had been detected due to the resin in carnauba wax (Harrin *et al.* 2017). These detected elements confirmed that the carnauba wax/TiO_2 composite coating was effectively formed on the filter paper surface.

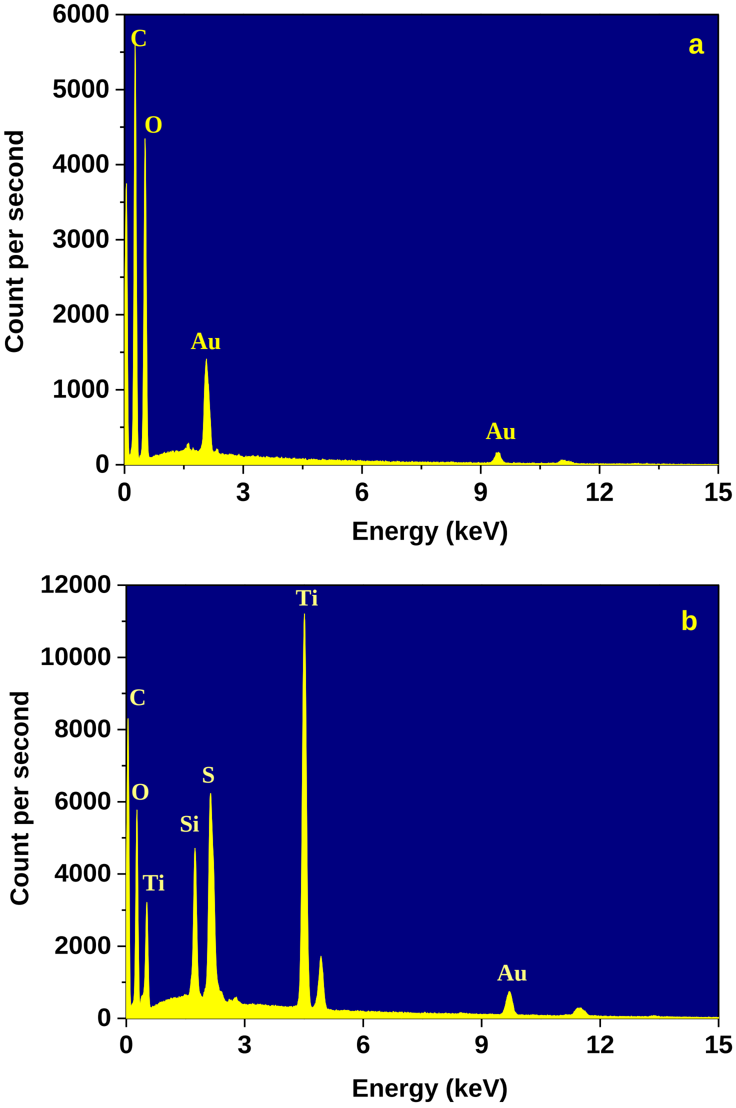

Fig. 1. The EDX spectra of (a) the pristine filter paper and (b) the hydrophobic filter paper

Hydrophobicity of Paper Surface

The original filter paper was entirely hydrophilic with a WCA of 0°. As is well known, the quality of coatings absorbed on the surface of the materials has an important impact on the properties of composite material, such as surface morphology, roughness, and wettability (Gao *et al.* 2014). In this work, the weight gain ratio (based on the dry filter paper) of the as-prepared filter paper was determined by the HDTMS-TiO_2/wax coating. The ratios of HDTMS-TiO_2 to carnauba wax in the composite coating were 0, 0.5/3, 1/3, 2/3, 3/3, 4/3, and 5/3, which are marked in Fig. 2a. As paper was dipped in the pure carnauba wax emulsion and HDTMS solution, it resisted water well but its WCA was only 125°. Adding HDTMS-TiO_2 into the wax-ethanol emulsion made a promotion in the WCA. The WCA of filter papers gradually increased with the increased weight gain of the HDTMS-TiO_2/wax. At the lower weight gain of 1.5%, the WCA reached 130.1°. The highest WCA 148.8° appeared at the weight gain of 6.4%.

As shown in Fig. 2b, the WCA of filter papers immersed in HDTMS-TiO_2 solution and then HDTMS solution was detected. The WCA of filter paper slowly increased when the weight gain of filter paper was below 10%. With 19.4% HDTMS-TiO_2 absorbed on paper, the WCA reached 148°. Clearly, to obtain the same WCA, it required more HDTMS-TiO_2 on the filter paper than the HDTMS-TiO_2/wax.

In this preparation of hydrophobic filter paper, the HDTMS-TiO_2/wax coating was expected to form a rough microstructure on the paper surface because microstructures on the material could help to enhance the hydrophobicity. The following immersion in HDTMS solution would further decrease the surface energy of the filter paper. Through testing by a particle size analyzer, the particle size of HDTMS-TiO_2 was 38 nm and the size of wax in ethanol was approximately 2 μm. The filter paper with the HDTMS-TiO_2/wax coating on the surface would have richer hierarchy microstructures than that of HDTMS-TiO_2 or carnauba wax. Therefore, the hydrophobicity of paper dipped in HDTMS-TiO_2/wax was better at the same weight gain.

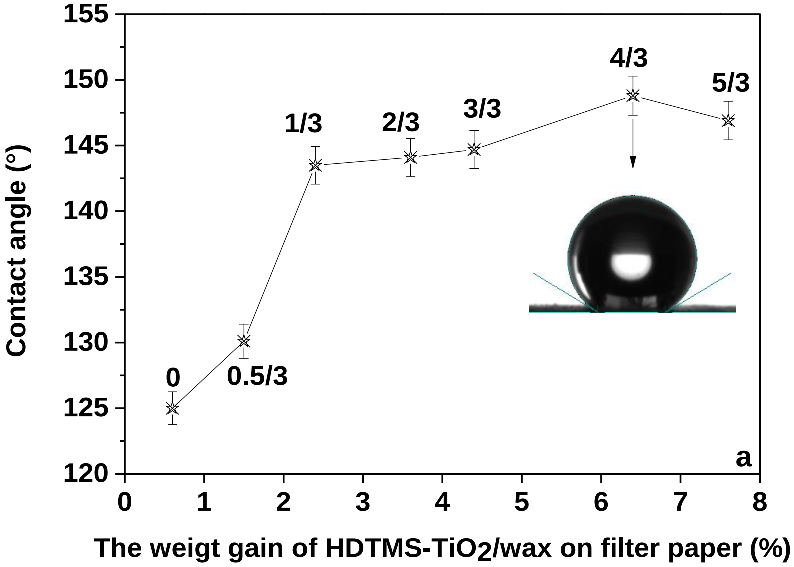

Fig. 2 (a). Contact angles of filter papers after treatment

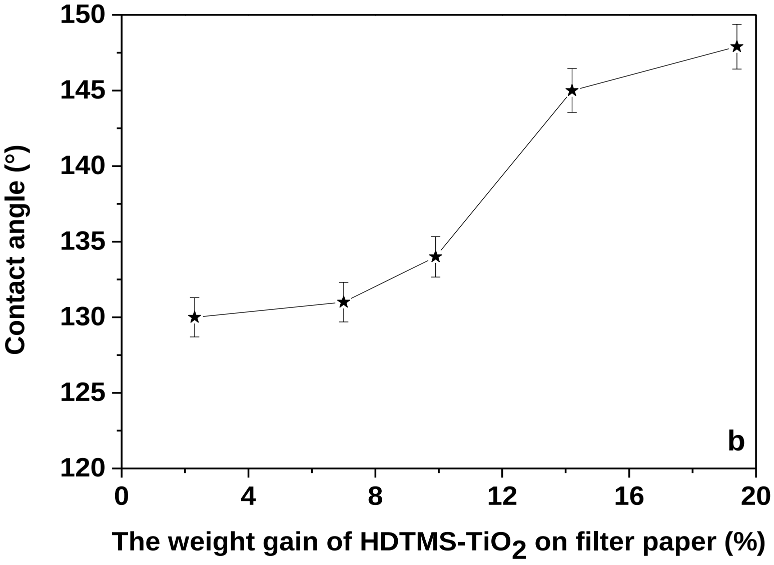

Fig. 2 (b). Contact angles of filter papers after treatment

Table 1. Particle Size of HDTMS-TiO_2 and Carnauba Wax

	Particle size
HDTMS-TiO_2	38 nm
Carnauba Wax	2 µm

Acid/Alkali-resistant Property

To detect the stability against acid or alkali, each paper sample was immersed in hydrochloric acid solution (pH = 1) or sodium hydroxide solution (pH = 13) for 4 h. The WCAs of the filter papers after immersion are shown in Fig. 3.

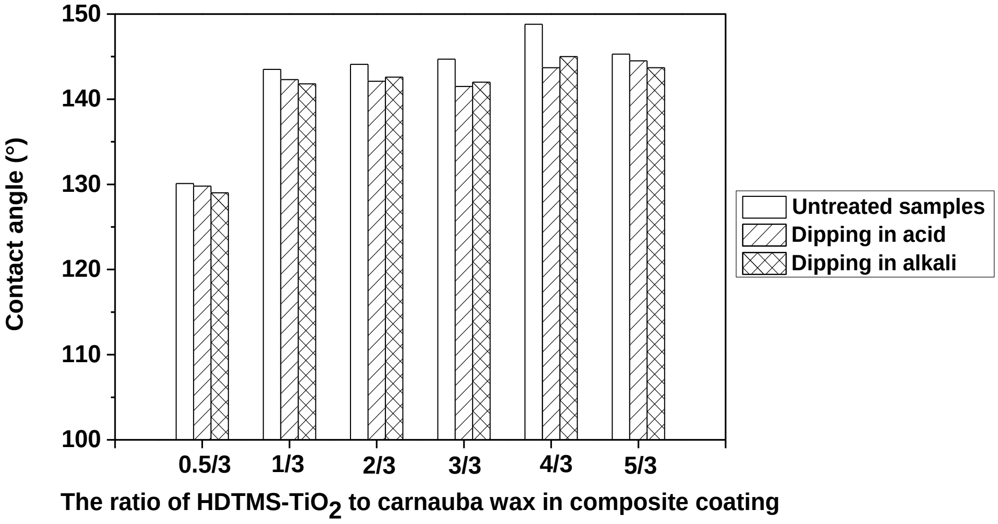

Fig. 3. The contact angles of filter papers before and exposure to acid/alkali

Compared with the WCA before immersion, the results indicated that the wetting characteristics of the obtained filter paper were essentially maintained after being dipped into a solution of acid or alkali. The WCA of filter paper only decreased < 5°. Chemical inertness of carnauba wax had proved to be quite advantageous, particularly in drug release studies (Reza and Haider 2003; Milanovic *et al.* 2011). The good acid/alkali-resistant property also showed that the hydrophobic coatings formulated using carnauba wax and HDTMS-TiO_2 would be helpful for the applications that require chemical inertness to exposure in certain fluids.

Surface Morphology of Filter Paper

The SEM images of the filter paper before and after the treatment are shown in Fig. 4. As seen from images a and b, the fibers interweaved to form the original filter paper and they consisted of thousands of microfibrils. After being dipped into the HDTMS-TiO_2/wax coating and dried at 100 °C, the surface morphology of the filter paper changed. In Fig. 4c, the fiber surface became rough with microstructures formed by the composite coating including nano HDTMS-TiO_2 beads and the petal-like carnauba wax flakes. In the close-up of Fig. 4d, the micro/nano structure was more obvious. As mentioned, a coarse surface is essential in the preparation process of materials with high hydrophobicity (Nosonovsky and Bhushan 2009). The petal/bead morphology formed on the composite coating was beneficial to improve the hydrophobicity of filter paper as the results showed in Fig. 2-a.

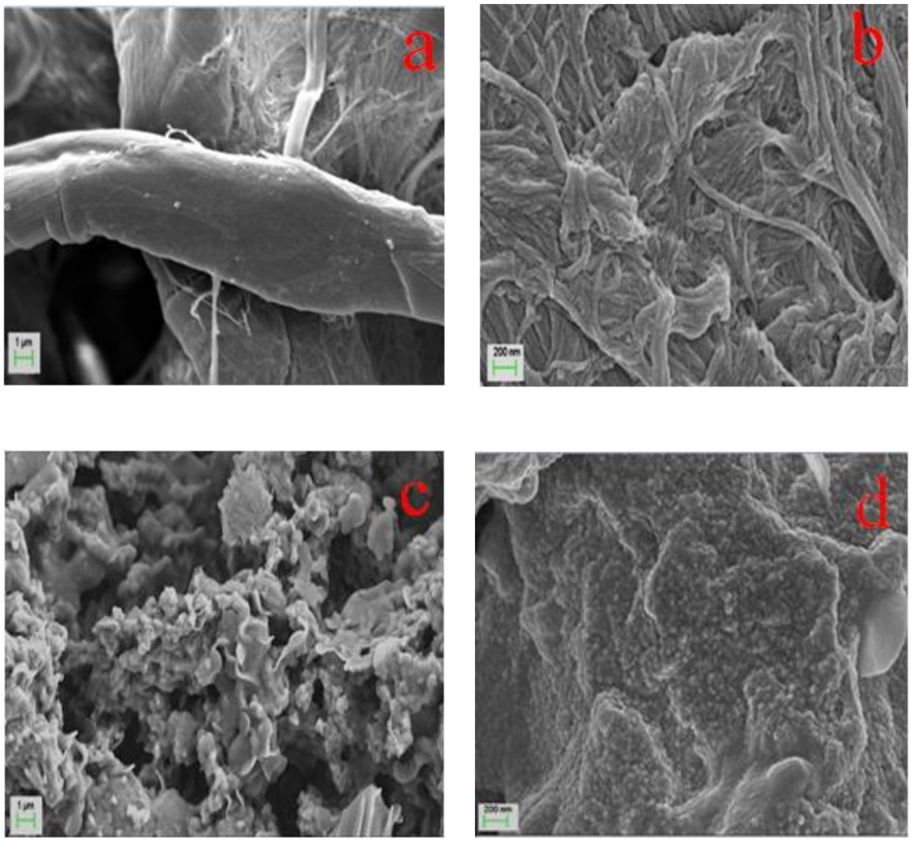

Fig. 4. SEM images of filter papers: a, b: the original filter paper; and c, d: filter paper after treatment (the concentration of HDTMS-TiO_2/wax used for coating in SEM images was 4/3)

Ability to Separate Water/Oil Mixture

The special wettability of the hydrophobic filter paper inspired the authors to apply it in water/oil separation. In this work, a mixture of diesel and water was separated by filter paper.

Through filtration, these hydrophobic filter papers effectively removed almost all water from diesel. In Table 2, the paper samples S1 through S5 corresponded to the samples in Fig. 2a (1/3 through 5/3). The water content in the water/diesel mixture was 100,000 ppm before separation. After the separation and filtration by filter papers, it decreased to 105 ppm to 404 ppm. The water removal efficiency reached 99.6% to 99.9%. It showed that the as-prepared filter papers had very good performance in the water/oil separation.

Samples S1 through S5 all had strong water resistance with WCAs over 140°, so there was no big difference in water contact angles of the five samples; water could not wet these filter papers even under 0.005 MPa vacuum degree. However, a little water would pass the filter papers through their pores. In Table 2, it was found that the water content decreased with decreased air permeability and pore diameter. Samples S4 and S5 had relatively lower air permeability and pore diameter, which prevented water from penetrating efficiently. In this work, the air permeability and pore diameter affected the final separation effect.

Table 2. Water/Oil Separation Ability of Filter Paper Samples

Ratio of HDTMS-TiO_2 to wax	Pore Diameter (μm)	Air Permeability (mL/min)	Water Content in Filtrate (ppm)
S1 (1/3)	2.83	832	404
S2 (2/3)	2.63	797	390
S3 (3/3)	2.24	731	229
S4 (4/3)	2.15	629	164
S5 (5/3)	2.24	715	105

CONCLUSIONS

1. A simple method was developed to prepare hydrophobic coating filter papers. The HDTMS-TiO_2/wax formed rough microstructures on the paper surface and the HDTMS solution further decreased the surface energy of paper. The water contact angles of all obtained filter papers were over 140°.
2. The obtained hydrophobic filter papers were stable against corrosive liquids such as acid/alkali solutions.
3. Hydrophobic filter papers separated water/oil mixtures. The water content in the water/diesel mixture decreased from 100,000 ppm to 105 ppm after separation and filtration. The porosity of filter paper played an important role in the separation and filtration.

ACKNOWLEDGMENTS

This research was supported by State Key Laboratory of Pulp and Paper Engineering (2016C14), the Special Project on the Integration of Industry, Education and Research of Guangdong Province (2013A090100013), the Fundamental Research Funds for the Central Universities (2015ZM174) and Open Funded Projects of Jiangsu Province Key Lab of Pulp and Paper Science and Technology (201519).

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Article submitted: May 13, 2017; Peer review completed: August 3, 2017; Revised version received and accepted: August 22, 2017; Published: September 6, 2017.
DOI: 10.15376/biores.12.4.7774-7783