Finishing of Cotton Fabrics with Aqueous Nano-Titanium Dioxide Dispersion and the Decomposition of Gaseous Ammonia by Ultraviolet Irradiation

Yongchun Dong,[1,2] Zhipeng Bai,[1] Liwen Zhang,[1] Ruihua Liu,[2] Tan Zhu[1]

[1]College of Environmental Science and Engineering, Nankai University, Tianjin 300071, People's Republic of China
[2]Institute of Material Science and Chemical Engineering, Tianjin Polytechnic University, Tianjin 300160, People's Republic of China

ABSTRACT: An aqueous dispersion of nano-titanium dioxide (nano-TiO$_2$) was prepared and mixed with a silicone softener to establish a finishing bath. Cotton fabrics were treated with this finishing bath with a pad–dry–cure process and were then characterized by X-ray diffraction and scanning electron microscopy. The gaseous ammonia was derived from an environmental condition simulated chamber. The specifically designed photocatalytic reactor was used to assess the factors, including the dosage of the aqueous dispersion of nano-TiO$_2$, the nature of the fabric, the direct dye, and the water-repellent agent, that affected the decomposition efficiency of ammonia in air. In addition, nano-TiO$_2$-finished fabrics were evaluated with respect to whiteness and breaking tension properties. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 286–291, 2006

Key words: degradation; irradiation; nanoparticles

INTRODUCTION

Different kinds of chemical additives have been widely applied in the construction processes of concrete buildings in recent years. However, the use of these chemical additives, especially antifreeze based on urea or ammonia compounds, has resulted in increasing indoor air pollution because of the emission of ammonia from indoor concrete walls. Standards and regulations to control indoor ammonia pollution have been enacted and developed in China.[1] It is a fact that ammonia is harmful to human health and the environment. The effect of ammonia on the health of animals and human bodies has been studied.[2] Several researchers have investigated indoor ammonia emission sources[3,4] and measured ammonia concentration in indoor air.[5–8] These studies reported that concentrations of ammonia were measured in different rooms in houses and in a range of public buildings with a variety of testing methods. In addition, remedial measures against high concentrations of ammonia in buildings have also been suggested.[9]

Oxidation is currently considered to be the most effective technology for decomposing airborne pollutants, and various oxidation processes have been studied, developed, and implemented in the past several decades. Ultraviolet (UV)-related technologies are very effective compared to other oxidation processes for the removal of contaminants in wastewater and air under considerably mild conditions. The hydroxyl free radical is the major species that initiates most of the UV-related processes to the oxidation of compounds in water or gaseous streams. Therefore, UV-related processes are referred as *advanced oxidation processes*. Among the UV-related processes, the UV/titanium dioxide (TiO$_2$) process has been considered a promising alternative for the decomposition of various refractory contaminants in aqueous or gaseous streams in past decades.

Coating of TiO$_2$ by impregnation is widely used by most researchers because the technique is easy and does not require any complicated equipment. The selection of basic material may influence the activity, homogeneity, and adhesion of the TiO$_2$ catalyst on the surface. However, it is difficult to replace spent TiO$_2$ catalyst from the reactors for practical uses. Therefore, various basic materials, including paper[10,11] and nonwowen textiles,[12] have been developed for possible application of the TiO$_2$ photocatalysis process in the future. However, there is little detailed information in the current literature concerning the decontamination of indoor ammonia with photocatalytic oxidation with TiO$_2$, especially based on fabrics or textiles.

In this study, an aqueous dispersion containing nano-titanium dioxide (nano-TiO_2) was prepared and mixed with a silicone softener to establish a padding bath. Cotton fabrics were finished with the padding bath with a pad–dry–cure process, and nano-TiO_2 finished fabrics were obtained. A specifically designed photocatalytic reactor and environmental condition simulated chamber were used to assess some factors affecting the ammonia removal efficiency, including the dosage of the aqueous nano-TiO_2 dispersion, the nature of the fabrics, the direct dye, and the water-repellent agent (WRA). In addition, nano-TiO_2 finished fabrics were evaluated with respect to whiteness and breaking tension properties.

EXPERIMENTAL

Materials

Commercially scoured, bleached, and mercerized cotton woven fabric and a polyester/cotton blend (blending ratio: 65/35) woven fabric were used in this study. These fabrics were further treated with a solution containing 2 g/L sodium carbonate and 2 g/L soap at boiling for 30 min and were then thoroughly washed with cold water and dried at ambient temperature.

Degussa P-25 TiO_2 powder (Degussa Co., Ltd., Düsseldorf, Germany) was employed as the photocatalyst without further treatment and was approximately spherical and nonporous with greater than 99.5% purity. Degussa P-25 TiO_2 powder contained about 80% anatase and 20% rutile, and the average particle size of the TiO_2 particles was 30 nm.[12] A commercial-grade silicone softener AM-200 from Fuzhou Botex Chemicals Co. (Fuzhou, China) and the WRA EC-50 from Nikka Chemicals Co. (Fukui, Japan) were used in this research. The dye used was Direct Black 15, which was not purified before use. All other chemicals were reagent grade.

Preparation of the aqueous nano-TiO_2 dispersion

The aqueous dispersion was prepared by the mixture of 7.5 g of Degussa P-25 TiO_2 powder and appropriate amounts of deionized water in an ultrasonic mixer. After 5 h of ultrasonic mixing, 0.625 g of polyglycol was added into aqueous dispersion and mixed under continuous magnetic stirring for 30 min. The TiO_2 aqueous dispersion was prepared with 3 wt % Degussa P-25 TiO_2 and 0.25 wt % polyglycol.

TiO_2 finishing of fabrics

The fabric samples were padded twice (take-up = 75%) with a treatment solution containing various amounts of the TiO_2 aqueous dispersion, silicone softener (10 g/L), and nonion wetting agent (2 g/L) on a laboratory padding mangle. After they were padded,
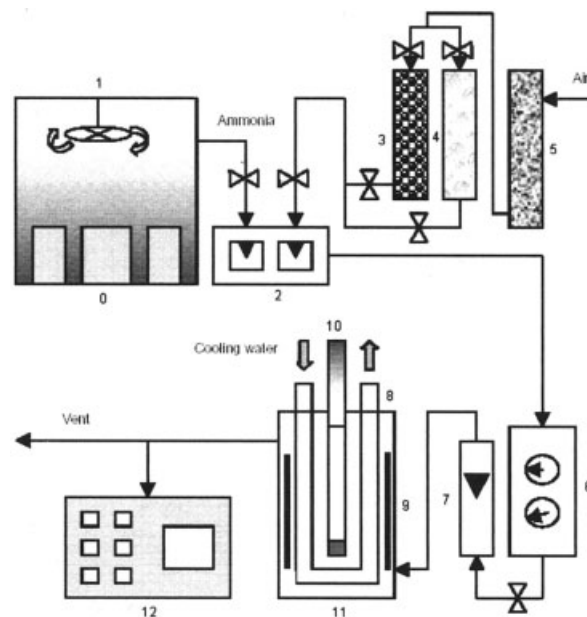
Figure 1 Schematic diagram of the photodegradation and testing system for ammonia: 0 = wall pieces; 1 = environmental chamber; 2 = gas mixer; 3 = dewater reagent; 4 = water bottle; 5 = activated carbon filter; 6 = thermo/humidity meter; 7 = flow meter; 8 = quartz shelter (inside cooling water); 9 = TiO_2-finished fabric; 10 = UV lamp; 11 = photocatalytic reactor; and 12 = ammonia detector.

the samples were immediately dried at 100°C for 2.0 min and cured at 170°C for 1.0 min.

Characterization and testing methods for the TiO_2-finished fabrics

The compositions of the TiO_2-finished fabrics were verified with a Rigaku Xd/Max-2500 X-ray diffractometer (Rigaku Corp., Tokyo, Japan) operating at 40 kV/100 mA with Cu Kα radiation. Scanning electron microscopy observations on specimens of TiO_2-finished fabrics were also done, on a Hitachi S-670 electron microscope (Hitachi High-Technologies Corp., Tokyo, Japan).

A Datacolor SF-600 Plus spectrophotometer connected to a personal computer was used to measure the Commission Internationale De Leclairage (CIE) whiteness of the TiO_2-finished fabrics. A tensile tester was used to determine the breaking strengths of the treated fabrics.

Ammonia photodegradation system

The photodegradation system used in this research was designed and consisted mainly of a small stainless steel environmental condition simulated chamber (1 m × 1 m × 1 m × 1.5 mm thick) and a glass photocatalytic reactor. The schematic diagram of the photodegradation and testing system for ammonia system is shown in Figure 1.
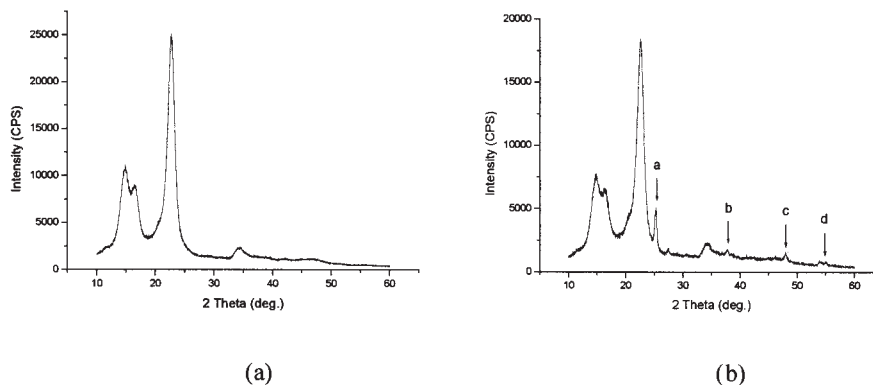
Figure 2 XRD spectrum of (a) untreated and (b) TiO_2-finished cotton fabrics.

A number of wall pieces were specially made with concrete and a small amount of antifreeze based on a urea compound and were used to simulate the indoor concrete wall of a typical room. These concrete wall pieces (500 mm × 200 mm × 300 mm for each piece, with four pieces in each experiment) were placed in the environmental chamber and served as an emission source of ammonia. The photocatalytic reactor was a 2.5-L fixed-bed glass reactor with a UV lamp. The UV lamp was obtained from Shanghai Yaming Co. (Shanghai, China) and emitted 365-nm lights. The TiO_2-finished fabric with an area of 0.022 m² was wound and fixed on the inner wall of the tubular photoreactor.

Photodegradation procedure and analytical method

The environmental chamber and photoreactor were thoroughly cleaned with a solution containing 2 g/L sodium carbonate and deionized water, respectively. Gaseous ammonia emitted from wall pieces in environmental chamber and clean dry air were mixed in a gas mixer and maintained constant to provide ammonia gas with a steady concentration. The temperature of the mixed gas flow in the photoreactor was kept at 20°C, and the humidity of the mixed gas flow reached a steady state. A NH_3 gas detector (TG-2400KBP; Bionics Instrument Co., Ltd., Tokyo, Japan) was used to determine the concentration of gaseous ammonia in the air from the photoreactor. The reaction was not considered to reach balance until the concentration of gaseous ammonia in the photoreactor was kept steady for 5 min. The ammonia concentration in the photoreactor at this time referred to the balance concentration of ammonia. The photocatalytic decomposition percentage of ammonia ($D_p\%$) at a constant humidity and temperature was calculated as follows:

$$D_p\% = \frac{C_0 - C}{C_0} \times 100 \tag{1}$$

where C_0 is the initial concentration of ammonia (ppm) and C is the residual concentration of ammonia (ppm).

RESULTS AND DISCUSSION

Characterization of TiO_2-finished fabrics

The cotton woven fabrics were selected as supporting materials for the loading of TiO_2 because their flexibility to being engineered. Moreover, the large surface area and a number of hydrophilic groups of the cotton fiber provided more active sites for the deposition of TiO_2 than general supporting materials. The X-ray diffraction (XRD) curve of the TiO_2 finished cotton fabric is presented in Figure. 2.

As shown in Figure 2, three major peaks (14.84, 16.38, and 22.68°) of the cellulose fiber were similar to those published in literature.[13] More importantly, a relatively strong reflection peak (25.28°, peak a) and three weak peaks (37.84°, peak b; 47.98°, peak c; and 53.90–55.12°, peak d) of anatase TiO_2 were also observed. Grain size was determined from the broadening corresponding X-ray spectral peaks by Scherrer's formula: $L = 0.90\lambda/(\beta \cos \theta)$, where L is the grain size, λ is the wavelength of X-ray radiation, β is the line width at half-maximum height, and θ is the Bragg angle between the incident radiation and the diffracting planes. On the basis of XRD analysis, the average L of anatase TiO_2 was 30.1 nm.

Figure 3 shows the scanning electron micrographs of the cotton fiber [Fig. 3(a)] and after TiO_2 finishing [Fig. 3(b,c)]. Figure 3(a) shows the surface structure of the cotton fiber (magnification = 5000×): a round surface that was very smooth to the touch. Figures 3(b) (magnification = 5000×) and 3(c) (magnification = 7000×) depict the morphological change in appearance of the cotton fiber after TiO_2 finishing; the cotton fiber surface was covered with TiO_2 particles and seemed to be somewhat rough and uneven. Therefore, we proved that the TiO_2 particles were loaded on the
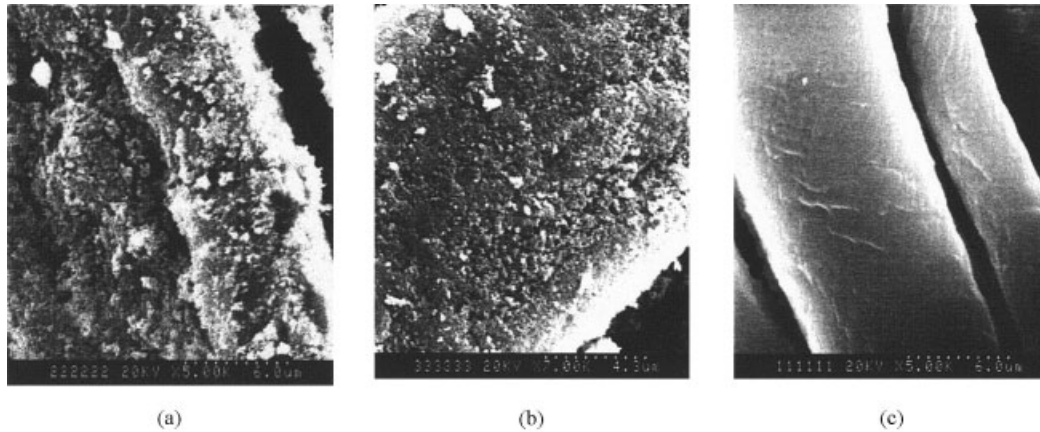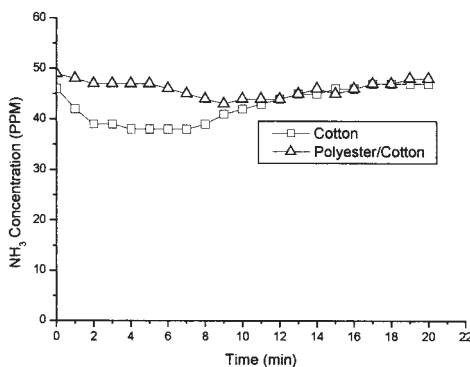
Figure 3 Scanning electron micrographs of (a) untreated cotton fibers and (b) TiO$_2$-finished cotton fibers and (c) a higher magnification image of TiO$_2$-finished cotton fibers.

cotton fiber with the pad–dry–cure process, but their distribution on the fiber surface was not even, possibly because of the aggregation of some fine TiO$_2$ particles.

Photocatalytic reaction of ammonia in air

The photocatalytic decomposition of ammonia by the 365-nm UV irradiation and in the presence of naked fabrics, especially pure cotton fabric, was found to be negligible within the reaction time studied, as shown in Figure 4.

As shown, the concentration of ammonia gradually decreased at the beginning stage of reaction but then came back to about the initial concentration level during the reaction time. This may have been due to the limited adsorption of ammonia on the fiber surface. Additionally, the adsorption of ammonia on the TiO$_2$ particles was also studied in this research and found to be minimal; therefore, the removal of ammonia contributing to the adsorption on TiO$_2$ particles during the UV/TiO$_2$ process could be neglected. The activity of the TiO$_2$ catalysts on the fabrics was assumed to be constant during the course of the reaction.

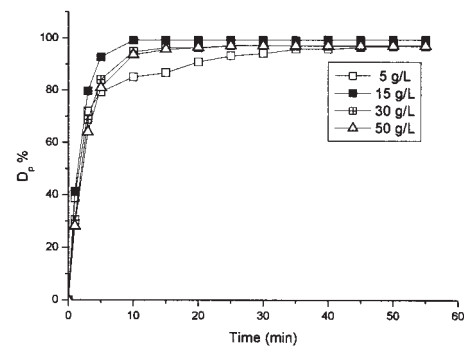### Dosage of the aqueous TiO$_2$ dispersion

The experimental results of gaseous ammonia photodecomposition with TiO$_2$-finished fabrics padded with different dosages of aqueous TiO$_2$ dispersions between 5 and 50 g/L in a finishing bath are given in Figure 5.

D_p% increased with time of the photocatalytic reaction, and this increasing tendency became level after a reaction time of 15 min. This means that most of the ammonia in the reactor was removed with the TiO$_2$-finished fabric during a relatively short time. Increasing the amount of the aqueous TiO$_2$ dispersion from 5 to 15 g/L in the finishing bath was accompanied with an enhancement in the degradation of ammonia. The most effective decomposition of ammonia in this study was obtained with the TiO$_2$-finished fabric processed with 15 g/L of the aqueous TiO$_2$ dispersion; there was also a small reduction in the decomposition of ammonia when the dosage of the aqueous TiO$_2$ dispersion exceeded 15 g/L in the finishing bath. This was due to the fact that the increasing dosage of the aqueous TiO$_2$ dispersion in the padding solution led to more TiO$_2$ particles being loaded on the fiber surface, which improved the decomposition efficiency of ammonia to a certain extent. However, an excessive

Figure 4 Photolysis of ammonia by the 365-nm lamp with the untreated fabrics.

Figure 5 Effect of aqueous TiO$_2$ dispersion dosage on D_p%.

TABLE I
Influence of Aqueous TiO$_2$ Dispersion Dosage on the Whiteness and Breaking Strength Retention (BSR)

|	Dosage of aqueous TiO$_2$ dispersion (g/L)				
	0	5	15	30	50
CIE whiteness	97.6	97.1	96.4	95.8	94.5
BSR (%)	100	96.4	94.3	94.5	93.5

quantity of the aqueous TiO$_2$ dispersion may have caused the aggregation of fine TiO$_2$ particles on the fiber surface and reduced the removal of ammonia.

On the other hand, it is obvious from the results shown in Table I that the whiteness and breaking strength of the TiO$_2$-finished cotton fabrics decreased slightly with increasing concentration of the TiO$_2$ dispersion in the finishing solution. This may have been due to a small amount of yellowing and damage of the treated fabrics caused by TiO$_2$ particles distributed unevenly on the fiber surface under the curing process.

Nature of the fabrics

For a given treatment condition, the cotton fabric and the polyester/cotton blend (blending ratio = 65/35) fabric were finished at the same concentration (30 g/L) of the aqueous TiO$_2$ dispersion.

Figure 6 depicts the difference in ammonia destruction between the TiO$_2$-finished cotton fabric and the polyester/cotton blend fabric. As shown in Figure 6, the TiO$_2$-finished cotton fabric was much higher than TiO$_2$-finished polyester/cotton fabric in terms of the decomposition of ammonia. This may have been because of the big difference in the chemical properties and microstructure characteristics between the cotton and polyester fibers. It is a fact that hydrophilic cotton fibers have a high moisture regain of 8.5% because it they are composed of cellulose molecules bearing hydroxyl groups; meanwhile, they have a relatively loose microstructure as a result of high amorphous regions and lower crystalline regions. Moreover, the same long cellulose chain molecules are organized in relation to each other in certain portions of their lengths and are disorganized in others.[14,15] In contrast, there are few polar substitutes in the molecular chain of hydrophobic polyester fibers. Furthermore, polyester fibers have a low moisture regain of 0.1–0.4% and a glass rod-like shape with a smooth surface.[14] Therefore, we believe that the cotton fibers may have exhibited a much higher adsorption affinity for ammonia than polyester fibers under the same environmental conditions by means of their good hydrophilicity and loose microstructure. The relatively high adsorption of ammonia onto cotton fibers may have accelerated the photocatalytic oxidation of ammonia on the surface of the cotton fibers. Also, if hydroxyl groups in the cel-
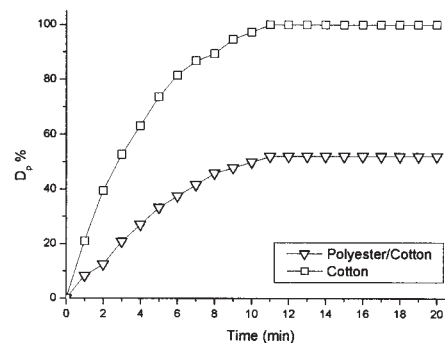
**Figure 6** Effect of different fabrics on D_p%.

lulose molecular chain were generally considered weak acid substitutes, they may have benefited the adsorption and photocatalytic degradation of ammonia on the surface of the cotton fibers to certain extent. In addition, it is possible that more TiO$_2$ particles were loaded on the surface of cotton fabric than on the polyester/cotton blend fabric because of their differences in hydrophilicity and adsorbability when we padded with the same concentration of finishing bath for a given process. Another probable explanation is related to the generation of hydroxyl radicals. When the TiO$_2$ particulates were excited by wavelengths below 385 nm of light irradiation, the first step was the generation of photoelectrons and photoholes on TiO$_2$ particulates [eq. (2)] followed by a reaction [eq. (3)] to yield the same active oxygen species, such as hydroxyl radicals. Then, these hydroxyl radicals could have attacked organic substrates and led to their degradation and mineralization.[16,17]

$$\text{TiO}_2 + h\nu \rightarrow (e_{cb}^-) + (h_{vh}^+) \rightarrow e^- + h^+ \qquad (2)$$
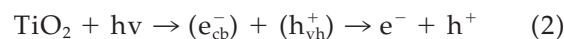
where hv is the photo-quanta or photo-energy, e_{cb}^- is the conduction band electron, h_{v6}^+ is the valence band hole, e^- is the photoelectron, and h^+ is the photohole.

$$h^+ + \text{OH}^- \text{ (or H}_2\text{O)}_{surf} \rightarrow \text{OH}^{\bullet}(+\text{H}^+) \qquad (3)$$

where OH$^-$ (or H$_2$O)$_{surf}$ is the hydroxyl groups of water molecules absorbed on the surface of TiO$_2$ particulates.
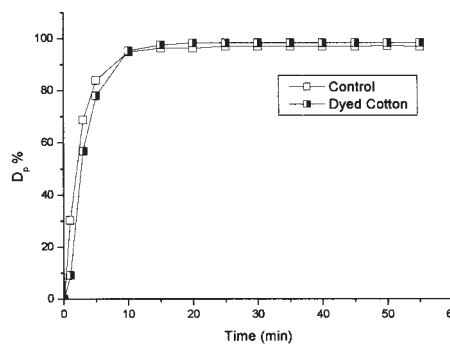
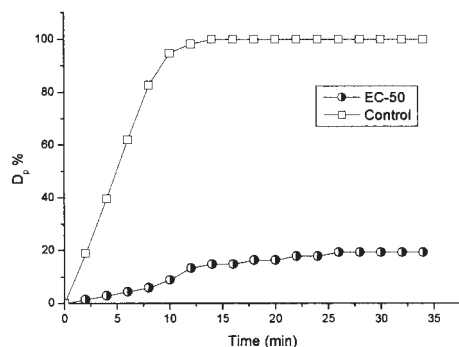**Figure 7** Effect of dyed cotton fabrics on D_p%.

Figure 8 Effect of WRA on D_p%.

For the TiO_2-finished cotton fabric, cotton fibers may have reacted [eq. (3)] with more water than polyester fiber to facilitate the production of hydroxyl radicals. Hence, the photocatalytic oxidation of ammonia could be improved. In a previous study, the decomposition of ethanol by a UV/TiO_2 process was enhanced with an increase in the relative humidity.[18]

Dyed fabric

To investigate the impact of the dyed fabric on the photooxidation of ammonia, cotton fabric dyed with a 2% on weight of fiber or fabric concentration of C. I. Direct Black 19 was also treated with a finishing solution containing a 30 g/L aqueous TiO_2 dispersion with a pad–dye–cure process under the same technical conditions as mentioned previously and was then used for the photodecomposition of ammonia.

In the comparison of the two decomposition curves of ammonia, Figure 7 shows that the photooxidation of ammonia was not affected much by Direct Black 19 on the cotton fabric. We believe that dyed fabric had little influence on the photooxidation of ammonia by the UV/TiO_2 process in this study.

WRA

The TiO_2 finishing of the cotton fabric was performed with a padding solution containing a 30 g/L aqueous TiO_2 dispersion and 30 g/L WRA EC-50 based on a fluorocarbon polymer instead of a silicone additive with the same method mentioned previously. This TiO_2-finished cotton fabric was examined to be water resistant and was also used for the photodecomposition of ammonia. For comparison, a control experiment, in which the WRA was absent in the padding bath, was carried out, the experimental results of which are presented in Figure 8.

We expected the ammonia decomposition efficiency of the water-resistant TiO_2-finished cotton fabric to be much lower than that of the control fabric. The decrease in the decomposition efficiency may have been mainly associated with the improved hydrophobicity of the cotton fabric surface.

CONCLUSIONS

The nano-TiO_2-finished fabrics were prepared with a finishing bath containing an aqueous nano-TiO_2 dispersion with the pad–dry–cure process and were evaluated with respect to the decomposition efficiency of ammonia in air, whiteness, and breaking tension properties. The results obtained indicate that gaseous ammonia in air was efficiently removed with nano-TiO_2-finished cotton fabrics by the 365-nm UV irradiation process. The decomposition efficiency of ammonia was much affected by the dosage of the aqueous TiO_2 dispersion and WRA in the finishing bath. The nano-TiO_2-finished cotton fabric was higher than the nano-TiO_2-finished polyester/cotton blend fabric in the decomposition efficiency of ammonia. Dyed cotton fabric had a similar decomposition capacity of ammonia to bleaching cotton fabric. The whiteness and breaking strength of the cotton fabric decreased slightly after nano-TiO_2 finishing. The need for a more complete comprehensive study is obvious.

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