

# A Novel Perfluorooctylated Triazine Pyridine Quaternary Ammonium Salt: Synthesis and Its Application on Cotton Fabrics Finishing

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**ABSTRACT:** A novel perfluorooctyl-containing triazine pyridine quaternary ammonium salt was designed and synthesized, which was applied to cotton fabrics by pad-dry-cure process. The treated fabrics showed good water and oil repellency, and washing durability. The water and oil repellent ratings were 100 and 6 respectively, and after 10 washing cycles, the water repellent rating was 90 and the oil repellent rating was 5. The modified specimen had the ultra

low critical surface energy and showed excellent repellency to selected liquids (water, tea, milk, wine, machine oil, and wooster sauce). © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 4561–4564, 2006

**Key words:** perfluoroalkylated compound; quaternary ammonium salt; water and oil repellent; critical surface energy.

## INTRODUCTION

It has been known that fluorocarbons have an extremely low surface free energy. Fluorinated coatings are the most important class of water and oil repellent finishes for textiles because of their excellent water and oil repellency, without impairing the textile's permeability to air or modifying the fabric's hand.<sup>1,2</sup> However, conventional finishing by the fluorinated coatings does not always show sufficient stability during use since the finishing agents used mostly form the surface layer only on the top of the fabrics and do not develop permanent chemical bonds to the textile substrate.<sup>3</sup>

Reactive dyes are famous for excellent washing color fastness. The reason is reactive dyes contain groups that can react with the hydroxyl groups in cellulose. Several types of reactive groups are found in reactive dyes. Triazine type is the most reactive one among them. We envisaged if triazine group was introduced into a compound, maybe it would be beneficial for improving wash durability.

In our ongoing research in this field, we designed a novel perfluorooctyl-containing triazine pyridine quaternary ammonium salt (FPQA). It contains both perfluorooctyl group and triazine pyridine quaternary ammonium salt, which can bind to cellulose fabric surfaces, and it could be a suitable surface modification agent for providing the treated cellulose fabric surface with durable water and oil repellent. We describe herein the synthesis of this ammonium salt (FPQA) and its application in the treatment of cotton fabrics.

## EXPERIMENTAL

### Materials

Sodium azide, hexadecyltrimethylammonium bromide ( $C_{16}H_{33}(CH_3)_3NBr$ ), Raney Ni, hydrazine hydrate ( $N_2H_4 \cdot H_2O$ , 85%), ethyl acetate, anhydrous  $MgSO_4$ , dichloromethane, methanol, cyanuric chloride,  $NaHCO_3$ , anhydrous  $Na_2SO_4$ , petroleum ether were used as purchased,  $CH_3CN$ , pyridine and ether were dried with 4A molecular sieves, and 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro-10-iododecane ( $C_8F_{17}CH_2CH_2I$ ) was prepared according to the reference 4<sup>4</sup>.

### Characterization

<sup>1</sup>H NMR spectra were recorded on a Bruker AV 400 (400 MHz) (Bruker Co., Faellanden, Switzerland) spectrometer with  $Me_4Si$  as an internal standard. <sup>19</sup>F NMR

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TABLE I  
Properties of Cotton Fabric Treated with FPQA<sup>a</sup>

Sample conc. (% owb)	Water repellency rating		Oil repellency rating	
	1 <sup>b</sup>	10 <sup>b</sup>	1 <sup>b</sup>	10 <sup>b</sup>
Untreated <sup>c</sup>	0	0	0	0
3.0	100	90	6	5

<sup>a</sup> Applied by pad-dry (3 min, 80°C), cure (5 min, 150°C).

<sup>b</sup> Number of laundering cycles before testing.

<sup>c</sup> Untreated cotton fabric.

spectra were obtained on Bruker AV 400 (376 MHz) spectrometer using CFCl<sub>3</sub> as an external standard, downfield shifts being designated as positive, all chemical shifts ( $\delta$ ) are expressed in ppm and coupling constants ( $J$ ) are in Hz, the following abbreviations are used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Mass spectra were recorded on a Finnigan-MAT-8430 (Finnigan Co) instrument using EI ionization at 70 eV. IR spectra were recorded on a Shimadzu IR-440 (Shimadzu Co., Japan) spectrometer. The contact angle was determined using an automatic video contact-angle testing apparatus OCA 40 (Dataphysics Co., Germany).

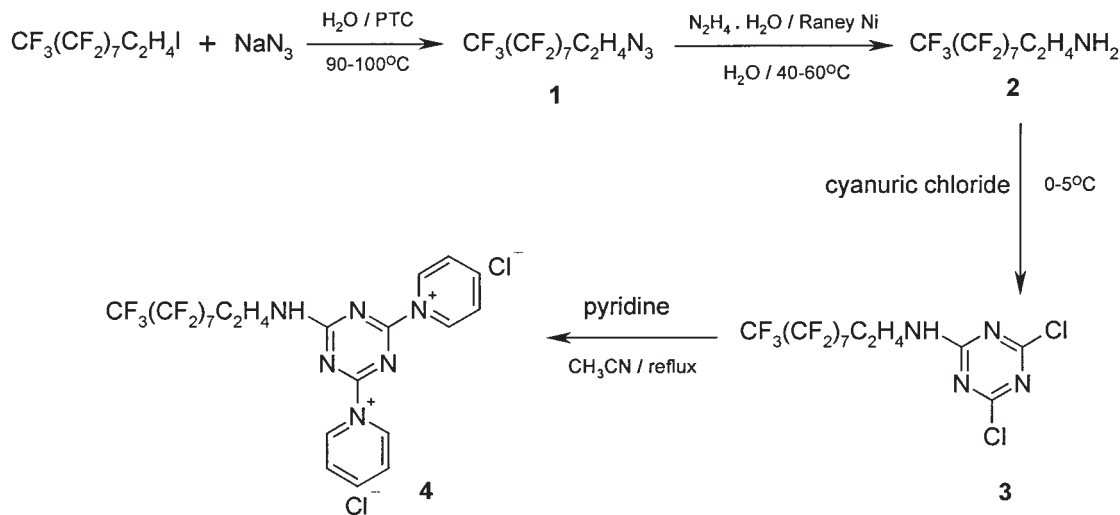
### Synthesis of finishing agent

The synthesis of FPQA was carried out as shown in Scheme 1. 1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10,-Hepta-decafluorodecyl) triaziridine **1**<sup>5-8</sup>: A mixture of C<sub>3</sub>F<sub>17</sub>CH<sub>2</sub>CH<sub>2</sub>I (11.5 g, 20 mmol), sodium azide (3.25 g, 50 mmol), hexadecyltrimethylammonium bromide (0.7 g, 2 mmol), and water (20 mL) was stirred at 90–100°C for 12 h. The aqueous phase was carefully

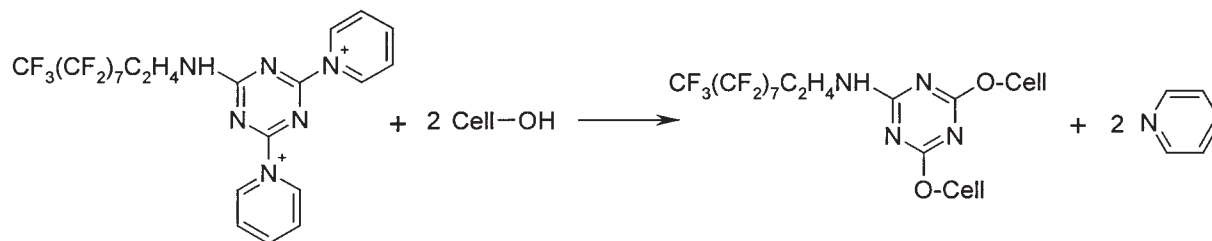
removed, 1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10,-hepta-decafluoro-  
decyl) triaziridine **1** was obtained by distillation and the fraction of 62–64°C/mmHg was collected (9.2 g, 94% yield).

3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Hepta-decafluoro-decan-1-amine **2**<sup>6-9</sup>: Compound **1** (40.0 g, 81.8 mmol) was charged into a 100 mL three-necked round-bottom flask, and then N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O (4.9 g, 98.2 mmol), Raney Ni (0.5 g), and water 40 mL were added. The reaction mixture was stirred at 40–60°C for 24 h. Then the mixture was extracted with ethyl acetate. The combined organic layer was dried over anhydrous MgSO<sub>4</sub>. The solvent was removed *in vacuo*. Purification of the residue by column chromatography on silica gel (dichloromethane: methanol = 10 : 1) gave compound **2** (17.0 g, 45% yield). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 1.0 (s, 2H), 2.1 (m, 2H), 3.0 (t, 2H), <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$ : -80.1 (m, 3F), -114.9 (m, 2F), -122.8 (m, 6F), -123.6 (s, 2F), -124.4 (s, 2F), -127.2 (s, 2F).

4,6-Dichloro-*N*-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10,-hepta-decafluodecyl)-1,3, 5-triazine-2-amine **3**<sup>10-13</sup>: Cyanuric chloride (4.8 g, 26 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (100 mL) and cooled to 0–5°C, aqueous NaHCO<sub>3</sub> (5%, 50 mL) was added, then a solution of compound **2** (12.1 g, 26 mmol) in methanol (25 mL) was added slowly. The reaction mixture was stirred for 1 h at 0–5°C, then for 5 h at room temperature. The organic layer was washed with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed *in vacuo*. Purification of the residue by column chromatography on silica gel (petroleum ether: ethyl acetate = 20:1) gave compound **3** (14.3 g, 90% yield). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 6.22 (s, 1H), 3.87 (m, 2H), 2.47 (m, 2H), <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$ : -80.7 (m, 3F), -113.6 (m, 2F), -121.6 (m, 6F), -122.6 (s, 2F), -123.4 (s, 2F), -126.2 (s, 2F); IR  $\nu_{\max}$  (cm<sup>-1</sup>, KBr): 3273, 3182,



Scheme 1



Scheme 2

1616, 1550, 1244, 1205, 1154; MS (EI, 70 ev)  $m/z$ : 612( $M^+ + 1$ , 20.8), 177, (100) 191 (86.14), 179 (60.34), 193 (52.04), 55.05 (26.33), 69.0 (21.7); Anal. Calcd. For  $C_{13}H_5F_{17}N_4Cl_2$ : C, 25.55; H, 0.82; N, 9.17; and Found: C, 25.64; H, 0.98; N, 9.07.

Perfluorooctyl-containing pyridine quaternary ammonium salt **4**: Compound **3** (1.02 g, 1.67 mmol) was dissolved in anhydrous  $CH_3CN$  (7 mL), a solution of pyridine (0.16 g, 2.0 mmol) in anhydrous  $CH_3CN$  (3 mL) was added slowly. The reaction mixture was stirred at  $50^\circ C$  for 1h. The solvent was removed *in vacuo*. The residue was washed with anhydrous ether to give quaternary ammonium salt **4** (1.1g, 87% yield) as a white solid.  $^1H$ -NMR (400 MHz,  $CDCl_3$ )  $\delta$ : 10.35 (m, 4H), 9.08 (m, 2H), 8.47 (m, 4H), 4.87(s, 1H), 4.16 (t, 2H,  $J = 6.4$ Hz), 2.78 (m, 2H),  $^{19}F$  NMR (376 MHz,  $CDCl_3$ )  $\delta$ : -80.1 (m, 3F), -114.9 (m, 2F), -122.8 (m, 6F), -123.6 (s, 2F), -124.4 (s, 2F), -127.2 (s, 2F); IR  $\nu_{max}$  ( $cm^{-1}$ , KBr): 3425, 3120, 1644, 1625, 1541, 1355, 1203, 1151; MS (EI, 70 ev)  $m/z$ : 769 ( $M^+$ , 0.12), 79(100), 177 (60.34), 52.05 (57.22), 191(56.55), 179 (37.8), 193 (36.45); Anal. Calcd. For  $C_{23}H_{15}F_{17}N_6Cl_2$ : C, 35.91; H, 1.96; N, 10.92; and Found: C, 35.69; H, 2.23; N, 10.67.

### Fabrics and treatment

Desized, scoured, bleached, and mercerized plain weave  $40 \times 40$  cotton weighed  $108.6 \text{ g/m}^2$ . Fabric samples were first immersed in an aqueous solution containing PFQA **4**, then padded with two dips and two nips to reach a wet pickup of 95–100%. The samples were then dried and cured in a curing oven at a specified temperature for a specified period of time. The concentrations were presented as % weight of bath (owb).

### Measurements

The water and oil repellent properties of the finished fabrics were measured according to AATCC test methods 22–2001 and 118–2002 respectively.<sup>14</sup>

## RESULTS AND DISCUSSION

It has been known that perfluoroalkyl compounds have extremely low surface free energies, and have

many important applications in low surface energy modification of various substrates. They are able to lower the critical surface tension ( $\gamma_c$ ) of the treated surface remarkably. In this study, the water and oil repellent effects of **4** on cotton fabrics were examined. The results were shown in Table I. The water repellent rating was 100 and the oil repellent rating was 6 when the concentration of **4** was 3.0%. These results reflected that the outermost layer of the treated fabrics might be fully covered by the perfluoroalkyl group,  $-CH_2CH_2(CF_2)_7CF_3$ , which has been confirmed to have a low surface free energy,<sup>15</sup> therefore, the treated surface has an excellent water and oil repellency.

Conventional fluorinated coating finishings do not always show sufficient stability during the use since the finishing agents used mostly form only surface layer on the top of the fabrics and do not develop permanent chemical bonds to the textile substrate. Triazine pyridine quaternary ammonium salt was reactive in the aqueous solution. It can react with hydroxyl groups of cellulose, at the same time pyridine was released, and the process was described in Scheme 2. FPQA **4** was just like a colorless reactive dye and perfluorooctyl group was linked to cotton fabric surface in this process. The results in Table I showed that the cotton fabrics treated with **4** had good washing fastness. Even after 10 washing cycles, the water repellent rating was 90 and the oil repellent rating was 5, respectively. This indicated that FPQA **4** was linked to cotton fabrics through permanent covalent bonds.

The surface properties of treated specimens were investigated by measuring contact angles of the pendant drop method. A homologous series of *n*-alkanes (decane, dodecane, tetradecane) and water were used as wetting liquid. Corresponding contact angle ( $\theta$ )

TABLE II  
Contact Angles of Treated Specimens for Different Test Liquids

	C14 <sup>a</sup>	C12 <sup>b</sup>	C10 <sup>c</sup>	Distilled water
Specimen <sup>d</sup>	87.9	79.2	64.3	121.1

<sup>a</sup> Tetradecane,  $\gamma = 26.7 \text{ mN/m}$ .

<sup>b</sup> Dodecane,  $\gamma = 25.4 \text{ mN/m}$ .

<sup>c</sup> Decane,  $\gamma = 23.9 \text{ mN/m}$ .

<sup>d</sup> Treated with FPQA.

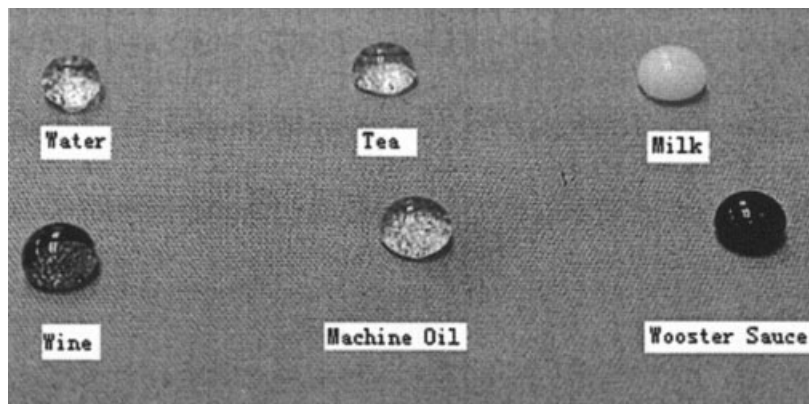


Figure 1 Photograph of the liquid repellency of the treated specimen.

were depicted in Table II. According to Zisman,<sup>16</sup> the homologous series of *n*-alkane can be used to reckon the critical surface energy of solid. When  $\cos \theta$  is plotted as a function of  $\gamma$  (the surface tension of the *n*-alkanes), the critical surface energy of solid can be obtained by extrapolation to  $\cos \theta = 1$ . The treated specimen showed the critical surface energy  $\gamma_c = 20 \pm 1$  mN/m, which was markedly lower than that of water and most oil. As shown in Figure 1, the modified specimen showed excellent repellency to selected liquids: water, tea, milk, wine, machine oil, and wooster sauce.

### CONCLUSIONS

In this study, we designed and synthesized a novel perfluorooctyl-containing triazine pyridine quaternary ammonium salt, and it was applied as a surface modification agent on cotton fabrics. The introduction of perfluorooctyl group made the treated fabrics show good water and oil repellent properties: the water and oil repellent ratings were 100 and 6 respectively; and the introduction of triazine pyridine quaternary ammonium salt made the treated fabrics show good wash durability: the water repellent rating was 90 and the oil repellent rating was 5 after 10 wash cycles. The critical surface energy of the treated specimen was

determined  $\gamma_c = 20 \pm 1$  mN/m. The treated fabrics showed excellent repellency to selected liquids: water, tea, milk, wine, machine oil, wooster sauce.

### References

1. Wang, J. G.; Mao, G. P.; Ober, C. K.; Kramer, E. J *Macromolecules* 1997, 30, 1906.
2. Grottenmuller, R. *Melliand Int* 1998, 4, 278.
3. Holme, I. *J Textile Inst* 1993, 84, 520.
4. Qing, F. L.; Ji, M.; Lu, R. H.; Yan, K. L.; Mao, Z. P. *J Fluorine Chem* 2002, 113, 139.
5. Szonyi, F.; Cambon, A. *J Fluorine Chem* 1989, 42, 59.
6. Roman, L.; Szonyi, F.; Bracon, F.; Cambon, A. *Synth comm* 1997, 27, 3125.
7. Trabelsi, H.; Szonyi, F.; Michelangeli, N.; Cambon, A. *J Fluorine Chem* 1994, 69, 115.
8. Szonyi, F.; Guennouni, F.; Cambon, A. *J Fluorine Chem* 1991, 55, 85.
9. Rolla, F. *J Org Chem* 1982, 47, 4327.
10. Brewer, S. A.; Burnell, H.; Holden, T.; Jones, B. G.; Willis, C. R. *J Chem Soc Perkin Trans* 1999, 2, 1231.
11. Thurston, J. T.; Dudley, J. R.; Kaiser, D. W.; Hechenbleikner, I.; Schaefer, F. C.; Hanser, D. H. *J Am Chem Soc* 1951, 73, 2981.
12. Zhang, W.; Nowlan, D. T. L.; Thomson, M.; Lackowski, W.; Simanek, E. E. *J Am Chem Soc* 2001, 123, 8914.
13. Durand, N. F.; Vessieres, A.; Heldt, J. M.; Bideau, F. L.; Jaouen, G. *J Organometal Chem* 2003, 668, 59.
14. AATCC Technical Manual 2003, 78
15. Neinhuis, C.; Barthlott, W. *Ann Bot* 1997, 79, 667.
16. Zisman, W. A. ACS, Washington, DC 1964, 1.