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Performance Comparison of New (Dendrimer, Nanoproduct) and Conventional Water, Oil and Stain Repellents

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Abstract
In this study, novel water, oil and stain repellent chemicals such as polymeric dendrimer containing fluorocarbon, nano sized fluorocarbon polymer, nano-silica acid and conventional agents such as paraffin emulsion containing zirconium salt and conventional FC (micro emulsion) compound were applied to cotton fabrics. After treatments, the water, oil and stain repellency, air permeability and water vapour permeability of all the fabrics treated were tested, and the effect of the chemical concentration, performance and washing resistance of all the chemicals were compared. In general, the water, oil and stain repellency results showed that new chemicals such as polymeric dendrimer containing FC and FC nanomolecules had better results than conventional ones in terms of performance and washing resistance. The performance of all the chemicals increased with a rise in chemical concentration. The air and water vapour permeability of all the fabrics treated were not negatively affected. FTIR analyses of the fabrics treated were also carried out.

Key words: *cotton, water-oil-stain repellency, dendrimer, nano-product, FTIR, air-water vapour permeability.*

Introduction

Nowadays, due to growing competition in the textile sector, the number of trends in the production and development of multi-functional, protective and comfortable clothes is on the increase. Water, oil and stain repellency treatments provide functionality and easy-care-for clothes.

The aim of water repellency treatment is to form a thin hydrophobic film on the fibre surface. Skin respiration and sweat transportation are not negatively affected due to the fact that fabric pores do not close [1]. The wetting of textile fabric can be explained by the physical phenomenon of the solid-liquid-air system (commonly known as gas). The boundary surface tension forces and water liquid on the fabric surface are indicated in ***Figure 1***. The ratio between these quantities at the equilibrium phase is described by Young equation [2]:

$$\gamma_S - \gamma_{SL} = \gamma_{LA} \cos \theta \qquad (1)$$

where, γ_S denotes the solid-air tension, γ_{LA} the liquid-air tension, and γ_{SL} the solid-liquid tension. If $\theta \leq 90°$, the fabric absorbs liquid and is hydrophilic, whereas if $\theta \geq 90°$, the fabric does not absorb liquid; it has a water repellency property [2].

Nowadays, the most important chemicals for oil and water repellency are fluorocarbon [FC] compounds. The efficiency of FC compounds is due to the structure of the bond between the F and C atoms. While the length of a C-F bond is 1.35 Ä, that of a C-C bond is 1.54 Ä. Because a C-F bond is shorter, the movement of fluorinated alkyl groups is lower, the F atom being strongly bonded with the C atom. This causes fluorocarbon compounds to have a much too low boundary surface tension. Therefore, liquids never penetrate into the fabric after water and oil repellent treatments [3].

Paraffin emulsions containing zirconium salt are adsorbed by fibres; paraffin and wax particles are bonded to the fibres via zirconium ions [1]. Paraffin emulsions containing zirconium salt provide good water repellency due to their zirconium ions holding onto fibres, and the fact that water repellent groups have good orientation on fibres surfaces [3].

Nanotechnology is increasingly attracting worldwide attention and has been introduced into other scientific and technological areas like robotics, biology, medicine, fibre optic communication networks, aerospace technology, advanced materials technology, chemical engineering and precision manufacturing. The properties that can be imparted to textiles using nanotechnology include water repellency, soil and wrinkle resistance, anti-bacteria, anti-static and UV-protection, flame retardation, and improvement of dyeability [4 - 5].

Dendrimer is a relatively new field of polymer chemistry defined by regular, highly branched monomers leading to a monodisperse, tree-like or generational structure. Synthesising monodisperse polymers demands a high level of synthetic control which is achieved through stepwise reactions, building the dendrimer up one monomer layer, or "generation," at a time. Each dendrimer consists of a core, internal cavities, branching units and closely-packed surface groups. The core molecule is referred to as "generation 0". Each successive repeat unit along all branches forms the next generation: "generation 1", "generation 2", and so on until the terminating generation. Dendrimers are generally used in genetics, medicine, biology and chemistry. Dendrimers are regarded as a more rapidly prepared and more economical replacement for special applications. They exhibit higher solubility and lower solution viscosity compared to linear analogues. In textile chemistry, dendrimers can be applied to textile fabrics to add water and oil repellency properties [6 - 7].

After washing, the textile materials treated with FC have to undergo heat treatment such as ironing and drying, because heat treatment is necessary for textile materials that have water and oil repellency properties again. But if the fabric is treated with an LAD (Laundry/Air Dry) fluorocarbon agent, heat treatment is not necessary [8].

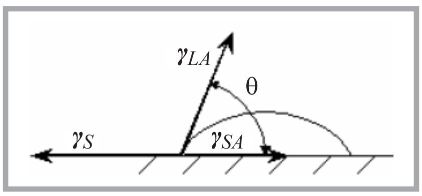

Figure 1. *Equilibrium state of a drop of liquid lying on a smooth solid surface [2].*

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Table 1. Physical properties of the cotton fabric.

Type of weave	Plain	
Fabric weight, g/m^2	138	
Linear density of the yarn, Ne	Weft	Warp
	20/1	22/1
Yarn density, picks/cm	21	25

In this study, novel water, oil and stain repellent chemicals such as polymeric dendrimer containing FC, FC nanomolecule, nano-silica acid and conventional agents such as paraffin emulsion containing zirconium salt and FC compounds were applied to cotton fabrics using the pad-dry-cure method. The performance and washing resistance of these chemicals were investigated, and the results obtained were evaluated.

Material and method

All the experiments were carried out with desized, scoured and bleached 100% cotton fabric. In ***Table 1*** the physical properties of this cotton fabric are given.

In ***Table 2*** the type and notations of the water, oil and stain repellents used in the experiments are given.

The finishing processes were realised with an Ernstbenz mark laboratory padder used for impregnation and an Atac GK4 mark laboratory stenter for drying and condensation. In these treatments six various water and stain repellents as well as four different oil repellents were applied to cotton fabrics at three different concentrations (25, 50 and 75 g/l). These chemicals at pH 4 were impregnated with 75% wet pick up and then dried at 100 °C for 5 minutes. Then all the samples were cured at 150 °C for 3 minutes in the stenter. The samples were divided into three groups, which were treated equally. The first group of fabrics was not washed, the second group of fabrics was washed once, and finally the third group of fabrics was washed five times in a Wascator machine according to Standard BS EN ISO 26330 (5A program). All the samples were dried and tested. After conditioning the fabrics for 24 hours in standard atmosphere conditions (temperature: 20 ± 2 °C, relative humidity: 65 ± 2%), water repellency tests of all the samples were performed according to Standard AATCC 22; oil repellency tests were carried out according to Standard AATCC 118; stain release tests were performed according to Standard AATCC 130; air permeability tests were performed according to Standard EN ISO 9237, and water vapour permeability tests were carried out according to Standard ISO 11092. Moreover, FTIR (Fourier transform infrared spectroscopy) analysis of the fabrics was carried out with Perkin Elmer Spectrum 100. All applications and tests were performed 3 times with each group of samples.

Statistical Analysis: The results (expressed as means/standard deviation) of all assays were compared using ANOVA, followed by a post hoc test (Duncan's test). For all statistical analyses, the software package SPSS 10.0 (Statistical Analysis Program) was used.

Results and discussion

In order to investigate the effect of such parameters, the type and concentration of repellent agents, and the washing time after treatment on the water, oil and stain repellency behaviour of the treated fabrics, statistical research was carried out. ANOVA for water, oil and stain repellency values indicated that these three parameters had a significant on the finishing performance of the fabrics. But the most important parameter among them is the type of repellent which gave the highest F value (4365.6) for the water repellency of the fabric treated. Secondly, the washing resistance of these chemicals was analysed; their performance decreased dramatically after washing, especially in the water repellency properties. On the other hand, the chemical concentration showed a statistically important effect on the finishing performance of the chemicals; however, the F values were lower when compared with the other parameters (***Table 3***).

Evaluating the water repellency results

Six various water repellents were impregnated into cotton fabrics at three different concentrations (25, 50 and 75 g/l). After the treatments, a Duncan Post Hoc test of the chemicals and the water repellency values of all samples were carried out, the results of which are given in ***Tables 4*** and ***5***.

Table 2. The chemical agents.

Water and stain repellents		Oil repellents	
Notation	Type	Notation	Type
A	conventional FC compound	A	conventional FC compound
B	paraffin emulsion containing zirconium salt	C	LAD-FC dispersion
C	LAD-FC dispersion	D	polymeric dendrimer containing FC
D	polymeric dendrimer containing FC	E	FC nanomolecule
E	FC nanomolecule	-	
F	nano-silica		

Table 3. ANOVA Tests of Between-Subjects Effects; df: degrees of freedom. F-ratio is the statistic used to test the hypothesis that the effects are real: in other words, that the means are significantly different from one another.

Source	Dependent Variable	Type III Sum of Squares	df	Mean Square	F	Sig.
Chemical	Water Repellency	141477.78	5	28295.56	4365.60	0
	Oil Repellency	284.44	5	56.89	-	-
	Dirty Motor Oil	36.90	5	7.38	106.28	0
	Olive oil	46.85	5	9.37	116.75	0
	Tea	86.74	5	17.35	234.19	0
	Coffee	155.57	5	31.11	672.06	0
Concentration	Water Repellency	1319.44	2	659.72	101.79	0
	Oil Repellency	52.11	2	26.06	-	-
	Dirty Motor Oil	2.11	2	1.06	15.20	0
	Olive oil	2.52	2	1.26	15.71	0
	Tea	7.11	2	3.56	48.00	0
	Coffee	4.86	2	2.43	52.50	0
Washing resistance	Water Repellency	52252.78	2	26126.39	4030.93	0
	Oil Repellency	87.11	2	43.56	-	-
	Dirty Motor Oil	4.78	2	2.39	34.40	0
	Olive oil	3.74	2	1.87	23.33	0
	Tea	0.86	2	0.43	5.81	0.004
	Coffee	11.86	2	5.93	128.00	0

__Table 4.__ Duncan Post Hoc test for type of water repellent; N: Total number of samples treated with the same chemicals. 1, 2, 3 and 4 indicate the name of the groups.

Chemical	N	1	2	3	4
F	27	22.22			
B	27		25.00		
C	27			84.44	
A	27				86.67
D	27				86.67
E	27				87.22
Sig.		1.000	1.000	1.000	0.46

__Table 5.__ Water repellency test results. Note: Water repellency test results were the grades (no unit) obtained from the standard scale in accordance with AATCC 22.

After treatment		no wash			Washing					
					one time			five times		
Concentration, g/l		25	50	75	25	50	75	25	50	75
Chemical	A	100	100	100	85	90	90	60	70	85
	B	60	80	85	0	0	0	0	0	0
	C	100	100	100	85	90	90	50	60	85
	D	100	100	100	80	85	85	75	75	80
	E	100	100	100	80	85	85	75	80	80
	F	60	70	70	0	0	0	0	0	0

__Table 6.__ Duncan Post Hoc test for types of oil repellent.

Chemical	N	1	2	3	4
A	27	2.11			
C	27		2.67		
E	27			2.89	
D	27				3.22
Sig.		1.0	1.0	1.0	1.0

__Table 7.__ Oil repellency values. Note: Oil repellency test results were the rating numbers (no unit) obtained from the standard table in accordance with AATCC 118.

After treatment		no wash			Washing					
					one time			five times		
Concentration, g/l		25	50	75	25	50	75	25	50	75
Chemical	A	2	2	3	1	2	3	1	2	3
	C	4	5	5	1	2	3	1	1	2
	D	3	6	6	2	4	4	0	1	3
	E	4	5	5	1	2	5	0	1	3

From the Duncan results it was clearly found that chemicals B and F were the lowest with respect to water repellency properties. Moreover, their washing resistances were also insufficient. Although the water repellency of chemicals D, E and A were statistically similar, the water repellency results of new chemicals such as D and E were higher than those for conventional ones. Furthermore, the washing resistances of new chemicals were better than those for the conventional ones, especially after 5 washings (***Table 4*** & ***5***).

Evaluating the oil repellency results

Four various oil repellents were impregnated into cotton fabrics at three different concentrations (25, 50 and 75 g/l). After the treatments, a Duncan Post Hoc test of the chemicals and the oil repellency values of all the samples were conducted, the results of which are shown in ***Tables 6*** & ***7***.

As seen from ***Table 7***, when the concentration increased, the oil repellency values rose, but after five washings these values decreased too much. In general, the washing resistances of all the chemicals were not enough, except at a concentration of 75 g/l.

Chemical D showed the highest oil repellency value, while chemical A provided the lowest oil repellency statistically (***Table 6***); the reason being that chemical

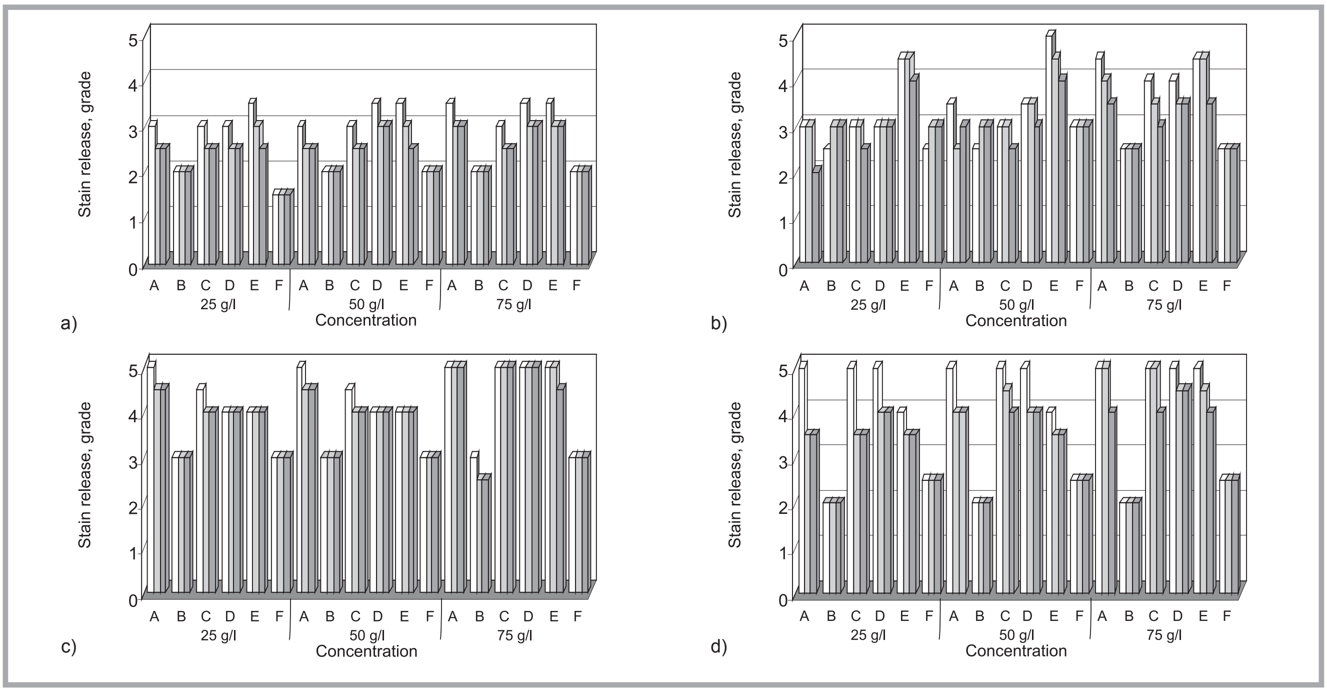

Figure 2. *Evaluation of the stain release performance for samples soiled with: a) dirty motor oil, b) olive oil, c) tea, d) coffee; □ - no wash, □ - one washing, ■ - five washings.*

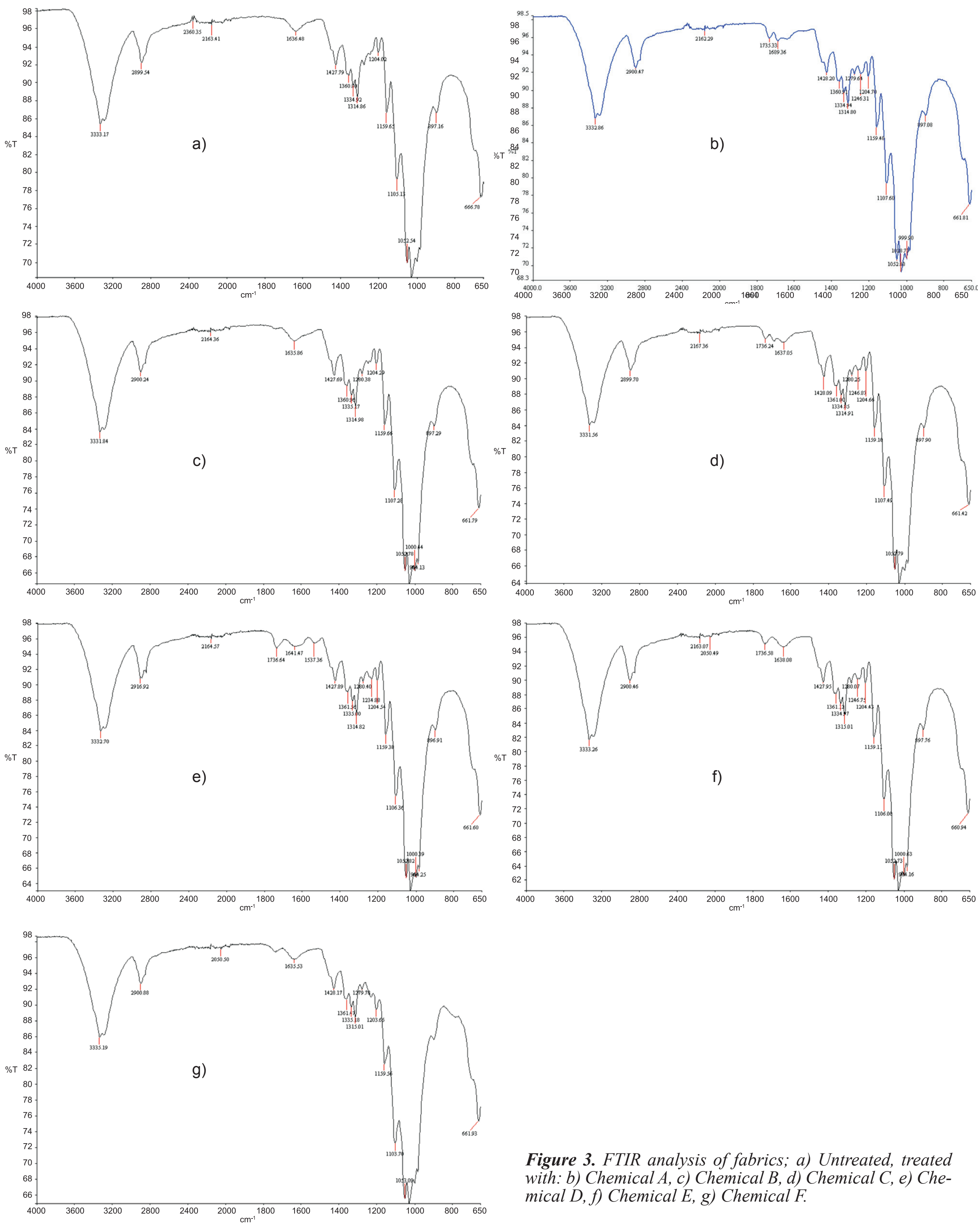

Figure 3. *FTIR analysis of fabrics; a) Untreated, treated with: b) Chemical A, c) Chemical B, d) Chemical C, e) Chemical D, f) Chemical E, g) Chemical F.*

D is a dendrimer and enhanced oil repellency by increasing the fluorine content in the outmost layer of a fabric, which provided long-lasting and breathable protection against water, oil, alcohol and fatty stains.

Evaluating the stain repellency results

Six various stain repellents were impregnated into cotton fabrics at three different concentrations (25, 50 and 75 g/l). After the treatments, all the samples were soiled with dirty motor oil, olive oil, tea and coffee. After soiling, washed and unwashed samples were evaluated with a special scale that is used in AATCC 130-1995. ***Figures 2*** show the results of evaluating the effect of finish on the appearance. In every chart the higher ratings indicate a better stain release effect and chemical performance for tea and coffee.

The dirty motor oil was very strong soiling. ***Figure 2.a*** (see page 78) shows that when the stain repellency performance of A, E and D was the best, that of F and B was the lowest. When the concentration of A and D increased, their performance improved. The effect of C and E was not dependent on the concentration. The washing resistances of all the chemicals were satisfactory except Chemical F. All FC containing chemicals did not allow the penetration of soiling into the fabric, removing impurities and soiling from the fabric with ease by laundry.

Figure 2.b (see page 78) indicates that, in general, there was no big difference between all the chemicals in terms of washing resistance except E. Chemical E (FC nanomolecule) also has better stain repellency results than the others. The effect of A and D increased with a rise in concentration.

As seen in ***Figure 2.c***, (see page 78) the washing resistances of all the chemicals were generally satisfactory. It can be said that the performances of all the chemicals were very high except B and F. When the concentration of all the chemicals increased, the performances improved.

When comparing the performances of all the chemicals with respect to tea soiling, we had similar results to those for coffee soils. But all the chemicals with respect to coffee soiling in terms of washing resistance showed worse results due to the fact that coffee soiling is harder than tea soiling (***Figure 2.d,*** see page 78).

FTIR analysis of samples

The infrared spectra of untreated and treated cotton fabrics were analysed to examine absorbance changes, and slips. In ***Table 8***, the transmittance peaks of untreated fabrics are given.

In ***Figure 3,*** (see page 79) FTIR analyses of the untreated and treated samples are given.

The fabrics treated with chemicals A, C, D and E showed peaks at 1246 cm^{-1} and 1735 cm^{-1} attributed C-F and $C=CF_2$, respectively (***Figures 3.b, d, e, f***, see page 79). The reason for these new bands being different from untreated fabric is that these chemicals are C-F based. But interestingly the FTIR bands of the fabric treated with Chemical D (polymeric dendrimer containing FC) also has 1537 cm^{-1} signals (***Figure 3.e,*** see page 79), which can be attributed to amide II (NH) modes on the basis of the dendrimeric structure of this chemical. However, Chemical E, which has an FC nanomolecule based structure, was analysed with FTIR to bring out its performance, in which bands of 1246 cm^{-1} and 1735 cm^{-1} ,the characteristics of C-F and $C=CF_2$ bonds, were examined. The T% (transmittance) values of these bands were measured, from which it was found that the T% of the 1246 cm^{-1} and 1735 cm^{-1} bands were lower when Chemical E was used instead of Chemical A (conventional FC compound). For example, the T% of the 1246 cm^{-1} band decreased from 92 to 89.5 (***Figures 3.b-f***, see page 79). As a result, it can be readily clarified that with chemical E, more FC molecules were applied and bonded to the fabrics because of their nanomolecular structure [13 - 17].

In the FTIR of the fabric treated with Chemical B, which is paraffin emulsion containing zirconium salt, no significant change was observed when compared with the untreated one, due to the fact that the characteristic bands of Zr-O bonds were 450–520 cm^{-1} (***Figure 3.e***) [18].

Evaluating the air permeability results

Six various water repellents were impregnated into cotton fabrics at three different concentrations (25, 50 and 75 g/l). After the treatments, air permeability tests of the unwashed fabrics were performed, and a Duncan Post Hoc test was carried out for these values.

Figure 4 indicates that the air permeability values of all the samples decreased slightly after finishing. The highest decrease (21%) in air permeability occurred after treatment with chemical F at a 50 g/l concentration. The lowest decrease (7%) was found when the fabric was finished with chemical A at a 75 g/l concentration.

Table 9 shows that the chemical type is important statistically; among the chemicals, Chemical A showed the lowest decrease in air permeability values, whereas Chemical F caused the highest . However, it can generally be said that there was no remarkable change in terms of the breathability of all the fabrics.

Evaluating the water vapour permeability results

Six various water repellents were impregnated into cotton fabrics at three different concentrations (25, 50 and 75 g/l). After the treatments, water vapour permeability tests of the unwashed fabrics were performed, the results of which are given in ***Figure 5***.

Table 8. *Infrared transmittance peaks (cm^{-1}) of untreated cotton fabrics [9-12].*

Untreated	Possible Assignment
3333.17	OH stretching
2899.54	CH_2 and CH_3 stretching
1636.48	Absorbed water
1427.79	C-H and CH_2 bending
1360.80	
1334.92	
1314.86	
1159.65	C-C ring breathing, C-O-C antisymmetric bridge stretching in cellulose and hemicellulose
1105.13	
1052.54	C-OH secondary alcohol

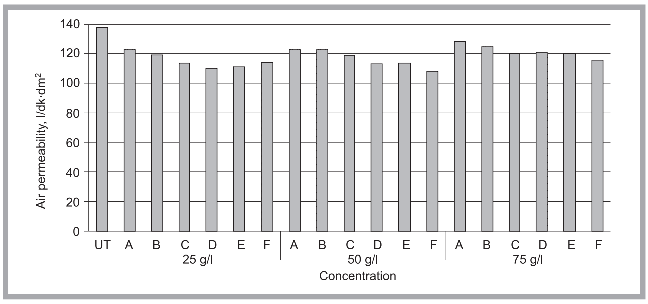

Figure 4. *Air permeability results.*

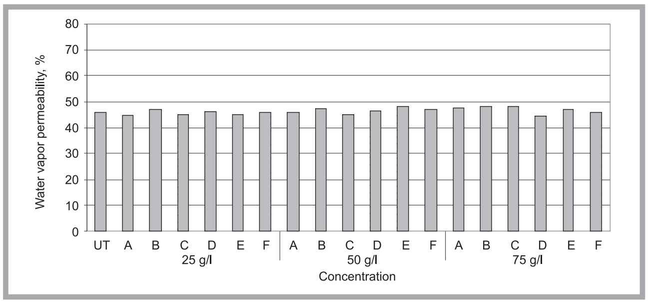

Figure 5. *Water vapour permeability results.*

Table 9. *Duncan Post Hoc test for air permeability.*

Chemical	N	1	2	3	4	5
F	18	112.78				
D	18		114.72			
E	18		115.11			
C	18			117.72		
B	18				122.50	
A	18					124.72
Sig.		1.00	0.20	1.00	1.00	1.00

It is known that after water repellency treatment, skin respiration and sweat transportation are not negatively affected due to the fact that the fabric's pores do not close [1]. Also in this study, like breathable textiles, the water vapour permeability of all the fabrics did not change greatly after treatment. According to ***Figure 5***, it can be said that there was no negative effect in terms of the water vapour permeability of all the fabrics.

Conclusion

The aim of this study was to compare the performances and washing resistances of new (dendrimer, nano-product) and conventional water, oil and stain repellents and to analyse the effect of chemical concentration. All the fabrics were treated with the same finishing processes under the same conditions. An analysis of the tests led to the following conclusions:

Water repellency results revealed the new chemicals such as polymeric dendrimer containing FC and the FC nanomolecule had better results than conventional ones in terms of performance and washing resistance. If the conventional FC compound is applied, a higher concentration of FC (75 g/l) is of great importance. In conclusion, all the FC compounds were more effective than the others. FC is an organic compound consisting of a perfluorinated carbon chain that forms a thin hydrophobic layer around the yarns, thus providing the yarn with a lower surface tension, since its surface tension is lower than most liquids. The modification of cotton fabric surfaces by use of FC compounds considerably improved the resistance of the fabrics to wetting, not only for water but also for oil and some stains. In this study, polymeric dendrimer containing FC and the FC nanomolecule were more successful than the others. Because dendrimers contain FC, they have an exceptionally low surface tension and, as a result, is particularly well suited to protecting textiles against moisture and staining. Furthermore, FC nanomolecules can provide high resistance for fabrics because of their large surface area-to-volume ratio and high surface energy, thus presenting better affinity to fabrics and leading to an increase in the washing resistance of the function.

For oil repellency, polymeric dendrimer containing FC (Chemical D) had the best performance. When the chemical concentration increased, oil repellency values rose, but after five washings these values decreased too much, except at a concentration of 75 g/l.

Stain release results for dirty motor oil and olive oil soiling clearly showed that especially the polymeric dendrimer containing FC, the FC nanomolecule and the conventional FC compound had better results than the others. When comparing the stain repellency performances of all the chemicals for tea soiling, we had similar and good results for coffee soiling without paraffin emulsion containing zirconium salt and nano-silica. The performances of all the chemicals are dependent on the concentration.

As a result of FTIR analysis, it was found that the F-C based chemicals were successfully applied to the fabrics. The fabric treated with Chemical D (polymeric dendrimer containing FC) showed 1537 cm^{-1} signals attributed to amide II (NH) modes on the basis of the dendrimeric structure of this chemical. The use of Chemical E instead of Chemical A (conventional FC compound) provided the fabrics with more bonded FC compounds because of its nanomolecular structure. However, Chemical B and F, which is paraffin emulsion containing zirconium salt and nano-silica, showed no significant change in the 650-4000 cm^{-1} bands.

The air and water vapour permeability of all the fabrics did not change greatly after treatments. It can be said that there was no negative effect in terms of the breathability of all the fabrics, and skin respiration and sweat transportation were not affected.

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