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CATIONIC POLYMERS AS FIXER PREPARATIONS OF PROTECTIVE FINISHING ON COTTON FABRICS

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Abstract. In this paper, the effect of cationic polymers on resistance of oleophobic finishing to washing and organic solvents action is investigated. It was established that the use of cationic polymer CP.2 increases resistance of the obtained protective finishing to 3-4 cycles of soap and soda treatments and significantly increases the resistance of oleophobic effect to the action of organic solvents.

Keywords: oleophobic treatment, finishing resistance, cationic polymers.

1. Introduction

In the time of growing demand for quality and competitiveness of products in textile industry, an important task is creation of chemicals and technology to provide complex consumer textile materials properties. One of the directions in the creation of protective surfaces is the production of textiles with oil-repelling properties. Oleophobization is a popular type of final treatment of textile materials, both of general and special purpose. Fabrics with such properties are widely used in the manufacture of work wear staff and oil refineries, fire, furniture upholstery materials, floor coverings, tablecloths, *etc.*

To create oleophobic materials one has to modify the surface energy of the material using oleophobic preparations – fluoride compounds, which have the lowest surface tension – 6.8 mN/m (compared to 20–35 mN/m for hydrocarbons and 72.75 mN/m for water). The action of these preparations is illustrated by the diagram shown in Fig. 1.

Water repelling preparations of different chemical nature (acrylic latexes, silicone polymers, pyridine compounds, *etc*.) do not provide the oleophobic effect because their surface tension is much higher than surface tension of oily liquids [1].

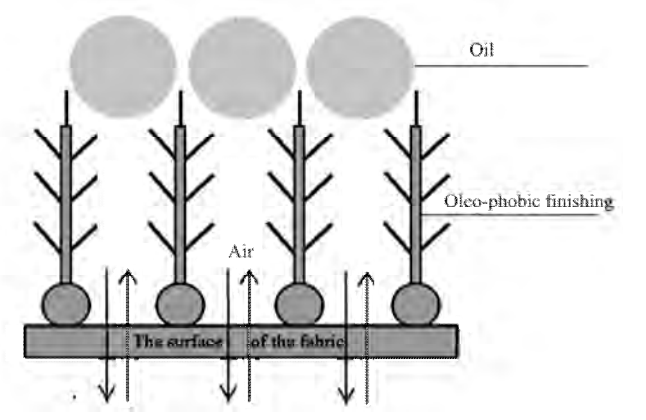

Fig. 1. The action scheme of fluorinated hydrocarbons

High quality processing is provided only by those fluorine-containing compounds which are capable of forming on the fiber a layer of tightly adjacent to each other and oriented outward extremely fluorinated hydrocarbon radicals. All this helps to minimize the free surface energy of the fiber, and, therefore, ensures a sharp decline in its wetting with water and oils. For the formation of such a layer on the fiber, side groups of the polymer main chain carbon in preparation for processing need to contain at least 6-7 fluorinated carbon atoms (CF_3–$(CF_2)_n$, where n = 5).

Polymeric carbon chain preparation provides free movement of CF_3– groups and their orientation on the fiber to form a protective coating. Replacing only one atom of fluorine for hydrogen in the CF_3– group of perfluorinated compounds dramatically increases their surface tension and reduces oleophobic properties, *i.e*. hydrogen impairs resistance of protective coating [2].

Providing textile materials with oleophobic effect is associated with the following problems:

– the tendency of oleophobic textile material to dry and wet pollution;

– impaired washability from contamination;

– sufficiently high oleophobic effect resistance.

These deficiencies manifest themselves due to a complex of reasons:

– increased pollution caused by the formation of thermoplastic oleophobic layer, tending to adhesively absorb pollution of different nature;

– impaired washing of oleophobic materials due to their poor wettability by detergents and difficult removing of contaminants from highly hydrophobic surface of textile material;

– insufficient stability of oleophobic effect on textile materials due to the ability of the oleophobic layer and textile material to swell during washing or dry cleaning. The different degree of swelling of the layers and fibers causes tearing off of the plastic layer from the surface of the fibers, *i.e.* flaking adhesion takes place. To improve stability of bonding between oleophobic layer and textile material suturing products (derivatives of urea, melamine, acrylamide) are introduced into the composition, which are capable of sewing the polymer layer and chemically reacting with the fiber. In the case of polyester fiber connection between oleophobic layer with fiber are purely mechanical [3].

As finishing processes intensification agents, foreign and domestic industry offer a wide range of textile auxiliaries with various chemical nature and properties. Of particular interest are cationic polymers, based on which multifunctional fixer preparations are created [4-8].

To improve stability of bonding between the oleophobic layer and the textile material, in this work it was proposed to use cationic polymers CP.1, CP.2, CP.3, and CP.4, produced in Russia, that differ by charge density and chemical structure (Table 1).

2. Experimental

The study was conducted on the painted cotton fabric art. 0-104 (produced by "PO TK-Donbass", Ukraine). As the fluoride compound Aquaphob Softech (produced by "MKS Devo", Turkey) preparation was used.

Table 1

Characterization of polymers used

Name	Chemical composition	The charge density, mg·eq/g
CP.1	Quaternary polyamine – based polymer epichlorohydrin and dimethylamine	4.8
CP.2	Strongly basic high molecular weight cationic polymer is synthesized by radical polymerizing the monomer dimethyldiallylammonium chloride	7.2
CP.3	The polycondensation product of epichlorohydrin and an aliphatic diamine	9.5
CP.4	The composite composition based on polyacrylamide and polydimethyldiallylammonium chloride	4.2

Table 2

Comparison of ZM and ISO 14419:2005 methods

ZM Method			ISO 14419:2005		
Liquid content in the mixture, % *n*-heptan:liquid paraffin	σ, mN/m	Oleophobic properties, c.u.	Composition	σ, mN/m	Oleophobic properties, points
100:0	20.0	150	*n*-heptan	19.8	8
90:10	20.5	140	*n*-octane	21.4	7
80:20	21.2	130			
70:30	21.9	120	*n*-decane	23.5	6
60:40	22.8	110			
50:50	23.6	100			
40:60	24.9	90	*n*-dodecanese	24.7	5
30:70	26.3	80	*n*-tetradecane	26.4	4
20:80	28.1	70	*n*-hexadecane	27.3	3
10:90	30.4	60	65:35 white mineral oils:	29.6	2
100	32.8	50	n-hexadecane, volume share	31.5	1

Notes: A – passing; clean, rounded blob; B – limit passing, round drop with partial darkening; C – no passing, a clear halo and (or) complete wetting; and D – failure to pass, complete wetting.

Oleophobic cotton was determined according to ISO 14419:2005, and in parallel by ZM method (Table 2). To this end, a series of standard liquid droplets were deposited on the cloth and kept in air for 3 min by using ZM method and 30 s – by ISO. Efficiency of oleophobic treatment was determined by the maximum surface tension of the liquid droplet, which stays on the fabric without wetting it for a specified period time. It should be noted that ZM method has more accurate calibration of oleophobic ratings from 150 to 50 conventional units (c.u.) at intervals of 10 units. According to ISO oleophobic ratings are evaluated on the scale from 1 to 8, where grade 6 by ISO corresponds to 3 ratings (100, 110, 120) and 7 – to 2 ratings (130 and 140) by ZM method.

Treated fabrics are considered quite oleophobic if the oleophobic degree by ZM method is 80–100 c.u., where for decorative and upholstery fabrics oleophobic degree should be 80 c.u. and for raincoat and coat fabrics – not less than 100 c.u. The developed method for determination of oil-repelling properties of fabrics is consistent with the average oil pollution of products during their use.

Resistance of oleophobic finishing to washing was determined according to standards by the method which is based on mechanical stirring of the investigated sample in washing solutions (4 g/l soap, 1 g/l of sodium carbonate) at 333 ± 2 K for 30 min.

Resistance of oleophobic finishing to chemical cleaning was investigated according to standards. The treated sample was pre-kept in desiccators, weighed to the nearest 0.01 g and dipped in a container of trichlorethylene (replaced by White spirit by ISO 25652-83), where it was kept during 30 min at a room temperature with periodical mixing without taking out from the solvent. After testing the sample was squeezed to remove excess solvent and dried to constant weight. Conclusion on finishing resistance to the action of the solvent was made based on the values of weight loss and checking of oleophobic properties.

3. Results and Discussion

The choice of the technological mode of cotton fabric processing by fluoride preparation Aquaphob Softech was made by fixing temperature variation from 363 to 393 K, with thermo-fixing at 423 K and without it (Table 3).

Table 3

The influence of the technological mode on resistance of the oleophobic processing to soap-soda treatments

Finishing composition	Concentration, g/l	Drying, K	Thermo-fixing, K	Time, min	Oleophobic properties before washing, c.u. (points)	Oleophobic properties after washing, c.u. (points)	
						Cycle soap-soda treatments	
						1	2
Aquaphob Softech	50	363	-	5	70B (4B)	80B (4A)	50B (2B)
	50	393	-	5	90B (5B)	80B (4B)	70A (4B)
	50	363	423	5	80B (5B)	80B (4B)	60B (3B)
	100	363	-	5	70B (4B)	80B (5B)	60B (3B)
	100	393	-	5	80B (5B)	70A (5B)	70B (5B)
	100	363	423	5	90B (6B)	70B (3B)	60B (2B)

Table 4

The influence of concentration of the fluoride preparation on resistance of the oleophobic processing to soap-soda treatments

Finishing composition	Concentration, g/l	Oleophobic properties before washing, c.u. (points)	Oleophobic properties after washing, c.u. (points)	
			Cycle soap-soda treatments	
			1	2
Aquaphob Softech	10	50C (1C)	-	-
	20	80B (4A)	50B(1B)	-
	30	80A (4A)	60B(2A)	-
	40	90B (5B)	70B(3B)	-
	50	90B (5B)	80B(4B)	70A(4B)
	60	90B (5B)	70B(3B)	50B(1A)
	70	90B (5B)	70B(3B)	50B(1B)
	100	80B (5B)	70B(3B)	60B(2B)

Table 5

Effect of cationic polymers on oleophobic properties

Finishing composition	Oleophobic properties before washing		Oleophobic properties after washing, c.u. (points) Cycle soap-soda treatments			
	c.u.	points	1	2	3	4
Aquaphob Softech – 50 g/l	90(B)	5(B)	80B(4B)	70A(4B)	-	-
CP.1 – 20 g/l; Aquaphob Softech – 50 g/l	80(B)	6(B)	60A(3A)	-	-	-
CP.2 – 7 g/l; Aquaphob Softech – 50 g/l	90(B)	6(A)	90B(6B)	90B(6B)	70B(5B)	70B(3B)
CP.3 – 5 g/l; Aquaphob Softech – 50 g/l	80(A)	5(B)	50A(3B)	-	-	-
CP.4 – 20 g/l; Aquaphob Softech – 50 g/l	60(B)	2(B)	70B(3B)	-	-	-

Table 6

Resistance of oleophobic effect to the action of organic solvents

Finishing composition	Oleophobic properties before processing		Oleophobic properties after processing	
	c.u.	points	c.u.	points
Aquaphob Softech – 50 g/l	90(B)	5(B)	70B	4(B)
CP.2 – 7 g/l; Aquaphob Softech – 50 g/l	90(B)	6(A)	90B	5(A)

It was established (Table 3) that the optimal technological processing mode is fabric impregnating with fluoride preparation Aquaphob Softech followed by drying at 393 K, allowing to ensure the oleophobic effect of 90 c.u. by ZM method and 5 points by ISO at the fluoride preparation concentration of 50 g/l. Increasing the preparation concentration to 100 g/l does not improve the oleophobic effect (Table 4).

Based on the previously conducted experimental studies [9] it was found that pretreatment of textile fabric cationic preparations CP.1, CP.2, CP.3, and CP.4 promotes the change of the negative electric charge of cellulosic fibers to positive, giving the prerequisites of using cationic preparations in oleophobic process to enhance bonding between cellulose fibers and anionic fluoride preparation.

In accordance with the foregoing, cotton fabric was pre-impregnated with solutions of cationic polymer concentration from 3 to 30 g/l, pressed to 90 % of weight gain, and then soaked with Aquaphob Softech preparation of 50 g/l concentration. The impregnated fabric was dried at 393 K for 5 min.

As a result, optimal concentrations of cationic polymers, that provide oleophobic properties of 6 points by ISO 14419:2005 and 90 c.u. by ZM method (Table 5) were selected.

Based on the data presented in Table 5, it is found that the protective effect obtained with the use of the preparation CP.2 is resistant to 3-4 cycles of soap and soda treatments at T = 333 K whereas without the cationic preparation pretreatment – to 1 cycle. The use of preparations CP.1, CP.3, and CP.4 leads to decrease of the oleophobic effect, which, in our opinion, is due to the chemical structure of the investigated cationic preparations.

The impact of CP.2 preparation on the resistance of the obtained oleophobic effect to the action of organic solvents is presented in Table 6.

According to the data presented in Table 6, pretreatment of cotton fabric by CP.2 preparation of 7 g/l concentration significantly increased oleophobic effect resistance to the action of organic solvents.

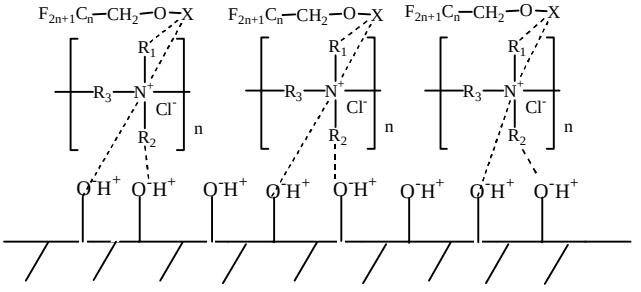

Fig. 2. A possible mechanism of cationic polymer action: R_1, R_2, R_3 – alkyl radical cationic polymer; X – active groups of fluoride compounds; ------ probable bond

In our opinion, "cotton fabric–oleophobic layer" bonding strengthening at the use of CP.2 preparation

occurs both at the expense of the electrostatic forces arising between fluoride preparation and cationic polymer, as well as at the expense of specific action of cationic polymer reactionary groups capable of formation of polymeric layer which fixes oleophobic preparation on a fabric in the course of heat treatment (Fig. 2).

Additionally, CP.2 preparation is capable of forming covalent bonds with cellulose fiber, which also enhances fixing oleophobic layer on the fabric. As a result, the obtained oleophobic finishing is characterized by high resistance to washing and dry cleaning.

4. Conclusions

1. On the basis of the conducted researches the use of cationic polymers to improve the resistance of oleophobic effect to washing and dry-cleaning action has been grounded.

2. The choice of the technological mode of cotton fabric oleophobization process as well as optimum concentrations of fluoride preparation Aquaphob Softech and cationic polymers CP.1, CP.2, CP.3, and CP.4 was performed.

3. It was established that the protective effect obtained using cationic polymer CP.2 with the concentration of 7 g/l is resistant to 4 cycles of soap and soda treatments at T= 333 K (without cationic preparation pretreatment – 1 cycle). The resistance of the resulting oleophobic effect to the action of organic solvents increases to 5 points by ISO 14419:2005 and to 90 c.u. by the ZM method.

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КАТІОННІ ПОЛІМЕРИ ЯК ПРЕПАРАТИ-ФІКСАТОРИ ЗАХИСНОГО АПРЕТУ НА БАВОВНЯНИХ ТКАНИНАХ

Анотація. *Досліджено вплив катіонних полімерів на стійкість олеофобного апрету до прання та дії органічних розчинників. Встановлено, що використання катіонного полімеру КП.2 підвищує стійкість отриманого захисного апрету до 3-4 циклів мильно-содових обробок; значно підвищує стійкість олеофобного ефекту до дії органічних розчинників.*

Ключові слова: *олеофобне оброблення, стійкість апрету, катіонні полімери.*