

IMPROVED SPIN FINISH FOR SYNTHETIC FIBRES: A NEW APPROACH TO SOLVING THE PROBLEM

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Based on an analysis of recent publications, a conclusion was drawn concerning the practical impossibility of creating multicomponent colloidal spin finishes with a defined level of processing properties. It was hypothesized that the principal solution of the problem of creating spin finishes for synthetic fibres consists of changing to the use of aqueous solutions of low-melting, ionogenic, film-forming polymers capable of large irreversible tensile strains at the temperature of orientational drawing and texturing of the fibres.

Textile auxiliary products (TAP) used in the manufacture of synthetic fibres, thread, and articles made from them can be divided into several independent groups [1]: TAP used in the synthetic fibre spinning stage; dispersers; levelers; antifoam agents; detergents; pH and redox-buffer mixtures; carriers; chemicals for final finishing. We will discuss the first group of products, combined in the literature under the term "spin finish."

The spin finish is an oiling system for controlling the state of the fibre; it has two functions: regulation of the friction level of polymer—polymer and polymer—other surface surfaces and dissipation of static electricity charges [2]. This product can formally consist of three components: oiling agent, emulsifier, and antistatic agent, but it usually also includes antioxidants, antimicrobials, pigments, and antifoam agents.

The list of the specifications for such compounds is very large [1-4] and usually also includes such indexes as thermal stability, power to wet the fibre and spread over it, adhesion to the fibre, weak foaming, weak migration into the polymer, and physiologic and toxicologic safety. The quality of a compound is also determined by the possibility of using it with some method of application on the fibre.

The choice of the type of oiling agent is a function of the desired fibre—fibre and fibre—metal friction level and the thermal stability requirements. Here thermal stability can be understood as low volatility, resistance to coagulation, duration of persistence of a liquid film on a hot surface, etc.

Mineral, animal, and vegetable oils are usually contained in oiling agents. However, in many compounds, a classic oiling agent is not required since its functions are successfully executed by the emulsifier and antistatic agent. This substitution becomes more comprehensible if we consider the concept of a slightly different role of the spin finish than the role indicated above.

As several investigators believe [5, 6], the main and unique goal of the finish — elimination of static electricity in fibres and thread — can be attained by two methods: first, by making the fibre hydrophilic and thus facilitating charge leakage (dissipation); second, preventing charge build-up by reducing the friction of fibres and yarns during movement in the processing equipment. In this approach, antistatic agents are divided into two types: those which dissipate static electricity charges and those which prevent build-up of static electricity. Blending these components should increase the antistatic effect, attaining synergism in many cases.

Giving the fibre compactness is the most important technological result of treating an as-spun fibre with a finish [3].

Since it is clear from the above that the creation of a modern compound for a spin finish is extremely complicated, the correct selection of a search strategy acquires primordial importance. For example, the strategy for such a search at the ISI Speciality Chemicals Plant (Leatherhead, Great Britain) consists of the following three directions.

The first direction involves a search for and selection of products which are potentially appropriate for use as one of the components of the finish, i.e., oiling agent, emulsifier, or antistatic agent. The investigators utilize an entire range of products

TABLE 1. Content of Components in Different Layers of an Emulsion [13]

Component	Component content, wt. %		
	upper layer	middle	lower layer
a	7.47	7.41	8.15
b	1.17	1.16	1.04
c	0.98	0.88	0.77
d	0.46	0.40	0.54

manufactured by the company, at the same time departing from the principle that there can be no success if each new finish composition is developed from the very beginning.

The second direction concerns improving the composition of the finish as a whole. By combining basic and newly selected products, compounds are created which should potentially satisfy certain defined requirements. All of the properties of the compounds obtained are compared with a series of control or standard compounds and if this is successful, they go into pilot-industrial and industrial testing in which the developers of the finish directly participate.

The third direction consists of work to improve the system for laboratory evaluation of the components and compound as a whole to the degree that the correlation between this evaluation and the test results in the enterprise utilizing the product would be clearer and the costs for conducting expensive industrial tests would be reduced.

Domestic investigators also essentially follow this strategy [7-10]. It is emphasized in [10] that the effectiveness of using some preparation for obtaining a product line is so significantly dependent on the implementation of the process that we can now speak of possible directions in the use of a concrete finish only in the most general way.

In light of these data, it is pertinent to state the question as follows: is it possible in principle to establish a sufficiently reliable correlation between the composition of a finish, which is always a multicomponent colloidal system, and the technological consequences of applying it on synthetic fibres and filaments?

It is very obvious that a positive answer to this question is possible when three invariable conditions are satisfied:

- the compound is micro- and macrohomogeneous;
- the composition of the compound on the surface of the fibre (filament) is identical to its composition in the oiling bath;
- the composition of the compound on the surface of the fibre is almost constant in the process change-overs following the spinning process.

However, recently published studies [11-16] suggest that none of these conditions are actually satisfied at all or are very rarely satisfied. Taking the example of a 10% aqueous emulsion whose oil phase consisted of four components (in %):

refined naphthene oil	75
alcohol ethoxylated with 2 moles of ethylene oxide	10
nonylphenol ethoxylated with 12 moles of ethylene oxide	10
coconut oil acid diethanolamide	5

it was shown in [13] that for external stability of the emulsion at room temperature for more than five months, the actual concentration of the components at different heights in the vessel was different (Table 1). This suggested that while it is aggregately stable on the whole, an aqueous emulsion of TAP can be compositionally inhomogeneous. Moreover, even in the case of contact of synthetic fibres with a compositionally homogeneous TAP emulsion, the identity of the compositions of the TAP in the bath and on the fibre should not be the rule, but instead a rare exception.

The results of the analyses of the starting oiling compound and composition of the finish going on polyethylene terephthalate fibre performed in [14] and reported in Table 2 clearly confirm this hypothesis.

The inconstant composition of the finish on the fibres during textile treatments is due to the thermal instability, particularly the hydrolytic instability [11] of carboxylic acid esters and alkylphenol ethoxylates on one hand and the solubility of the components of the finish in the amorphous phase of fibre-forming polymers [15, 16] on the other hand.

TABLE 2. Results of the Analysis of the Initial Oiling Compound and Composition of Finish Going on Polyethylene Terephthalate Fibre [14]

Component	Content of component, wt. %	
	initial compound	finish on fibre
Monoalkyl phosphate	0.139±0.019	0.023±0.003
Dialkyl phosphate	0.188±0.015	0.045±0.003
Polyethylene glycol monoester	0.161±0.006	0.042±0.004
Polyethylene glycol diester	0.067±0.009	0.037±0.006
Total	0.555	0.147

TABLE 3. Composition and Physical Properties of Ternary Copolyesters Based on Sulfophthalic Acid, Polyethylene Glycol, and Diglycol Terephthalate [20]

No.	Copolyester		t_m , °C	EEC,** meq/g	Sulfur. % content, wt	$\rho \cdot 10^{-10}$ at 65% relative humidity, Ωcm	
	composition*	concentration of component, mole %				I***	II
1	Na-SPA	30.0	184-190	1.15	207	48.0	80.0
	PEG	1.2					
2	Na-SPA	30.0	170-170	0.78	2.0	26.0	7.5
	PEG	3.3					
3	Na-SPA	25	149-160	1.0	1.5	25.0	14.0
	PEG	10					
4	Na-SPA	20	115-125	0.85	1.3	2.7	1.6
	PEG	25					

*Na-SPA: sulfophthalic acid sodium salt; PEG: polyethylene glycol.

**EEC: equilibrium exchange capacity.

***I: concentration of copolyester in water bath used for processing fibre, 0.5 wt. %, II: 1.0 wt. %.

The major conclusion thus follows from the above that the problem of creating multicomponent colloidal TAP whose use is associated in advance with certain technological consequences is most probably primarily insoluble. As a consequence, in all cases where the oiling system must be colloidal, it is necessary to use the search strategy clearly formulated in [2] and successfully implemented for production of synthetic fibres and filaments [7-10] and production of textile materials [17].

However, the problem consists of whether the spin finish for synthetic fibres must obligatorily be a colloidal solution.

For a correct answer, it is important to keep in mind that the tradition of using aqueous emulsions as oiling and brightening agents came to the man-made and then also the synthetic fibre industry from the textile industry, where such products began to be widely used in cotton spinning at the end of the 1920s [18, 19] when it was necessary to satisfy two apparently incompatible requirements: easy sliding of fibres in the flyer frame to attain a high degree of drawing of the fibres and good cohesion of the fibres in the yarn to ensure its mechanical strength.

Fabrication of yarn from blends of natural and chemical fibres, the same as from chemical fibres alone, requires the same approach. For this reason, the use of emulsions whose oil component coats each fibril, ensuring its "individuality," on one hand and a sufficient level of interaction with neighboring fibres on the other is totally justified.

A different situation arises when synthetic complex fibres used for fabricating knitted fabrics (articles) and household or industrial cloth must be given compactness, antistatic, and optimum friction properties. In these cases, it is important for the

fibre to behave as a unified whole, and for this reason, the strength of the interfilament contacts attained by their bonding in the direct or figurative sense must be high enough.

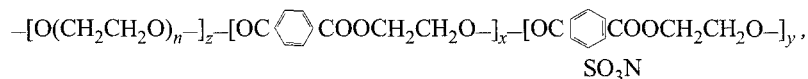
In other words, with respect to application of a spin finish on synthetic fibres not undergoing subsequent stapling, an analogy with loom sizing of fibres is suggested. However, the main difference between these processes consists of the fact that the polymer film applied on the synthetic fibre during spinning should be capable of large (hundreds of percent) irreversible tensile strains without perturbation of the integrity at the temperature of orientational drawing and texturing of the fibres. Since this film must give the fibres antistatic properties and the process of applying it on the fibre is environmentally safe, the polymer used for this purpose must be water-soluble, ionogenic, and capable of being transformed into a viscous, spontaneously nonfluid, but easily deformed melt at the temperature of the indicated processes which does not hinder structural rearrangements of the polymer from which the fibre is spun. In addition, the protective film formed on the surface of the fibre should have the technologically necessary friction level with respect to the surface of the thread-guide fittings.

It is very obvious that such polymers as starch, carboxymethyl cellulose, polyvinyl alcohol, polyacrylates, products of hydrolysis of polyacrylonitrile, and even high-molecular-weight polyethylene glycols do not satisfy these requirements. We should undoubtedly consider specially synthesized multicomponent heterochain polymers containing fragments of different functional (in light of solving the problem posed) directionality in amounts which would ensure attaining the optimum properties with respect to one or more types of synthetic fibres.

Going from multicomponent colloidal spin finishes to products which are an aqueous solution of a multicomponent copolymer has the following major advantages:

- the real polymer solution is always homogeneous;
- the composition of the film formed on the surface of the fibre is not a function of the process parameters of application of the product;
- due to the nonvaporizability of the polymers and their relatively high thermal stability in comparison to low-molecular-weight products of similar chemical structure, the composition of the protective film is almost invariable in all process changes following fibre spinning;
- as a result of decreasing the amount of gaseous products liberated in orientational drawing and texturing of the fibres, the working conditions for personnel servicing this equipment improve significantly;
- the film can contain a covalently bound dye and act as a marker;
- at the necessary time, the film can be removed from fibres or articles by simply treating them with water.

As an example illustrating the practical feasibility of this general idea, the properties of ternary copolyesters of the following general formula



forming a sufficiently elastic thermostable (decomposition temperature of 325-335°C) film with ionic conductivity and hydrophilicity on the surface of Lavan fibre according to [20], are reported in Table 3.

The data cited are primarily interesting because they demonstrate the absence of a direct correlation between the concentration of sodium sulfonate groups in the copolyester and the antistatic properties of such a polymer.

The picture is different if the surface electric resistance of the films is compared with the ratio of rigid (glycol terephthalate and glycol sulfophthalate) and flexible (ethylene oxide) units in the copolymer:

Copolymer	$[-\text{OCH}_2\text{CH}_2-] / [-\text{OCH}_2\text{CH}_2\text{OCO}-\begin{array}{c} \diagup \\ \diagdown \end{array}-\text{CO}-]$	$\rho \cdot 10^{-10}, \Omega \cdot \text{cm}$
1	0.28	48.0
2	1.16	26.0
3	3.03	25.0
4	9.10	2.7

TABLE 4. Some Physicochemical Characteristics of Caprolactam and PEG-400 Block Copolymers [23]

No.	$\frac{[-\text{OCH}_2\text{CH}_2-]}{[-\text{NH}(\text{CH}_2)_5\text{CO-}]}$	$d, \text{kg/m}^3$	Moisture absorption, wt. %	T_m, K	Dyeability,* g/kg
1	0	1136±1	3.70±0.20	493±1	2.1±0.3
2	0.135	1151±8	4.71±0.03	492±1	4.4±0.1
3	0.315	1146±3	5.3±0.2	483±2	5.0±0.2
4	0.725	1133±5	5.6±0.3	476±1	6.2±0.3
5	1.450	1102±4	8.35±0.01	443±2	—

*Estimated with sorption of cobalt phthalocyanine disulfonic acid sodium salt.

TABLE 5. Solubility of Caprolactam and Polyethylene Glycol Block Copolymers [23]

Solvent	[-OCH ₂ CH ₂ -]/[-NH(CH ₂) ₅ CO-] ratio		
	0	0,135	1,450
Benzyl alcohol	S.h.	S.h.	S.r.
Ethylene glycol	I.s.	S.h.	S.h.
Ethanol	I.s.	S.h.	S.r.
Ethanol H ₂ O (1:1)	I.s.	S.h.	S.h.

Notation: i.s.: insoluble; s.h.: soluble when heated; s.r.: soluble at room temperature.

In the given case, it is totally appropriate and obvious to speak of the clear tendency toward improvement of the antistatic indexes of the copolymer as the concentration of flexible and hydrophilic ethylene oxide units in it increases. The positive role of the —SO₃Na group primarily consists of giving the copolymer water solubility.

This hypothesis is totally in agreement with both the results of studies on synthesis of water-soluble aromatic polymers [21] and with our data [22, 23] on the effect of the ratio of [—NH(CH₂)₅CO—] and [—OCH₂CH₂—] fragments in the macromolecules of copolymers based on caprolactam and polyethylene glycol on the solubility and other physicochemical properties of these copolymers.

The data reported in Tables 4 and 5 show that changing from pure polycaprolactam to a copolymer containing 1.45 ethylene oxide units per caprolactam unit on average is accompanied by a significant increase in the hydrophilicity and accessibility of the polymer for large organic molecules. However, it still does not acquire properties of water solubility, in contrast to the ternary copolyester containing only 0.28 ethylene oxide units per ethylene terephthalate (ethylene phthalate) unit if approximately every other one of the latter units contains a sulfo group in the salt form.

From this point of view, selecting the type and concentration of ionogenic group in the macromolecule of the copolymer is primarily dictated by the conditions of satisfying the water solubility requirements while simultaneously preserving the low meltability of the polymer.

The results recently obtained in the Department of Chemical Fibre Technology at Ivanovo State Chemical Engineering University show that the problem of developing an assortment of heterochain polymers which satisfy all of the requirements

noted above is unconditionally solvable and as a consequence, the prospect of changing to a primarily new (solution-type) spin finish in fabrication of synthetic fibres is not utopian.

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