

# **industrial processes**

## **Treatment of textiles in an organic solvent medium**

COMMISSION OF THE EUROPEAN COMMUNITIES

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Comitextil Scientific Research Centre

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TREATMENT OF TEXTILES IN AN ORGANIC SOLVENT MEDIUM

SCIENTIFIC AND TECHNICAL REPORT

This report describes and presents the results of a scientific research project in the textile field, carried out jointly, at Community level, by several laboratories in various member countries of the EEC.

It relates to research topic N°2 of a so-called initial "feasibility" programme, the two other topics of which deal with "The heat treatment of chemical fibres" (N° 1) and "Fire-proofing by radiation grafting" (N° 3).

The collective nature of this research, resulting from its synergetic effect, enables the necessary effectiveness threshold to be reached and the results obtained to be placed at the disposal of all the undertakings in the sector.

Devised in the framework of the Strategy for the European textile sector, this programme, like the one which follows on from it, is based on the objectives for common policies prescribed for industrial competitiveness, economic and social profit and regard for the consumer.

It is being carried out at the instigation of and under the direction of the Comitextil's Scientific Research Management Centre, with the financial assistance of the EEC Commission.

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October 1979

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SUMMARY

The aim of the research was to examine the possibilities of replacing certain finishing treatments in an aqueous medium by treatments in a solvent medium, with the aim of lessening pollution and making energy savings.

The programme consists of a theoretical subject and three cases of practical application.

In the theoretical study, the solvents-textile materials interactions, principally for the PER/polyester system, were examined.

The practical applications are:

- the extraction of oligomers, more particularly from polyester and polyamide,
- the dyeing of wool in a solvent medium and the extraction of surface impurities,
- the extraction of non-fixed dyes from polyester textile materials.

I.

INTRODUCTION

In our industrialised world, serious environmental pollution problems, one of the aspects of which is water pollution, are increasingly frequently having to be faced. It is therefore logical that the discharge of effluents should be regulated and controlled by the public authorities.

This means that in order to meet these requirements, the effluents will have to be treated within the undertakings themselves before being discharged into surface waters or use will have to be made of communal waste treatment plants, to which a fee will have to be paid depending on the volume of effluent and the amount of pollution caused.

In the textile sector, it is chiefly finishing firms which are faced with the problem. Textile finishing processes are traditionally carried out in an aqueous medium, thus producing huge quantities of effluents which are full of chemical products. In West Germany, for example, textile finishing is in eighth place for water consumption and the production of effluents.

In addition, the current market demands textile goods the colours of which are particularly fast. This is also the case for certain finishes. This involves the use of dyes and chemical products which are only degradable with difficulty and which, due to the fact that even in small concentrations they colour the effluents and give the observer the impression that the pollution is even greater.

Furthermore, good quality water is become increasingly scarcer and therefore expensive.

There are several solutions for resolving, or lessening, the problems of water in the finishing industry:

- reduction in the volume of effluents: e.g. short liquor processes (discontinuous) or the "minimum concentration" technique (continuous),
- purification of effluents: e.g. by chemical, biological or physico-chemical treatment,
- elimination of the production of effluents: e.g. by treatments in a solvent medium.

Numerous studies on the purification of effluents have enabled various systems to be perfected.



The objective of this particular research project is to examine the possibilities offered by the third possibility: finishing treatments in a solvent medium. The solvents can indeed be recovered in their pure state after use thanks to distillation and with relatively low energy consumption, and the wastes contained in these baths are recovered either in compact form or in paste form, in such a way that solid waste is obtained rather than the waste streams being polluted. Nevertheless, the future possibilities for this technique vary widely depending on the textile finishing fields. As far as pre-washing and finishing are concerned, it has already been brought in relatively widely, as shown *inter alia* by the wide range of machines for sale on the market.

As far as dyeing in a solvent medium is concerned, the euphoria of the initial period has given way to a sensible and realistic way of seeing things.

The use of solvents as carriers for chemical products does indeed pose a number of problems which have been unknown up to now, which means that for the time being optimal operational security and thus generalised application is not possible.

In this Community study, an attempt has been made to co-ordinate the work carried out by laboratories in various EEC countries and to evolve as a group a programme which, as a result of the study of the important parameters and of the suggestions for application, will enable European textile manufacturers to be in possession of basic data enabling solvent treatment techniques to be used.

The research project consists of a theoretical part and a practical part.

It was necessary to obtain some more basic knowledge about the interactions between the various solvents and textile materials. In this part of the programme, special attention is paid to perchlorethylene-polyester interaction. A second part is given over to the study of the extraction by solvents of polyester and polyamide 6.6. oligomers. The two other practical studies relate to the solvent medium dyeing of wool and the extraction by solvents of surface impurities on the one hand and the extraction of non-fixed dyes after thermosol dyeing of polyester on the other. For the two applications, the influence of the most important parameters was determined.

II.

INTERACTION BETWEEN TEXTILE MATERIALS AND SOLVENTS

When the use of organic solvents as a carrier medium in textile finishing was first examined, it was realised that this technology presented not only advantages but also gave rise to a number of new problems.

One phenomenon which plays a very important part is the swelling of fibrous materials in an organic solvent medium, i.e. the absorption of the solvent by the textile.

Certain industrial treatments in a solvent medium are dependent on the swelling of the fibres.

To quote a few examples:

- . the modification of synthetic fibres to improve their dyeing affinity,
- . certain treatments to obtain dimensional stability for textile or synthetic goods,
- . the "Prograde" (R) and "Sanforset" (R) processes, which are applied industrially to cotton yarns with the aim of improving lustre, dyeing behaviour and mechanical properties,
- . the cleaning of synthetic textiles in a solvent medium. Thus, at the present time, 30% to 50% of the treatments used in cleaning synthetic knitware involve the use of perchlorethylene (PER),
- . the desizing of fabrics.

Organic solvents can also give rise to varying degrees of swelling reduction, which is necessary in certain finishing treatments and must be avoided for others.

It is clear that swelling behaviour must be well known if it is wished to examine the possible use of organic solvents in the textile industry. This is why this subject is dealt with in the first section of this research project.

Work was directed towards the "polyester-solvents" system, where stress was laid on perchlorethylene.

The following points were examined:

- the absorption of solvents by polyester fibres: the swelling in equilibrium values and the kinetics of sorption,
- the shrinkage of fibres and developments in the shrinkage tension resulting from a treatment in a solvent medium,
- the variation in the vitreous transition temperature of polyester resulting from swelling,
- the desorption of the solvents absorbed by the polyester.

1. The textile materials used

The tests were carried out on various types of polyester:

- polyester filament (polyethylterephthalate), dtex 150 f 48, bright: non-set, textured,
- Vestan <sup>(R)</sup> fibre (polycyclohexane-1, 4-dimethylalterephthalate), 16 dtex 17/10, bright,
- Diolen 42, a polyester with improved dyeing affinity.

The samples are treated beforehand by extraction for 30 min. with petroleum ether (low boiling point) in a Soxhlet.

2. The tests carried out

2.1. Absorption

2.1.1. Measurement method and description of the test

The absorption of the solvent by the fibre was principally determined by gravimetry in a nitrogen atmosphere using a thermo-balance (model TGS-1 of the Perkin-Elmer brand). The tests were carried out on samples of 5 mg of fibre rolled into 3 mm to 4 mm in diameter balls. They were treated with the solvent in a thermostatically controlled chamber at different temperatures and for various lengths of time. Before the quantity of solvent absorbed is determined, the non-absorbed solvent on the surface of the fibre must be eliminated. For PER, the impregnated sample is placed in the measuring apparatus, where the non-absorbed solvent evaporates very quickly at constant speed. During this stage the recorder produces a very steep time/desorption curve which stops suddenly after a certain period of time; the non-absorbed solvent is then eliminated. The desorption of the solvent absorbed, which is inside the fibre, continues very slowly. By extrapolation of the two parts of the graph, the G1 weight of the sample: textile + solvent absorbed can be determined.

The temperature of the balance is then raised to 200-240°C; the solvent absorbed evaporates. This evaporation is over when the weight of the sample remains constant at a G 2 value. The quantity M of the solvent absorbed by the fibres is then:

$$M = G_1 - G_2$$

For certain solvents, such as alcohols, trichloroethylene or methylene chloride, the point of inflection is less pronounced and extrapolation gives less reliable results. Other solvents, such as dimethylformamide, which have a higher boiling point and a low vapour pressure, are very strongly fixed to the surface of the fibres and it is practically impossible to eliminate the solvent on the surface completely at room temperature. In this case the samples are squeezed in a piece of cotton cloth and cleaned with a solvent with a low boiling point, such as diethyl ether, which does not penetrate into the fibre. After this treatment the measurements can be made using the method described above.

In order to determine very small quantities of PER in polyester, the measurements were made by pyrolysis in conjunction with a Perkins-Elmer 990 chromatograph during the gaseous phase. The samples were then heated in a pyrolysis cell at 250°C and the PER extracted by the nitrogen was brought into the chromatograph.

#### 2.1.2. Results

Table 1 shows the swelling in equilibrium values for various types of polyester treated in PER at 120°C.

It was noted that at this temperature the solvent is very quickly absorbed by the polyester fibres and that after only a few minutes relatively high swelling in equilibrium values are reached. As in industrial treatments, the textile may be under tension or with more or less unrestricted shrinkage, the tests were also carried out on yarns of constant length.

Table 1 - Absorption of PER by polyester fibres at 120°C

Fibre	Absorption of PER (g/100 g)
Polyester, filament, non-set, unrestricted shrinkage	9.8
Polyester, filament, non-set no shrinkage	8.3
Diolen 42	11.6
Vestan (R)	13.1

The above figures show that the swelling in equilibrium value does not depend solely on the chemical composition of the polyester but also on the chemical treatments to which the fibre has been subjected; after texturing, absorption of the solvent falls and is slower.

It was also found that the heat-setting temperature has an important role to play. Figure 1 shows the swelling rates as a function of the heat-setting temperature of the polyester set without tension.

Absorpt. of PER

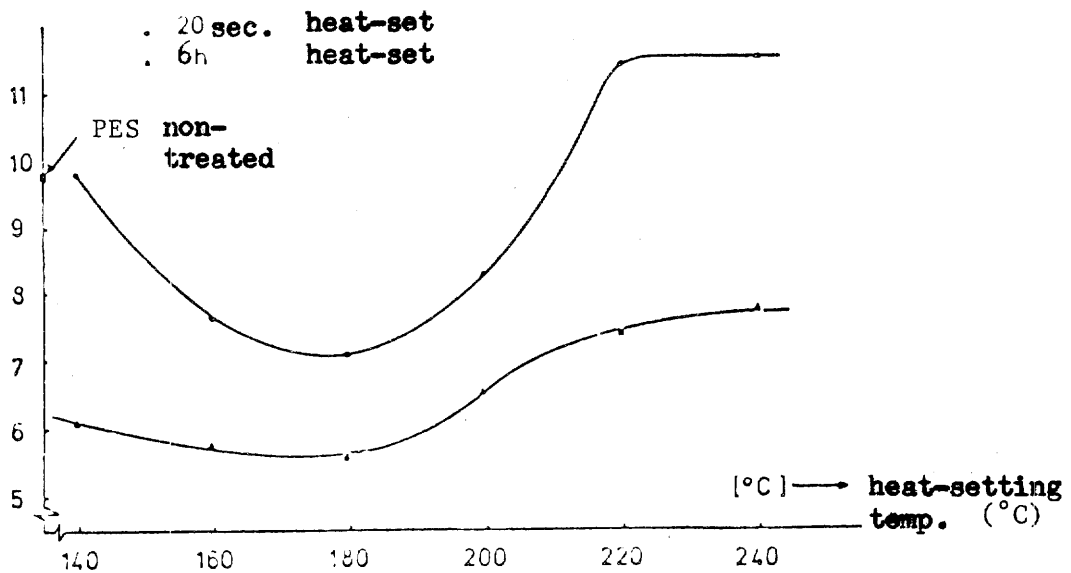


Fig. 1 - Influence of the heat-setting temperature on the absorption of PER by polyester at 120°C.

The absorption of the solvent decreases up to a setting temperature of 180°C and then proceeds to increase, as is the case for dyeing affinity. This curve's profile is determined by the interaction of two opposing effects:

- . the Röntgen diagrams show that with a rising setting temperature the lateral arrangement in the fibre increases. Consequently, the density of the yarn increases and this leads to a drop in the absorption of PER,
- . the rise in the setting temperature produces increasing differentiation between the amorphous and crystalline areas. The accessible areas become more "porous" and the absorption of PER increases.

Simultaneously with these very rapid phenomena, a very slow crystallisation process is to be noted during the treatment of polyester yarns. However, industrial heat-setting hardly exceeds 15 to 30 sec. and this crystallisation process is not then over. It was therefore interesting to carry out the same absorption tests a second time on the polyester, which this time was treated for 6 h, in a vacuum, without tension, at the various setting temperatures already used for the 20 sec. treatment. A period of 6 h was chosen because it is stated in literature on the subject that crystallinity no longer changes after 6 h of treatment, with the result that the fibrous structure then depends solely on the treatment temperature and the length of the treatment no longer has any influence.

In comparison with the samples treated for 20 sec., it is to be noted that in materials treated for 6 h the degree of crystallinity is higher, as the amorphous areas are proportionately fewer; the absorption of PER thus diminishes in the same ratio (fig. 1). The curve, however, looks the same as for shorter treatment times: it reaches a minimum at 180°C and then rises owing to the increasingly marked contrast between the amorphous and crystalline areas.

The exertion of tension on the textile material also influences swelling; external tension interferes with swelling.

In industry, textiles are often treated at temperatures below 120°C. This is the case for instance with regard to the pre-washing of knitted fabrics, certain finishing treatments, washing operations after continuous dyeing. Absorption at lower temperatures was thus measured. It was found that when the treatment temperature falls as low as 30°C, the quantity of solvent absorbed is the same as in treatment at boiling point.

Table 2 below gives the swelling in equilibrium rate for the various types of polyester, as a function of the treatment temperature:

Table 2 -

Treatment temp. (°C)	Swelling rate (g/100g)				
	Polyester			Non-set Vestan	Non-set modified Polyester (b)
	non-set	set (a)	textured		
40	11.4	-	-	-	-
50	11.2	-	-	13.0	10.3
60	10.8	6.8	7.0	-	-
70	10.5	6.9	-	13.1	-
80	10.0	7.0	7.0	13.5	11.4
90	-	7.1	-	-	-
100	9.8	-	7.5	-	-
120	9.8	7.2	8.0	13.1	11.6

(a) heat-setting at 180°C for 20 sec., without tension,

(b) polyester with improved dyeing affinity.

It is interesting to note that for conventional non-set polyester the swelling in equilibrium rate decreases slightly when the temperature rises, in contrast to the values noted for modified polyester.

If the swelling in equilibrium rate remains constant with the temperature, the sorption speed falls sharply, with the result that in industrial treatments, which are generally short, absorption is nil or very slight (fig. 2).

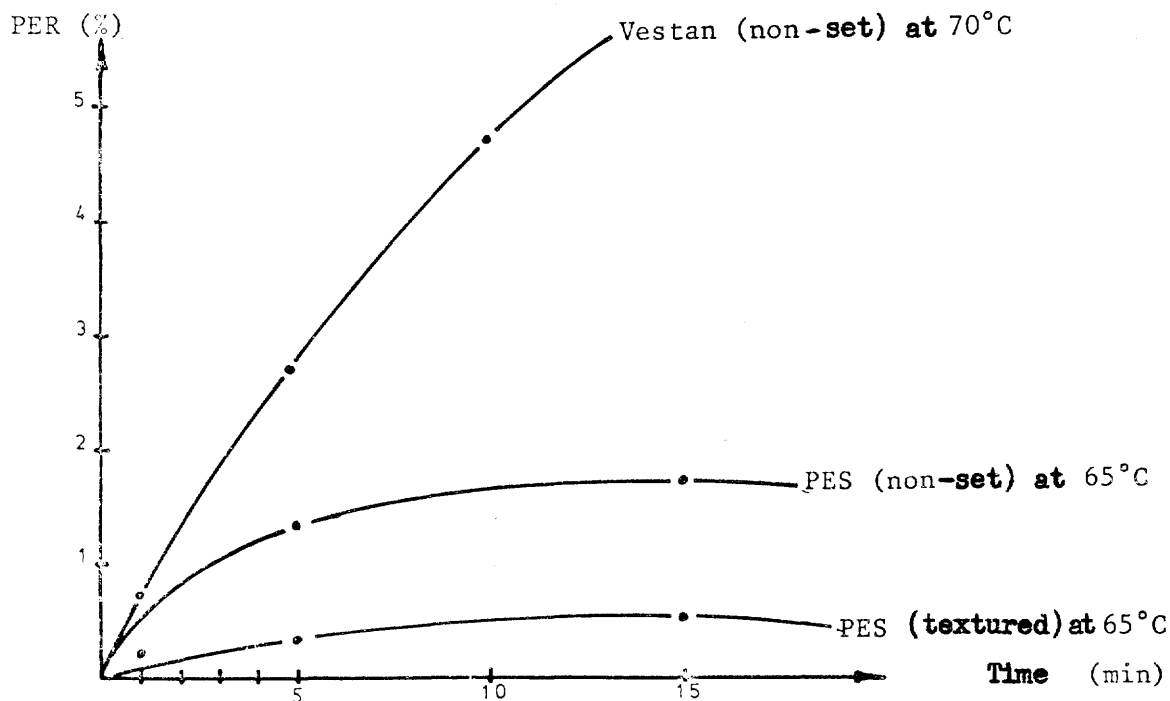


Fig. 2 - The absorption of PER into polyester fibres

The above figure shows that for a treatment temperature of 65° to 70°C, textured polyester contains only 0.5% to 0.7% of PER after 15 min. The non-set fibre absorbs a little more solvent: 1.8% to 2%, while absorption is highest for non-set Vestan: ± 6%

Continuous cleaning machines operate at temperatures of 20° to 50°C and the treatment time is 30 to 60 sec. Under these circumstances, absorption of solvent is minimal (fig. 3), < 0.05% for polyester.



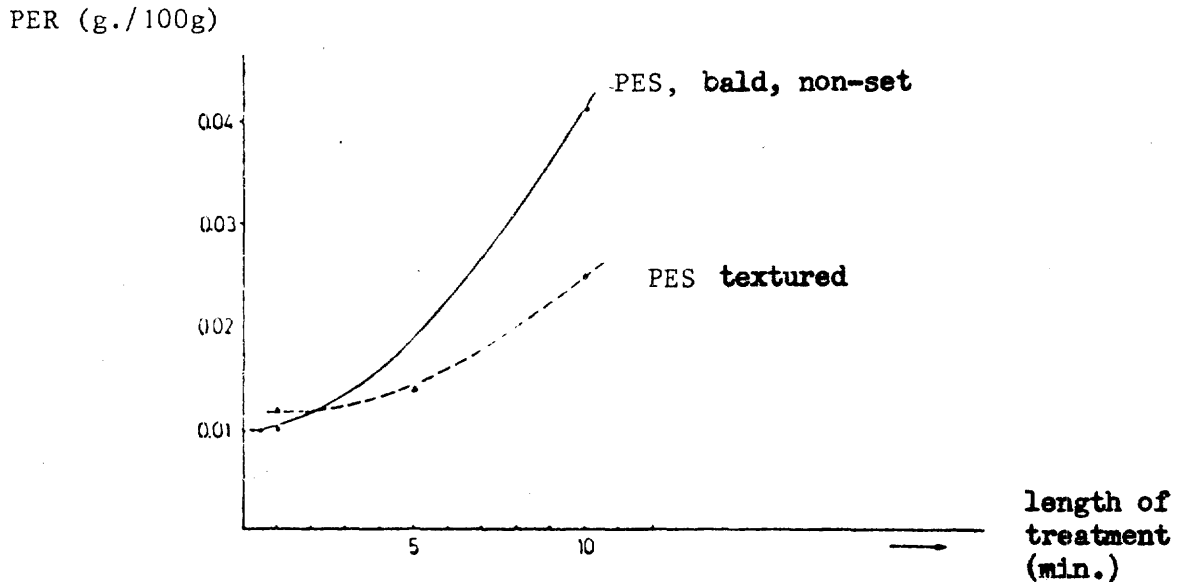


Fig. 3 - Absorption of PER by polyester during a cleaning treatment at 30°C.

After this cleaning, the textile impregnated with PER is air-dried at 100-140°C. Under these circumstances the fibre may well absorb a little PER, which will remain after cooling. Very small quantities are concerned, however, as under current conditions in industrial treatments, PER loss totals only 1% to 3%, and account must be taken of the fact that this loss is not caused solely by absorption of PER but other phenomena may play a part, such as for instance leakages in the equipment, draining off with the escaping air, in the distillation waste, in the water separation.

With the aim of studying the kinetics of PER sorption by polyester, the relative swelling value was determined:  $\frac{Q_t}{Q^\infty}$ .

where  $Q_t$  = swelling after a period of time  $t$

$Q^\infty$  = swelling in equilibrium.

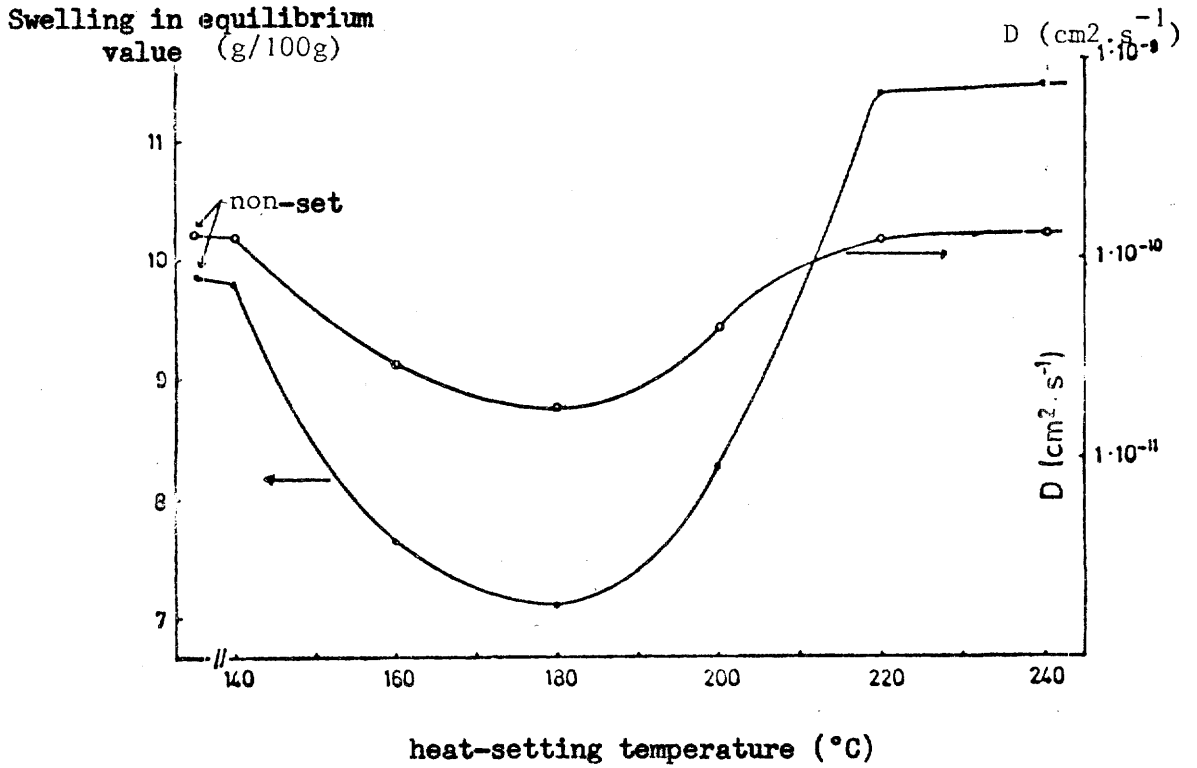
The apparent coefficients of diffusion were then calculated roughly (3) for various temperatures; they are given in table 3.

Table 3 - Apparent coefficients of diffusion for the absorption of PER into polyester.

Temperature (C°)	Ds - 10 <sup>11</sup> (cm <sup>2</sup> / s)	
	Non-set polyester	Set polyester (a)
50	0.026	-
60	0.190	-
70	0.405	0.076
80	1.41	0.266
90	8.0	1.607

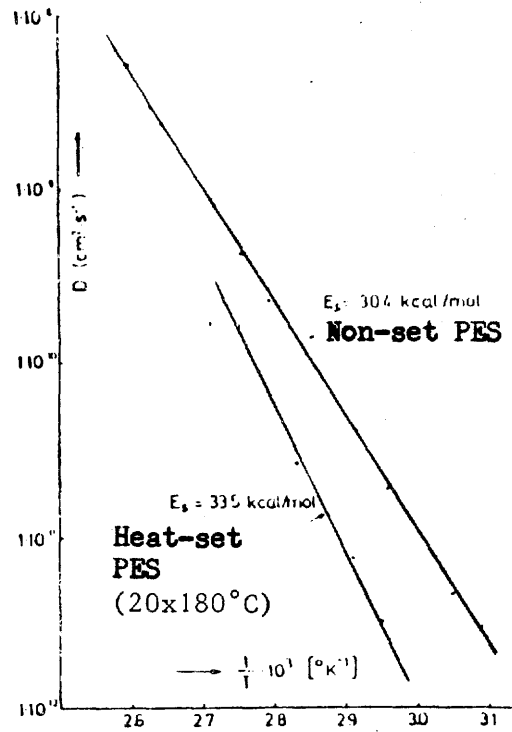
(a) : 180° C, 20 sec.

It is to be noted that the diffusion of PER in the fibre is slowed down considerably when the latter has been subjected to a prior heat treatment, where account must be taken of the influence of the temperature of the heat treatment, which is similar to that recorded for the swelling in equilibrium rate (fig. 4).



**Fig. 4** -- Apparent coefficients of diffusion and swelling in equilibrium rate of PER in polyester yarns at 80°C, as a function of the heat-setting temperature.

When the logarithm of the coefficient of diffusion and the reciprocal of the PER bath temperature are correlated, a linear relation is obtained. The slope of this straight line enables apparent mean values of activation energy for the diffusion of PER in polyester to be determined (fig. 5).



**Fig. 5** - log D as a function of  $1/T^\circ$  for the absorption of PER into polyester fibres

For the various types of polyester tested, the following values were found:

Es (kcal/mol)	Fibre
30.4	<b>Non-set polyester</b>
33.5	Polyester <b>set at</b> 180° C
15	Vestan

These relatively high values indicate that the diffusion of PER is determined by the mobility of the segments of the polymer chains. Similar values are obtained for the absorption of dyes into polyester. The measurements made show in addition that for the temperature field in question, the activation energies are constant, which would mean that this range from 50° to 120°C is above the vitreous transition temperature of the polyester/PER system.

## 2.2. Shrinkage and changes in the shrinkage tension of polyester in PER

### 2.2.1. Measurement method and description of the test

The continuous filament polyester yarn is treated with PER in an isothermal container. After a specific treatment time, changes in the length of the yarn are measured using a cathetometer. The samples which are without tension in the treatment container are taken out briefly for each measurement. A low weight is attached to the end of the yarn, which is thus in a taut position for measurement.

The shrinkage tension which appears when a polyester yarn of constant length is allowed to swell in various solvents was measured using apparatus specially made for this purpose.

### 2.2.2. Results

The absorption of solvents reduces the intermolecular interactions in the polymer and causes segments of the chain to break up. The mobility of the molecule chains in the polymer is thus increased and the tensions accumulated during spinning and stretching are relaxed. When the yarn is subjected to a treatment without tension, this relaxation takes the form of shrinkage of the yarn. Figure 6 shows the shrinkage isotherms of polyester in PER, where the time scale is logarithmic.

Shrinking

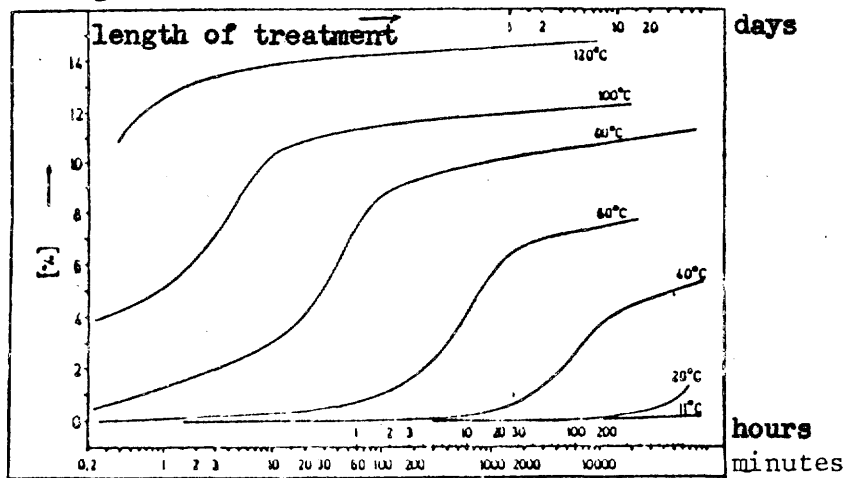


Fig. 6- Changes in the shrinkage of polyester fibre in PER.

In dyeing conditions, where the temperature is about 120°C, rapid and extensive shrinkage is to be noted, whereas between 20°C and 60°C, and for the lengths of time generally used for cleaning with solvents, the length of the fibres does not change.

Generally speaking, the shrinkage process consists of three phases:

- . an induction period,
- . a period where the maximum shrinkage speed is reached,
- . a "post-shrinkage" phase.

These phases are particularly well defined for solvents more active than PER, for example methylene chloride.

A linear relation is obtained between the maximal shrinkage speed according to the Arrhenius equation and the treatment temperature, the slope of which enables the shrinkage activation energy to be determined. Its value is 30.5 kcal/mol, which corresponds to the activation energy for the diffusion of PER in polyester (fig. 5). This concordance is not surprising as both the absorption of solvent molecules and shrinkage are due to molecular interactions between the chain segments.

In addition to the shrinkage phenomena, it is also interesting to examine the shrinkage tensions which come into play when the length of the fibres remains constant. During chemical and heat treatments, the molecular re-arrangements develop a force, in the direction of the longitudinal axis of the filaments, which can be measured, on condition that the length of the sample is kept at a constant value.

Fig. 7 shows the development of the shrinkage tension as a function of the treatment time, at various temperatures.

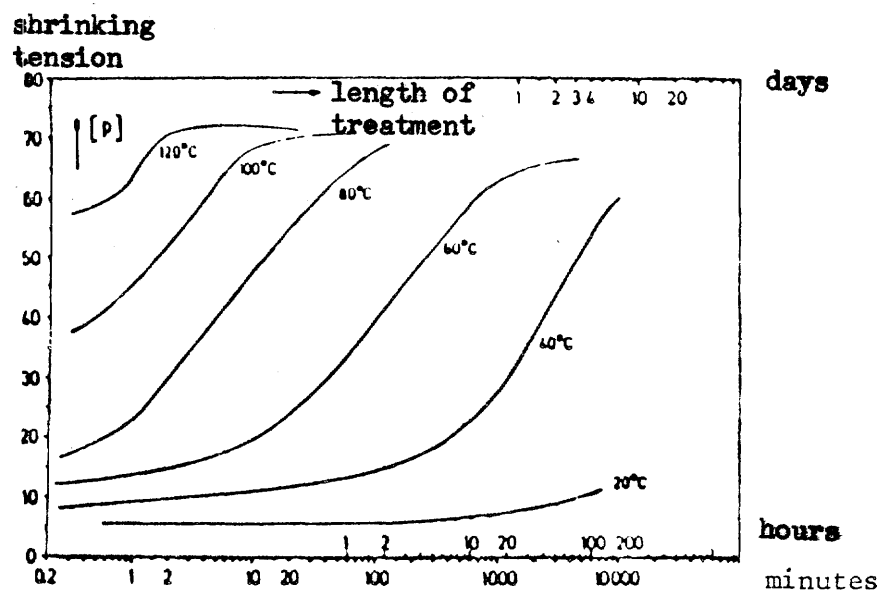


Fig. 7-- Changes in the shrinkage tension of polyester yarns in PER.

While shrinkage in equilibrium, in the absence of tension, increases with a rising temperature, shrinkage in equilibrium tension seems, as far as the temperatures in question are concerned, to be less influenced by temperature. The same finding was made about solvents other than PER.

It should be noted that the changes in the shrinkage tension result from two opposing effects; on the one hand, swelling causes a change in the structure resulting in a shrinkage of the fibre, on the other a treatment without shrinkage can give rise to a relaxation of tensions. This latter effect becomes more marked with rising temperatures, and this can result in the end in the shrinkage tension not increasing with the temperature, as in the case of unrestricted shrinkage.

### 2.3. The change in the vitreous transition temperature of polyester by swelling in PER

#### 2.3.1. Measurement method and description of the test

The vitreous transition temperature can be determined using two methods:

- . By charting the shrinkage in equilibrium value as a function of the temperature, a linear relation is obtained. The extrapolation of this relation up to zero shrinkage point enables a temperature value to be found which roughly corresponds to the vitreous transition temperature.
- . In the case of the interaction between polyester and PER, the vitreous transition temperature was determined using a dilatometer, type TMA-500, made by the firm Heraeus, Hanau.

#### 2.3.2. Results

The fall in the vitreous transition temperature is a measurement for the interaction between the polymer and the solvent. In this particular work it was determined using the two methods described above. In the second method it is a question of dynamic shrinkage, or possibly lengthening measurements of fibres at rising temperatures, where the change in the length of the fibres only takes place when the treatment temperature is higher than the vitreous transition temperature of the amorphous areas.

The samples are placed in a thermo-mechanical measuring machine, where they are subjected to a specific weight and heated at a constant temperature. Changes in length are continuously recorded.



The sample of non-set yarn (2 g) begins to shrink as soon as the crystallisation area is reached. By extrapolation of the parts of the curve obtained, a vitreous transition temperature of 89°C is found (fig. 8).

length of the fibre

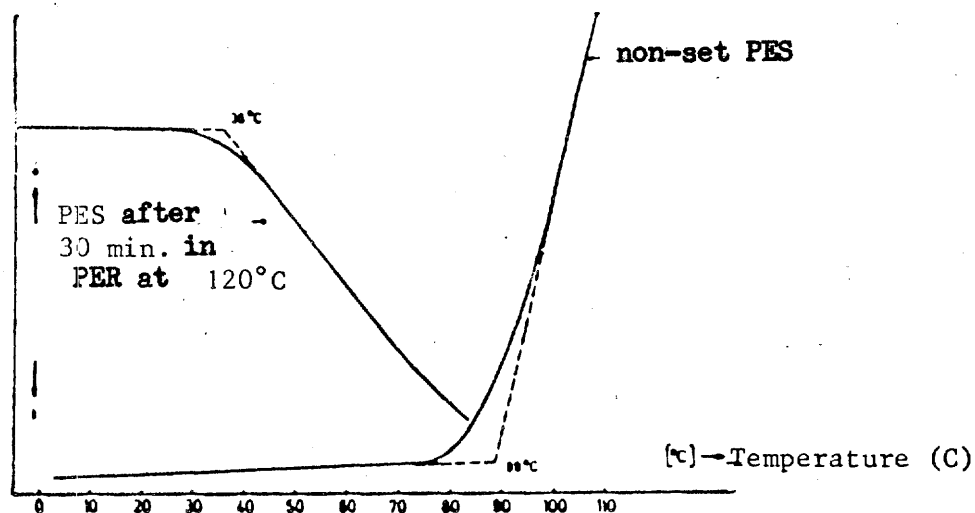


Fig. 8 - Thermodynamic analysis of polyester yarn.

When the fibres are saturated with solvent using a treatment with boiling PER for 30 min., thermo-mechanical analysis no longer shows any shrinkage. The weight to which the sample is subjected should be so high (20 g) in this case that the sample lengthens after reaching crystallisation temperature (fig. 8). In this way, a vitreous transition temperature of  $\pm 36^\circ\text{C}$  was obtained for this sample. This sharp fall in the crystallisation temperature explains inter alia the improvement of polyester dyeability in PER baths.

## 2.4. The desorption of PER from polyester fibres

### 2.4.1. Measurement method and description of the test

The desorption of the solvent as a function of the drying time and temperature was analysed using a sample of polyester treated with PER at 90°C until the swelling in equilibrium rate was reached, i.e. after 2 h. In the initial stage this sample was then placed in PER atmosphere and at drying temperature in a container, fitted with a temperature control system.

Drying was then continued in a vacuum for various lengths of time. The traces of solvent left in the fibre were determined by gravimetry using a thermobalance.

### 2.4.2. Results

A particularly important problem as regards the industrial application of the treatments of textiles in a solvent medium is the elimination of the solvent absorbed by the fibres during the treatment. This elimination, which must be rapid and complete, is generally essential for ecological, economic and qualitative reasons.

As shown by the absorption measurement tests, the fibre absorbs very little PER in the moderate conditions used for pre-cleaning. The surface-fixed solvent is easily eliminated and poses no problems in practice. In contrast to textiles impregnated with water, the drying of textiles impregnated with PER uses less energy, as the specific heat and the evaporation heat of PER are much lower than those of water.

This is not, however, the case where PER treatments of polyester at higher temperatures, such as dyeing for instance, are concerned. The relatively large quantity of solvent absorbed by the fibre is not so easily eliminated by drying, as shown by fig. 9, for non-set polyester yarns containing 9.3% PER and heat-set polyester yarns containing only 7% PER.

PER content (g/100g)

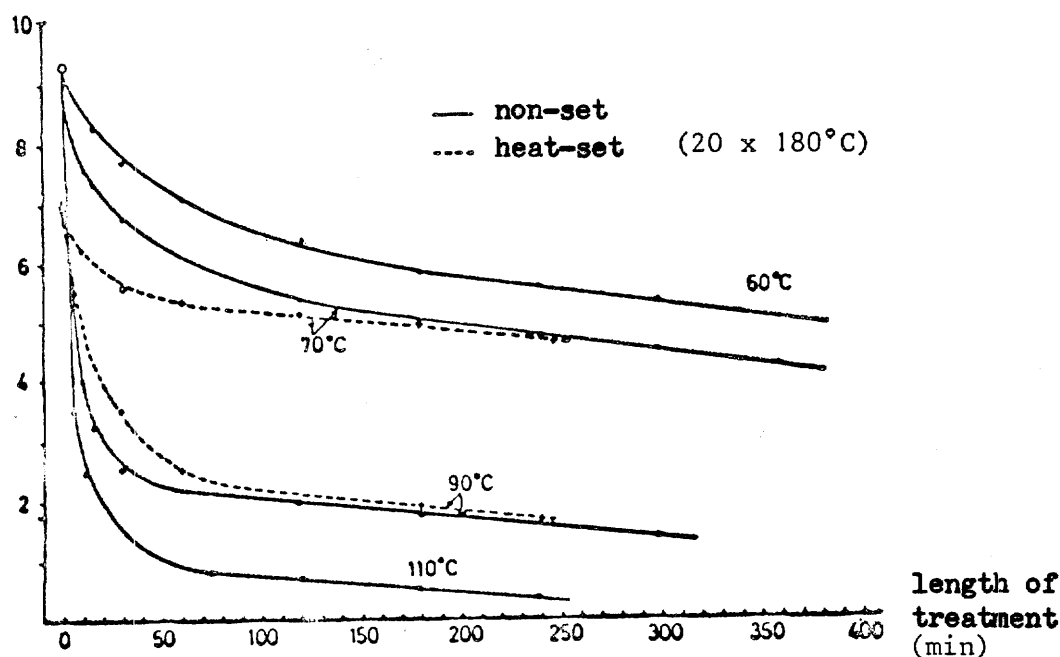


Fig. 9 - Desorption of PER from polyester yarns.

Desorption consists of two clearly visible phases. The first is quicker, and its speed and duration are a function of the temperature. It is followed by a second phase, which is much slower, where the speed of desorption no longer depends, or depends only to a very slight extent, on the temperature. It is interesting to note that as far as heat-set yarn is concerned, desorption in the first phase is slower than for non-set yarn, but the speed is about the same in the second phase.

Fig. 10 shows desorption for an even longer drying time.

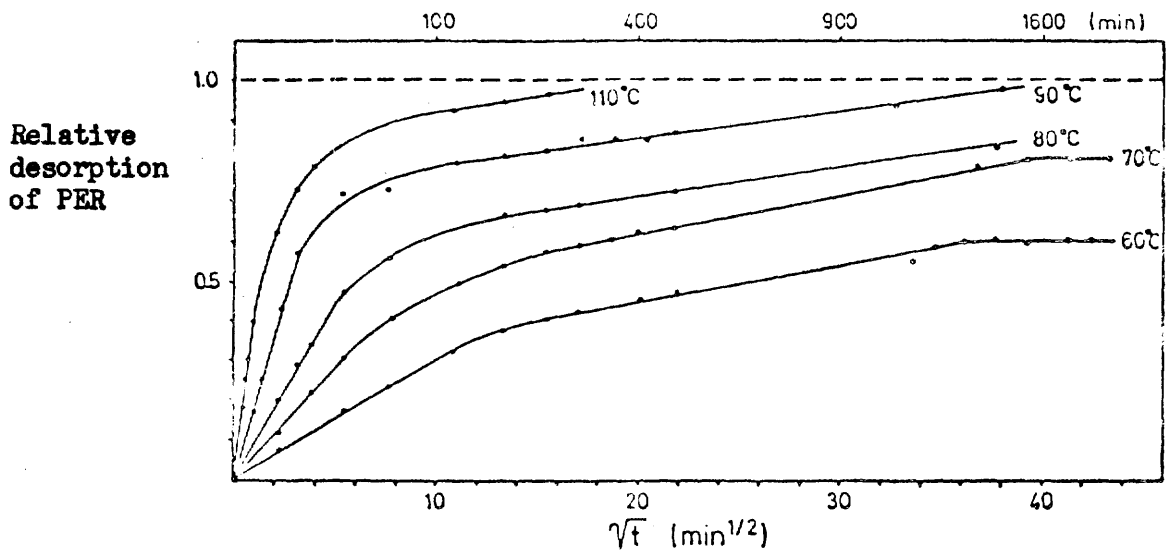


Fig. 10 - Desorption of PER from polyester yarns.

The graph shows the relative fall in the quantity of PER as a function of the square root of the drying time. The initial phase, where temperature plays a part, corresponds to an activated process of the Arrhenius type. For both heat-set and non-set yarn the activation energy for desorption is 26 kcal/mol.

As the drying gradually progresses, the vitreous transition temperature of the polyester fibre, which initially dropped from 90°C to 30°C through the absorption of the solvent, progressively rises.

Since, during the desorption of the solvent, the outer layer of the yarn loses the solvent more rapidly, it is in this area first that the vitreous transition temperature will reach the drying temperature. It can thus be supposed that at that time the desorption of the solvent inside the fibre will be far slower (phase 2). When the vitreous transition temperature of the whole fibre reaches, by continuing desorption, the drying temperature, desorption can stop completely. This occurs when the drying temperature is well below the vitreous transition temperature of the dry fibre, this being the case up to  $\pm 70^{\circ}\text{C}$ ; it is only at temperatures above  $80^{\circ}\text{C}$  that the complete elimination of PER is possible. Account must, however, be taken of the fact that even at  $100\text{--}120^{\circ}\text{C}$  it is not possible to eliminate the PER completely in economically justifiable times (fig. 9 and 10). Traces of PER can easily be eliminated at very high temperatures, i.e. at  $180^{\circ}\text{C}$  in 30 to 60 sec., but under these circumstances air pollution and recovery problems arise, with the result that this method should be abandoned.

More rapid desorption is possible when the rise in the vitreous transition temperature of the polymer during elimination of the solvent is less sharp. This is the case when the heat treatment is carried out in the presence of water vapour. In the presence of water, the vitreous transition temperature drops by about  $20^{\circ}\text{C}$ . For industry, the use of saturated or superheated vapour seems to be the only means of eliminating PER from polyester, after dyeing in a solvent medium, for instance.

## 2.5. The behaviour of polyester in other solvents

As a complement to the study on the swelling of polyester fibres in PER, similar tests were carried out with other solvents: alcohols, ether, ketones, nitriles, acid amide and chlorinated hydrocarbon. Below is a report on the results obtained, with particular reference to absorption.

Table 4 gives the swelling in equilibrium values measured by gravimetry.

**Table 4 - Swelling in equilibrium values of non-set polyester fibres in organic solvents at 50°C.**

N°	Solvent	(cal/cm <sup>3</sup> ) <sup>1/2</sup>	Swelling in equilibrium values (g/100 g)
1	iso-propanol	11.5	0.9
2	methanol	14.28	2.1
3	acetonitrile	11.9	4.1
4	2-methoxyethanol	12.06	4.4
5	dimethylformamide	12.14	4.8
6	propionitrile	10.5	5.2
7	acetone	9.77	7.0
8	<b>ethyl acetate</b>	9.1	7.8
9	tetrahydrofurane	9.52	9.7
10	<b>methylene chloride</b> (*)	9.53	9.8
11	1,1,1-trichlorethane	8.57	9.8
12	perchlorethylene	9.36	11.2
13	trichlorethylene	9.28	12.7
14	dioxane	10.0	12.8
15	chloroform	9.21	15.1
16	1,1,2,2-tetrachlorethane	9.85	16.3

(\*) at 25°C.

If the kinetics of sorption of the solvents is examined, it is found that if the ordinate of the relative swelling values  $Q_t/Q^\infty$  and the abscissa of the root of the treatment time are plotted, straight lines are obtained in the first phase for the following solvents: isopropanol, methanol, acetonitrile, 2-methoxyethanol, proprionitrile, acetone, ethyl acetate, tetrahydrofurane, 1,1,1-trichlorethylene, perchlorethylene and dioxane. These solvents are absorbed in accordance with a controlled diffusion process.

Methylene chloride, trichlorethylene, chloroform and 1,1,2,2-tetrachlorethane behave differently. Here the sorption curves are S-shaped, especially for lower treatment temperatures, i.e. at the beginning the

speed of sorption increases in time. This behaviour can be caused by the appearance, in the first phase, of swelling tensions in the fibre which are subsequently eased, thus enabling the concentration of solvent in the outer layer of the fibre to increase after a certain time.

Table 5 gives the mean value of the apparent coefficients of diffusion for the absorption of the various solvents by the polyester yarns, mainly at 50°C. For solvents where the swelling is delayed at the beginning, a maximum swelling speed is obtained. With regard to the determination of the speed of diffusion at various temperatures, the activation energies for the sorption process have also been given (table 5). It is to be noted that of all the solvents, methylene chloride is absorbed the quickest. Even at a relatively low temperature (10°C), the swelling in equilibrium value is reached in about a minute. Chloroform is also diffused into the fibre fairly quickly, while of all the solvents examined at 50°C, perchlorethylene and 1,1,1-trichlorethane are the most slowly absorbed. This latter point is of practical importance for the textile cleaning process, as oily substances and preparation products on the surface must be eliminated, without large quantities of solvents being allowed to penetrate into the fibre. It is found, therefore, that in this connection, in addition to perchlorethylene, 1,1,1-trichlorethane is also suitable. Furthermore, methylene chloride can be interesting whenever certain finishing products, such as dyes or carriers, have to be fixed into polyester fibres quickly and in moderate conditions.

It is interesting to examine the connections between the swelling values and the specific characteristics of the solvents.

**Table 5- Apparent coefficients of diffusion and activation energies for the absorption of solvents into non-set polyester yarns.**

solvent	(cm <sup>3</sup> /mol)	D <sub>s</sub> .10 <sup>10</sup> (cm <sup>2</sup> /s)	activation energy (kcal/mol)
<b>methylene chloride</b>	63.6	58 (10° C)	10
chloroform	80.7	15.8 (20° C)	11
1,1,2,2-tetrachlorethane	102.7	20 (46° C)	26
acetonitrile	52.9	16.2 (50° C)	22
methanol	38.4	7.0 (50° C)	11.5
acetone	73.4	6.9 (50° C)	25
tetrahydrofurane	81.2	6.0 (50° C)	18
trichlorethylene	90.2	4.7 (50° C)	15
propionitrile	70.3	2.2 (50° C)	30.5
<b>ethyl acetate</b>	98.5	1.3 (50° C)	11
dioxane	85.2	0.96 (50° C)	23
2-methoxyethanol	79.1	0.76 (50° C)	12
perchlorethylene	100.4	0.038 (50° C)	31
1,1,1-trichlorethane	101.7	0.026 (50° C)	16

It is logical to seek out first of all a connection between the sizes of the particles diffused and the speed of diffusion or possibly the activation energy, where it should be found that for larger particles the speed of diffusion decreases and the activation energy increases. It can nevertheless be seen from table 5 that such a simple correlation does not exist. This is not surprising as the size and mobility of the solvent particles are not the only influential factors and this influence is often minimal.

In addition, the interactions of the segments of the chains of polymer molecules among themselves and the interactions among the segments of the chains and the extraneous molecules diffused inside are important. If the apparent activation energies of speed of diffusion are expressed in terms of the parameter of solvent solubility  $\delta L$ , there is still no



satisfactory connection. On the other hand, an interesting connection is obtained when the quantity of solvent used and  $\delta L$  (figure 11) are compared. Here are two fields with the maximum number of interactions for  $\delta L$  values of about 9.5 - 10 and 12.0 - 12.2. These results tally with previous research work, which showed similar connections between the solubility parameters and the crystallization phenomena, induced by the solvents, of amorphous polyester and between the fall in vitreous transition temperature and shrinkage in polyester fibres.

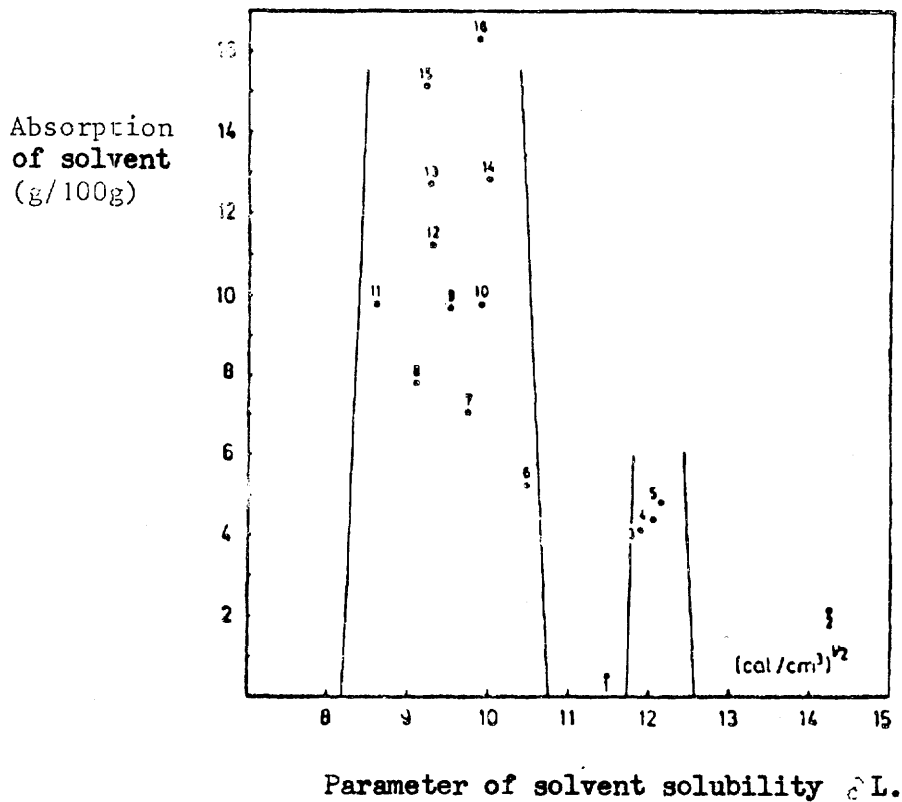


Figure 11 - Quantity of solvent absorbed by the polyester, as a function of the parameter of solvent solubility  $\delta L$ .

Given that pronounced polymer swelling phenomena are to be expected whenever the  $\delta$  - polymer ( $\delta =$  polyester 10.7) is equal to or approximates the  $\delta$  - solvent, the case of polyester is surprising in that 2 peaks of interaction are to be noted. Weigmann and collaborators recently gave the following explanation for this: if polyester is considered as a copolymer with the alternating groups  $-\text{CO}-\text{C}_6\text{H}_4$  ( $\delta = 9.8$ ) and  $-\text{CO}-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$  ( $\delta = 12.1$ ), the solvents which, in accordance with their  $\delta_L$  value, can enter into interaction with one of the two groups, will produce the phenomena observed, to a greater or lesser extent, such as the absorption of solvent, the fall in the vitreous transition temperature, the shrinkage phenomena. The breaking of the intermolecular interactions among the aromatic groups is particularly effective for this purpose.

Finally, the problem of the desorption of solvents from polyester fibres will be tackled briefly. As for PER, the desorption of the other solvents is slower than their absorption. This behaviour can be illustrated by taking methylene chloride as an example. Methylene chloride, a solvent which could acquire enormous importance in the manufacturing industry for the treatment of polyester, is absorbed at room temperature in 1 min. up to the swelling in equilibrium value. If it is then dried at room temperature, the fibre still contains about 70% to 80% of the solvent absorbed after 60 min. At higher temperatures, the speed increases but desorption does not occur in economically acceptable times (figure 12). As in the case of perchlorethylene, it is more advantageous to extract the solvent using a steaming process (figure 12).

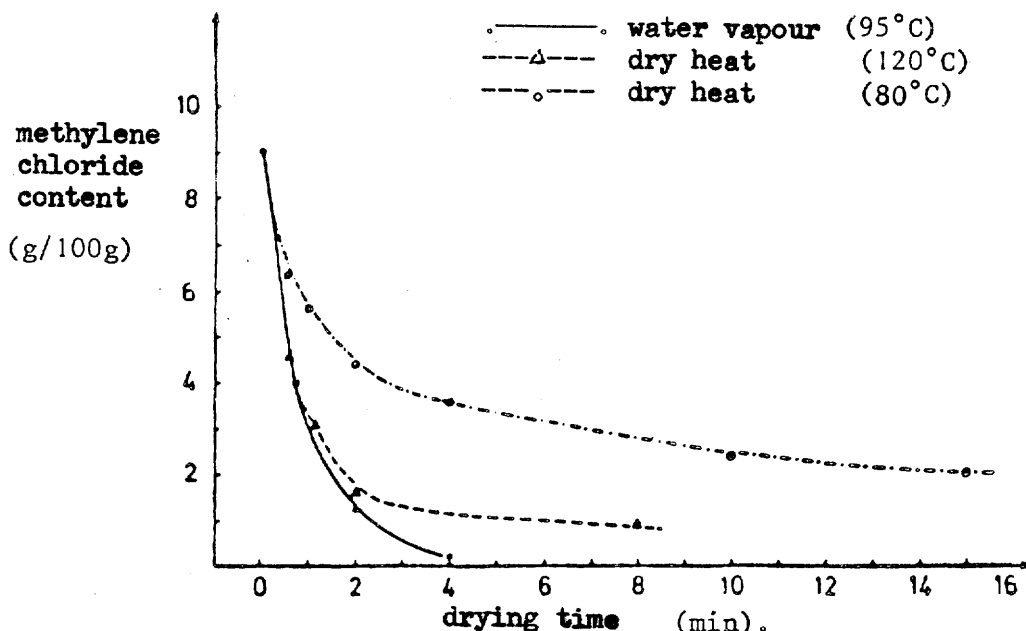


Figure 12 - Desorption of methylene chloride from polyester fibres.

III.

EXTRACTION OF OLIGOMERS

While the action of dissolving or extracting of substances extraneous to the fibre, such as grease, natural waxes, oilings, sizings, finishing agents, etc., is normally involved when solvents are present, there is also an extraction phenomenon relating to certain constituent parts of the textile material with which it is essential to be acquainted prior to the industrial application of treatments in a solvent medium. These parts are oligomers, the first end products of polymerisation, the small size of which results in greater solubility in solvents than is the case for the rest of the polymer.

The solvents penetrate into the textile material and reach the oligomers by sorption. Under the action of the solvent, migrations of these parts from the inside to the outside of the fibres may occur. This phenomenon may be the cause of certain dyeing faults, interfibre frictions, handle defects in the goods, etc. and may give rise to difficulties during the manufacturing process, precipitation in the baths and deposits on the inside surfaces of the machines, gummy deposits and blocking-up of the mechanical parts, dust during spinning, etc.

The following points are studied:

- whether or not the partial or total elimination of oligomers is beneficial,
- whether a treatment in a solvent medium is likely to produce new oligomers in the fibrous structure,
- how the fibre-solvent interactions develop according to the nature of the solvents,
- to what extent the migration or extraction of oligomers produces pores.

The research work was given over to the behaviour of polyester oligoesters and of polyamide 66 oligoamides, in various types of solvent: reactive or inert type, dyeing and cleaning solvents, mixtures, aqueous emulsions.

1. The textile materials used

1.1. Polyester

- standard polyester yarn (Tergal), non-dyed, 167 dtex/30 ends, stretched
- Tervira yarn, tested before and after texturing
  - original yarn: 0
  - false twist yarn: FT
  - set false twist yarn: SFT
- standard polyester yarn after various heat treatments in the laboratory at 100°C or 185°C lasting 3 h.

## 1.2. Polyamide

### . 1st batch: oiled yarns

- standard fine yarn for hosiery, 78 dtex, 7 ends, before texturing,
- fine yarn for garments, 44 dtex, 13 ends, with a mat or non-mat finish: mat, semi-mat, bright, high tenacity bright, milobal,
- medium yarn 78 dtex, 7 ends, after various heat treatments with shrinkage or lengthening (220°C),
- coarse yarn for carpets, 2150 to 2800 dtex, 136 ends, after texturing.

### . 2nd batch: non-oiled yarns

- medium yarn 76 dtex, 18 ends, semi-mat, obtained by conventional stretch spinning,
- coarse yarn, bright obtained by wet spinning:  
2150 dtex, 136 ends with integrated stretching,  
2800 dtex, 136 ends with integrated stretching and texturing.

## 2. Tests carried out.

### 2.1. On polyester

#### 2.1.1. Description of the tests

The various types of polyester are treated with the following solvents:

- water,
- perchlorethylene,
- trichlorethylene,
- dioxane,
- methanol,
- dichloromethane,
- xylene.

The treatments are:

- So-called "global" extraction of oligomers:
  - . either full bath, 3 h at 100°C with the water or PER solvents, 64°C with methanol, 40°C with dichloromethane, 20°C with methanol and dichloromethane,
  - . or 12 h Soxhlet extraction with trichlorethylene or full bath with flow back, 7 h with xylene, as used by other research workers.

- Selective extraction of the surface oligomers: full cold bath treatment, 5 min., with dioxane.
- Repeated treatments with perchlorethylene, with the aim of totally extracting the oligomers present in the material at the outset and of checking whether or not they form new oligomers during the treatments. The operation consists, prior to the initial treatment with PER and between each treatment, of extracting the oligomers which may have migrated to the surface, by the brief action of dioxane at a cool temperature.

After these treatments, the oligoesters extracted are analysed using the following methods:

- . qualitative and semi-quantitative analysis by chromatography on a thin layer, using the chromatographic plate and the development method recommended by Valk and the Peebles' irrigational solvent mixtures.

The operational methods followed are thus as follows:

- thin layer of fluorescent silica gel (Merck F 254) on aluminium plate,
- irrigation by the specific mixture:
  - . (C): chloroform-ether 90 : 10 for cyclic oligomers
  - . (L): chloroform-ethanol 90 : 10 for linear oligomers.
- development by examination of the chromatogram under ultraviolet light with a 254 nm wavelength. Violet spots on a yellow background are developed.

A diagram showing the appearance of the chromatograms is given in figure 13.

- quantitative analysis: several techniques for analysing the solvent after treatment are possible:
  - A): ponderal: weighing of the dry matter,
  - B): spectrophotometric: measurement of the UV absorption of the solution using the terephthalic nucleus' capacity to absorb at 240 nm,
  - C): chromatographic: separation and measurement of the depths of shade of the spots or of the absorption of the state of each spot in the vapour phase.

These methods and their application to practical problems of analysis are described in literature on the subject.

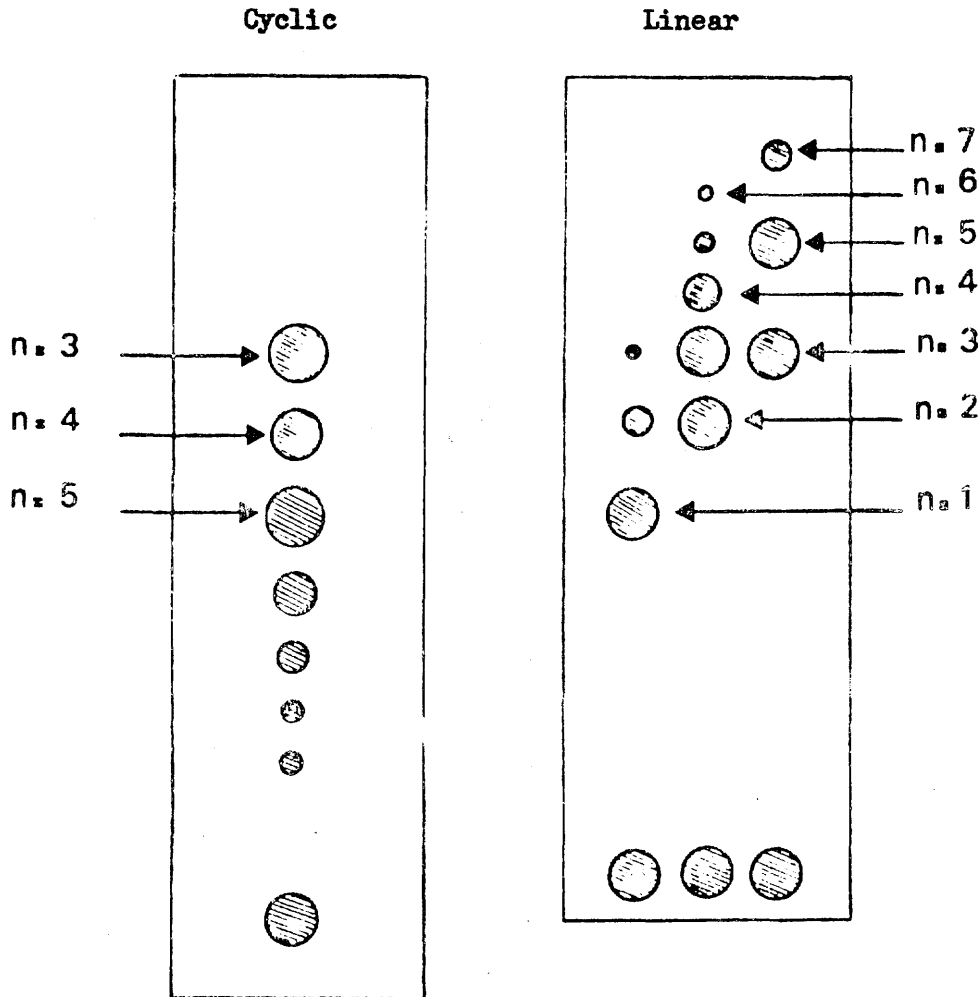


Figure 13 - Chromatographic separation of the oligoesters on a thin layer.

### 2.1.2. Results

It should be remembered that oligomers are very short chains, composed of less than 10 monomers which, in polyester's case, are 97% cyclic type, and thus hydrophobic in nature. The cyclic trimer being the major component part, it can be considered to be representative of all oligomers in their behaviour in a solvent medium (1-3; 1-4).

Table 6 lists the treatment conditions and the results provided by the chromatograms. The sizes and depths of shade of the spots depend upon the quantities of oligomer displaced and are represented on the table by the signs:

t	= trace	x	= pale shade
xx	= deeper shade	xxx	= very deep shade

The spots are classified in descending chromatographic order from the solvent front to the initial or deposit point. The cyclic oligomer spots are sufficiently deep in shade and clear to be identified with the reference products. The linear oligomers are coloured trails, which cannot be identified owing to the very small proportion of them present.

It is found that all the customary solvents, including those to be used for de-oiling, extract oligomers.

According to the hydrophobic or hydrophilic nature, the solvent solubilizes to a greater or lesser extent the cyclic oligomers, which have no terminal position, and the linear oligomers, with free hydroxyl and carboxyl terminal positions.

Thus, water extracts practically no cyclic oligomers but on the other hand draws out the trace linear oligomers; similarly, alcohols such as methanol have little action. Chlorinated solvents, on the other hand, trichlorethylene and above all perchlorethylene, extract far more. The aromatic solvents, benzene and xylene, also extract large quantities of oligomers.

When the results obtained with methylene chloride are examined, it is found that this solvent extracts a large proportion of polyester products; these are cyclic and linear oligomers, but also other parts of the fibre such as fibrils. This solvent is indeed recognised as being very active vis-à-vis polyester, having a swelling and de-crystallising effect on the material.

The thin layer chromatographic method applied here is not sensitive enough to evaluate the variations in migration of the oligomers towards the outside in solvent baths before and after texturing (samples O, FT, SFT).

After a second extraction, the treatment solution again gives an oligomer chromatogram which is identical to that of the first extraction. The hypothesis that all the oligomers initially present in the sample are not identically accessible to the solvent during the first extraction is more plausible than that of the formation of new oligomers during the chemical treatment in a solvent medium.

**Table 6 - Extractable fractions of oligoesters using various solvents.**

Sample examined	Treatment solvent		Oligomers extracted				
	Nature	Conditions time tempera- ture	chromatographic spots				
			Cyclic		Linear		
			G-t <sub>n</sub>	Proportion	Number	Depth of shade	
standard Polyester (oiled)	Water	3h, 100° C	n = 3	t	5	t	
	Perchloroethylene	3h, 100° C	impurities of the solvent	xxx	3	t	
			n = 2	xx			
			n = 3	xxx			
				n = 4	xx		
				n = 5	x		
			non-identified	t			
	Twice 3 h, 100° C	id.	id.	id.	id.		
Methanol	3 h, E=64° C	n = 3	x	2	t		
Methanol	3 h, 20° C	n = 3	t	trails	t		
Trichloroethylene	12 H E = 87° C	impurities of the solvent	x	2	t		
		n = 2	t				
		n = 3	xxx				
			n = 4	x			
			n = 5	x			
		non-identified					
Dioxane	5 mm E = 101°	n = 2	t	5	t		
		3	xx				
		4	x				
		5	t				
		non-identified					
Dioxane	5 mm 20°	id.	id.	id.	id.		
Polyester O FT SFT	Xylene	6 h E = 135°	impurities of the non-identified solvent	x	3	t	
			n = 2	x			
			n = 3	xxx			
			n = 4	x			
			n = 5	t			



The structure of the material also has an influence on the extractability of the oligomers.

Table 7 gives the proportions of oligomers extracted by successive treatments in the case of a polymer with an internal structure variously modified by heat treatment:

- the repeated actions of the solvents tend to rid the material of its constitutive oligomers, the proportion rapidly decreases and no oligomers are produced by degradation, at least after five PER treatments each lasting 3 h, which confirms the hypothesis put forward above.

Table 7 - Quantitative analysis by weighing of the dry matter, results expressed in oligoester content per 100 PEIP.

Successive treatments	Solubilization of the oligomers - Dry matter %		
	None	100° C, 3. h	185 °C, 1/2h
Purification			
a) - de-oiling (cold temperature isooctane)		0.03	
b) - elimination of the surface oligomers (dioxane)		0.13	
<b>Actions of dry heat</b>			
<b>Successive extractions:</b>			
Dioxane (/ mm, 20° C)		~ 0	0,30
PER (3 h, 100° C)	0.13	0.125	0.10
Dioxane	0.13	0.05	0.35
PER	0.05	0.02	0.05
Dioxane	0.02	0.02	0.19
PER	0.002	0.003	
Dioxane	0.2	0.006	
PER	0.02	0.005	
Dioxane	0.008	0.008	
PER	0.004	0.02	

- For thermally modified material, there are two cases to be considered:
- . if the temperature is average (100°C), the extraction rate of the treated polymer is identical to and even somewhat lower than that of non-treated polymer.
- . if the temperature is high (185°C), the extraction rate is very high.

Non-treated polymer:  $0.13 + 0.013 + 0.05 + 0.02 = 0.33\%$

Polymer (100°):  $0.125 + 0.050 + 0.020 + 0.020 = 0.215\%$

Polymer (185°):  $0.30 + 0.10 + 0.35 + 0.05 + 0.19 = 0.99\%$

The penetration of the material by the solvent, which conditions the solubilization of the oligomers and their extraction, depends on the internal structure of the polymer and in particular its microporosity.

It was shown that heat produces a re-arrangement of the pores, with the disappearance of the medium-sized pores and the creation of more numerous small and large pores, without any appreciable change in the total porosity volume.

Using this result as a basis, it can be considered that at 100°C the number of small pores increases, which would restrict the penetration of the solvent into the material and, as a consequence, the migration of the internal oligomers towards the periphery, resulting in slightly lower extraction rates; at a higher temperature (185°C), however, there would be a sharp increase in the wide diameter pores aiding penetration of the solvent and thus facilitating migration of the oligomers towards the periphery, with resulting higher extraction rates.

From this study, it would appear that the action of solvents on the extraction of oligomers is modified by the conditions of the heat treatments to which the material may have been subjected previously and which may have modified the state of the internal microporous structure.

## 2.2. On polyamide

### 2.2.1. Description of the tests

The textile material is treated with the solvents generally used for dyeing and dry cleaning, and also with other solvents from the same families. They are applied pure, in mixtures or in aqueous emulsions.

- water,
- alcohols, methanol, ethanol, isopropanol,
- perchlorethylene,
- R 113 or trifluorotrchloroethane,

- binary mixtures 90/10 perchlorethylene + methanol; perchlorethylene + ethanol; perchlorethylene + isopropanol,
- ternary solvent mixtures: perchlorethylene + R 113 + methanol 5/90/5,
- aqueous emulsions in the presence of the emulsifier Ultravon SL IWA 200% CIBA-GEIGY: perchlorethylene + water + Ultravon 1 1 50 ml/3 g and 1 1 50 ml/0.2 g.

Account was taken of certain solvents giving dry residue in the ponderal results of the first batch of samples. For the second, the solvents (apart from E 114) were distilled.

The solvent treatments are carried out in an open bath, ratio 5 g/200 ml, for a relatively long time, 1 h, to increase extraction at 65°C, in the case of dyeing, or at 25°C, in the case of dry cleaning.

The method of analysis consists of carrying out an extraction using a suitable solvent and analysing the solution qualitatively and quantitatively.

Two techniques are suitable:

- A - Ponderal
- B - Chromatographic.

As in the case of polyesters, each of these methods has its pros and cons.

For the chromatographical technique, preliminary tests were carried out on Sephade, i.e. thin layer and column, then the following conditions were established:

- Separation by fraction chromatography on a silica gel column (type Lichrosorb Si60 10 µm Merck); the oligomers are separated in 20 to 25 min. by elution at room temperature with an 18% 95% ethanol aqueous solution, under a pressure of 350 to 400 psi. Figs. 14 and 15 illustrate the appearance of the chromatograms obtained after various solvent treatments.
- Quantitative analysis of the eluate by chromatographic-spectrophotometric coupling with measurement of the absorption with a wavelength of 210 nm and with reference to known quantity peaks of reference oligomers.
- Preparation of the reference oligomers by preparative chromatography and checking of their purity using IR spectrography.

Analysis is restricted to the most important oligomers and those most easily detectable in UV: the cyclics  $n = 1$  to 4.

The oligoamides in the initial textile material are quantified by ethanol extraction in a Soxhlet for 6 h (Recommendation ISO R 599-1967). The fraction of oligoamides extracted by the solvent treatment and the fraction remaining in the fibre after this treatment are analysed in the same way.

Morphological examination of the fibres using electron microscope scanning enables the surface products to be observed and the presence of crystallised oligomers and their specific shapes to be followed in particular.

Preparation of the sample for analysis consists of de-oiling the fibre in an anionic type detergent bath and a thermic after-treatment, the optimal conditions for which are determined by systematic preliminary tests, the fibres being fixed on a metal frame.

The observation using electron microscope scanning is carried out either two or twenty-four hours after the heat treatment.

The photographs on pages 53/54 show the fibre enlarged 5 000 times.

### 2.2.2. Results

Qualitatively, the oligomers are a relatively varied mixture of short chains consisting of cyclic ( $N^{\circ} 1, 2, 3, 4$ ) and linear molecules, where three types of terminal groups are possible: diamine, dicarboxylic and amino acid. Quantitatively, 2% to 2.5% of oligomers, including 1.6% of cyclics (monomers 0.68%, dimer 0.68% and trimer 0.23%) (1-5, 1-6, 1-7) are isolated from polyamide 66.

#### 2.2.2.1. Oiled yarns

##### . Interference of oiling products

These are extracted to a greater or lesser extent in the solvent medium, as proved by the special odour and oily appearance of the dry residue. Thus, the ponderal results will always be a little too high.

CHROMATOGRAPHIC SEPARATION IN THE LIQUID PHASE  
OF THE OLIGOAMIDES EXTRACTED IN VARIOUS  
SOLVENT MEDIA

Fig. 14  
WATER

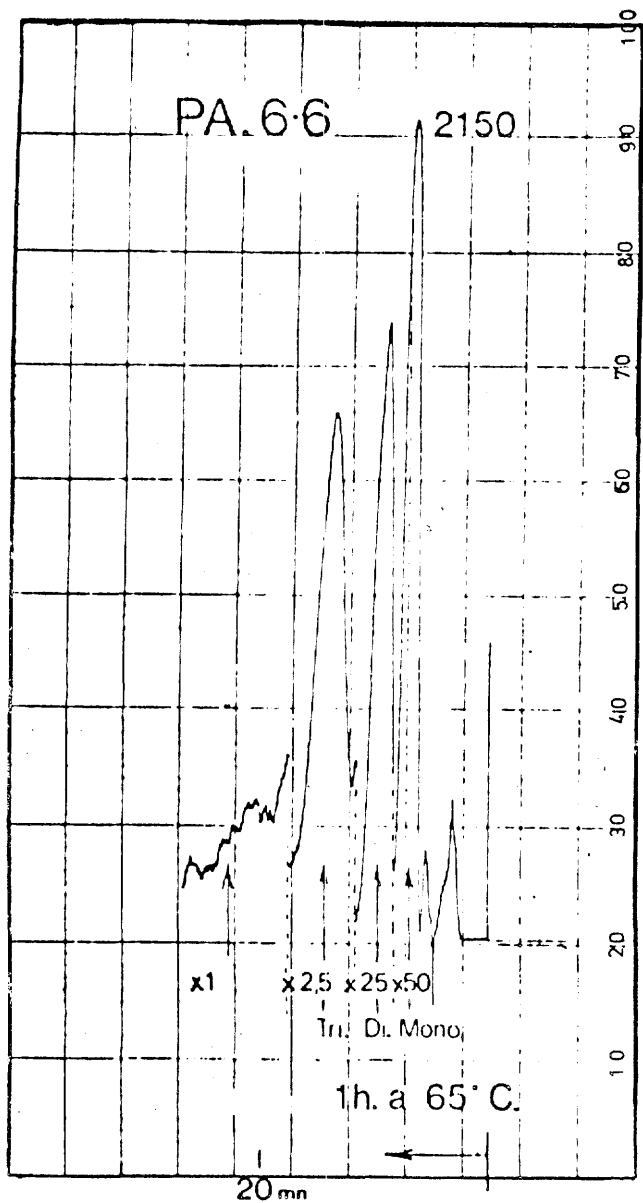
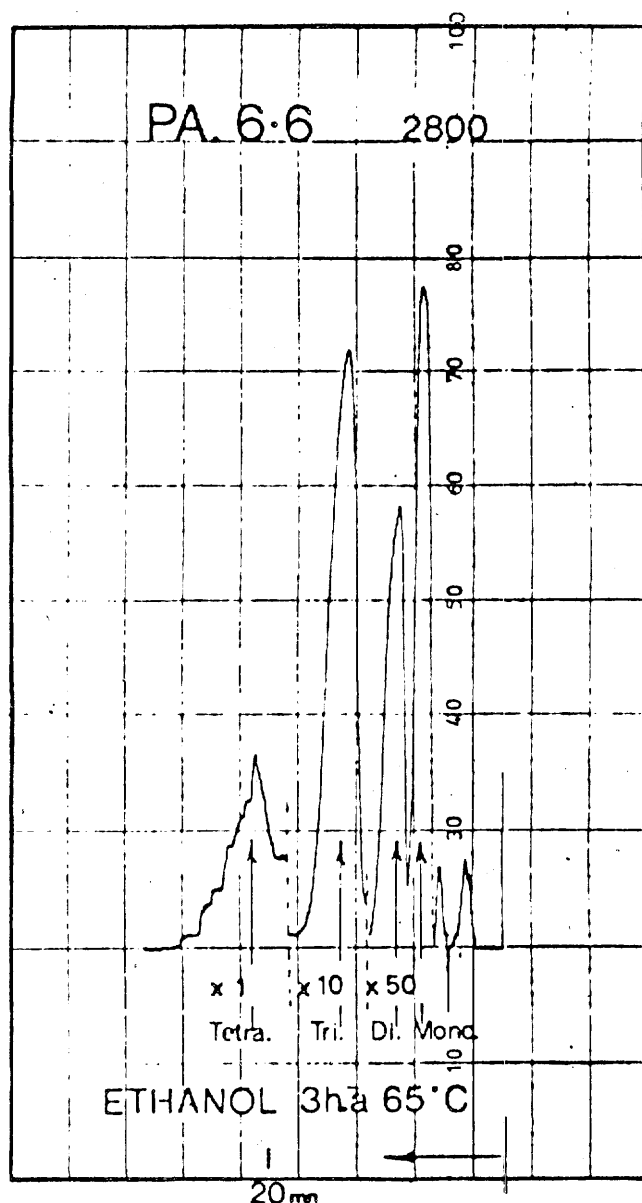


Fig. 15  
ETHANOL



. Comparison of the various yarns

Table 8 gives the proportion of oligoamides in the initial yarns. The proportions obtained are of the same order, 1.6%, for all the yarns except the polyamide carpet, where the added value (2.16%) may be due to "overoiling" before texturing.

Table 8 - Quantitative analysis of the "oligomers" (\*) in the initial yarns (ponderal method)

Sample	%	Mean
P.A. carpet	2.17	2.16
	2.15	
P.A. Standard (non-textured)	1.61	1.64
	1.67	
P.A. bright	1.53	
	1.75	
P.A. semi-mat	1.58	
	1.70	
P.A. mat	1.59	1.60
	1.60	
P.A. bright high tenacity	1.54	
	1.50	

(\*) "Oligomers" in inverted commas, as all the extractable matters are concerned. The results are calculated in relation to the weight of the polyamide.

Dulling has no influence.

- . Action of various solvents
- using the ponderal method

Table 9 - % of oligoamides in polyamide 6-6

Polyamide 6-6	Yarn/Carpet 2785 dtex			Yarn/Hosiery 78 dtex			Mat.yarn/Shirts 44 dtex		
	1 Ext.	2 Remain -ing	3 Total	1 Ext.	2 Remain -ing	3 Total	1 Ext.	2 Remain -ing	3 Total
Original material (no extraction)	2.16			1.64			1.60		
Extractions:									
Water	1.31	1.14	2.45	0.74	0.90	1.64	0.78	0.93	1.71
Methanol	2.01	0.14	2.15	1.57	0.10	1.67	1.66	0.05	1.71
PER	0.58	1.59	2.17	0.50	1.31	1.81	0.66	1.27	1.93
PER + Meth.	2.61	0.30	2.91	1.78	0.21	1.99	1.91	0.20	2.11

Table 9 above gives the rate of oligoamides extracted and remaining in the fibre for the various yarns.

For a single material, the proportions of extracts (column 1) vary according to the solvents. In the case of the aqueous emulsion, no significant value is indicated, as the proportion of emulsifier chosen was too large and unduly distorted the ponderal result. Depending on the material, the extraction characteristic of each solvent remains the same.

- using the chromatographic method

Qualitatively, three spots appearing quite visibly on a thin layer and three peaks on a column are to be observed. These products are identified by the IR spectrograph as being cyclic oligomers  $n = 1, 2$  and  $3$ . The higher cyclic oligomers spots are too weak, being traces, as are the linear oligomers. A semi-quantitative evaluation is obtained by comparing the relative depth of the shades of the different spots or surface of the peaks; the order of classification of the solvents according to their extracting power is confirmed and the proportions of oligomers extracted decrease from  $n = 1$  to  $n = 4$ .

2.2.2.2. Non-oiled materials

Table 10 lists the proportion of global oligoamides (column A) and of each of the principal cyclic oligomers ( $n = 1$  to  $4$ ).

Table 10- % of cyclic oligomers,  $n = 1$ , in the original non-oiled materials

Description of the polyamide 66	Amounts							
	A	B					Total 1+2+3+4	Difference A - Total
		n = 1	2	3	4			
78 dtex 18 ends (integrated stretching)	1.60	0.332	0.403	0.180		0.915	+ 0.245	
2150 dtex, 136 ends (integrated stretching)	1.04	0.338	0.392	0.127	0.02	0.877	+ 0.163	
2800 dtex, 136 ends (integrated stretching + texturing)	1.12	0.338	0.399	0.165	0.013	0.916	+ 0.204	

The results are calculated according to the weight of the sample of polyamide for analysis.

A = ponderal method

B = chromatographic method

The solubilization of the oiling appears if a comparison is made between the values in column A of this table, of the order of 1% to 1.6%, and those in table 9, between 1.60% and 2.20%. However, the positive difference between the A values and the total, 4 oligomers, seems to indicate the existence of other products not detected by the chromatographic method.



It is also found that after texturing the proportions extracted are of the same order as before texturing, but systematically a little higher.

Table 11 enables the influence of the nature of the solvent on various types of polyamide, with identical temperature and treatment time, to be followed, while table 12 enables the influence of the temperature and treatment time of the various solvents on a single polyamide to be followed.

The various extracting powers of the solvents are classified in the following descending order:

alcohols, methanol, the most active, water  
the mixtures: PER-alcohols, PER aqueous emulsion,  
and lastly PER on its own, the least active.

In view of the low proportions of the most active components (alcohol, water) in the usual mixtures, the extracting powers of these media are high: 0.78% and 0.45%, synergetic effect of the mixtures and emulsions.

It is to be noted that at 65°, extraction is substantial; at room temperature extraction of the oligoamides is practically zero in the case of PER and the aqueous emulsion. The solvent containing fluorine, on the other hand, seems to have great extracting power: 0.53%. Yet there is no question of oligomer extraction; chromatography does not detect any; the values in the B columns are low, but it detects many other products such as impurities in the non-distilled solvent, or oiling, as the part of the sample for analysis near the bottom of the bobbin may have been contaminated by the oiled yarn from the beginning of the winding.

It is found that extraction increases with time, but only slightly after an hour. The length of the treatment would appear to be conducive to the extraction of the higher less soluble oligomers,  $n = 3$ , for instance.

In table 12, if a comparison is made between the respective amounts of the four cyclic oligomers analysed in the material before treatment and in the fractions extracted by the various solvents, several anomalies are to be observed in the proportions which, insofar as they are significant seem to indicate in particular that water extracts a little less dimer: 0.28%, while methanol and above all the PER and methanol mixture extract more, 0.364% and 0.402% respectively.

**Table 11 - Analysis of the extractable fraction of oligoamides of various non-oiled polyamides as a function of the nature of the solvent, under the same temperature and time conditions.**

**Column A:** Ponderal method - Global extractable fraction

**Column B:** Chromatographic method, i.e. the sum of the cyclic oligomers n = 1 to 4 quantified separately.

Description of the polyamide	Solvent treatment 1 h at 65° C	Quantitative analysis Extractable fractions	
		A	B 1+2+3+4
78 dtex 18 ends	<b>Water</b> <b>1st test</b>	0.63	0.384
	<b>2nd test</b>	0.57	0.444
	Methanol	1.16	0.874
	PER	0.10	0.038
	PER + Methanol	0.77	0.538
2150 dtex 136 ends	<b>Water</b>	0.43	0.353
	Methanol	0.87	0.758
	PER	0.26	0.012
2800 dtex 136 ends textured	<b>Water</b>	0.83	0.670
	Methanol	1.11	0.856
	PER	0.15	0.03
	PER + Methanol	0.78	0.870
	PER + <b>Water + Emulsifier</b>	0.45	0.067

**Table 12-** Analysis of the extractable fraction of polyamide (2800 dtex), as a function of the solvent, the temperature and the time.

Solvent treatment		A.	B					
Nature	Conditions		n = 1	n = 2	n = 3	n = 4	1+2+3+4	
None		1.12	0.338	0.399	0.165	0.013	0.916	
Water		0.83	0.324	0.282	0.064	~ 0	0.670	
(Methanol)		1.11	0.338	0.364	0.142	0.012	0.856	
(Ethanol)		1.05	0.335	0.372	0.120	0.012	0.839	
Alcohols	(Isoprop. 65° C, 1h)	0.65	0.244	0.175	0.038		0.457	
Chlorinated	(PER)	0.15	0.03	~ 0	~ 0	~ 0	0.03	
Mixed	(PER+Meth.)	0.78	0.309	0.402	0.148	0.011	0.870	
	(PER+Eth.)	0.65	0.339	0.300	0.064		0.703	
	(PER+Isopr.)	0.35	0.172	0.152	0.019		0.343	
Emulsion	(PER+Water+emuls.)	0.45	0.047	0.017	0.003		0.067	
Chlorinated Containing fluorine	: PER R 113 (PER+Water+emuls.)	25 ° C, 1 h	~ 0	~ 0	~ 0	~ 0		
Mixed	(PER+113+emuls.)		0.53					
			~ 0					
			0.30	0.194	0.038	0.002	0.234	
			30 min.	0.306	0.323	0.112	0.012	0.753
Alcohols	(Ethanol)	65° C						
		( 1 h	0.335	0.372	0.121	0.012	0.840	
		( 2 h	0.309	0.354	0.135	0.012	0.810	
		( 3 h	0.326	0.396	0.160	0.018	0.900	

### 2.2.2.3. The surface of the fibres

The first tests with electron microscope scanning were carried out on medium yarns 78 dtex, 7 ends, as such, and after industrial heat treatments at 22°C, in various stretching or shrinkage conditions.

On the surface of the fibres non-uniformly abundant and non-uniformly crystallised deposits are to be observed and when the fibre is de-oiled, the spinning jet stripes become very apparent (photo 1).

The experiments showed firstly the interest of carrying out a thermal after-treatment before the electron microscope scanning, the deposits being more numerous and observation made easier, and secondly the influence of the time of observation, 2 h after the after-treatment hardly any well formed crystals can be seen, whatever the temperature and length of this treatment, but the deposits are most abundant at low temperatures; 24 h after, on the other hand, the appearance of the crystals depends on the temperature of the after-treatment; the best formed and most abundant crystals after 5 min. at 170°C.

The tension conditions during the industrial heat treatment also have an influence. Thus the superficial deposits decrease when the tension on the yarn increases: they are more numerous on a yarn treated with 6% shrinkage than 4.2%, etc. shrinkage.

In addition, the shapes of the crystals seem a little different on the samples treated with extensive shrinkage or at constant length.

These initial tests enabled the most favourable conditions for carrying out good observation to be found and revealed the influence of the temperature and state of tension of the material on the kinetics of migration and crystallisation of the surface oligoamides.

The second tests were carried out on materials with different shapes, round and tetralobal sections, and relate to the action of solvent treatments. In this case, the thermal after-treatment which is the most suitable for electron microscope scanning is 2 min. at 140°C.

Before the solvent treatment, there are fairly numerous ill-defined deposits on the surface of the round section standard yarn.

After treatment in water or in PER, the surface becomes smoother, as if it has been "cleared", and there are several types of deposits: micro-needles and large crystals, start of "crystallisation".

For the special carpet yarn with a tetralobal section, the same observations as above can be made, but more clearly, as the quantities of deposits are greater in all cases than for standard yarn. This is consistent with the differences in content analysed in the two yarns (see table 8).

Photographs illustrate the examination:

- . after treatment in water, the deposits are long patches or form "run-outs", especially on the lateral surfaces of the concave parts of the lobes (photo 4), the convex parts being smooth (cleared),
- . after treatment with PER, the clustering together of the oligomers is quite apparent in the cavity of the lobes (photo 5). The thermal after-treatment renders the flat crystalline shape of these deposits visible (photo 6).

For the conclusions, it can be considered that the results on non-oiled material will be more reliable than those on normal oiled material.

It is shown that any solvent treatment extracts oligoamides at a warm temperature and that the extraction is a function of the nature of the solvent and of the various principal oligoamides.

Water is a very dissolvent medium owing to the hydrophilic nature of the oligoamides, as can be readily assumed from their formulae; perchlorethylene, on the other hand, is not very active at all; the PER + alcohol mixtures and the aqueous emulsions of PER, although having a little less power of extraction than water, still have a not inconsiderable action, particularly the alcohol mixture.

If the change in porosity brought about by various spinning methods is not marked, that caused by prior heat treatments, even texturing, becomes clearly visible: rise in the extraction rate and in the surface migration rate.

The role of the shape of the fibre is also clearly shown.

Thus, any treatment with shrinkage, leading to an increase in the diameter of the fibre, facilitates migration. Stretching, leading to a decrease in the diameter and flattening of the pores, has the opposite effect.

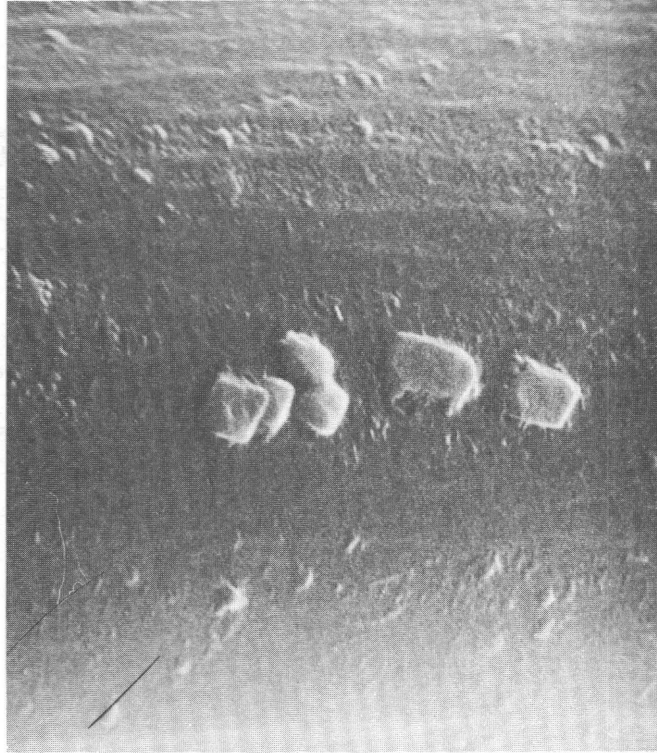
If the surface of the fibre is even, round section, extraction is homogeneous, but if there are cavities in the surface, tetralobal section, the action of the solvent is heterogeneous, the convex parts are more exposed and thus "cleared" of the oligomers present on the surface; the oligoamides, on the other hand, are kept in the concave parts, clustered together in the cavities.

Now any localized distribution on the surface, i.e. presence or otherwise of a cluster of oligoamides, is a heterogeneous modification, which may have repercussions on the future behaviour of the material.

ELECTRON MICROSCOPE SCAN OF THE SURFACE OF A STANDARD POLYAMIDE  
6-6 YARN (Round section)

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PHOTO 1



ELECTRON MICROSCOPE SCAN OF A SPECIAL POLYAMIDE YARN FOR CARPETS  
(Tetralobal section) VARIOUS SHAPES OF DEPOSIT

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PHOTO 2

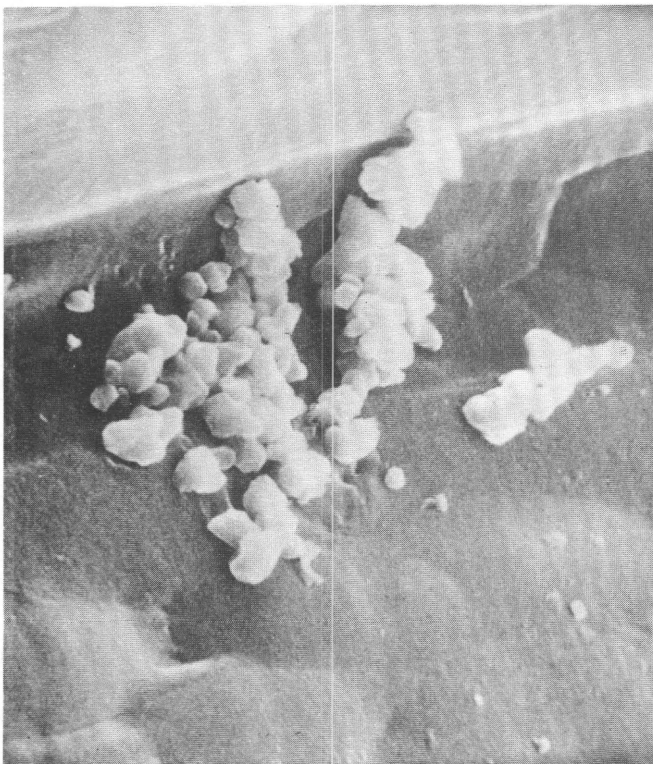
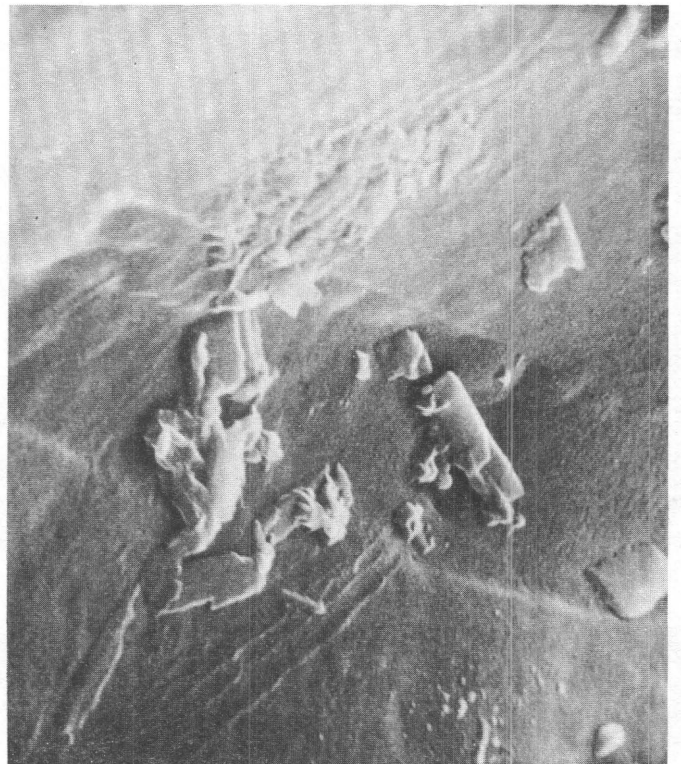


PHOTO 3



ELECTRON MICROSCOPE SCAN OF THE ACTION OF SOLVENTS ON SPECIAL YARN  
FOR CARPETS

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WATER

PHOTO 4



PERCHLORETHYLENE

PHOTO 5

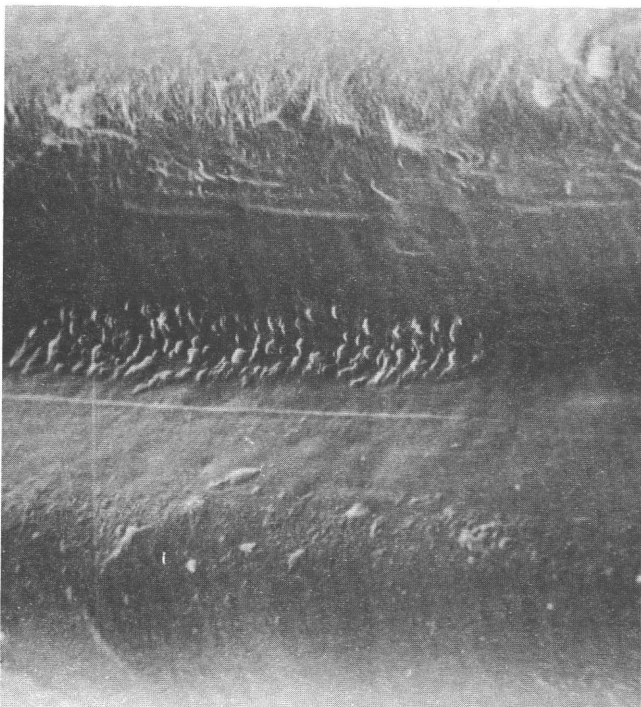
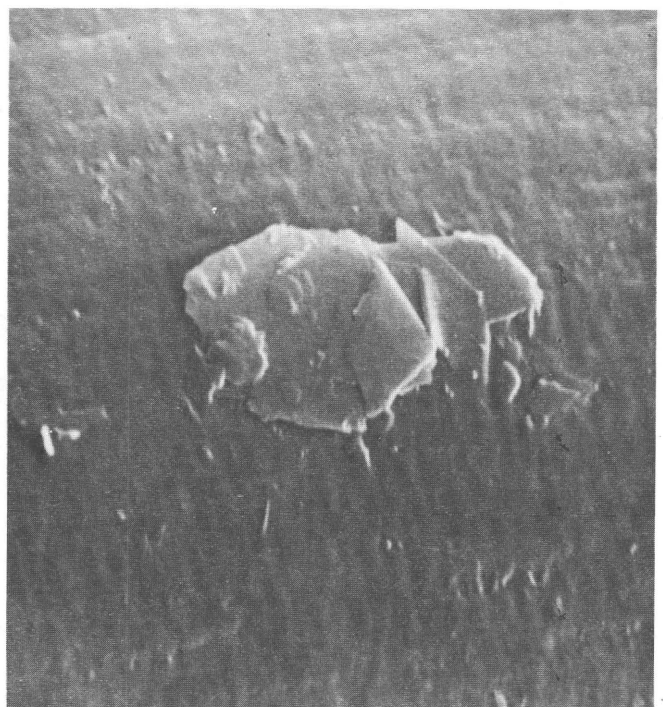


PHOTO 6





IV. DYEING OF WOOL AND EXTRACTION OF SURFACE IMPURITIES

1. The dyeing of wool in a solvent medium

It has been shown that anhydrous wool swells a very great deal, i.e. by 21.5%, when it is soaked in a PER/HAc (acetic acid) mixture, of 10% v/v. Furthermore, this swelling is similar at 55°C and 90°C. The dyeing tests are, therefore, carried out at these temperatures.

Various parameters were examined:

- the PER/HAc ratio,
- the dyeing temperature
- the wool's degree of humidity,
- the nature of the dye.

Through a series of dyeing tests at room temperature, supplemented by certain results obtained from other studies, an attempt was made to pinpoint more accurately the dyeing in a solvent medium mechanism, and more especially the fixation of the dye.

1.1. Textile materials used

- Combed sliver Australia LW 67: average diameter: 20.8  $\mu\text{m}$ ;  
pH of the aqueous extract: 5.9;  
alkaline solubility: 16.4%  
urea-bisulphite solubility: 57.4%.
- "Pure wool" fabrics, 4 twill, two end warp and weft yarn, metric count N° 24; weight to the square metre: 240 g, alkaline solubility: 14.3%.

1.2. Dyeing processes and measurement methods

Discontinuous dyeing process:

The dyeings are carried out in a ground in balloon-flask with a condenser on top. There is no mechanical agitation of the material. The liquor ratio usually used is 1:50, in order to ensure better levelling. The tests were carried out at a constant temperature using a "Praxitest 100" machine, specially developed for dyeing in a solvent medium; in this case, the liquor ratio is 1:25. With the discontinuous process, the material used always takes the form of combed sliver.

Continuous dyeing process:

Laboratory equipment for continuous dyeing was developed. The process consists of first of all impregnating the yarn in an organic solution of dye at 100-105°C for 10 to 20 seconds. The material is drawn along and squeezed gently with a "Ilma" padder; it is then dried in a "Fleissner" ventilated drier for 5 to 10 minutes at 120°C. In the case of wool, it is necessary to steam the material for at least 30 sec. to get rid of the residual acidity.

Before dyeing, the organic solution of dyes is filtered in order to eliminate the "superfluous elements" from the dye: during impregnation there is also partial fixation of the dye. This is why the concept of pick up rate does not have the same value as during cold padding in an aqueous system.

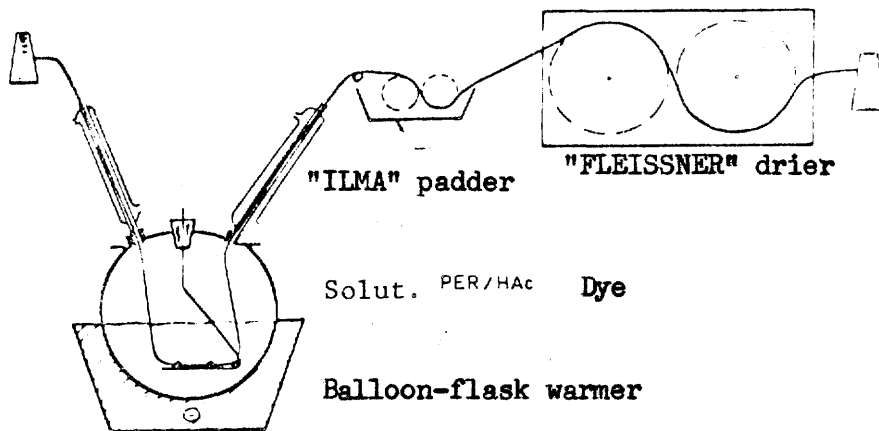


Figure 16 - Diagram of the dyeing equipment.

Determination of the quantity of acid fixed on the wool:

20 ml of the PER/HAc solution are titrated by a known titre of KOH/Ethanol solution, in the presence of thymolphthalein in an alcohol solution as an indicator.

Determination of the quantity of water desorbed by the wool:

The volumetric determination of the quantity of water in the solvent is made using the Karl Fischer method; determination of the end of the reaction is carried out electro-chemically (Dead Stop End Point Method) using a device consisting of a platinum double electrode, a reactor, a Radiometer ABU 12 automatic burette, a Radiometer 51 pH-metre and a TTT 11 titrator.

Measurement of the shrinkage percentage on the fabric:

The method applied has only relative values and departs from more elaborate methods. Using a 15 cm long, 5 cm wide steel plate, a rectangle is drawn on the fabric, which has lain for 24 hours, and prior to treatment. After dyeing, the fabrics are dried and after lying flat for one night in the same atmosphere as the non-treated fabric, the shrinkage percentage compared with the latter fabric is determined.

Measurement of the bath exhaustion:

The dyeings carried out at 55° and 90°C are done in a "Linitest" machine. The dyes are dissolved in acetic acid, then the quantity of PER is added; the solution thus obtained is filtered. The exhaustion curves are determined by colorimetry (Spectrophotometry, Beckman, model B), after dilution of an aliquot part of the dye bath with acetic acid. For a single dye concentration standard curves were made for each concentration of HAc in PER.

### 1.3. The tests carried out

#### 1.3.1. Influence of the quantity of HAc in a mixture with PER

##### 1.3.1.1. Description of the test

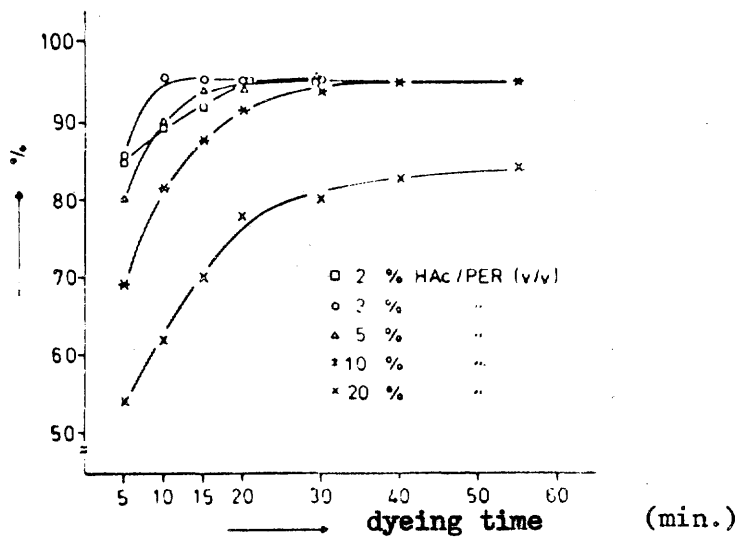
The tests were carried out at 55°C using the "pure wool" fabric, non-dried (dry weight: 0.898 g), 0.5% of dye, Polar Yellow 5 G N, liquor ratio 1:20. The percentage of acid used was between 2% and 20%. Tests with a percentage of acid above 20% were not carried out, as from the economic viewpoint it is more advantageous to use low proportions of HAc.

##### 1.3.1.2. The results

Figure 17 shows that the fixation of the dye is rapid (less than 30 minutes), when the percentage of acid is 10% or less.

If the bath exhaustion as a function of the percentage of acid in PER is shown on a graph, it is found that maximum fixation is situated in the region of 3% to 5% of acetic acid, irrespective of the dyeing time, with one exception, however, when the dyeing time is 30 minutes or more (see figure 18).

**Exhaustion**



**Figure 17** - Bath exhaustion as a function of dyeing time.  
Conditioned wool, temperature 55°C.

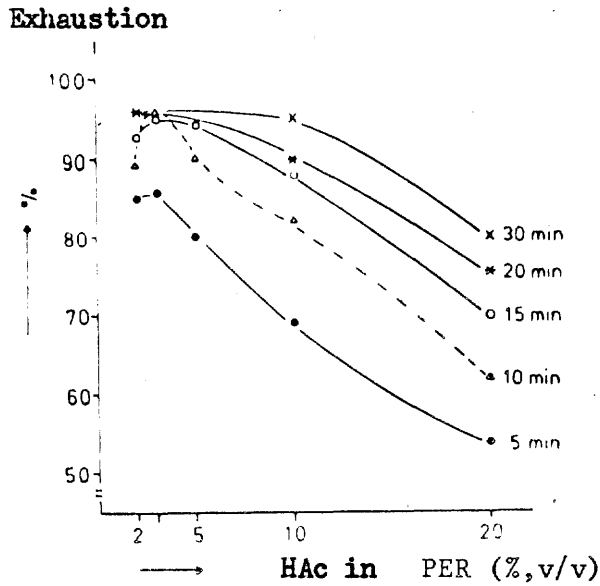
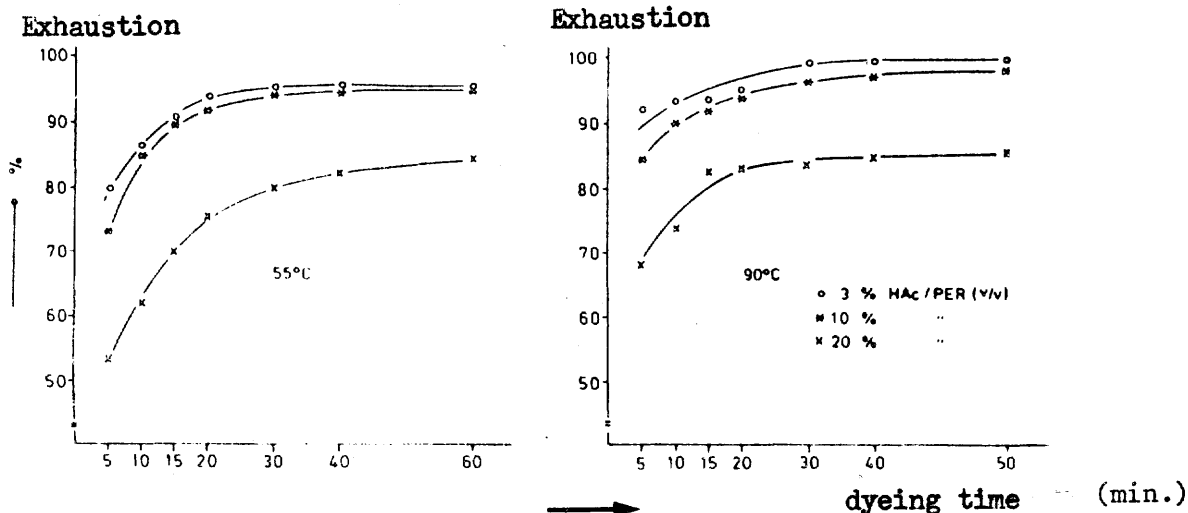


Figure 18 - Bath exhaustion as a function of the percentage of acetic acid in a mixture in PER. Conditioned wool, temperature 55°C.

1.3.2. Influence of the dyeing temperature

As already noted above (15), the swelling of anhydrous wool in the PER/HAc mixture, 10%, v/v, is identical at 55° and 90°C. The dyeing results confirm this, even though in this particular case anhydrous wool was not used. There is, however, a slight increase in the bath exhaustion percentage at 90°C when the PER/HAc/20% mixture is used, during the first 15 minutes of dyeing, as shown by figures 19 A and 19 B.



Figures 19 A and 19 B - Bath exhaustion as a function of dyeing time. Liquor ratio 1:20; 1% of Polar Yellow 5 G N; (conditioned wool), temperature 55° and 90°C.

1.3.3. Influence of the wool's degree of humidity on the fixation of the dye

Further to the results obtained in other studies (16), the influence of the wool's degree of humidity was studied. A "conditioned" wool (dry weight = 0.898 g) and an anhydrous wool were used. (The latter was dried overnight at 150°C in a ventilated oven).

As regards the influence of the percentage of acid in PER on the bath exhaustion, it is to be observed that, contrary to what was obtained for conditioned wool (figure 18), the best dye bath exhaustion is obtained when the proportion of acid in the PER is the highest, i.e. 30%, irrespective of the length of dyeing (figure 20).

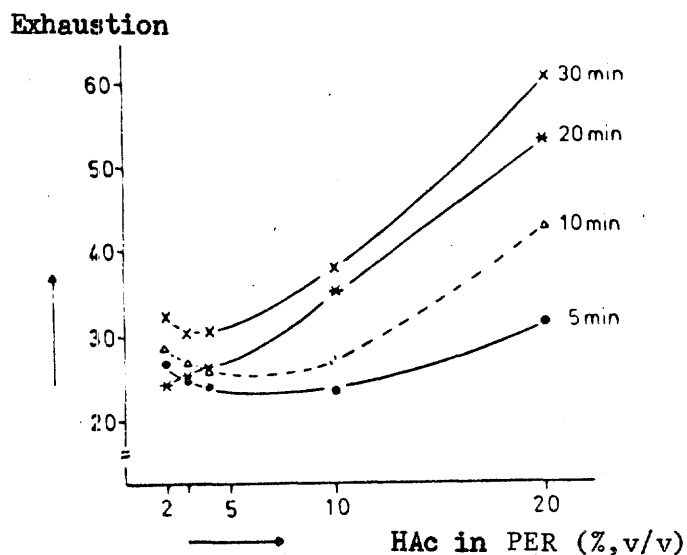
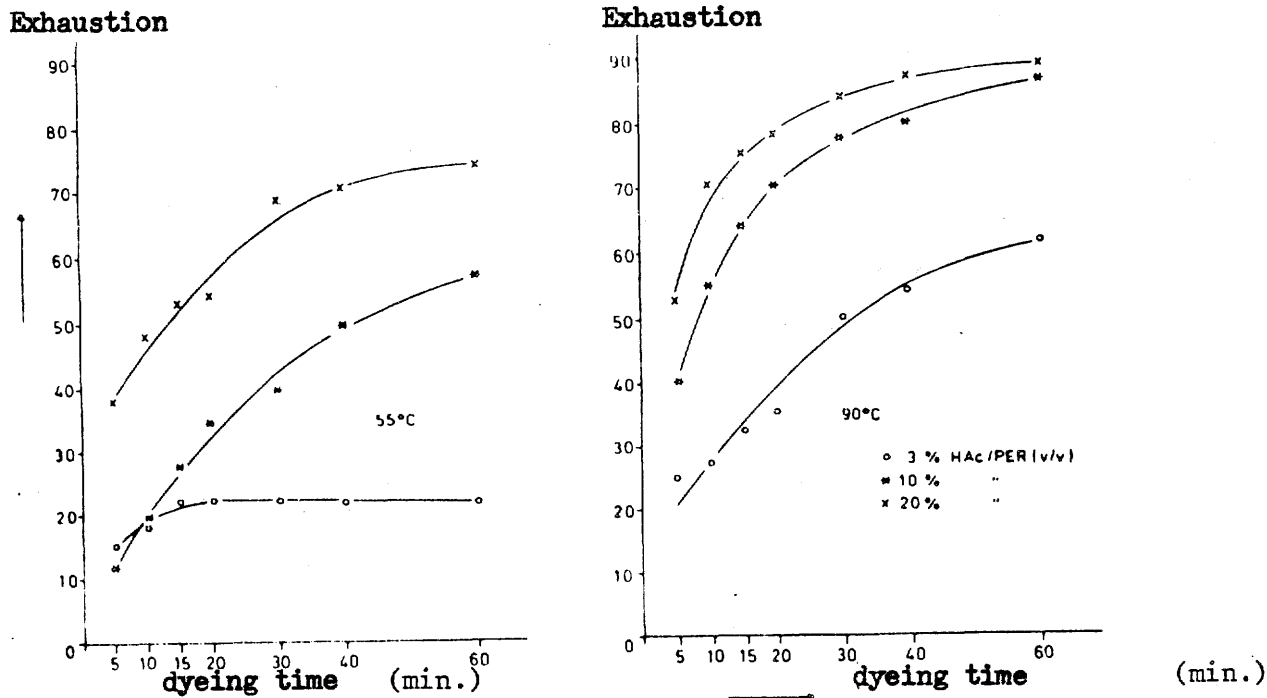
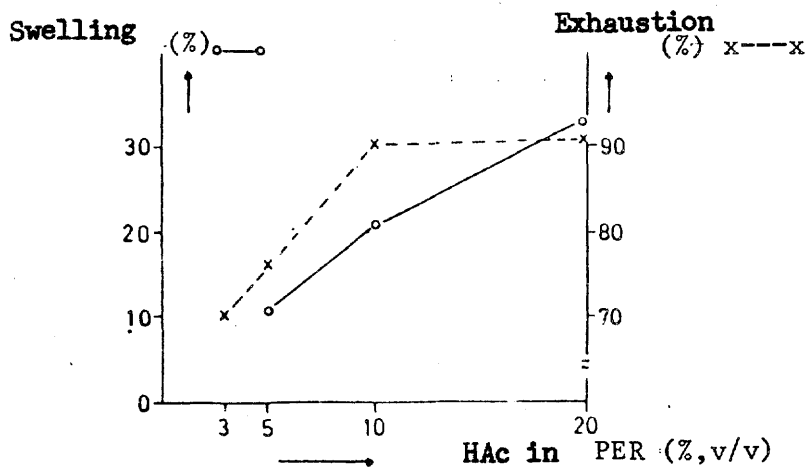


Figure 20 - Bath exhaustion as a function of the percentage of acetic acid in a mixture in PER. (Anhydrous wool); temperature 55°C.

The influence of temperature on the fixation of the dye on the anhydrous wool was studied. It is found (figures 21 A and 21 B) that the bath exhaustion is markedly greater at 90°C than at 55°C. This result is, at first sight, inconsistent with those obtained previously (15), in the case of the swelling of wool and the fixation of the dye (figure 22); thus, in addition to swelling, other parameters come into play during dyeing in a solvent medium.



**Figure 21 A and 21 B - Influence of the temperature and the percentage of acetic acid in a mixture with PER, on bath exhaustion (anhydrous wool)**



**Figure 22 - Influence of the quantity of acetic acid in PER on the swelling of anhydrous wool and on bath exhaustion.**



The dye bath exhaustion as a function of the water content of the wool was also examined. In addition to the anhydrous wool and the conditioned wool, the same substance, dried for relatively short times at 150°C (1.5 and 10 minutes) was used. Figure 23 shows that a 1 min. drying time at 105°C for wool reduces the fixation of the dye for conditioned wool from 92% to 37%.

This result is important for practical applications. Indeed, as the material's degree of humidity has an important influence on bath exhaustion and as at the present time working in dyeing with a constant degree of humidity is practically out of the question, it is found that dyeing in a purely organic medium poses a new problem which is difficult to resolve, especially in the case of wool.

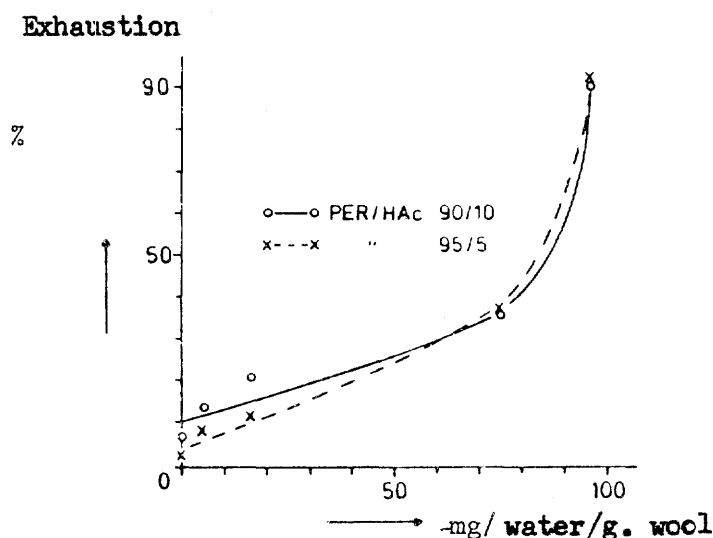


Figure 23 - Influence of the degree of humidity of the wool on the bath exhaustion. Temperature 55°C; dyeing time 20 min.; liquor ratio 1:30; 1% Polar Yellow 5 G N.

#### 1.3.4. Influence of the nature of the dye

It was interesting to study the maximum fixation of the dye on the fibre as a function of the percentage of acetic acid in PER, by using different dye classifications and sizes. A normal acid dye, Polar Yellow 5 G N, and a 1 : 1 metal complex dye, Neolane Orange G, were compared: the maximum fixations as a function of the percentage of acetic acid in PER are different.

After 10 minutes of dyeing at 55°C, the maximum fixation is obtained with 5% HAC in PER, when Polar Yellow 5 G N is used, while it is higher than 10% HAC in PER for Neolane Orange G (figure 24). During the two tests, however, the bath exhaustion percentage falls when the percentage of HAC in PER is higher than 10%, which can partially be explained by the fact that the solubility of the dye in the solvent system increases when the quantity of HAC increases and thus the affinity of the dye for the fibre decreases.

After 60 minutes of dyeing, the swelling of the fibre is sufficient to obtain a maximum of dye fixed (Polar Yellow 5 G N), with 3% to 10% of HAC; it is only when the percentage of HAC is higher than 10% that fixation decreases. In the case of Neolane Orange G fixation increases notably when the percentage of HAC in PER rises from 3% to 10%, which can be explained by the fact that in this area the swelling of the fibre increases when the percentage of HAC rises. When the percentage of HAC in PER is 20%, better fixation of Neolane Orange G is obtained compared with Polar Yellow 5 G N, which is more soluble in the mixture PER/HAC 80/20 (v/v) than Neolane Orange G.

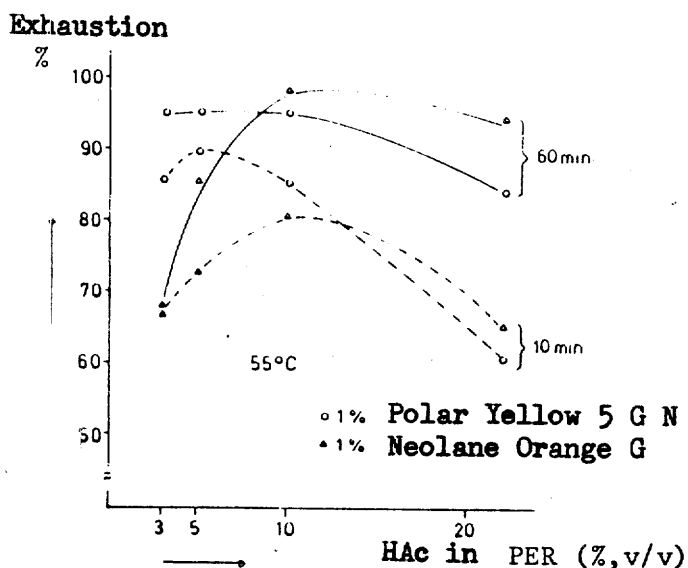


Figure 24 - Influence of the nature of the dye on bath exhaustion.

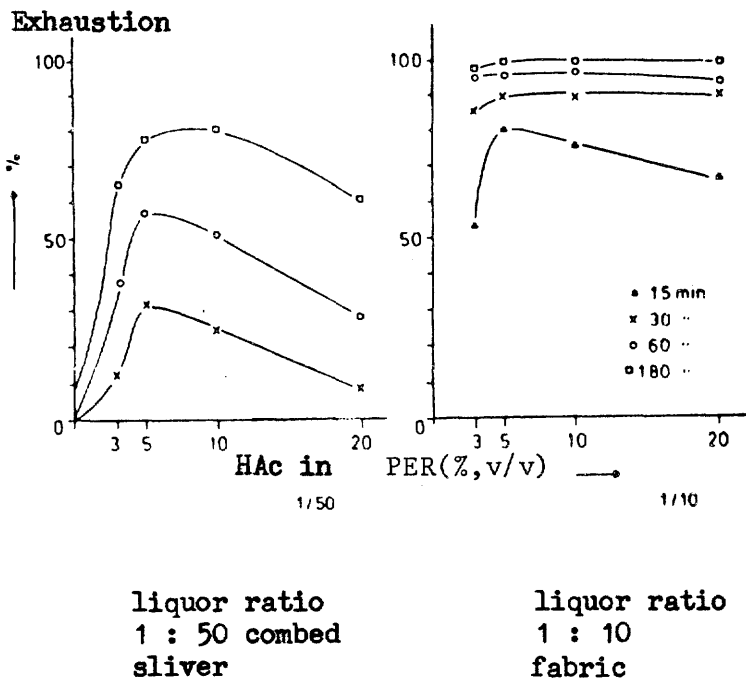
1.3.5. The dyeing mechanism and the fixation of the dye

We wished to pinpoint more accurately the dyeing in a solvent medium mechanism and more particularly to explain the maximum dye fixation obtained as a function of the percentage of Hac in PER. So as to make the measurements more accurate and also to use the results obtained in previous studies (16), we worked at room temperature (22° - 25°C) in this set of tests.

During the dyeing, the material is agitated backwards and forwards at 100 agitations/min. The dye used is Polar Yellow 5 G N, 1% on the weight of the material.

1.3.5.1. Bath exhaustion

As in the tests carried out previously at 55 and 90°C, maximum dye fixation is found when the percentage of acid in PER is around 5% (fig. 25). However, when the liquor ratio is low, 1 : 10, this maximum is only to be observed during the first few minutes of dyeing (fig. 26). The important influence of the liquor ratio 1 : 10 should be noted; fixation is complete after 60 min. of dyeing. It amounts to only 80% when the liquor ratio is 1 : 50. This difference will be explained in the next point.



Figures 25 and 26 - Influence of the percentage of acetic acid in a mixture in PER on bath exhaustion. Temperature 22°C.

In addition to the liquor ratio, the type of material, sliver or fabric, also influences bath exhaustion (fig. 27).

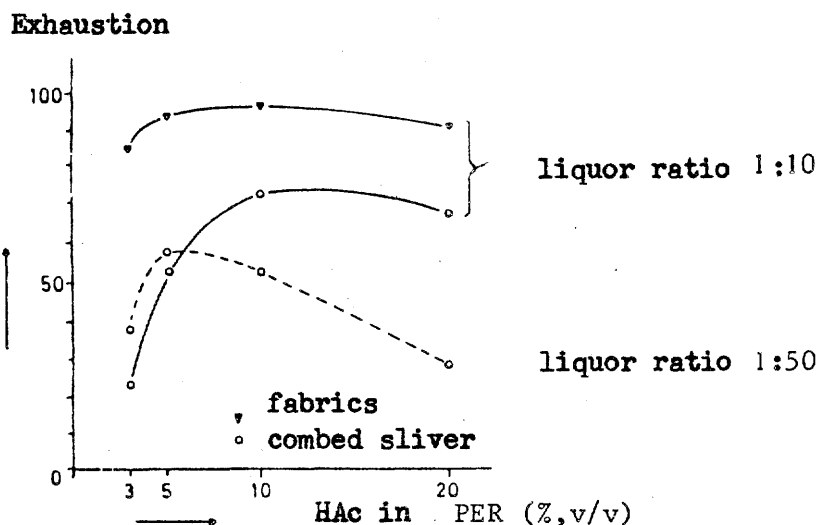


Figure 27 - Influence of the liquor ratio and of the percentage of acetic acid in a mixture in PER on bath exhaustion. Temperature 23°C; dyeing time 60 min.; 1% Polar Yellow 5 G N.

#### 1.3.5.2. Quantity of water desorbed by the wool in the PER/HAc mixture

The quantity of water desorbed by the conditioned wool in the PER/HAc mixture was determined using the classic Karl Fischer method, slightly modified. The increase in the quantity of water in the solvent after impregnation of the wool in the PER/HAc mixture during contact times varying between 10 and 60 minutes was measured; slight agitation of the solution was applied during the treatment.

Certain results are given in figure 28. It is to be noted first of all that there is a big difference in the desorption of water from the wool, according to whether the liquor ratio used is 1 : 10 or 1 : 50. If it is logical that desorption should be greater when the liquor ratio is high, it is surprising that this desorption can be 100% higher when a liquor ratio of 1 : 50 is used, especially as the contact time, 10 or 60 minutes, does not increase desorption, except in the case of the PER/HAc mixture (20%). It should be noted that where the liquor ratio is 1 : 10, desorption is low as long as the percentage of HAc in PER is 10% or less, but that the quantity of water desorbed, using the 20% PER/HAc mixture is seven times higher than with the 10% PER/HAc mixture. On the other hand, desorption increases regularly with the rise in the volume of HAc in PER, when the liquor ratio 1 : 50 is used.

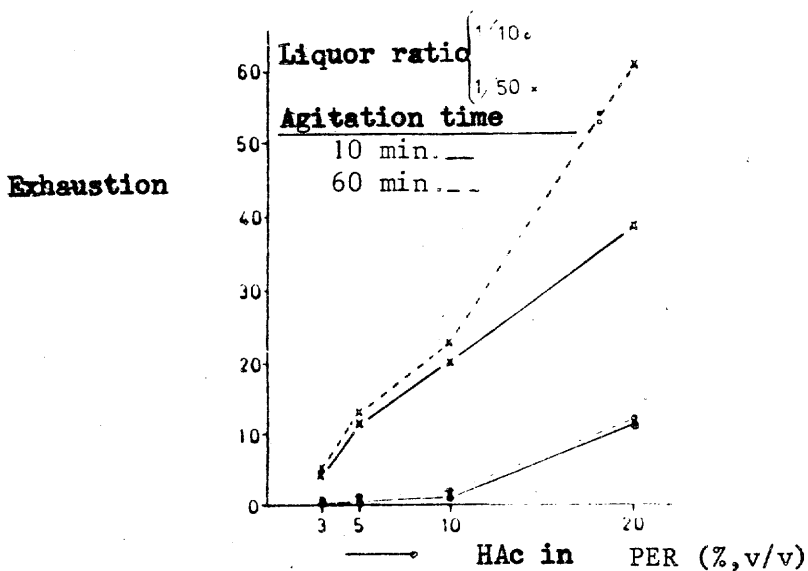


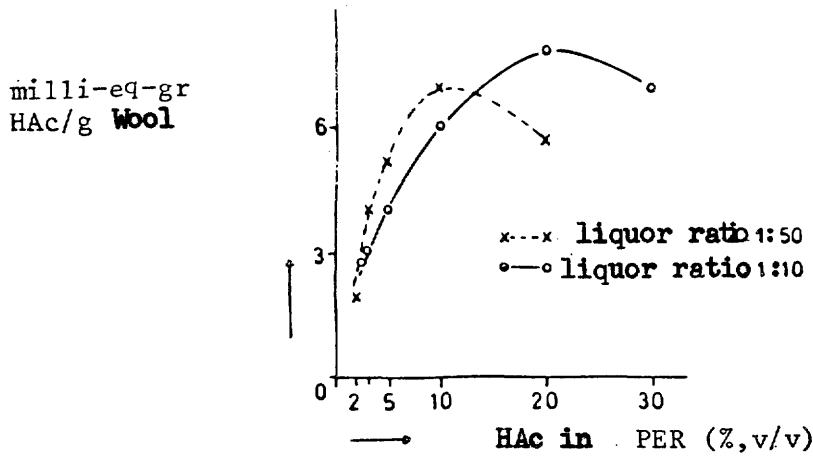
Figure 28 - Measurement of the desorption of water contained in the wool.

1.3.5.3. Quantity of acid fixed on the wool

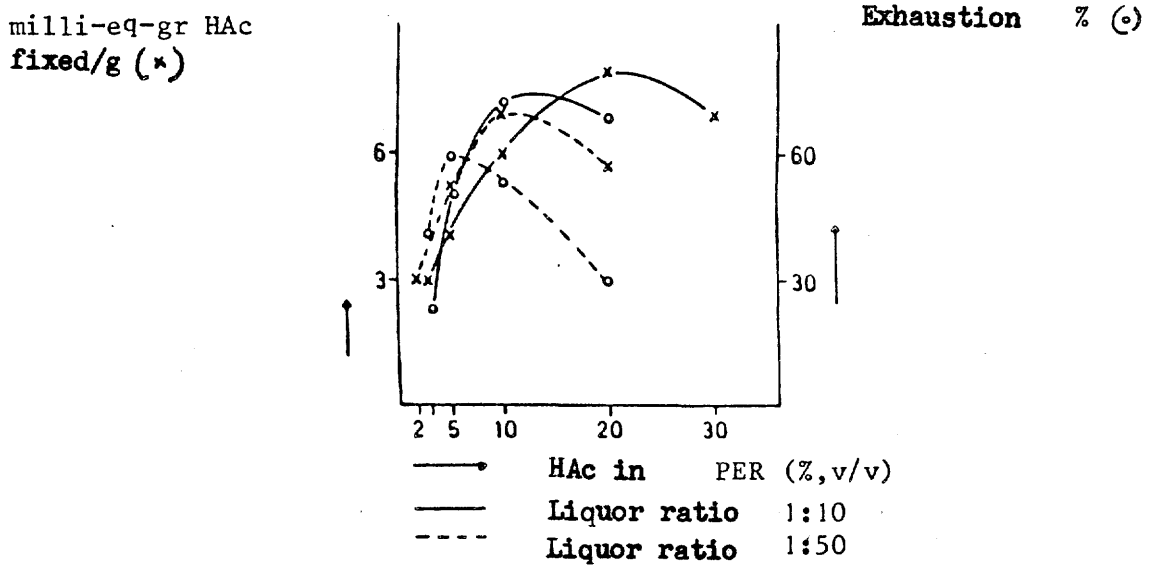
The quantity of acid fixed on the wool (conditioned combed sliver, LW 67), after 60 minutes of agitation at room temperature, was measured as a function of the percentage of acetic acid in PER. Two liquor ratios were used, 1 : 10 and 1 : 50. The results are given in figure 23. It is to be noted that whatever the liquor ratio used, a maximum of acid absorption is passed through. However, when a 1 : 50 liquor ratio is used, the maximum is situated in the region of 10% acetic acid, whereas with a liquor ratio of 1 : 10, the maximum is displaced to the region of 20% acetic acid. The explanation for these maximum absorptions can be supplied by figure 28. It is to be noted, indeed, that the desorption of water is much greater when a 1 : 50 liquor ratio is used. This may explain the fact that maximum acid absorption is situated in the region of 10% of acetic acid in PER. According to the "Drei Komponenten-Systemen" theory, put forward by H. Böhme, acid absorption by wool is at a maximum when the quantity of water in the PER/HAc mixture is near saturation point.

1.3.5.4. Connections between the quantity of acid absorbed, the bath exhaustion percentage, the quantity of water desorbed by the wool and the fabric shrinkage percentage.

If the maximum quantity of acid absorbed by the wool and the maximum percentage of dye bath exhaustion as a function of the percentage of acetic acid in the PER/HAc mixture (figure 30) are examined, it is found that the maximum amount of dye fixed always precedes the maximum acid absorption, which indicates that the quantity of acid fixed on the wool is only a partial function of the relative quantity of dye absorbed by the fibre.



**Figure 29** - Absorption of HAc by wool, as a function of the percentage of acetic acid in a mixture with PER. Contact time: 60 min; Temperature 22°C; (combed sliver)



**Figure 30** - Quantity of HAc fixed by wool and bath exhaustion as a function of the percentage of acetic acid in a mixture with PER. Temperature 22°C; reaction time 60 min.



The bath exhaustion percentage, the quantity of acid absorbed, the water desorbed by the conditioned fabric and the shrinkage percentage were finally determined on the "pure wool" fabric, in the same conditions. The operational conditions were as follows: liquor ratio 1 : 10; temperature: 23°C; dyeing time: 10 min; Polar Yellow 5 G N: 1%.

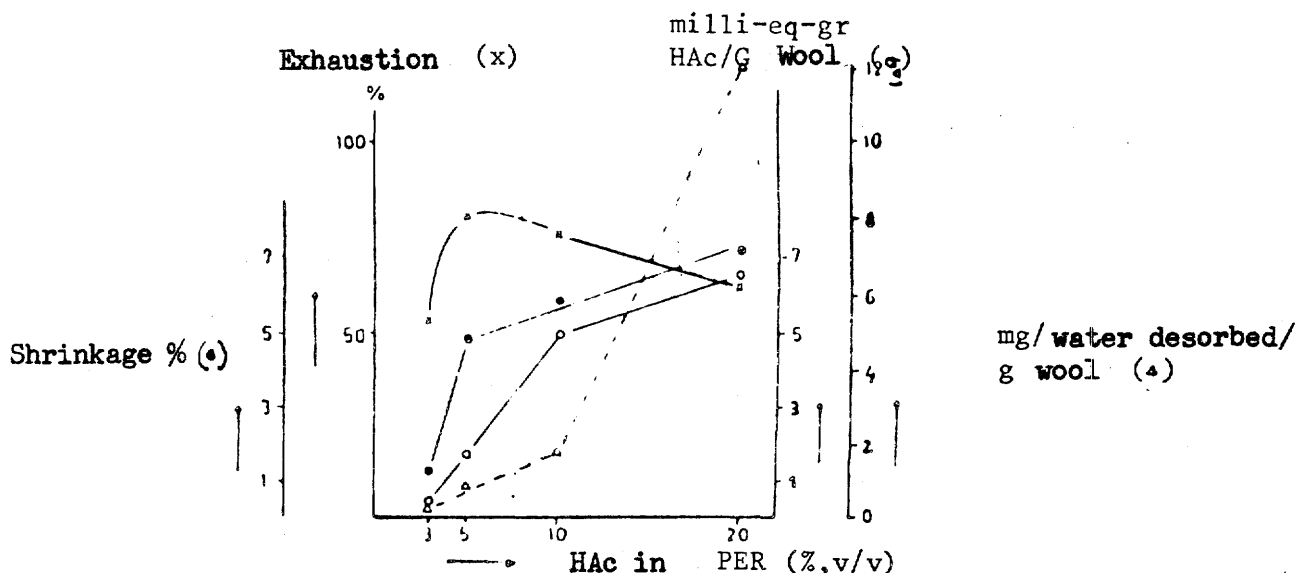


Figure 31 - Shrinkage, bath exhaustion, quantity of acid absorbed and water desorbed by the "pure wool" fabric percentages, as a function of the percentage of acetic acid in a mixture with PER.  
Liquor ratio: 1 : 10; reaction time: 10 min.

The various results given in figure 24 show that:

- Up to a concentration of 10% HAc in PER, the absorption of HAc by wool is very rapid, whereas the desorption of water is very low; it is only when the concentration of HAc in PER is over 10% that the desorption rate rises sharply.

These two opposite effects enable maximum fixation to be obtained, given that, in these conditions, the wool is still swollen and that the dye penetrates easily, being brought on to the fibre by the acetic acid.

- The shrinkage percentage and the quantity of acid fixed run parallel. No explanations have been found for this finding to date.
- If in this test maximum HAC fixation is not obtained, it is due to the low liquor ratio used (1 : 10); in this case, the maximum occurs when the concentration of HAC in PER is over 20% (see figure 30).

## 2. Extraction of the surface substances from wool

The quantity of substances extracted from industrially cleaned wool with most solvents is relatively low (under 1.5%). This quantity of lipo-protein substances is also greater when, before extraction, the wool is partially reduced or oxidized. Nevertheless, this slight extraction of substances can considerably modify the dyeing or adhesion properties of polymers on wool.

The study relating to the dyeing of wool in a solvent medium showed the synergetic effect of the perchlorethylene/glacial acetic acid mixture. We wanted to seek out a similar effect for the extraction, by mixtures of organic solvents, of the lipo-protein substances from cleaned wool. The shrink proofing treatment for wool does indeed necessitate a fairly elaborate pre-treatment: scouring, chlorination, reducing treatment, washing. These treatments are very expensive and chlorination, in particular, is somewhat harmful to wool. This pre-treatment in an aqueous medium is mainly carried out to extract the surface substances from the wool.

Although the influence of an ethyl alcohol action on wool treatment has already been studied by Speakman, Bradbury, Mackinson and Farnworth, no study exists on extraction from wool cleaned with mixed solvents, to prepare the material for shrink proofing treatments.

### 2.1. The textile materials used

- "Pure wool" single jersey knitted fabric
- Combed sliver 21  $\mu$ m.

2.2. The solvents and the conditions of extraction

Main solvent: perchlorethylene

Co-solvents: series of aliphatic alcohols up to C<sub>4</sub>; benzyl alcohol.

- Low agitation extraction at room temperature, for 1 h max; liquor ratio 1 : 10.
- Extraction with Soxhlet extractor (with 6 siphonages) - After extraction, the mixture of solvents is filtered and distilled in a vacuum and in a nitrogen atmosphere.

2.3. The tests carried out

The results given in table 13 relate to the substances extracted from a single jersey knitted fabric after soaking in the solvents at ordinary temperature for one hour.

Table 13 - Percentage of substances extracted as a function of the percentage of alcohols in the mixture.

Alcohol	Percentage of alcohol in PER (v/v)						
	0	5	10	85	90	95	100
Methanol	0.472	1.683	1.907	2.183	1.848	1.656	1.646
Ethanol	0.474	-	1.235	1.066	1.039	1.156	0.921
Isopropanol	0.479	0.473	0.790	0.791	0.700	0.662	0.678

It can be seen, from the values mentioned in table 13, that the addition of a small quantity of alcohol (5%, 10%) to PER doubles or quadruples the quantity of substances extracted: in addition, the colour of the extract changes markedly, it goes from dark yellow (with 100% PER) to brown-black in the case of PER/Methanol mixtures. It is therefore found that, all other conditions being equal, the lower the molecular weight of the alcohol, the more surface substances are extracted from wool. This result tallies with the "pore size" theory, already put forward by Speakman.

The percentage of protein nitrogen on the substances extracted by the solvents was also determined. In this case, an optimal percentage of alcohol in PER (see table 13) is no longer to be found. On the contrary, the percentage of protein nitrogen increases regularly with the quantity of alcohols in PER (table 14).

Table 14 - Percentage of protein nitrogen in the substances extracted.

% of methanol in PER (v/v)	0	5	10	85	90	95	100
% of nitrogen	0.78	0.94	1.04	1.05	1.04	1.09	1.11

The knitted fabrics which have been pre-treated by solvents or mixtures of solvents are shrink-proofed using anionic resins (Hercoset) or cationic resins (Polyacrylates). The results show that one hour of extraction at ordinary temperature do not lead to any marked improvement in the shrink-proof nature of the single jersey knitted fabric treated with resins. Extraction by solvents over 24 hours, however, greatly improves the resin's adhesion to the wool and thus increases its shrink-proof nature, both for anionic and cationic resins. However, as pre-treatment in a solvent medium takes a great deal of time, it cannot be contemplated industrially.

V. EXTRACTION OF NON-FIXED DYES FROM POLYESTER TEXTILE MATERIALS

In this last part of the research project, the possibility was examined of carrying out certain steps in the textile finishing process in a solvent medium, more particularly the continuous cleaning of polyester after thermosol dyeing, at the same time retaining the same fastness properties as those obtained using the reducing treatment in an aqueous medium.

In industry, thermosol dyeing on pure polyester is not very widespread. It is, on the other hand, very common for polyester/cotton goods and this study is the first stage of research into the effectiveness of after-cleaning in solvents after thermosol dyeing of the polyester/cotton mixture, where account must be taken of the presence of a second fibre and a second type of dye.

The use of perchlorethylene for the after-cleaning of polyester has not yet been applied in industry and literature on the subject is limited (50, 51, 52). The only application known of at the present time is after-cleaning after dyeing with new types of dyes specially developed for use in a solvent medium. The aim of this study is now to test common dyes.

1. Textile materials used

"Grilene" polyester fabric, 155 g/m<sup>2</sup>, yarn N° 20 x 2.

2. The dyes and measurement methods

<u>Dye</u>	<u>Chemical characteristics</u>
C.I. Disperse Yellow 198	monoazo
C.I. Disperse Red 60	anthraquinone
C.I. Disperse Blue 81	anthraquinone
C.I. Disperse Blue 94	monoazo
Black	mixture of various dyes.

The black dye is a mixture of various dyes and is not clearly defined. For the laboratory tests only Disperse Blue 81 was used. The other dyes were tested on semi-industrial equipment, as was a trichomy dyeing process.

The dry and wet rub fastness of the colours was tested in accordance with standard DIN. 54.021.

### 3. The laboratory tests

A diagram of the laboratory apparatus is shown in fig. 31. After thermosol dyeing, the polyester fabric is placed in a specially designed laboratory Jig. The material passes continuously in front of a jet nozzle, which sprays the after-cleaning bath under invariable pressure.

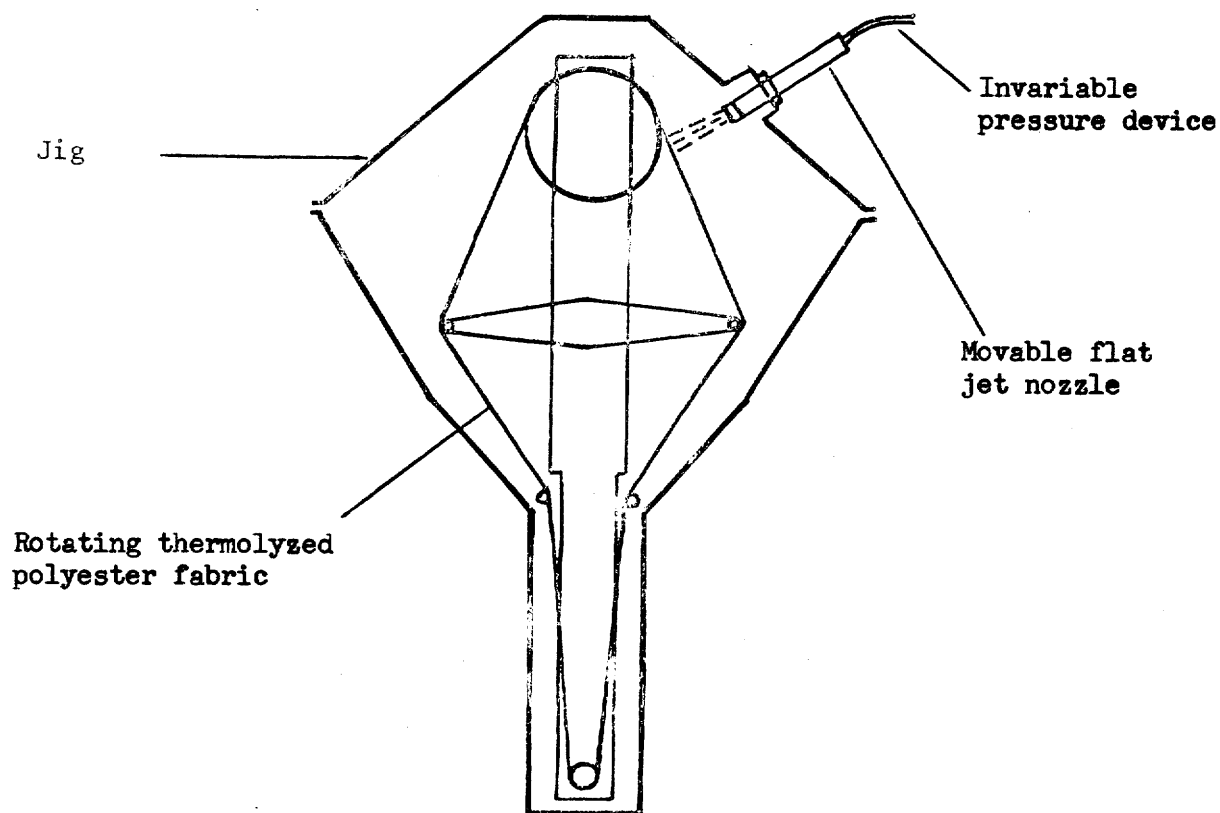


Figure 31 - Laboratory equipment for the after-cleaning examination with solvent using the spraying process.

The basic principle is that after thermosol dyeing, there are, on the surface of the polyester, particles of non-fixed dyes encrusted in the auxiliary products, which are water soluble. For PER to be able to reach this non-fixed dye, it must therefore be applied fairly vigorously. This was why pressure spraying was preferred. The cleaning bath is composed of PER containing 15 g/l of water and 3 g/l of a commercial surfactant of the water/oil emulsifier type.

### 3.1. Influence of the addition of water

Right from the first tests with C.I. Disperse Blue 81, it was found that in order to achieve fastness ratings 4-5, obtained with the conventional reducing treatment, a certain quantity of water was necessary. Figure 32 gives the results obtained as a function of the quantity of water in PER. It will be noted that for a concentration of 3 g/l surfactant, 15 g/l water is sufficient.

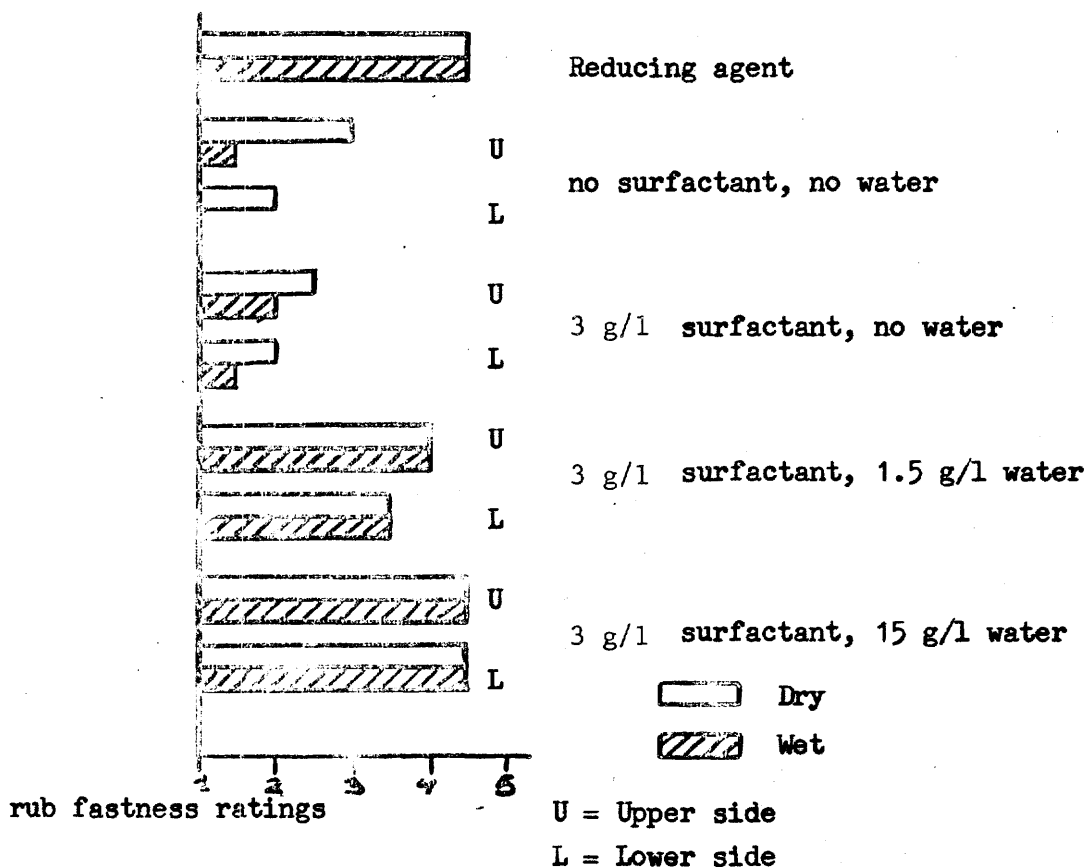


Figure 32 - Influence of the concentration of surfactant and of water in the PER bath on the rub fastness ratings of thermosol dyeings. Dyeing at 4%; pressure of the jet nozzle: 6 bars; speed 6 m/min.; space between the jet nozzle and the fabric: 35 mm; spraying angle: 60°; spraying and test: on both sides.

The influence of water is logical if the fact that the dye is designed for the aqueous medium and contains water soluble auxiliary products is taken into account. Its extraction from the textile material will therefore be made easier if an adequate quantity of water is used.

### 3.2. Influence of the mechanical action

The laboratory tests also enabled the influence on the elimination of the encrusted dye of agitation of the textile in the PER bath to be demonstrated.

As shown in figure 34, the penetration of the solvent into the textile material in the dyeing equipment is inadequate for the desired fastness ratings to be achieved: no more than rating 2 can be achieved. After agitation of the samples, ratings of 3-4 are achieved. The same fastness ratings were achieved when the material was agitated in a rotating dyeing machine.

Fastness ratings 4-5 were achieved with this same movement in a dry cleaning machine drum. However, the fastness ratings obtained with the conventional reducing treatment were only equalled by after-cleaning using sprayed solvent.

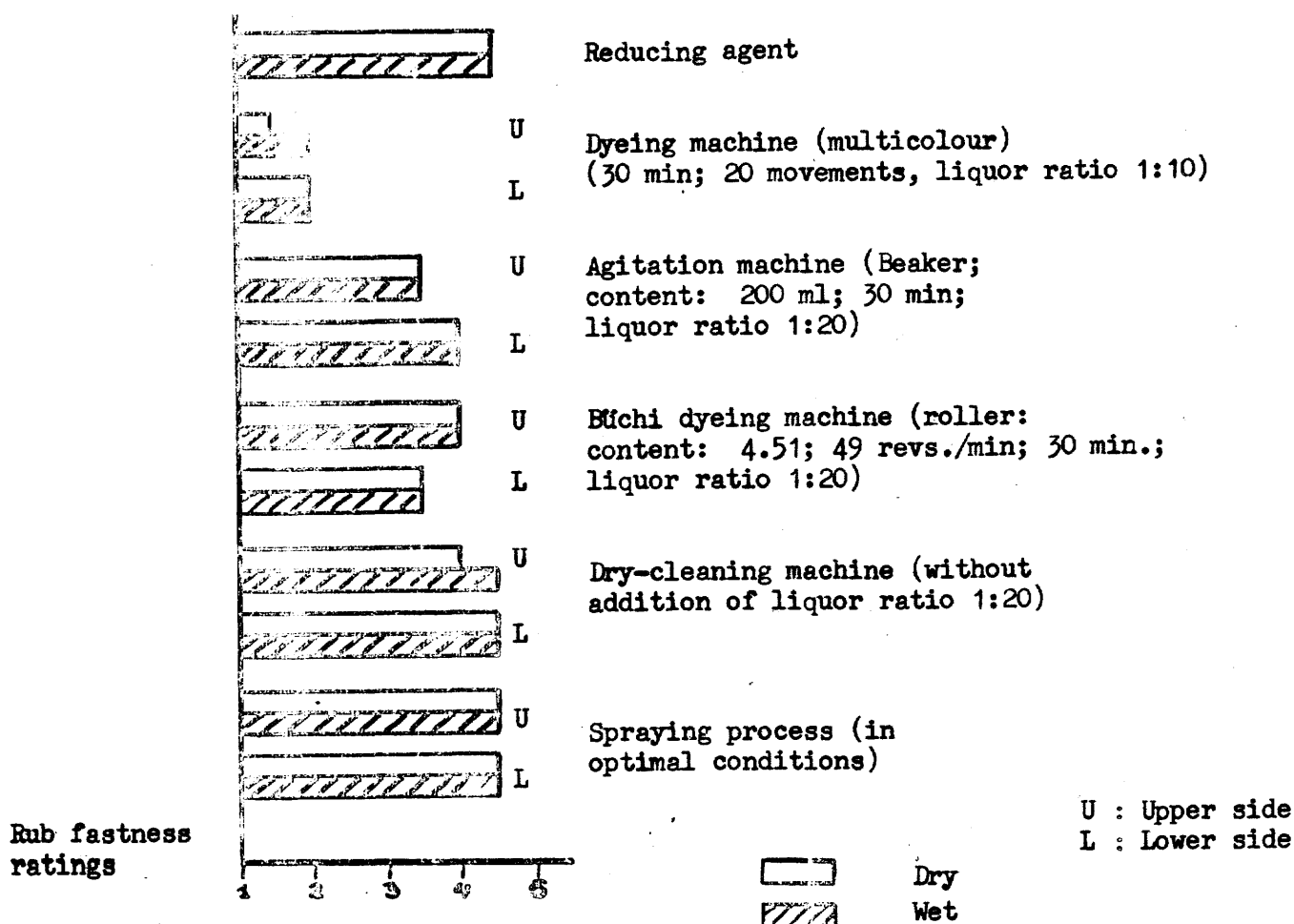


Figure 33 - Relation between the rub fastness obtained with an after-cleaning in solvent and the process chosen. (surfactant XIX: 3 g/l; water 15 g/l).

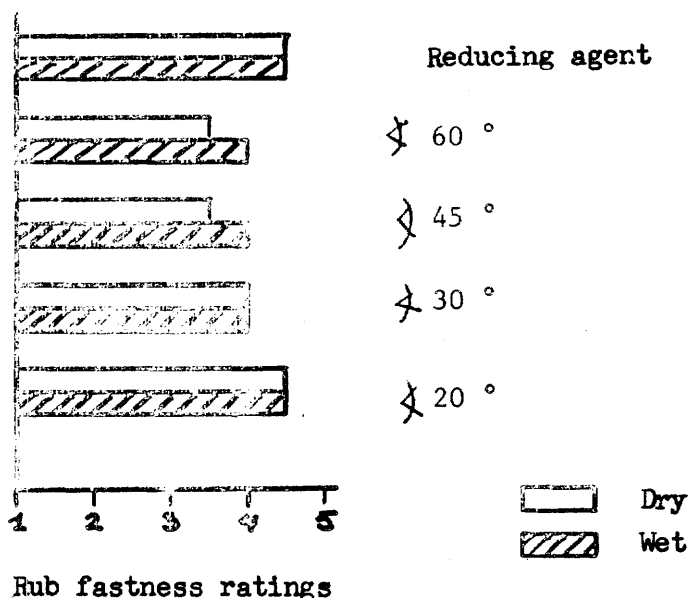


### 3.3. Influence of the spraying conditions

The spraying parameters which were examined were:

- the angle of the jet nozzle, spraying angle,
- the jet nozzle opening,
- the pressure of the jet nozzle,
- the distance between the jet nozzle and the fabric,
- the speed at which the fabric passes,
- the number of sprays, on 1 or 2 sides,
- the need for possible extra ends in the bath.

As an example, the influence of the spraying angle is illustrated by fig. 34. It is found that for a specific distance between the jet nozzle and the fabric, fastness improves when the spraying angle decreases; at 20° the values obtained using the conventional reducing treatment are achieved. This result is logical as the solvent is concentrated on a smaller strip of fabric if the spraying angle is narrow, while the solvent is spread over a bigger surface when the spraying angle is wider. One drawback with a narrow spraying angle is that, owing to the small surface of fabric reached, a relatively large number of sprays will be necessary to cover the whole width of the fabric. Nevertheless, by choosing a properly adjusted pressure and opening for the jet nozzle, it is possible to work with a wider spraying angle without affecting the fastness.



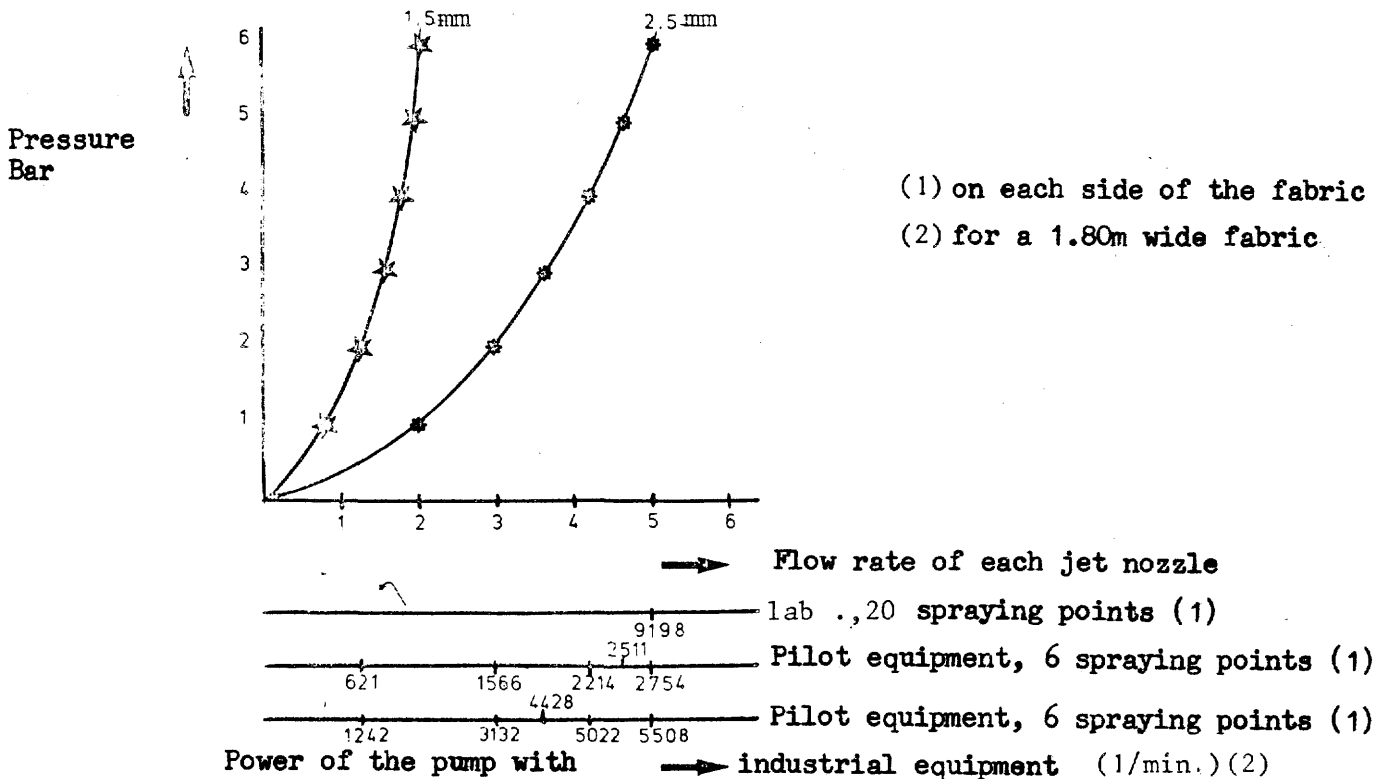
**Figure 34** - Influence of the spraying angle on the rub fastness ratings of thermosol dyeings.  
Dyeing at 4%; jet nozzle opening: 2.5mm; jet nozzle pressure: 6 bars; distance spray-fabric: 35mm; speed of passage: 6m/min.; spraying: 10 times on each side; test: upper side.

The laboratory tests enabled the optimal spraying conditions to be determined:

- spraying angle : 60° which enables a 40 mm wide strip of textile material to be treated
- jet nozzle opening : 2.5 mm
- jet nozzle pressure : 6 bars
- jet nozzle/textile distance : 35 mm where the width of the 40 mm strip is maintained
- spraying : 20 times on the two sides, i.e. 20 consecutive spraying points on each side of the fabric.

These laboratory-determined conditions are unsatisfactory for two reasons:

- A pressure of 6 bars with a jet nozzle with a spraying angle of 60° and an opening of 2.5 mm in diameter requires a solvent flow rate of 5.2 l/mm (figure 35). For a fabric width of 1.80 m and 20 spraying points on each side, a 9200 l/min. pump would be necessary. This power is economically impossible and would considerably increase investment and running costs. In practice, the power of the pumps is generally ± 1000 l/min.



**Figure 35** - Relation between the flow rate and the power of the pump on the one hand and the spraying pressure and the jet nozzle opening on the other. Spraying angle 60°.

- As a result of the force with which the solvent is sprayed on to the fabric, the textile characteristics could deteriorate. This is particularly true in the case of bulky goods where the formation of the bulked appearance should come about without any external mechanical action.

4. Tests on pilot equipment

A diagram of the pilot equipment is given in fig. 36.

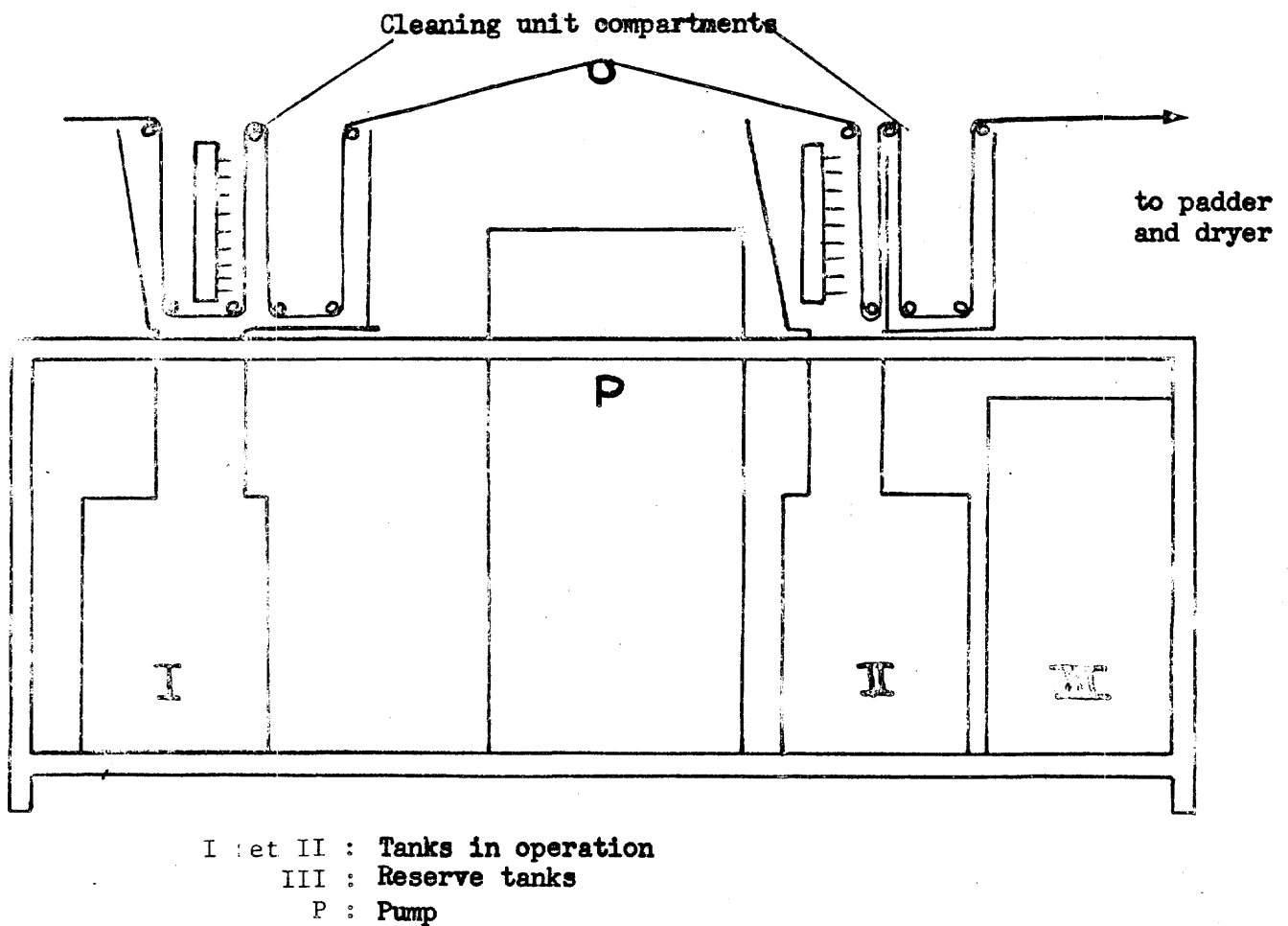


Figure 36 - Diagram of the pilot equipment for after-cleaning in perchlorethylene after thermosol dyeing using the spraying process.

The equipment has two cleaning unit compartments, divided into a spraying section and an impregnation section. In the first compartment the upper side of the fabric is sprayed, in the second one the lower side. After leaving the washing unit compartments, the fabric is driven towards B&W C 400 continuous equipment where it is first squeezed in a padder and then dried in a dryer.

The cleaning bath is contained in two tanks. A third tank contains pure solvent. The pump used enables there to be spraying pressures up to 7 bars. The cleaning bath leaves tank III and is pumped via tanks I and II respectively to the cleaning unit compartment. The spraying pressures can be adjusted with pistons and the pipes are fitted with manometers for adjustment and checking. Figure 37 shows the fabric's route in the two compartments.

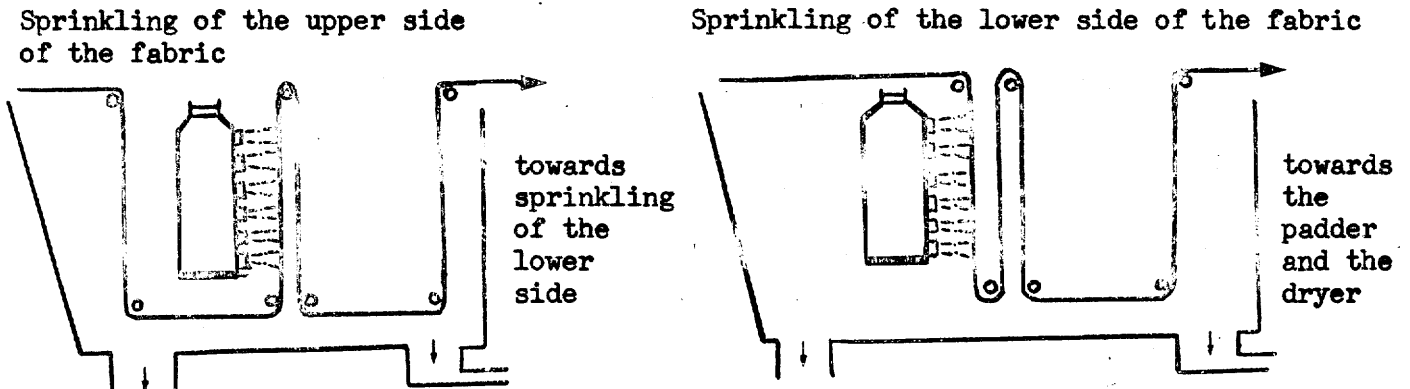


Figure 37 - The passage of the material through the cleaning unit compartments of the pilot equipment.

The solvent is sprayed on to a 15 cm wide strip of textile, at a distance of 35 mm, from 6 spraying points each containing 4 jet nozzles with a spraying angle of 60°. The points are arranged in such a way that first the upper side, then the lower side of the fabric are treated. The cleaning bath drains away immediately and goes back into the pumping circuit.

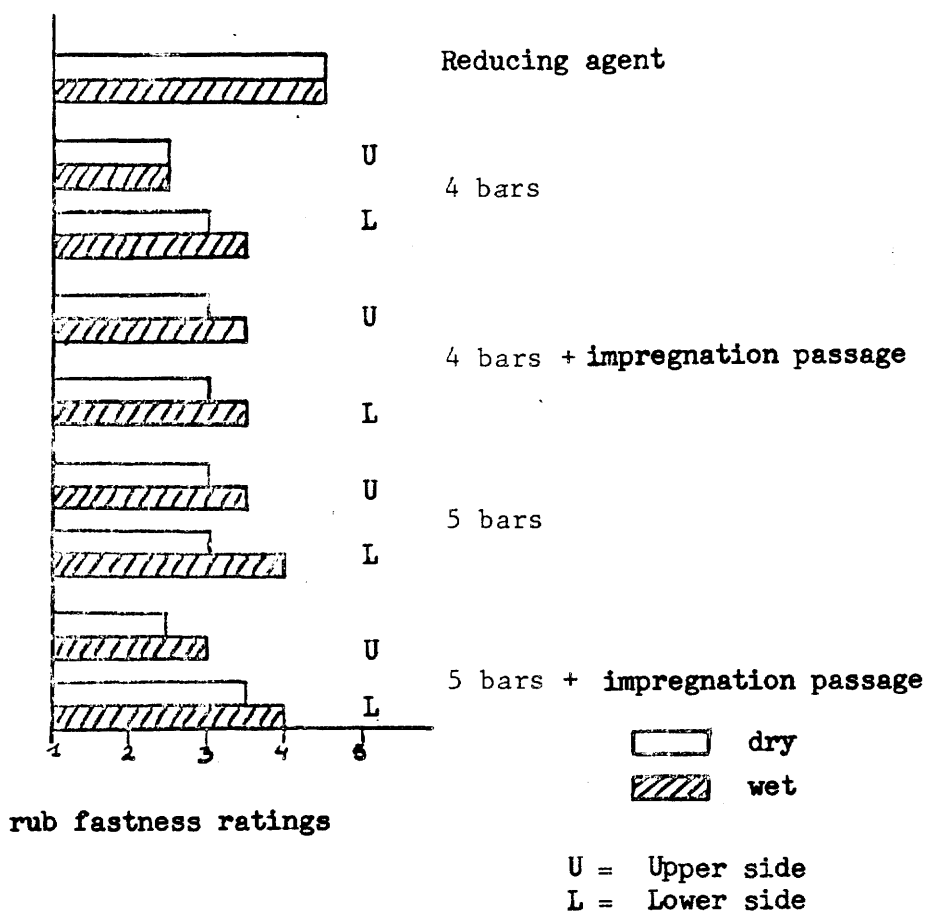
The impregnation section enables there to be possible impregnation of the fabric with the cleaning bath, enabling the dyes already freed by the spraying to be eliminated. The PER temperature is 40°. It is obtained by the operation of the pump and is measured by a thermocouple joined up with a recorder. The speeds of passage of the fabric are 6 m/min. and 10 m/min.

The tests on the pilot equipment are designed to remedy the difficulties caused by the theoretical conditions determined in the laboratory, i.e. to reduce spraying pressure from 6 bars to 5 or even 4 bars without changing the fastness ratings.

For this purpose, the compartments include an impregnation section filled with cleaning liquid.

For a single passage of the fabric and with 6 spraying points per side, the reduction from 6 to 5, or from 6 to 4 bars on the pilot equipment would mean a reduction in pump capacity of from 9200 to 2500, or of from 9200 to 2200 l/min. on industrial equipment. Fig. 38 gives the results of the tests for a fabric passage speed of 6 m/min.

It is found that in these conditions, a pressure of 4 or 5 bars is inadequate and that an additional impregnation has very little effect; the tests were thus continued without impregnation.

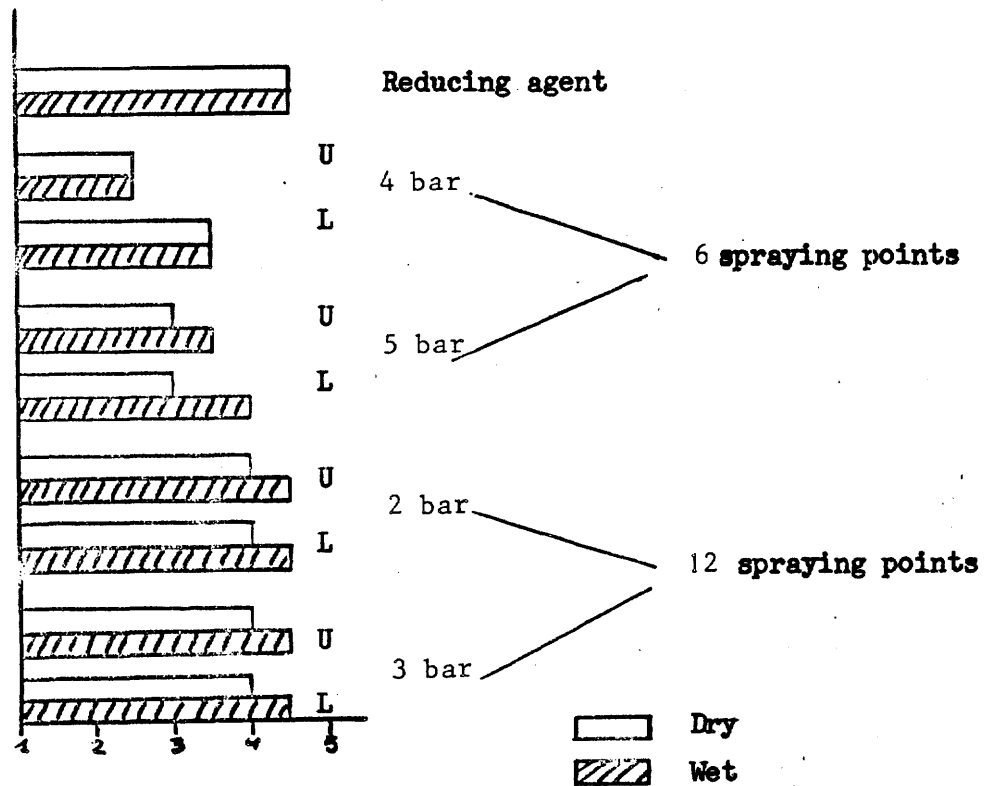


**Figure 38** - Tests on the pilot equipment: Influence of spraying pressure and of an additional impregnation passage on the rub fastness ratings of thermosol dyeings. Dyeing at 4%; jet spray opening: 2.5 mm; bath temperature: 40°C, jet nozzle-fabric distance: 35 mm; speed of passage: 6 m/min.; spraying points: 6 on each side of the fabric.

#### 4.1. Influence of the number of spraying points

The decrease in the mechanical action resulting from the higher pressure cannot be offset by an impregnation. The number of spraying points was therefore doubled, the fabric passing through the machine twice. The results obtained are given in fig. 39.

When the number of spraying points is doubled, the rub fastness ratings obtained are better and it is possible to reduce the pressure from 4 to 2 and from 5 to 3 bars respectively. It should, however, be noted here that the spraying pressure, i.e. the mechanical action on the non-fixed dye exerted by the jet nozzle, is not the only factor which affects fastness but that the frequency of repetition of the operation is also very important.



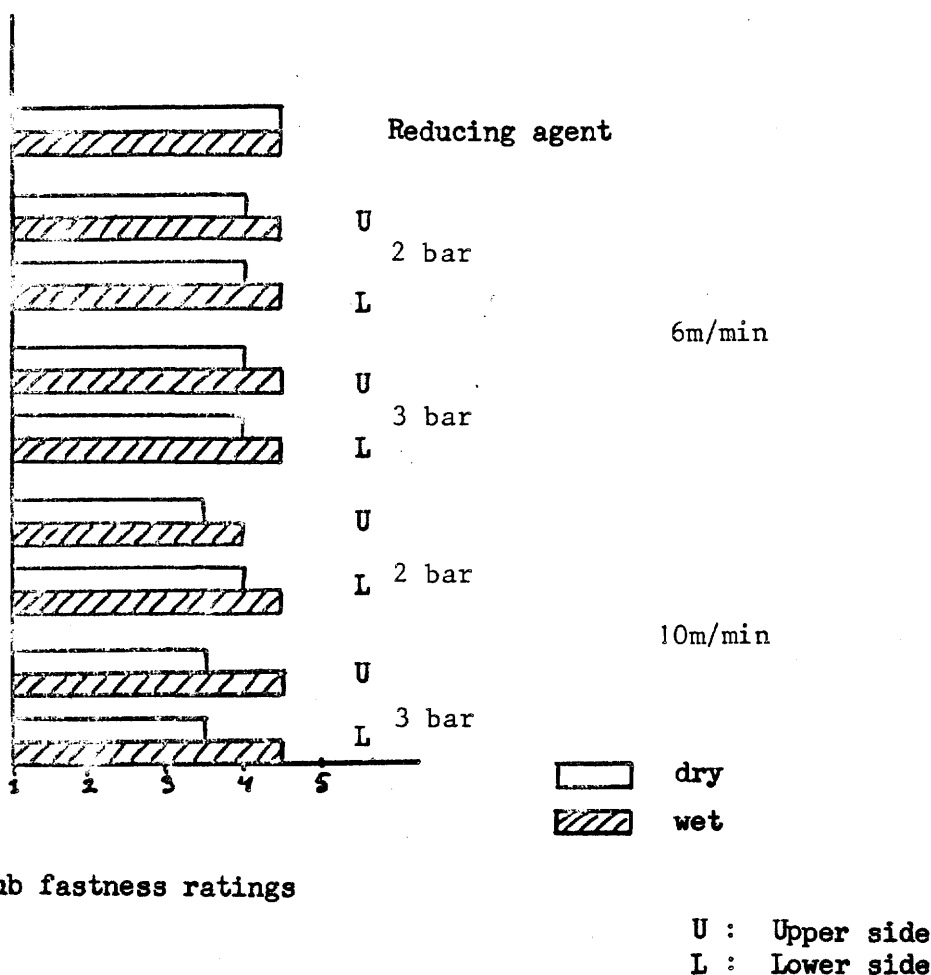
Rub fastness ratings

U = Upper side  
 L = Lower side

**Figure 39** - Tests on pilot equipment: Influence of the number of consecutive spraying points per side of the fabric on the rub fastness ratings of thermosol dyeings for 2 spraying pressures.  
 Dyeing at 4%; jet nozzle opening: 2.5 mm; bath temperature: 40°C; distance jet nozzle-fabric: 35 mm; speed of passage of the fabric: 6 m/min.

4.2. Influence of the speed of passage of the fabric

In addition to reducing pressure, it is preferable to increase the speed of passage of the fabric; the profitability of continuous equipment is indeed determined inter alia by the speed of production. With the two speeds possible on the pilot equipment, 6 and 10 m/min., the influence of the speed on fastness ratings was examined (fig. 40).



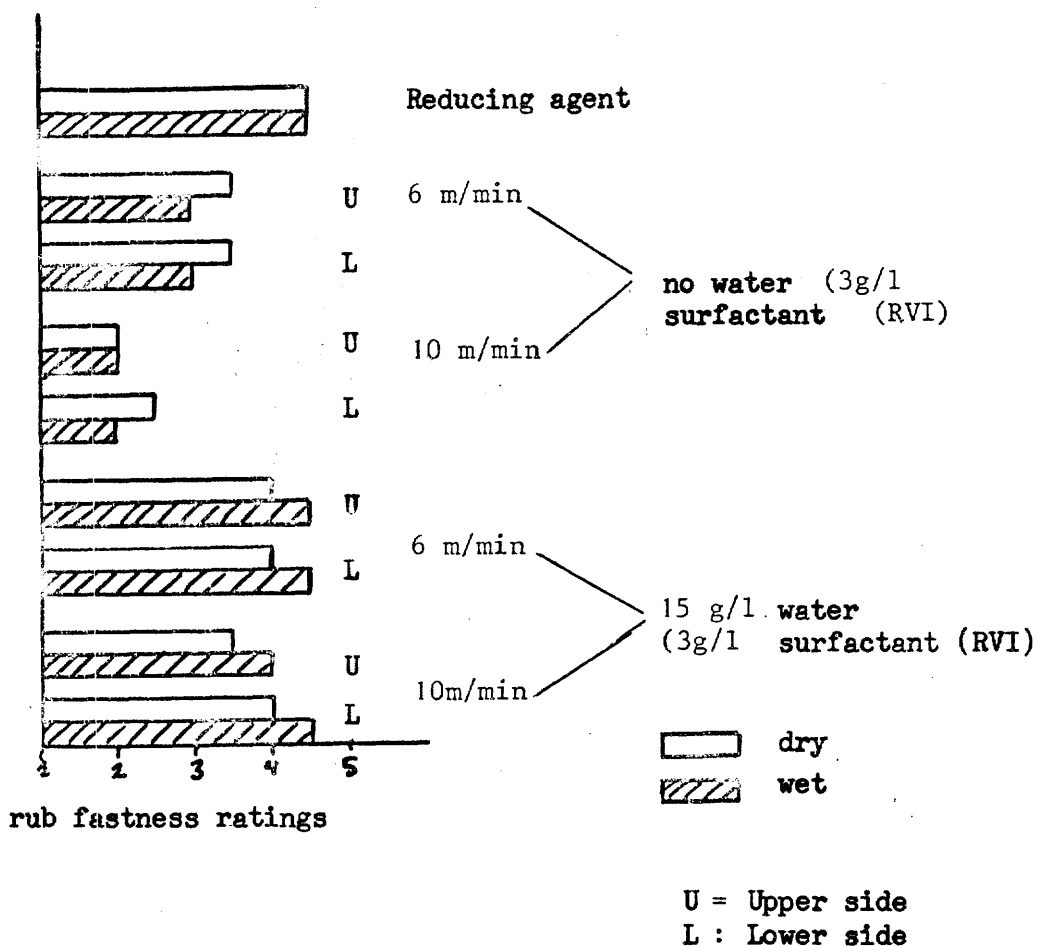
**Figure 40** - Tests on pilot equipment: Influence of the speed of passage of the fabric on the rub fastness ratings of thermosol dyeings with 2 spraying pressures. Dyeing at 4%; jet nozzle opening: 2.5 mm; bath temperature: 40°C; jet nozzle-fabric distance: 35 mm; spraying points: 12 on each side of the fabric.

It is found that for pressures of 2 and 3 bars respectively and the slow speed of 6 m/min., dry or wet rub fastness ratings of 4 and 4-5 respectively are obtained, as with the conventional reducing treatment. At 10 m/min., the rub fastness ratings, particularly dry, decrease by about one unit. This is due to the fact that the passage time of the fabric in the spraying section, and thus the duration of contact between the fabric surfaces and the sprayed liquid, is too short with a speed of 10 m/min.; 6 sec. With a speed of 6 m/min., it is 10 sec.

#### 4.3. Influence of water

The tests described above were carried out with a PER mixture, containing 3 g/l surfactant and 15 g/l water. The importance of water having been shown in the laboratory tests, they were repeated on pilot equipment. Fig. 41 gives the results for 2 speeds of fabric.





**Figure 41** - Tests on pilot equipment: influence of the water content of the perchlorethylene bath on the rub fastness ratings of thermosol dyeings for 2 speeds of passage of the fabric.

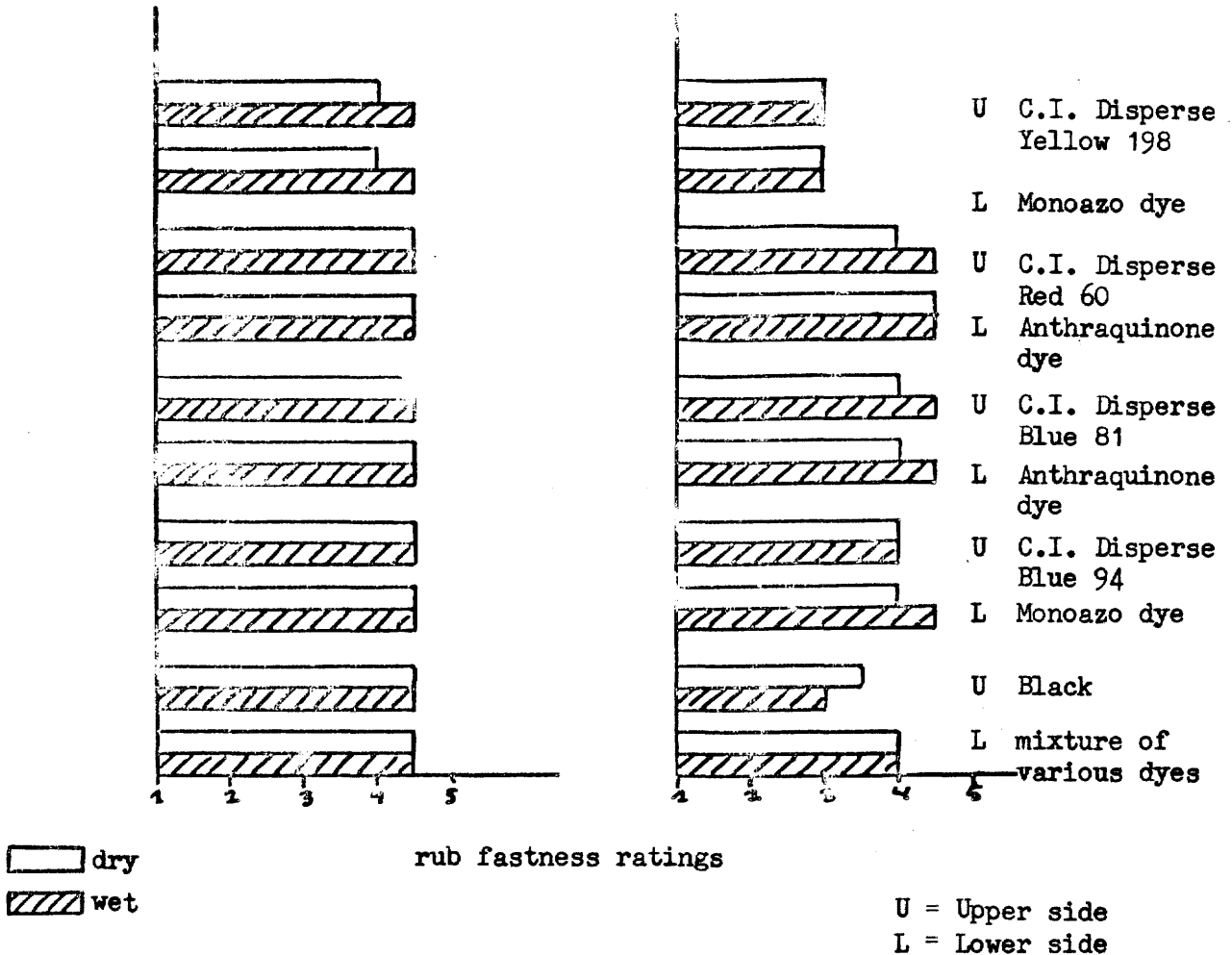
Dyeing at 4%: jet nozzle opening: 2.5 mm; bath temperature: 40°C; spraying pressure: 2 bars; spraying points: 12 on each side of the fabric.

The cleaning in solvent without water gives fastness ratings below 4 for the slower speed and even below 3 for the speed of 10 m/min. The emulsifier alone is not therefore capable of eliminating the non-fixed dyes with the solvent. A certain amount of water is therefore necessary: it serves as a solvent for the soluble elements in the dye, in which the latter is encrusted.

#### 4.4. Influence of the type of dye and of the shade strengths

The previous tests were carried out with C.I. Disperse Blue 81, an anthraquinone dye. The study was broadened to include other commercial disperse dyes of different chemical composition and dyeings of 1% to 4%. The fixation rate is 92% to 96%, except for the yellow dyeing, where it is only 80%.

Figure 42 shows the rub fastness ratings obtained with an after-cleaning in PER as a function of the various dyes used and as a function of the shade strength.

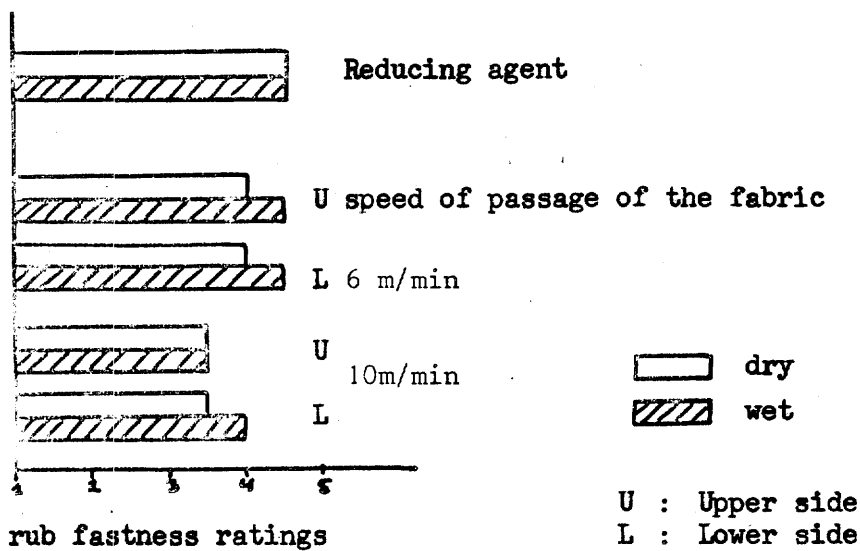


**Figure 42** - Tests on pilot equipment: rub fastness ratings of various thermosol dyeings of various shade strengths. Jet nozzle opening: 2.5 mm; spraying pressure: 2 bars; spraying points: 12 on each side of the fabric; bath temperature: 40°C; speed of passage of the fabric: 6 m/min.

For light shade strengths, about 1%, fastness ratings of 4-5 are obtained. In this case, there is no objection to substituting a cleaning in a solvent medium for the conventional reducing treatment, which causes considerable pollution.

For certain very dark shade strengths, about 4%, such as yellow and black, the fastness only reaches a value of 3 or 3-4.

Many dyes used alone behave differently during dyeing from when they are combined with other dyes. Cleaning in PER after a mixed thermosol dyeing was therefore also examined. The test was carried out with a dark olive shade, obtained by mixing dyes C.I. Disperse Yellow 198, C.I. Disperse Red 60 and C.I. Disperse Blue 81. Figure 43 gives the results obtained for two speeds of passage of the fabric.



**Figure 43** - Tests on pilot equipment: Rub fastness of a thermosol mixed dyeing. Dyeing at 4%; dark olive; jet nozzle opening: 2.5 mm; spraying pressure: 2 bars; spraying points: 12 on each side of the fabric; bath temperature: 40°C.

For the speed of 6 m/min., fastness ratings of 4 and 4-5 are obtained. As in the previous tests, a reduction in fastness when the speed of passage of the fabric increases can be expected for mixed dyeings.

4.5. Influence of the spraying pressure and of the diameter of the jet nozzle

One means of lowering the cost of the PER cleaning treatment is to reduce the power of the pump other than by reducing the pressure. The previous tests showed that as far as the effectiveness of the cleaning and the rub fastness are concerned, a reduction in pressure from 4 to 2 bars is justified (cf. figure 37). This means that for a 60° angle jet nozzle with 2.5 mm opening, 12 spraying points on each side of the fabric and a fabric width of 1.5 m, the power of the pump in industrial equipment can be reduced from 4430 to 3130 l/min., i.e. by 30% (figure 35).

Another possible way of reducing the power on industrial equipment is to work with 2 bars, but with a jet nozzle opening of 1.5 mm. In principle, the power of the pump could be reduced from 3130 to 1240 l/min., i.e. a 60% reduction.

Figure 44 gives the rub fastness ratings obtained for deep shade strengths after spraying with 2.5 and 1.5 mm jet nozzles, the pressure being 2 bars.

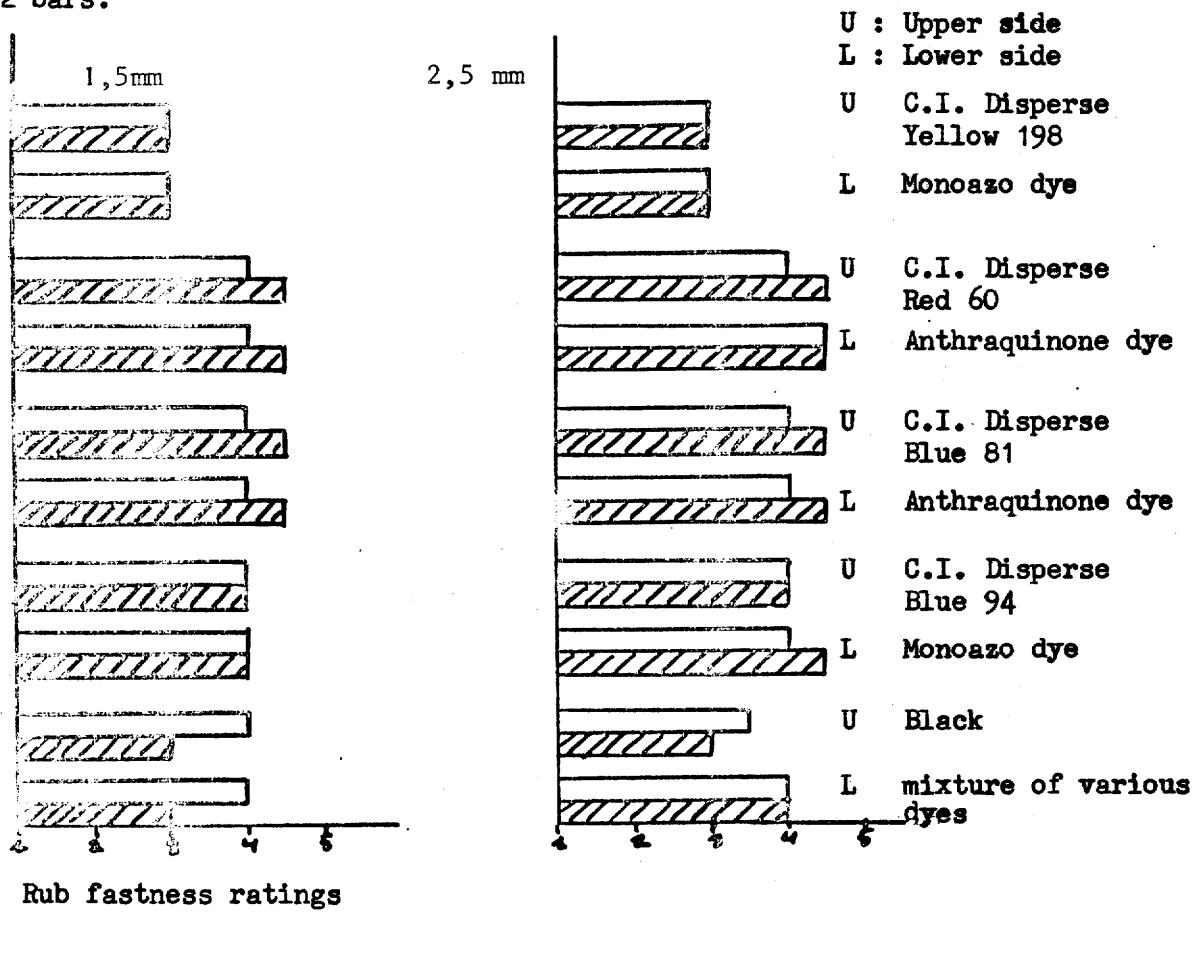


Figure 44 - Tests on pilot equipment: Influence of the jet nozzle opening on the rub fastness ratings of thermosol dyeing. Dyeing at 4%; spraying pressure: 2 bars; spraying points: 12 on each side of the fabric; bath temperature: 40°C; speed: 6 m/min.

It was found that with small jet nozzle openings, satisfactory fastness ratings can be obtained: 4 and 4-5. Only the critical colours, yellow and black, give poorer results. The lower bath volume resulting from the reduction in the jet nozzle opening seems to have no influence on the extraction of the non-fixed dyes.

It can thus be concluded that, even for relatively dark shade dyeings of 4%, with a jet nozzle opening of 1.5 mm and a spraying pressure of 2 bars, a satisfactory rub fastness is obtained, which means that a 1240 l/min. pump, of ordinary capacity and economically justified for industrial application, can be used.

For safety reasons, the jet nozzle opening cannot be too small, otherwise there is a risk that it may become obstructed by an accumulation of fibres.

#### 4.6. Influence of the type of surfactant

The rub fastness was examined using 4 types of surfactant, I - IV, in the spraying conditions given: jet nozzle opening: 1.5 mm; spraying pressure: 2 bars; 12 spraying points on each side of the fabric; speed of passage of the fabric: 6 m/min. The cleaning bath contains 15 g/l water and 3 g/l surfactant.

The results are given in figures 45 to 48.

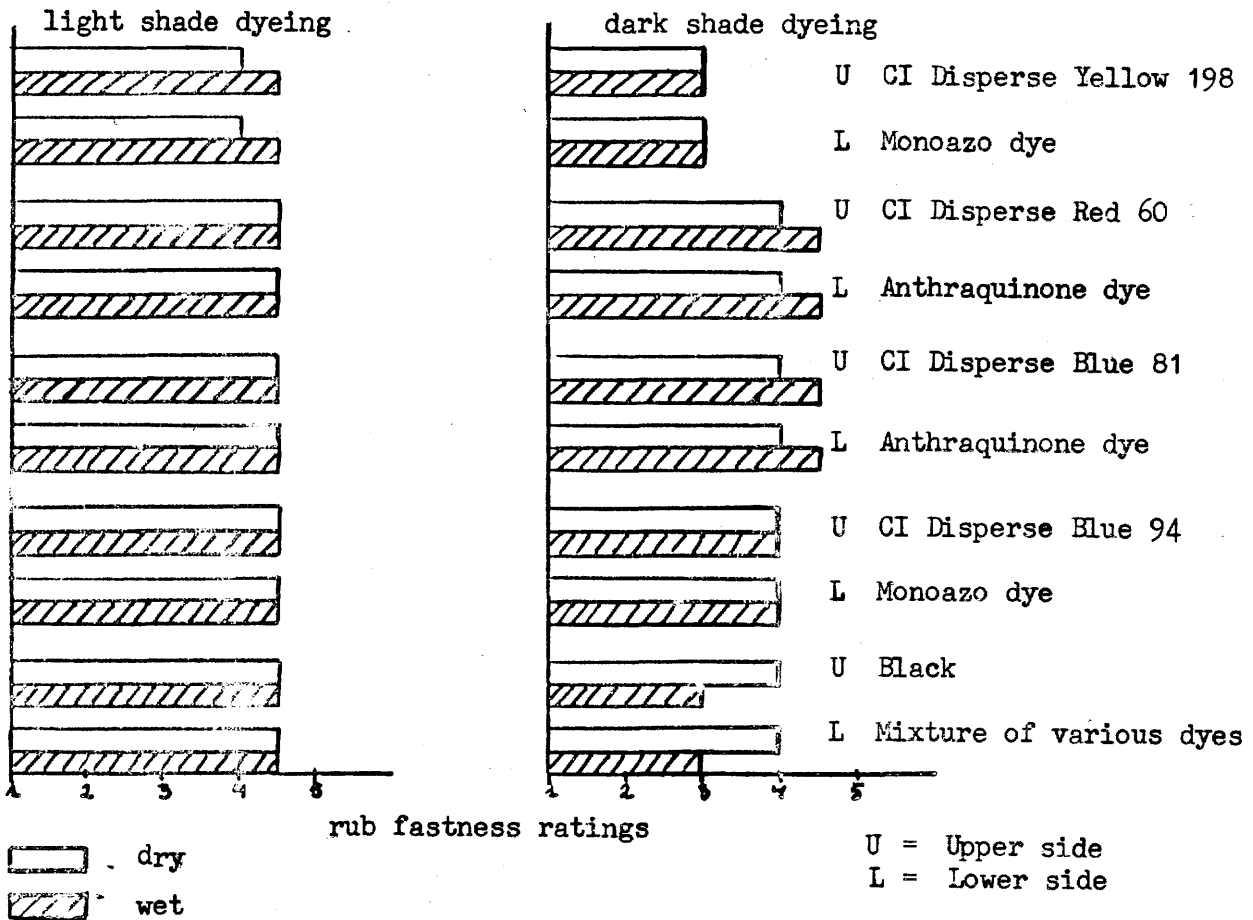


Figure 45 - Tests on pilot equipment: Influence of the addition of 3 g/l surfactant I and 15 g/l water on the rub fastness ratings of thermosol dyeings of various depths. Jet nozzle opening; 1.5 mm; temperature 40°C; spraying pressure: 2 bars; speed of passage of the fabric: 6 m/min.; 12 spraying points on each side of the fabric.

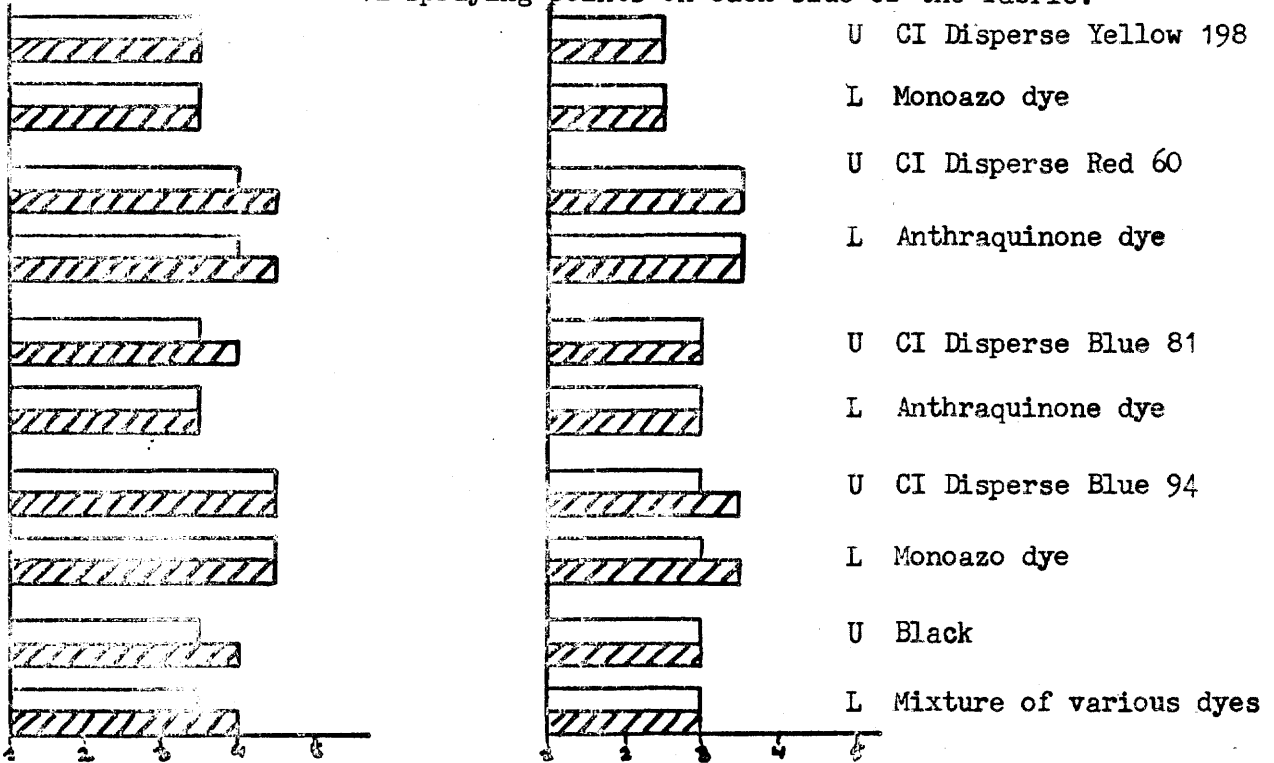
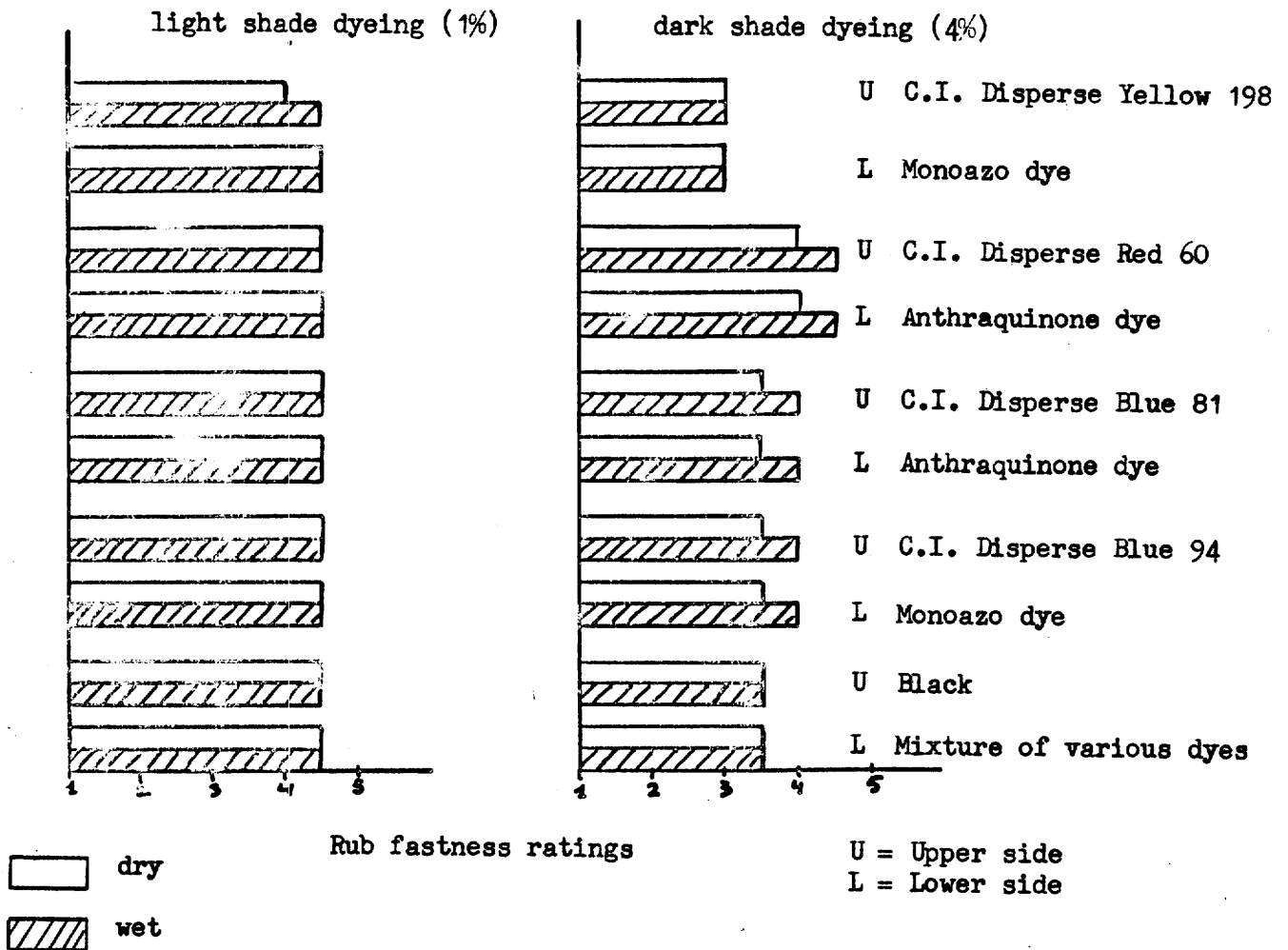
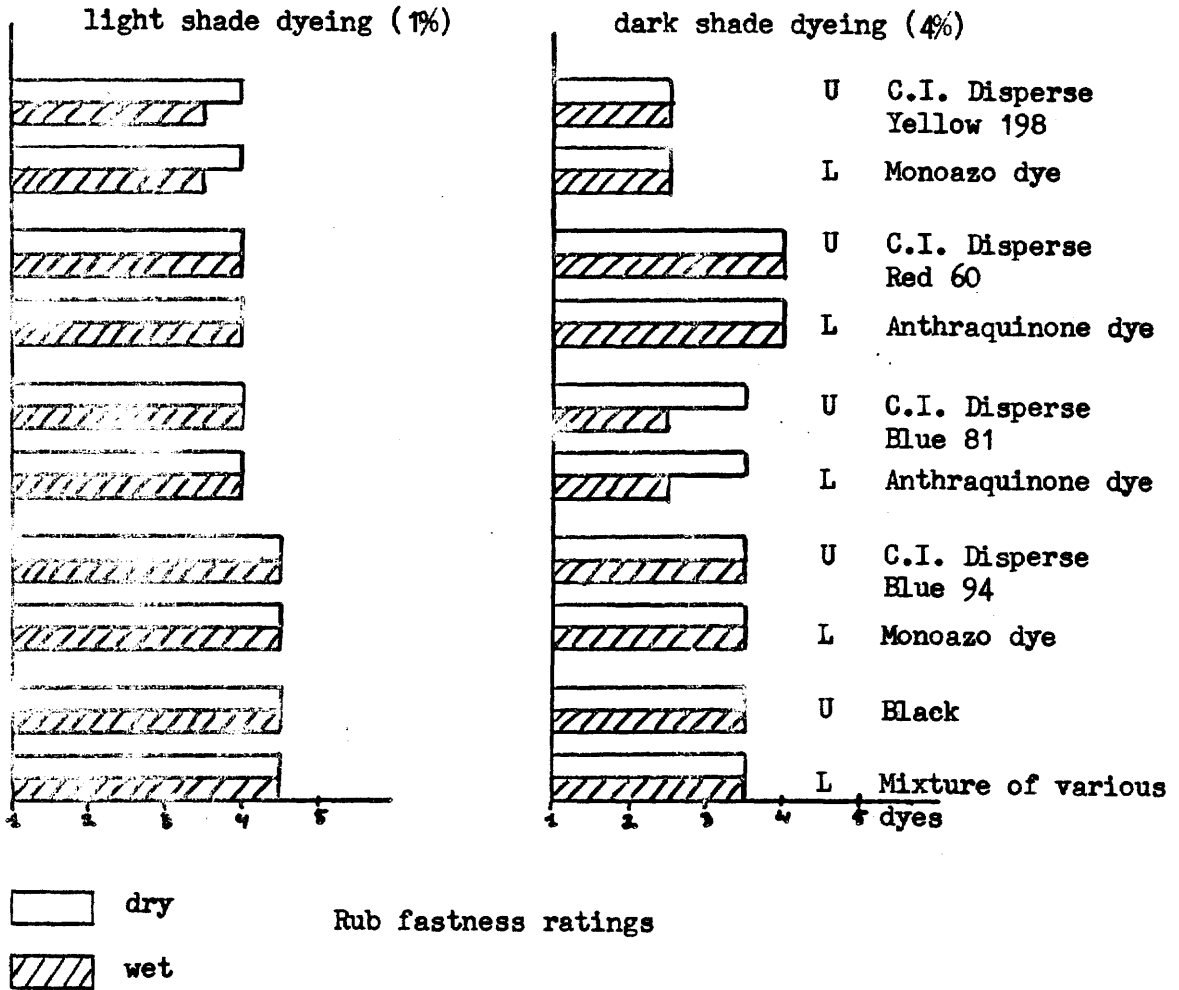


Figure 46 - Tests on pilot equipment: Influence of the addition of 3 g/l surfactant II and 15 g/l water on the rub fastness ratings of thermosol dyeings of various depths. Jet nozzle opening: 1.5mm; temperature: 40°C; spraying pressure: 2 bars; speed of passage of the fabric: 6m/min; 12 spraying points on each side of the fabric.



**Figure 47** - Tests on pilot equipment. Influence of the addition of 3 g/l surfactant III and 15 g/l water on the rub fastness ratings of thermosol dyeing of various depths. Jet nozzle opening: 1.5 mm; temperature: 40°C; spraying pressure: 2 bars; speed of passage of the fabric: 6 m/min.; 12 spraying points on each side of the fabric.



**Figure 48** - Tests on pilot equipment: Influence of the addition of 3 g/l surfactant IV and 15 g/l water on the rub fastness ratings of thermosol dyeings of various depths. Jet nozzle opening: 1.5 mm; temperature: 40°C; spraying pressure: 2 bars; speed of passage of the fabric: 6 m/min.; 12 spraying points on each side of the fabric.



In order to assess the effectiveness of the surfactant, the results obtained for the light shades are used as a basis.

Of the various surfactants tested, type I gives the best results, for both light and dark shade depths. Of the latter, only yellow and black do not reach value 4. The results are slightly less good for surfactant III.

Types II and IV are less effective, as the fastness ratings obtained are 4 or less, even for "non-critical" light shades. The results are similar for dark shades.

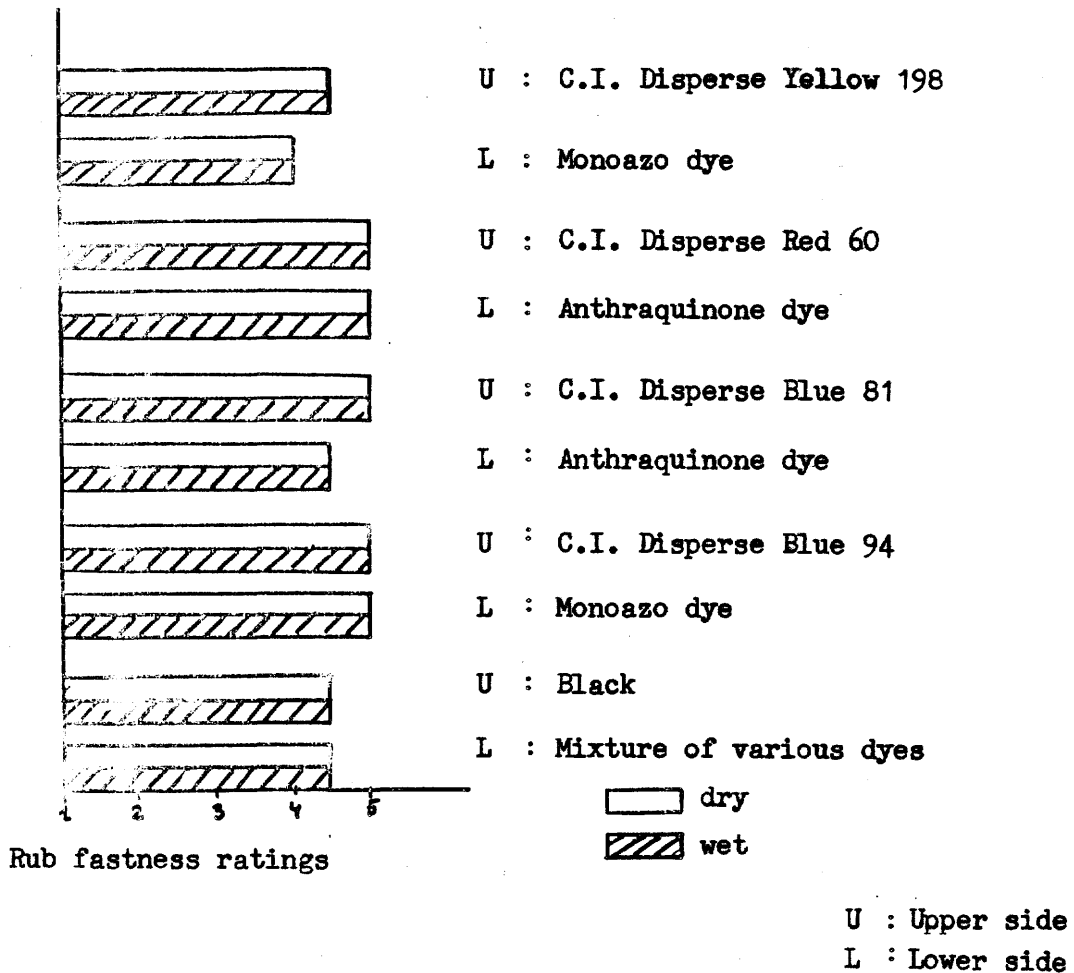
For all practical purposes, it can be concluded that for extraction by solvent spraying of non-fixed dyes, the effectiveness varies depending on the nature of the surfactants. In any case, preference should be given to the surfactant which, even for critical dyes, which are difficult to extract, gives satisfactory results in optimal spraying conditions.

## 5. Industrial tests

The industrial tests were carried out on Bøwe type C 740 continuous equipment. The cleaning solvent is sprayed on to the fabric by 4 high pressure jet nozzle hoses, with a pressure of 4 bars and one low pressure jet nozzle, with a spraying pressure of 1 bar. The speed of passage of the fabric is 6 m/min.

The results of the industrial tests are given in figure 49.

Even for very difficult shades (at 4%), the fastness ratings are at least 4.



**Figure 49** - Industrial tests: rub fastness ratings of thermosol dyeings. Dyeing at 4%; jet nozzle opening: 3 mm; 4 high pressure jet nozzles: each 4 bars; one low pressure jet nozzle: 1 bar; speed of passage of the fabric: 6 m/min.; bath temperature: about 25°C; two passages: 8 unilateral spraying points.

It can be concluded that the principle of the after-cleaning of polyester in PER after thermosol dyeing is valid. In this specific application, it is possible therefore to replace, without reducing the rub fastness of the colours, the conventional reducing treatment, which produces large quantities of very polluted effluents, with a treatment in a solvent medium, which does not harm the environment.

The aim of further research work should therefore be to adapt the process for common industrially processed textile goods.

VI.

GENERAL CONCLUSIONS

1. Interactions between the textile materials and the solvents

It was found that the swelling rate at equilibrium is not dependent on the treatment temperature. The speed of sorption, on the other hand, varies considerably with the temperature.

The swelling rate is also a function of the chemical composition of the polyester, of the prior heat treatments to which the fibres have been subjected and of the temperature of these treatments.

2. Extractions of oligomers using solvents

All the solvents tested dissolve oligomers, whereas mixtures and emulsions have a synergetic effect which occurs to a greater or lesser extent. The extracting power depends on the nature of the solvent and the textile material.

At high temperatures such as those used in dyeing, large quantities of oligomers are extracted, while at moderate temperatures, for example dry cleaning, there is almost no extraction.

3. Dyeing in a solvent medium and the extraction of surface substances from wool

The fixation of the dye on wool dyed in a solvent medium, i.e. in a mixture of PER/HAc, is a function of the quantity of HAc (contained in this mixture or in the wool).

The percentage of extractable materials is a function of the nature and concentration of a co-solvent.

4. Extraction of non-fixed dyes from polyester textile materials

The tests showed that it is possible to substitute an after-cleaning with PER for the conventional reducing treatment after thermosol dyeing. The necessary number of spraying points, the jet nozzle opening and the spraying pressure were determined.

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The aim of the research was to examine the possibilities of replacing certain finishing treatments in an aqueous medium by treatments in a solvent medium, with the aim of lessening pollution and making energy savings.

The programme consisted of a theoretical subject and three cases of practical application.

In the theoretical study, the solvents-textile materials interactions, principally for the PER/polyester system, were examined.

The practical applications are:

- the extraction of oligomers, more particularly from polyester and polyamide,
- the dyeing of wool in a solvent medium and the extraction of surface impurities,
- the extraction of non-fixed dyes from polyester textile materials.

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