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Charged Solvent System using
some Reactive Disperse and
Acid Dyes**

by

J.P.M. Brandt

**SOUTH AFRICAN
WOOL AND TEXTILE RESEARCH
INSTITUTE OF THE CSIR**

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DYEING OF NYLON 66 FROM A CHARGED SOLVENT SYSTEM USING SOME REACTIVE DISPERSE AND ACID DYES

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ABSTRACT

The suitability of certain reactive disperse dyes and acid dyes for dyeing ©Nylon 66 from an aqueous charged perchloroethylene system was investigated.

For the reactive disperse dyes low to very good exhaustion values were obtained. Fixation values were inferior to good. No general trend in both exhaustion and fixation was found compared to aqueous dyeings, thus not allowing a general prediction of dyeing behaviour from the solvent system.

Acid dyes can be applied without cationic complexing agents, provided they are able to dissolve or disperse in the dyebath composition. Dyeings of adequate levelness and wet fastness were obtained with both reactive disperse and acid dyes.

INTRODUCTION

Mounting energy costs and strict environmental protecting legislation are already strongly affecting the textile industry and are expected to influence dyeing and finishing methods even more in the near future. Much work has been done so far to reduce or to solve energy and effluent problems arising from dyeing, using different techniques.

One method of obtaining improved water economy involves the use of short liquor ratios which resulted in a foam dyeing method (Sancowad process)¹. To avoid problems relating to aqueous dyeing such as pollution, the necessity of pre-scouring, lengthy dyeing cycles and the large latent heat of evaporation of water, solvents other than water have been employed for dyeing. Dyeing in ammonia or ammonia-alcohol has been patented^{2,3}. Another possibility is the replacement of water by organic solvents. The following points are considered to be advantageous in this respect: saving of water, auxiliaries, energy, time, alleviation of effluent problems and process integration.

The selected organic solvent should have a low latent heat and be resistant to hydrolysis and decomposition by heat. It also should be commercially available within a reasonable cost limit, non-flammable, non-poisonous or at least easy to handle and almost completely recoverable. Most of these requirements are fulfilled by perchloroethylene⁴. Unfortunately, however, perchloroethylene cannot perform all the functions of water during dyeing because of its nonpolar character. Water swells some fibres, this being necessary for satisfactory dyestuff diffusion. It dissolves ionic dyes and establishes a suitable partition coefficient in the case of

(b) Acid/alkali technique

Dyebath preparation and dyeings were carried out according to appropriate pattern card instructions¹⁴.

D. DYEING METHODS FOR NYLOMINE DYES

(All percentages on mass of fabric)

(1) Solvent dyeing:

Recipe

10 g fabric, 100 g perchloroethylene, 1,2 or 4% Emulgator 20 FB 1002, 1 or 2% [®]Matexil LC-CWL, X% Nylomine dyestuff and 50% aqueous solution containing 3% CH₃COONH₄, 3% CH₃COOH (30%), adjusted with CH₃COOH to pH 5,7 or containing 3% (NH₄)₂SO₄ and 3% CH₃COOH (30%) for a pH of 4,2.

Procedure

1. After dissolving a multiple charge of dyestuff and Matexil LC-CWL in water, an aliquot was added to the perchloroethylene containing the emulsifier.
2. To obtain a stable emulsion the dyebaths were tumbled for 5 to 10 min at 45°C.
3. A series of fabric samples was entered into the respective dyebaths and the dyeing cycle commenced. After 15 min at 45°C the temperature was raised to 90 to 95°C over 30 min and maintained at that temperature for 45 min. At appropriate times during the dyeing cycle, samples were removed in order that exhaustion values could be determined as described subsequently under E.

In the case of Nylomine Blue CG the method had to be changed to the following for reasons of solubility:

After dissolving a multiple charge of dyestuff and emulsifier in perchloroethylene, an aliquot was added to 5 ml aqueous buffer solution containing Matexil LC-CWL. Points 2 and 3 were carried out as described in the original procedure.

(ii) Aqueous dyeing¹⁵

Recipe

10 g fabric, 200 ml aqueous buffer solution at pH 5,2 containing 3% CH₃COONH₄ and 3% CH₃COOH (30%), 1% Matexil LC-CWL and 3% Nylomine dyestuff.

Procedure:

Dyeing was carried out in an Ahiba laboratory dyeing machine in the manner described under 3 above. The degree of exhaustion was determined as described under E.

E. DETERMINATION OF EXHAUSTION CHARACTERISTICS OF PROCINYL AND NYLOMINE DYES

After dyeing, fabric samples were rinsed once with 50 ml and twice with 25 ml ethanol and the ethanol liquor added to the residual dye liquor.

The resulting dye liquor was either extracted with ethanol, and this solution used for spectrophotometric analysis, or the dyeing liquor was diluted with ethanol to obtain a homogeneous liquor suitable for spectrophotometric analysis.

F. DETERMINATION OF COVALENT FIXATION (PROCINYL DYES)

Fabric samples (1 g) were extracted with water/pyridine (80/20) in a soxhlet for at least 60 min, the resulting solution made up to volume and the concentration of extracted dyestuff determined spectrophotometrically.

Fastness to washing and to both alkaline and acid perspiration were determined by standard methods^{1,6}.

RESULTS AND DISCUSSION

Procinyl dyestuffs:

Because these dyestuffs are not dissolved but only *dispersed* in the perchloroethylene system, high speed stirring of the dyebath emulsion immediately before use is essential to avoid settling of the dyestuff and consequent unlevel dyeings. Stirred dyebaths should be used within 15–30 min. Tumbling alone seems to be insufficient to produce a stable emulsion.

The low exhaustion values associated with the dyeing of polyester with disperse dyes from an aqueous charged perchloroethylene system^{11,12} have not been found to exist for the Procinyl dyestuffs when dyeing Nylon 66 (Table I, Fig 1–6). For both Procinyl Red GS and Yellow GS the exhaustion values from the solvent system are better than those obtained from an aqueous system, while the Procinyl Blue RS shows a lower exhaustion. It appears that no general trend for the exhaustion can be predicted when changing from aqueous to solvent dyebaths. Selection of suitable dyes giving high exhaustion values in the solvent system may nevertheless be possible. In this connection it is interesting to note that NaHCO_3 increased the degree of exhaustion of Procinyl Red GS (Fig 7).

As in aqueous dyebaths the Procinyl dyestuffs with low reactivity required temperatures higher than 90°C to develop the best fixation values (Fig. 2) in the charged solvent system. Since a mixture of perchloroethylene and water forms an azeotrope which boils at 87°C under atmospheric pressure, pressurised equipment is necessary to obtain optimum fixation rates.

The concentration of dyestuff in the dyebath showed no significant influence on the exhaustion in the concentration range investigated (Fig. 1, 3).

Dyeing with reactive disperse dyestuffs from an inert solvent would offer the advantage of reducing the possibility of further hydrolysis of the reactive group and so promoting reaction between dye and fibre. However, the presence of water is desirable for reasons mentioned above. Figs. 1, 4 and 5 show that fixation increased with increasing exhaustion rates, the exception being Procinyl Blue RS when using the NaHCO_3 -method (Fig. 3). Compared with aqueous dyeings, lower fixation was obtained with Blue RS, about similar fixation with Yellow GS and better fixation

with Red GS. Neither fixation nor exhaustion values showed a general trend.

Although dyeings from aqueous dyebaths showed only small differences in exhaustion and fixation when employing either the NaHCO_3 -method or the acid/alkali method (Table I), the influence of the method of dyeing in a charged solvent dyeing was investigated (Figs. 5 and 6). Procinyl Yellow GS showed slightly better results using the NaCHO_3 -method and Procinyl Blue RS significantly better results using the acid/alkali method. The suitability of each method, therefore, seems to depend on the dyestuff used. It should be noted that in the case of the acid/alkali method an increase in pH decreased the degree of exhaustion (Figs. 5 and 6).

Solvent dyeing techniques usually shorten the time considered necessary to obtain maximum exhaustion and fixation. For the aqueous dyeing with Procinyl dyes a dyeing time of 120 min is recommended when using the NaHCO_3 -method¹³. Dyeing from the charged solvent system results in maximum fixation after a dyeing time between 60 and 90 min, thereby conserving both energy and time.

Wet fastness tests (ISO wash test No. 3, ISO alkaline and acid perspiration tests) showed a close agreement between the solvent dyed and aqueous dyed samples with the exception of Procinyl Blue RS (Table II).

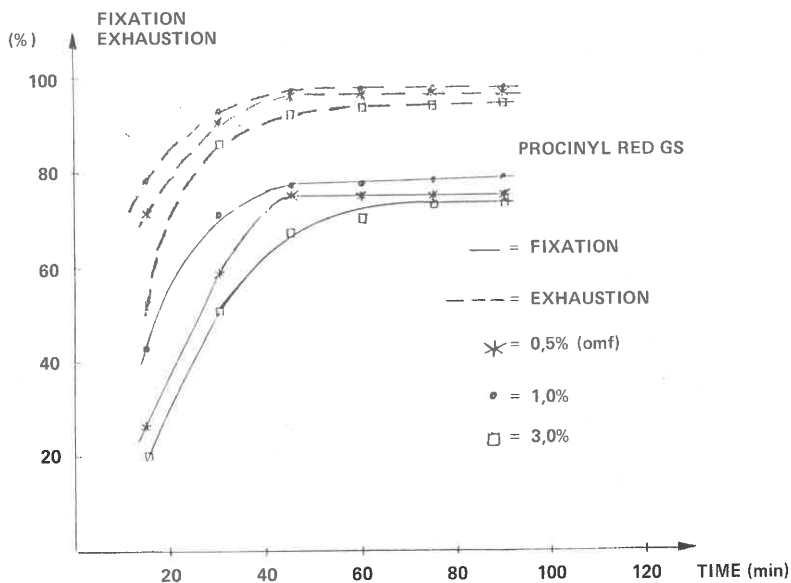


FIGURE 1
Exhaustion and Fixation for Procinyl Red GS (NaHCO_3 -method), Final Temperature 100°C

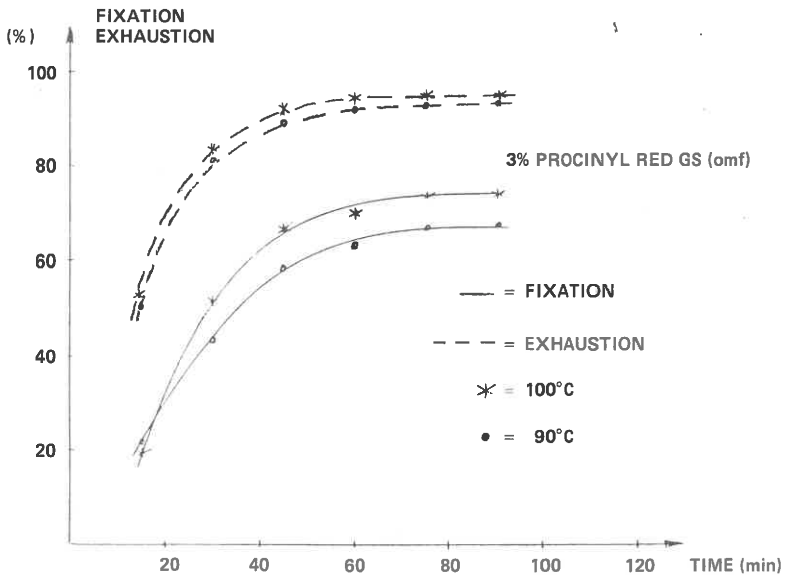


FIGURE 2

Influence of Temperature on Exhaustion and Fixation for Procinyl Red GS (NaHCO₃-method)

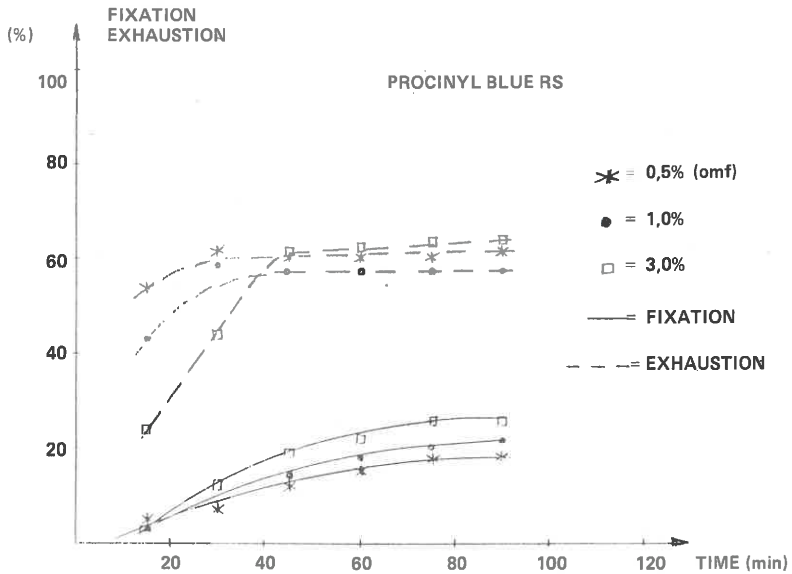


FIGURE 3

Exhaustion and Fixation for Procinyl Blue RS (NaHCO₃-method), Final Temperature 100°C

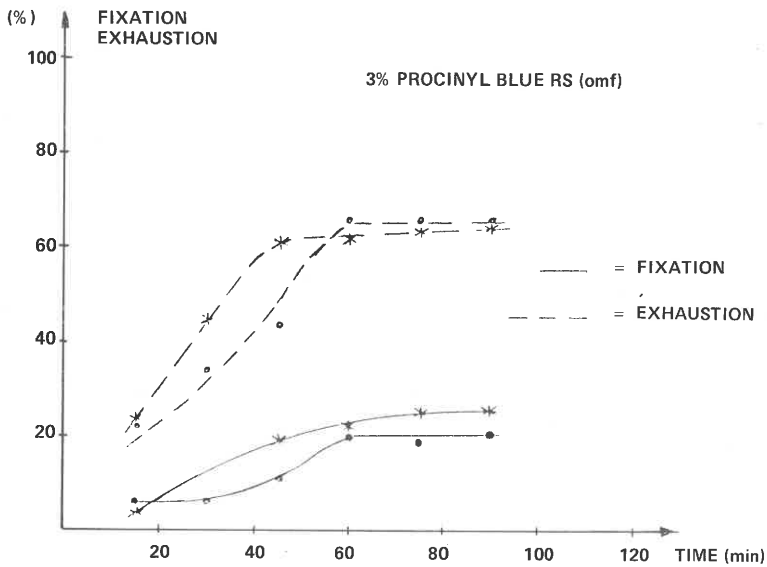


FIGURE 4

Influence of Temperature Regulation during Dyeing for Procinyl Blue RS (NaHCO_3 -method)

- ★ Temperature increased from 50°C to 100°C within 30 min., kept at 100°C for further 60 min.
- Temperature increased from 50° to 70°C within 15 min., kept at 70°C for 30 min, then further increased to 100°C within 15 min and kept at 100°C for 30 min.

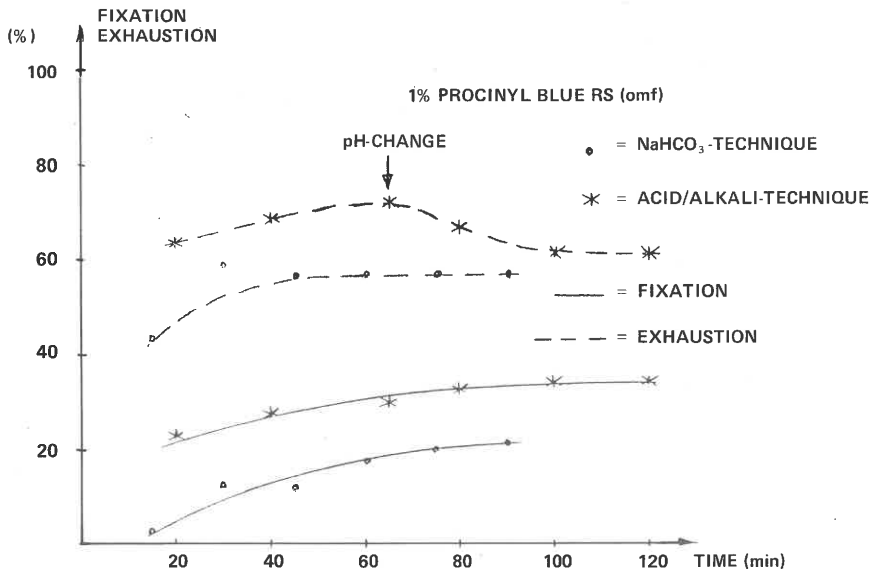


FIGURE 5

Influence of Dyeing Method on Exhaustion and Fixation for Procinyl Blue RS, Final Temperature 100°C

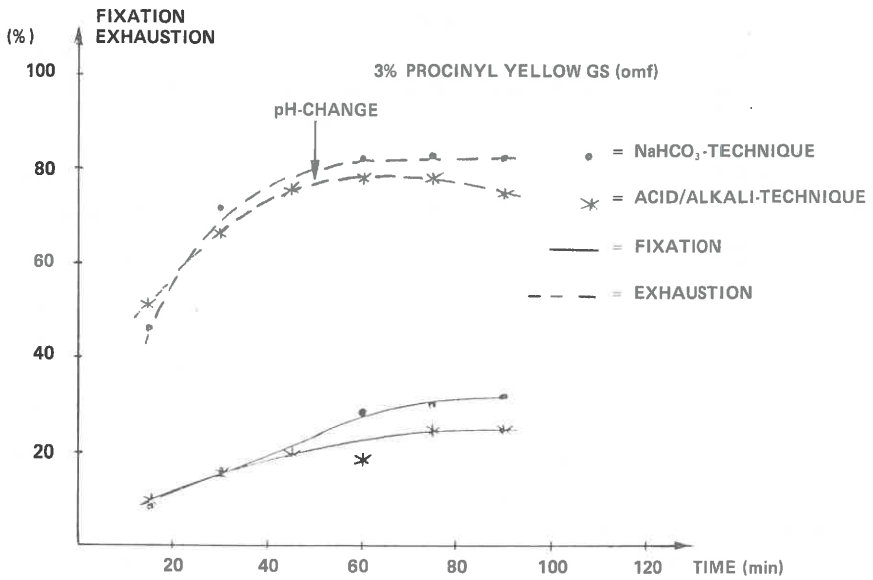


FIGURE 6
 Influence of Dyeing Method on Exhaustion and Fixation for Procinyl Yellow GS, Final Temperature 100°C

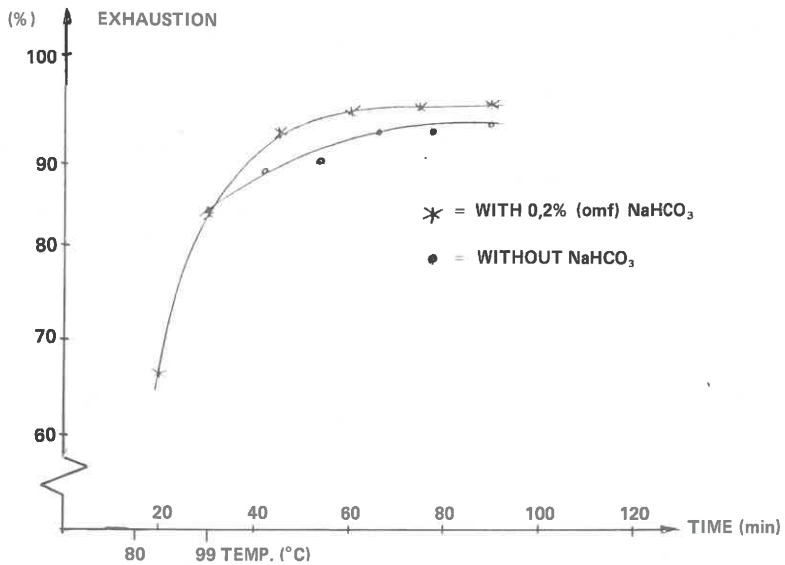


FIGURE 7
 Influence of NaHCO₃ on Exhaustion for 3% Procinyl Red GS (omf), Final Temperature 100°C

TABLE I

COMPARISON OF EXHAUSTION AND FIXATION VALUES IN
AQUEOUS AND SOLVENT DYE BATH

Dyestuff (3% omf)	Dyeing Method	Exhaustion (%)	Fixation (%)
Procinyl Red GS	Solvent NaHCO ₃	95,0	74,3
	Aqueous NaHCO ₃	88,2	60,2
	Acid/Alkali	83,3	59,0
Procinyl Blue RS	Solvent NaHCO ₃	64,0	25,7
	Aqueous NaHCO ₃	92,6	85,2
	Acid/Alkali	88,8	77,8
Procinyl Yellow GS	Solvent NaHCO ₃	81,9	31,9
	Aqueous NaHCO ₃	74,8	32,9
	Acid/Alkali	74,0	29,3

Nylomine dyestuffs

Nylomine dyes are sufficiently soluble for dyeing from aqueous baths. However, the use of the solvent dyeing techniques restricts the amount of water to such an extent that the required amount of dyestuff is not completely soluble in every case. Nylomine Red A-2B was adequately soluble whereas Yellow A-3G was used mainly in a dispersed state because of its low solubility. In both cases, however, satisfactory dyeings were obtained.

Dyeing with Blue C-G was found to be difficult at higher concentrations (3 *per cent*, omf). It is not completely soluble in the available amount of water and because of its tarry consistency it could not be dispersed properly, and *uneven* dyeings resulted. Therefore the preparation of the dye bath was changed as described under *Experimental*. Using this modified method Nylomine Blue C-G was almost soluble in perchloroethylene containing the emulsifier, but precipitated after addition of the buffer solution and shaking. This was followed by a migration of the bulk of the precipitated dyestuff to the aqueous phase. It was hoped that a smaller size of dyestuff particles could be obtained via precipitation, therefore

TABLE II

PROCINYL DYESTUFFS : RESULTS OF PERSPIRATION TESTS AND WASH TESTS

Dyestuff	% omf	Dyeing Method	Max. dyeing temp. (°C)	Perspiration Test						Wash Test		
				pH 8			pH 5,5			ISO No. 3		
				Staining of		Change in colour	Staining of		Change in colour	Staining of		Change in colour
				Nylon	Wool		Nylon	Wool		Nylon	Wool	
Procinyl Red GS	3	Solvent NaHCO ₃	100	3-4	3-4	5	3-4	4	5	4	5	5
	3	Solvent NaHCO ₃	90	3	3-4	5	3-4	4-5	5	4	5	5
	1	Solvent NaHCO ₃	100	4	4-5	5	4-5	5	5	4-5	5	5
	0,5	Solvent NaHCO ₃	100	4-5	5	5	4-5	5	5	4-5	5	5
	3	Aqueous NaHCO ₃	100	3-4	4-5	5	4	4-5	5	4	5	5
Procinyl Yellow GS	3	Aqueous Acid/alkali	100	3-4	4	5	3-4	4-5	5	3-4	5	5
	3	Solvent NaHCO ₃	100	4-5	4-5	5	4-5	5	5	3-4	4	5
	3	Solvent Acid/alkali	100	4	4-5	5	4	5	5	3	4	4
	3	Aqueous NaHCO ₃	100	4-5	5	5	4-5	5	5	3-4	4-5	5
	3	Aqueous Acid/alkali	100	4-5	5	5	4-5	5	5	3-4	4-5	5
Procinyl Blue RS	3	Solvent NaHCO ₃	100	3	4	4-5	3-4	4	4-5	2-3	4-5	3
	3	Solvent NaHCO ₃	100	3-4	4-5	4-5	3-4	4	5	2	5	4
		prolonged exhaustion time										
	1	Solvent NaHCO ₃	100	4	5	5	4-5	5	5	3	4-5	4
	1	Solvent Acid/alkali	100	4	4-5	5	4-5	5	5	3-4	5	4
Procinyl Blue RS	0,5	Solvent NaHCO ₃	100	4-5	5	5	5	5	5	3-4	5	4
	3	Aqueous NaHCO ₃	100	4-5	5	5	4-5	5	5	2-3	5	5
	3	Aqueous Acid/alkali	100	4	4-5	5	4	5	5	2-3	5	5

resulting in a better dispersed dyestuff. Level dyeings could be obtained when employing the modified method.

The results of dyeing nylon with Nylomine Blue C-G are shown in Fig. 8. The use of higher concentrations of emulsifier (4 per cent omf) results in very low exhaustion (55 per cent). Reduction of the emulsifier concentration increased the exhaustion to over 80 per cent but resulted in unlevel dyeings. An increase in the amount of retarder (Matexil LC-CWL) from 1 per cent to 2 per cent (omf) as recommended for certain dyestuffs¹⁵ improved the levelling without decreasing the exhaustion, especially when a lower pH was employed. Dyeings with only 1 per cent Blue C-G (omf) were of acceptable levelness. The resultant exhaustion values (between 82 and 85 per cent) are close to the values which should be achieved in aqueous dyeings (80–90 per cent)¹⁵. Exhaustion values for both Nylomine Red A-2B and Yellow A-3G were much higher than 90 per cent and were only influenced to a limited extent by the concentration of dyestuff used (Figs. 9 and 10). Levelling was satisfactory. Wet-fastness properties (alkali and acid perspiration tests, ISO wash test No. 3) for solvent and aqueous dyeing were similar. (Table III).

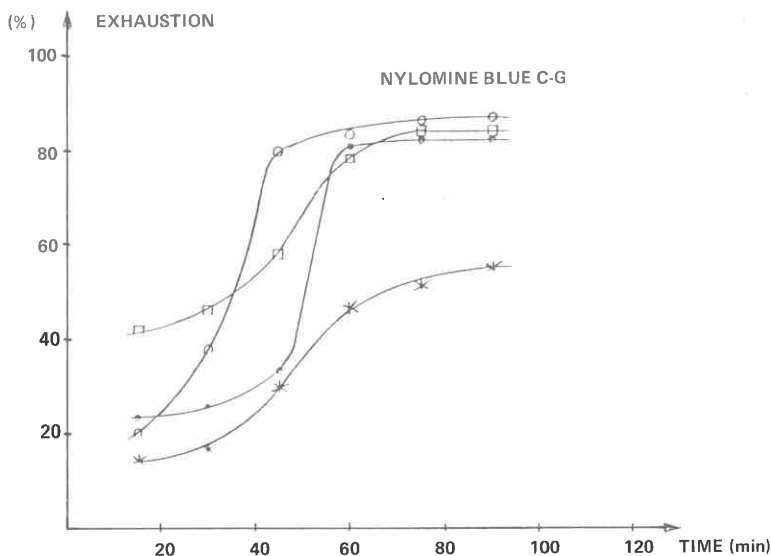


FIGURE 8
Exhaustion of Nylomine Blue C-G

Curve	% Dyestuff (omf)	% Emulgator 20 FB 100% (omf)	% Matexil LC-CWL (omf)	Buffer pH
★	3	4	1	5,7
●	3	1	1	5,7
□	3	1	2	4,2
○	1	2	1	5,7

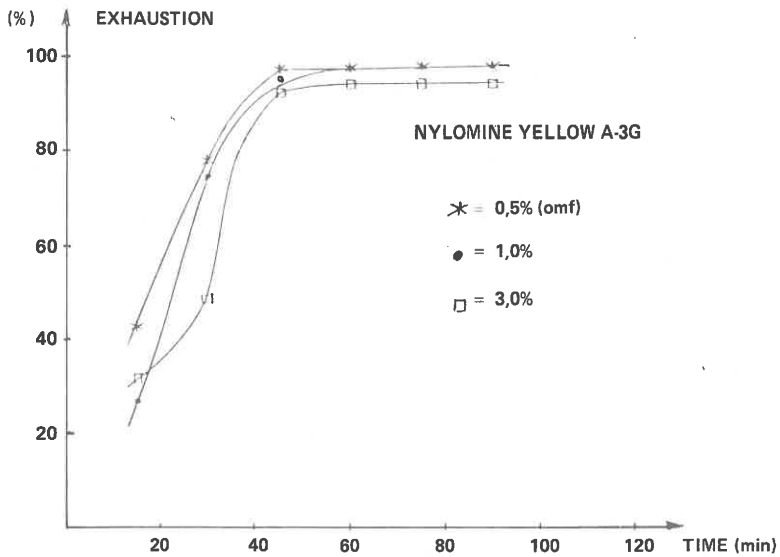


FIGURE 9
Exhaustion of Nylomine Yellow A-3G, Buffer pH 5,7 1% (Emulgator 20 FB 1002 (omf), 1% Matexil LC-CWL (omf))

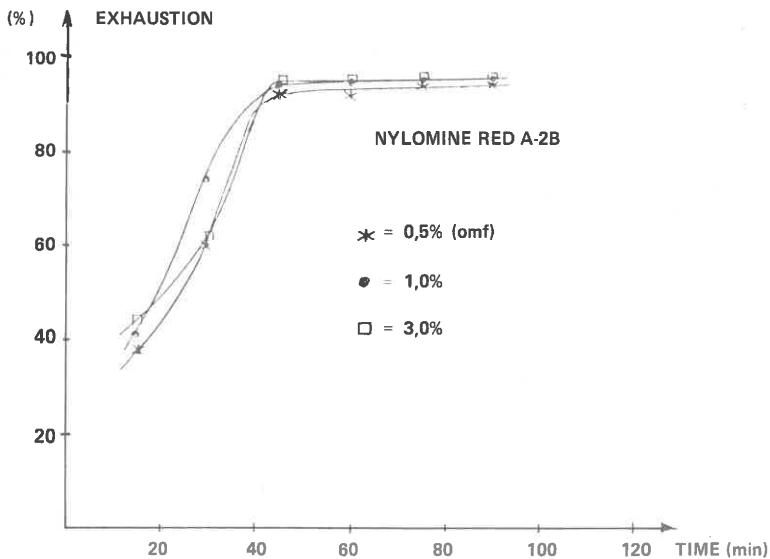


FIGURE 10
Exhaustion of Nylomine Red A-2B Buffer pH 5,7 , 1% Emulgator 20 FB 1002 (omf), 1% Matexil LC-CWL (omf)

TABLE III

NYLOMINE DYES: RESULTS OF PERSPIRATION AND WASH TESTS

Dyestuff (Percentage, omf)	Dyeing Method	Buffer pH	Emulgator 20 FB 1002 % omf	Matexal LC- CWL % omf	Perspiration Test						Wash Test		
					pH 8			pH 5,5			ISO No. 3		
					Staining of		Change in Colour	Staining of		Change in Colour	Staining of		Change in Colour
					Nylon	Wool		Nylon	Wool		Nylon	Wool	
Nylomine (3,0) Red A-2B (1,0) (0,5) (3,0)	Solvent	5,7	1	1	3-4	4	5	4	4-5	2	4-5	4	
	Solvent	5,7	1	1	4-5	5	5	5	5	3	4-5	5	
	Solvent Aqu.	5,7	1	1	5	5	5	5	5	4	5	5	
Nylomine (3,0) Yellow A-3G	Solvent	5,2	0	1	3	3-4	5	5	3-4	2-3	4-5	5	
	Solvent	5,7	1	1	3-4	4	5	5	3-4	4	5	4	
	Solvent	5,7	1	1	4-5	4-5	5	5	4-5	5	5	5	
Nylomine (3,0) Blue C-G (3,0) (1,0) (3,0)	Solvent	5,7	1	1	5	5	5	5	5	5	5	5	
	Solvent	5,2	0	1	3-4	3-4	5	5	3-4	4	4-5	5	
	Solvent Aqu.	5,2	1	2	2-3	2-3	Unlevel	5	2-3	2-3	4-5	4	
	Solvent	4,2	2	1	5	5	5	5	5	5	5	5	
	Solvent	5,7	2	1	3	3	5	5	3-4	3-4	5	5	
	Solvent Aqu.	5,2	0	1	3	3	5	5	3-4	3-4	5	5	

SUMMARY AND CONCLUSIONS

In contrast to low exhaustion values reported by other workers for dyeing polyester with disperse dyes from solvent systems, solvent dyeings of Nylon 66 with certain reactive disperse dyes showed exhaustion values superior to the corresponding values for aqueous dyeings. Solvent dyeings resulted in fixation values which can be lower or higher than values obtained from aqueous dyeings. Both exhaustion and fixation values showed no general trend when compared with aqueous dyeings.

The solvent technique offers the advantage of significantly shorter dyeing times when using reactive disperse dyes. Wet fastness properties of solvent and aqueous dyed samples were found to be in close agreement.

From these results it may be concluded that, in principle, solvent dyeing of Nylon 66 with reactive disperse dyes is possible, but it requires a correct selection of dyestuffs in terms of exhaustion and fixation characteristics.

The acid dyestuffs investigated in this study can be used without problems in a charged solvent dyeing system, provided that they can be dissolved or properly dispersed in the aqueous phase. Exhaustion values higher than 90 *per cent* can be achieved. The use of complexing agents is unnecessary.

Acid dyestuffs not properly dissolved or dispersed under solvent dyeing conditions require modified methods to obtain satisfactory dyeings. Wet fastness properties were found to show no significant difference to those obtained from aqueous dyeings.

Small amounts (1 to 2 *per cent* omf) of emulsifier were found to be sufficient to stabilise the dyebath emulsions for both reactive disperse and acid dyestuffs.

Although solvent dyeing of nylon using reactive or acid dyes is possible, the dyes should be carefully selected.

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THE USE OF PROPRIETARY NAMES

The product names ® Procynyl, ® Nylomine, ® Matexil and ® Nylon 66 are registered trade marks of Messrs ICI Ltd. The fact that chemicals with proprietary names have been used in this report in no way implies that SAWTRI recommends them, or that there are not others which may be of equal or even better value.

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