

**SAWTRI
TECHNICAL REPORT**



No. 265

**A Laboratory Process for Dyeing Wool
with Reactive Dyes from a Charged
Solvent System Using a Single Emulsifier**

by

M. B. Roberts and Cornelia Botha

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

**P. O. BOX 1124
PORT ELIZABETH
REPUBLIC OF SOUTH AFRICA**

ISBN 07988 0694 X

A LABORATORY PROCESS FOR DYEING WOOL WITH REACTIVE DYES FROM A CHARGED SOLVENT SYSTEM USING A SINGLE EMULSIFIER

by M.B. ROBERTS and CORNELIA BOTHA

ABSTRACT

A relatively simple technique has been devised whereby wool may be satisfactorily dyed with reactive dyes from an aqueous charged perchloroethylene system. Dyeings of adequate depth, levelness and wet fastness may be achieved with shorter liquor ratios and boiling times than are currently employed in aqueous dyeing.

KEY WORDS

Dyeing – emulsion – perchloroethylene – reactive dyes – wool.

INTRODUCTION

Several workers^{1, 2, 3} have drawn attention to the theoretical economic advantages of solvent dyeing systems, namely, a great reduction in water consumption, less aqueous effluent and significant reduction in energy requirements. Judging from the market penetration of solvent dyeing techniques, these factors have not proved sufficiently attractive to the industry.

Recent increases in fuel costs, however, together with an increasing awareness of problems associated with water supply and effluent purification have served to provide fresh stimulus for research in this field. It is possible that industry may revise its attitude towards solvent dyeing.

Results to date on the dyeing of ionic fibres with ionic dyes from a non-polar solvent indicate the necessity of incorporating small amounts of polar solvents in the system. The polar solvent serves to dissolve the dye and to swell the fibre^{4, 5, 6}. Water has been the obvious choice, but its use with solvents such as perchloroethylene results in the formation of low-boiling azeotropes and thus dyeing with reactive dyes in such a medium is likely to give rise to inadequate exhaustion and inferior covalent fixation. The use of pressurised equipment as a means of obtaining higher temperatures has been criticised on the grounds that the complicated machinery would render such a process prohibitively expensive⁷.

Further objections to the charged system have been the large quantities of expensive chemicals required to produce a satisfactory emulsion and the

low shade depths obtainable as a consequence of the inadequate solubility of reactive dyes in the small amount of polar solvent in the charge. Van der Merwe and van Rooyen⁷ indicate the need for 12,5 *per cent* (o.m.f) emulsifying agents and Swanepoel and Roesstorff⁽⁸⁾ found that only 27 *per cent* of reactive dyes tested possessed sufficient solubility to permit dyeing to a depth of 2,5 *per cent*.

Several workers have devised charged systems which exclude water but this action has frequently caused other problems. Van der Merwe and van Rooyen⁷ substituted polyhydric alcohols for water but found difficulty in removing them from the fibre after dyeing. Meissner and McIver⁹ attempted the solubilisation of the anionic dye in the non-polar solvent by complex formation with a cationic surfactant but achieved satisfactory dyeing only after the addition of small amounts of water or acetic acid or both.

The present authors, having re-appraised the results of previous work in the light of present day circumstances, consider that it is not essential to eliminate the use of water entirely, and that the use of pressurised equipment should not be automatically excluded. High temperature dyeing equipment is commonplace and machinery manufacturers are familiar with the technology.

This paper outlines a laboratory process by which wool may be satisfactorily dyed from an aqueous charged solvent system at short liquor to goods ratios requiring only small quantities of emulsifier.

EXPERIMENTAL

All wool double jersey fabric was used throughout the project. It was chlorinated with 4,5 *per cent* DCCA¹⁰ at pH 3,2 and 20°C to prevent felting during dyeing. Samples (5 g) were dyed in stainless steel capsules in a Linitest apparatus.

After first preparing a multiple charge of dye dissolved in water, previously adjusted to pH 4,5 with acetic acid and 1 *per cent* o.m.f. ammonium sulphate, an aliquot was added to the perchloroethylene containing the emulsifying agent, Emulgator 20 FB 1002, a trial product obtained from Ciba-Geigy¹¹. This procedure was adopted in order to overcome problems of handling small quantities and was designed to result in an aqueous charge of 50 *per cent* (o.m.f).

After agitating for 5 min using a magnetic stirrer, the emulsion was tumbled in the Linitest at 30°C for 5 min prior to the addition of the fabric. The temperature was then raised to 100°C in 40 min and maintained at 100°C for the requisite time.

Aqueous dyeings were carried out in an Ahiba laboratory dyeing machine for purposes of comparison. The use of different machines for solvent

and aqueous dyeings was considered to be of little significance. Dyebaths were prepared according to the appropriate pattern card instructions. Samples were entered at 30°C (40°C in the case of the Procilans), raised to the boil in 40 min and maintained at 100°C for 60 min.

Exhaustion values were determined by spectrophotometric analysis of the residual dye liquor after centrifuging at 12 000 r.p.m. for 30 min. In the case of solvent dyeings, the dyed samples were soaked in 2 x 25 ml portions of ethanol to remove entrained liquor. The alcoholic extracts were added to the residual liquor and the whole made up to volume with ethanol to give an optically clear solution.

All dyed samples were treated at pH 8,5 in an ammonia bath at 80°C for 20 min, rinsed in a 1 *per cent* formic acid bath and air-dried, the purpose of this treatment being to remove most of the dye not covalently bound to the fibre. The ammonia extracts were analysed spectrophotometrically to determine the amount of dye removed.

Covalent fixations were determined by extraction of 1 g samples with water-pyridine (80 : 20) in a vertical soxhlet. The extracts were centrifuged at 12 000 r.p.m. for 30 min.

Values for exhaustion and covalent fixation after ammonia treatment and aqueous pyridine extraction are expressed as a percentage of dye originally applied to the fibre.

A Harrison-Shirley Digital Colorimeter was employed to determine XYZ values and chromaticity co-ordinates. Colour differences (ΔE) between corresponding solvent dyed and aqueous dyed samples were calculated in AN (42) units according to the standard equation¹². Reflectance values were obtained from a Zeiss Elrepho reflection photometer and K/S values calculated from the Kubelka-Munk equation¹³.

The dyeings were tested for fastness to washing¹⁴ and alkaline perspiration¹⁵.

RESULTS AND DISCUSSION

The most significant feature of this particular technique appears to be the efficiency of the emulsifying agent, Emulgator 20 FB 1002. The use of minimal quantities of this product has enabled satisfactory dyeings to be achieved.

Table I shows the effect of variation in emulsifier concentration. It may be seen that level dyeings of acceptable exhaustion and covalent fixation can be achieved with only 1 *per cent* (o.m.f) emulsifier. No improvement was observed with concentrations in excess of this figure. This small quantity contrasts sharply with the 12,5 *per cent* (o.m.f) of a mixture of sodium dodecyl benzene sulphonate and lauryl monoethanolamine required

in the process devised by van der Merwe and van Rooyen⁷.

TABLE I

EFFECT OF VARIATION OF EMULGATOR 20 FB 1002 CONTENT UPON EXHAUSTION AND FIXATION CHARACTERISTICS OF SOLVENT DYEINGS

Emulgator Concentration (% o.m.f)	Exhaustion (%)	Percentage Dye on Fibre after	
		Ammonia Treatment	Aq. Pyridine Treatment
C.I. Reactive Red 84			
0,25 } 0,50 }	Unlevel		
1,0	99	86	83
2,0	97	86	80
C.I. Reactive Yellow 39			
0,25 } 0,50 }	Unlevel		
1,0	99	85	82
2,0	98	85	82
C.I. Reactive Blue 69			
0,25 } 0,50 }	Unlevel		
1,0	98	88	84
2,0	96	87	85

In the aqueous dyeing of wool with reactive dyes, it is customary to boil for 60 min in order to induce the maximum covalent fixation and consequent optimum wet fastness properties. Van der Merwe and van Rooyen⁷ reported that solvent dyeing techniques have resulted in maximum covalent fixation values after only 40 min. In view of the increased emphasis upon energy conservation, this factor assumes greater importance and it was considered essential to check this feature in the present process. Table II shows that after about 30 min at the boil the exhaustion and covalent fixation values had reached a maximum and their magnitude was similar to that achieved in dyeing at the boil for one hour in aqueous media.

The effect of increasing dye concentration upon exhaustion and covalent fixation is shown in Table III. The present process gives results similar to those obtained by conventional aqueous dyeing. The poor fixation values exhibited by both solvent and aqueous dyed samples at the 5 *per cent* (o.m.f) level are not unexpected. The manufacturers pattern card does not recommend the application of any of the three dyes at depths in excess of 3 *per cent* (o.m.f).

The relationship between reflectance of dyed material and dyestuff concentration is shown in Figs 1 – 3 and Table IV. The graphs show excellent agreement between solvent and aqueous dyed samples and also a reasonable linear relationship between dyestuff concentration and Kubelka-Munk function. Deviations from linearity at higher concentrations are to be expected.

Solvent dyeing processes require the solvent to be reclaimed by distillation at the completion of the dyeing cycle. There is inevitably a loss of solvent in each processing cycle which, if it becomes greater than about 2 *per cent*, may render the process economically unsound. One method of reducing this loss is to minimise the volume of liquor required. To this end, the possibility of low liquor to goods ratios was examined. Table V shows that satisfactory dyeings could be obtained with a ratio as low as 5 : 1. The use of such low ratios will also contribute to a reduction in energy consumption, particularly when it is borne in mind that heat must be applied during both dyeing cycle and solvent reclamation.

In order that the applicability of the process to commercial ranges of reactive dyes might be tested, members of the Lanasol, Hostalan, Procilan and Verofix series were examined at 2 *per cent* depth, together with comparable aqueous dyeings. Chromaticity co-ordinates, colour difference, exhaustion and covalent fixation values, alkaline perspiration and wash fastness (ISO 3 Method) characteristics were determined and the results are tabulated in the Appendix.

The colour difference values (ΔE) were, in most cases, small showing that dyeings of similar hue and depth could be obtained by this method.

The wet fastness properties of solvent dyed and aqueous dyed samples were in very close agreement.

TABLE II
EFFECT OF BOILING TIME UPON EXHAUSTION AND FIXATION
CHARACTERISTICS OF SOLVENT AND AQUEOUS DYEINGS

Time at Boil (min)	SOLVENT			AQUEOUS		
	Exhaustion (%)	Percentage Dye on Fibre after		Exhaustion (%)	Percentage Dye on Fibre after	
		Ammonia Treatment	Aq. Pyridine Treatment		Ammonia Treatment	Aq. Pyridine Treatment
C.I. Reactive Red 84						
0	98	78	74	88	77	67
15	99	82	78	94	85	71
30	99	83	81	94	86	75
45	99	86	82	98	84	79
60	99	88	82	99	88	82
C.I. Reactive Yellow 39						
0	99	81	79	76	64	57
15	99	85	83	90	81	67
30	99	88	86	94	86	77
45	99	88	85	96	87	83
60	99	89	85	96	87	82
C.I. Reactive Blue 69						
0	98	84	81	86	66	60
15	99	89	86	94	76	71
30	99	89	85	96	87	82
45	99	89	86	98	90	84
60	99	89	85	98	89	84

TABLE III

EFFECT OF DYE CONCENTRATION UPON THE EXHAUSTION AND FIXATION CHARACTERISTICS OF SOLVENT AND AQUEOUS DYEINGS

Dye conc. % (omf)	SOLVENT			AQUEOUS		
	Exhaustion (%)	Percentage Dye on Fibre after		Exhaustion (%)	Percentage Dye on Fibre after	
		Ammonia Treatment	Aq. Pyridine Treatment		Ammonia Treatment	Aq. Pyridine Treatment
C.I. Reactive Red 84						
0,25	99	85	81	97	71	67
0,50	99	87	83	97	81	77
1,0	99	85	82	96	85	80
2,0	99	86	84	98	86	83
5,0	97	50	47	91	57	51
C.I. Reactive Yellow 39						
0,25	99	84	80	93	82	77
0,50	99	87	83	95	89	83
1,0	99	90	84	95	89	84
2,0	99	86	83	94	83	79
5,0	99	36	33	72	38	34
C.I. Reactive Blue 69						
0,25	98	83	81	97	91	85
0,50	98	87	83	97	91	86
1,0	98	89	84	97	91	83
2,0	98	87	84	97	87	80
5,0	98	54	49	83	58	52

TABLE IV

THE RELATIONSHIP BETWEEN REFLECTANCE, K/S AND DYE CONCENTRATION FOR SOLVENT AND AQUEOUS DYEINGS

Dye Conc. (% omf)	Solvent		Aqueous	
	R	K/S	R	K/S
C.I. Reactive Red 84				
0,25	10,50	3,814	9,80	4,151
0,50	6,30	6,968	5,80	7,652
1,0	2,40	19,84	2,10	22,82
2,0	1,40	34,72	1,30	37,46
5,0	0,70	70,43	0,80	61,50
C.I. Reactive Yellow 39				
0,25	9,10	4,540	7,90	5,369
0,50	4,40	10,38	4,00	11,52
1,0	2,50	19,01	2,30	20,75
2,0	1,40	34,72	1,30	37,46
5,0	1,00	49,00	1,10	44,56
C.I. Reactive Blue 69				
0,25	5,45	8,197	4,80	9,441
0,50	3,25	14,45	3,10	15,14
1,0	1,50	32,34	1,30	37,46
2,0	0,50	99,00	0,45	112,0
5,0	0,20	249,0	0,20	249,0

TABLE V

EFFECT OF VARIATION OF LIQUOR-TO-GOOD RATIO UPON EXHAUSTION AND FIXATION CHARACTERISTICS OF SOLVENT DYEINGS

Liquor-to-Goods Ratio	Exhaustion (%)	Percentage Dye on Fibre after	
		Ammonia Treatment	Aq. Pyridine Treatment
C.I. Reactive Red 84			
2,5 : 1	Dyeings unlevel		
5,0 : 1	99	92	87
10,0 : 1	99	87	83
20,0 : 1	96	86	82
C.I. Reactive Yellow 39			
2,5 : 1	Dyeings unlevel		
5,0 : 1	99	90	84
10,0 : 1	99	88	84
20,0 : 1	97	85	82
C.I. Reactive Blue 69			
2,5 : 1	Dyeings unlevel		
5,0 : 1	98	92	86
10,0 : 1	97	90	85
20,0 : 1	94	85	83

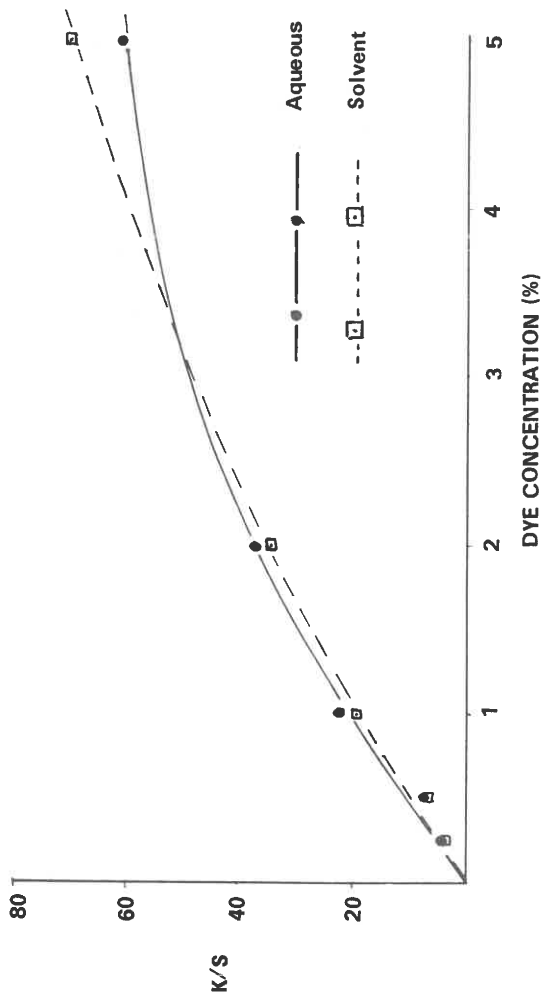


Fig 1 Relationship between reflectance of dyed wool and dye concentration --
 Reactive Red 84

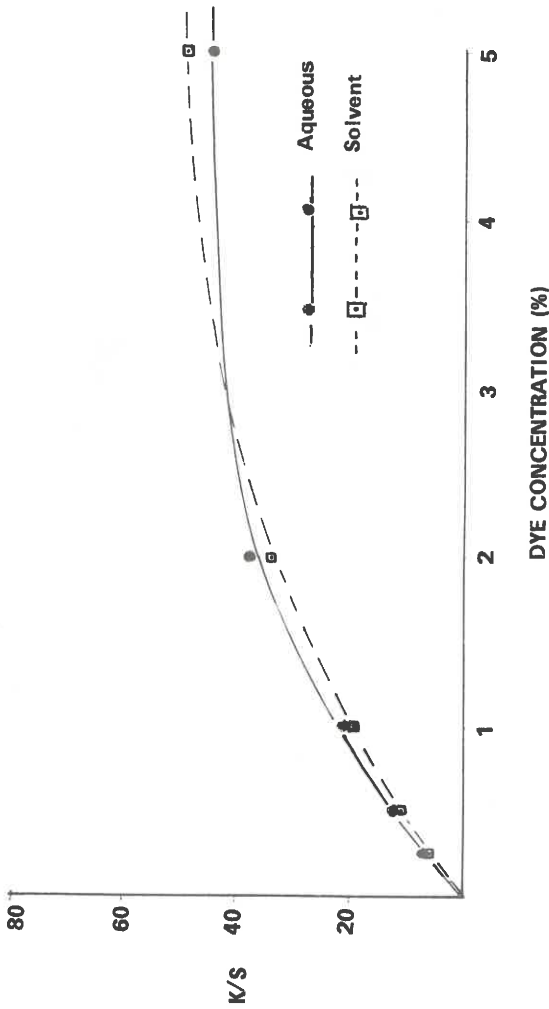


Fig 2 Relationship between reflectance of dyed wool and dye concentration —
Reactive Yellow 39

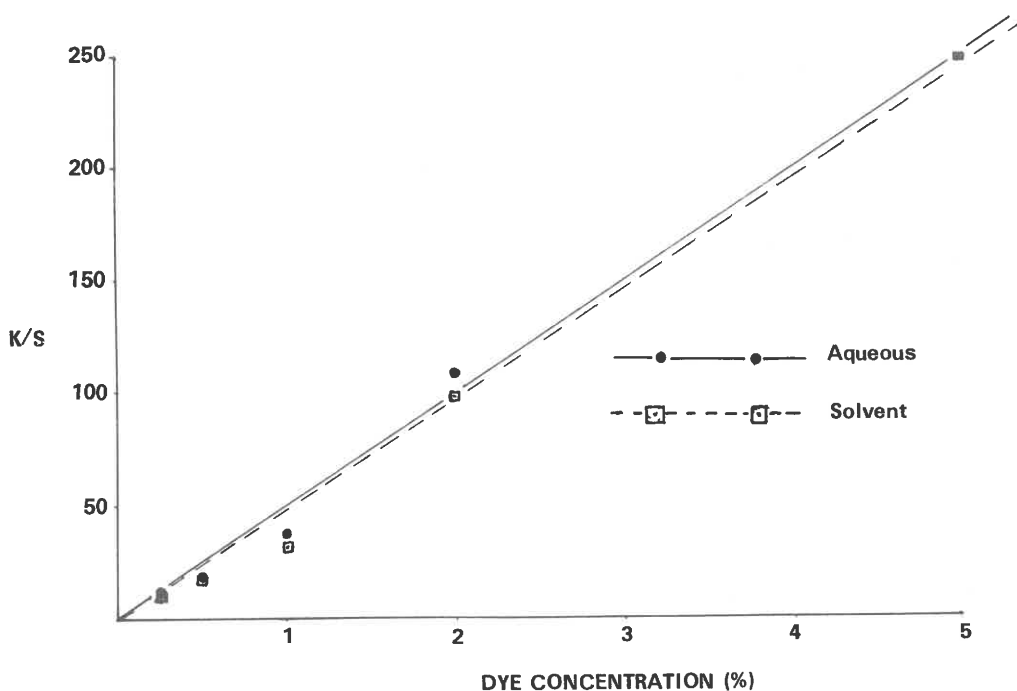


Fig 3 Relationship between reflectance of dyed wool and dye concentration – Reactive Blue 69

SUMMARY AND CONCLUSIONS

A system for the dyeing of wool with reactive dyes from an aqueous charged perchloroethylene system has been devised whereby the wet fastness properties, hue, depth and brightness characteristics are comparable with those obtained by conventional aqueous dyeing.

Difficulties associated with previous methods such as the retention of auxiliaries by the fibre and the necessity of using large quantities of expensive emulsifying agents have been eliminated.

The low liquor to goods ratio and shorter time at the boil could make a significant contribution towards the reduction of energy consumption.

It is hoped to translate this laboratory process to a larger scale after which further results will be published.

ACKNOWLEDGEMENTS

The authors wish to thank Mrs C. Bellingham and Miss Y. Mannell for the colour difference calculations and Miss P. Schouten for general assistance. Permission to publish from the South African Wool Board and Messrs Ciba-Geigy, Basel, Switzerland is also gratefully acknowledged.

USE OF PROPRIETARY NAMES

The fact that products with proprietary names have been used in this investigation in no way implies that there are not others of equal or greater merit.

REFERENCES

1. Brunnschweiler, E., Färben aus organischen Lösungsmitteln allgemeine Überlegungen und Grundlagen, *Textilveredlung*, **4**, 745, (1969).
2. Sieber, J.H., Verfahrenstechnische und apparative Betrachtungen über die Textilausrüstung in Perchloräthylen mit kontinuierlich und diskontinuierlich arbeitenden Ausrüstungsmaschinen, *Textilveredlung*, **4**, 761, (1969).
3. Miličević, B., The Use of Non-Aqueous Solvents in Colouration and Textile Processing, *Rev. Prog. Col.*, **1**, 49, (1969).
4. Mecheels, J., Physikalische und Chemische Grundlagen des Färbens und Ausrüstung aus organischen Lösungsmitteln, *Textilveredlung*, **4**, 749, (1969).
5. Hildebrand, D., and Kuth, R., Das Färben in organischen Lösungsmitteln nach dem ionischen Mechanismus. *Melliand Textilber*, **53**, 569, (1972)
6. Miličević, B., Zur Problematik des Färbens aus organischen Lösungsmitteln, *Textilveredlung*, **4**, 213, (1969).
7. Van der Merwe, J.P., and van Rooyen, Annette, The Laboratory Dyeing of Wool from a Non-Aqueous Medium Using Reactive Dyes, *S. African Wool and Text. Res. Inst. Techn. Rep. No. 206* (1973).
8. Swanepoel, O.A., and Roesstorff, Lynette, Dyeing of Wool from a Charged Solvent System, *S. African Wool and Text. Res. Inst. Techn. Rep. No. 137* (1970).
9. Meissner, H.D. and McIver, B.A., Solvent Dyeing of Wool with a Reactive Dye/Surfactant Complex, *S. African Wool and Text. Res. Inst. Techn. Rep. No. 231* (1974).
10. Weideman, E., and Grabherr, Hilke, The Effect of Temperature and pH of DCCA Solutions on the Shrink Resistance of Woven Wool Fabrics during

- Continuous Application, *S. African Wool and Text. Res. Inst. Techn. Rep. No. 254* (1975).
11. Strydom, M.A., Private Communication.
 12. Maclaren, K., The Adams-Nickerson Colour-difference Formula, *J. Soc. Dyers Col.*, **86**, 354 (1970).
 13. Kunz, J. and Lebensaft, W., *Farbmessung*, Lapp, Mönchengladbach, p.56 (1967).
 14. Standard Methods for the Determination of Colour Fastness of Textiles, *Soc. Dyers and Col.*, 3rd Ed., Bradford, p.104 (1962).
 15. *Ibid*, p.71.

ISBN 07988 0694 X

**Published by
The South African Wool and Textile Research Institute
P.O. Box 1124, Port Elizabeth, South Africa,
and printed in the Republic of South Africa
by P.U.D. Repro (Pty) Ltd., P.O. Box 44, Despatch**

