ELSEVIER
Dyes and Pigments 45 (2000) 43–49
DYES and PIGMENTS

The fastness, to repeated washing, of reactive dyes and pre-metallised acid dyes on nylon 6,6

S.M. Burkinshaw*, Young-A. Son, S.N. Chevli

School of Textile Industries, The University, Leeds LS2 9JT, UK

Received 5 September 1999; received in revised form 24 September 1999; accepted 13 October 1999

Abstract

Standard depth dyeings were prepared using three, unsulfonated 1:2 pre-metallised acid dyes as well as three reactive dyes on knitted nylon 6,6 fabric and the fastness of the dyeings to 20 repeated wash tests was determined. In the case of the three pre-metallised acid dyes, while aftertreatment with a commercial syntan/cation system as well as a modification of this commercial system reduced both the rate and extent of dye loss during repeated washing, the extent of dye loss which occurred was not unsubstantial. In contrast, the dyeings obtained using the three commercial reactive dyes suffered considerably lower dye loss during repeated washing. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Nylon 6,6; Reactive dyes; Pre-metallised dyes; Repeated washing

1. Introduction

Nylon 6,6 is dyed predominantly using acid dyes (including pre-metallised acid dyes). However, the level of wash fastness displayed by members of this dye class, especially the non-metallised representatives, on nylon 6,6 often leaves much to be desired and recourse to an aftertreatment is usually necessary to achieve adequate fastness to washing [1]. The most common aftertreatment used, is the single-stage application of a synthetic tanning agent (syntan) to the dyed material. It has been demonstrated that the effectiveness of a commercial syntan in improving the wash fastness of various non-metallised acid dyes [2,3] and pre-metallised acid dyes [4,5] on nylon 6,6 could be enhanced by the subsequent application of a cationic agent to the syntanned, dyed material, as exemplified by the first such commercial *syntan/cation* system, the Fixogene AC (Uniqema) aftertreatment process. It is proposed [1,2] that this two-stage aftertreatment process results in the formation of a large molecular size, low a aqueous solubility, complex between the anionic syntan and the cationic compound within the dyed fibre.

While textile usage of nylon 6,6 has been invigorated of late as a result of the enhanced tactile and visual aesthetics offered by microfibre nylon 6,6, the wash fastness of acid dyes on microfibre nylon 6,6 is generally lower than that on its conventional decitex counterpart [1] and aftertreatments with a syntan and the syntan/cation system are less effective on dyed microfibre nylon 6,6 [1,2,4,5].

In recent years, the fastness of dyeings towards repeated washing has become increasingly important, not only for dyed nylon 6,6 but for other

---

* Corresponding author Tel.: +44-113-233-3722; fax: +44-113-233-3704.

E-mail address: s.m.burkinshaw@leeds.acu.uk (S.M. Burkinshaw).

PII: S0143-7208(99)00096-0

dye/fibre systems [6,7], in response to increased consumer and retailer demands. In the context of dyed nylon 6,6, the Fixogene AC process recently wash shown to be highly effective in improving the fastness of 2:1 pre-metallised acid dyes on both conventional decitex and microfibre nylon 6,6 to repeated wash tests [5]. However, although this particular commercial syntan/cation system was more effective than a single syntan aftertreatment in improving the fastness over 10 washes, the extent of dye loss and staining of adjacent fibres during washing was not insubstantial.

Theoretically, reactive dyeings on nylon 6,6 should, by virtue of the covalent nature of the dye–fibre bond, display excellent fastness to repeated washing without recourse to an aftertreatment. Although several papers have recently detailed the generally very high level of fastness that can be achieved using various types of commercial reactive dye on nylon 6,6 to single washing [8–14], the level of fastness which can be achieved towards repeated wash fastness testing has not received attention.

The purposes of this work were to firstly determine the level of fastness displayed by typical reactive dyeings on nylon 6,6 to repeated washing and then to compare this to that achieved using nylon 6,6 which had been dyed with acid dyes and aftertreated with a commercial syntan/cation system (Fixogene AC). In addition, a modification was made to the Fixogene AC process in that the usual cationic component, Fixogene CXF, was replaced by the cationic fixing agent, Solfix E (Ciba-Geigy), which is intended for the aftertreatment of direct dyeings on cellulosic fibres. This was done so as to determine whether the use of the reactive, cationic fixing agent, Solfix E, would be more effective than the recommended, non-reactive cationic agent, Fixogene CXF in the Fixogene AC system.

2. Experimental

2.1. Materials

Scoured, knitted nylon 6.6 fabrics (78f68; 1.15dtex per filament) were generously supplied by Du Pont (UK). The dyes used in this work were kindly supplied by Crompton & Knowles (Table 1) Commercial samples of the syntan, Fixogene AXF, the cationic agent Fixogene CXF and the nonionic surfactant Lanapex R were generously supplied by Uniqeme. A commercial sample of the cationic agent Solfix E was supplied by Ciba-Geigy.

All the other chemicals used were laboratory grade reagents.

2.2. Procedures

2.2.1. Dyeing

All dyeings were carried out in 200 cm^3 stainless steel dyeing pots housed in a laboratory scale, Zeltex Polycolor PC 1000 dyeing machine. The dyeing method used for the acid dyes and the reactive dyes are shown in Fig. 1; McIlvaine buffers [15] were used to achieve the two pH values used. All dyeings were carried out using a 25:1 liquor ratio to 1/1 standard depth [16] except for the black shades where identical visual depths of shade were produced because of the difficulty of obtaining either the standard Black/DK or standard Black/LT using reactive dyes on nylon 6,6.

2.2.2. Fixogene AXF (syntan) aftertreatment

Samples which had been dyed using the acid dyes were aftertreated with the commercial syntan in sealed, stainless steel dye pots, of 200 cm^3 capacity, housed in a Zeltex Polycolor PC 1000 laboratory scale dyeing machine employing a liquor ratio 20:1. At the end of dyeing, the dyed samples were removed, rinsed thoroughly in tap water and allowed to dry in the open air. The aftertreatment method is given in Fig. 2.

2.2.3. Fixogene CXF and Solfix E (cationic agent) aftertreatment

The dyed and syntanned nylon 6.6 samples were aftertreated with either of the two cationic polymers in sealed, stainless steel dye pots, of 200 cm^3 capacity, housed in a Zeltex Polycolor PC 1000 laboratory scale dyeing machine using a liquor ratio of 20:1 (Fig. 3). At the end of dyeing, the dyed samples were removed, rinsed thoroughly in tap water and allowed to dry in the open air. The reactive dyed samples were washed off using 3 g l^{-1} Lanapex R

Table 1
Dyes used

Commercial name	C.I. generic name	Maker
Neutrilan Bordeaux K-RL	C.I. Acid Red 182	Crompton and Knowles
Neutrilan Yellow K-RL	C.I. Acid Yellow 137	
Neutrilan Black K-BL	C.I. Acid Black 194	
Cibacron Red F-B	C.I. Reactive Red 184	Ciba-Geigy
Cibacron Yellow F-3R	C.I. Reactive Orange 91	
Cibacron Black F-2B	None ascribed	

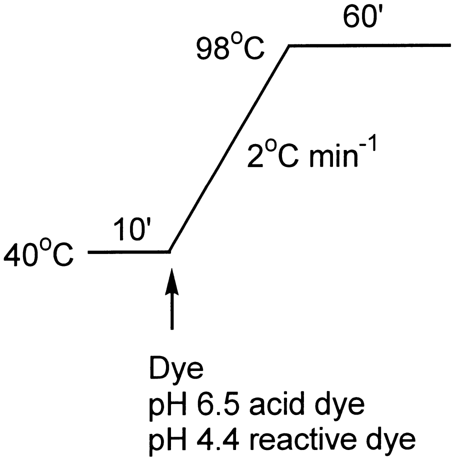

Fig. 1. Dyeing method.

and 1 g l^{-1} Na_2CO_3 at 60°C for 20 min and were then rinsed in cold running water for 5 min.

2.2.4. Colour measurement

All measurements were carried out using an X-rite Match-Rite™ spectrophotometer coupled to a PC using illuminant D_{65}, 10° standard observer with the specular component excluded and the UV component included. Each fabric was folded once so as to give two thickness and an average of four readings was taken each time.

2.2.5. Wash fastness

Wash fastness tests were made according to the ISO C06/C2 wash test method [17]. The reduction in colour strength ($\Delta K/S$) that occurred as a result of repeated washing was calculated using Eq. (1) in which the subscripts 1 and 2 represent, respectively, before and after 5,10,15 or 20 wash tests.

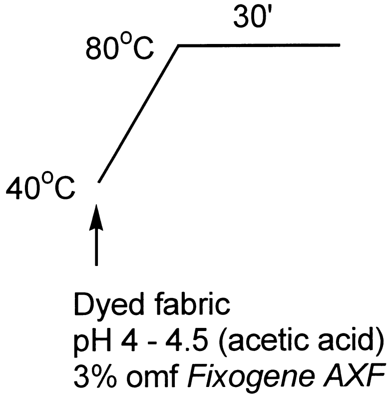

Fig. 2. Aftertreatment with syntan (Fixogene AC).

$$\Delta K/S = \left(\frac{K_1/S_1 - K_2/S_2}{K_1/S_1}\right) \times 100 \qquad (1)$$

3. Results and discussion

Fig. 4 shows the reduction in colour strength ($\Delta K/S$ values) that occurred when a 1/1 standard depth shade of C.I. Acid Red 182 was subjected to 5,10,15 and 20 repeated ISO C06/C2 wash tests. It is evident that the colour strength of the dyeing decreased with increasing number of washes and that dye desorption from the dyed sample occurred progressively as the number of washes increased. The results displayed in Fig. 4 also reveal that aftertreatment with the two-stage syntan (Fixogene AXF)/cation (Fixogene CXF) system reduced both the rate and the extent of dye loss that occurred as a result of repeated washing. The colorimetric data displayed in Table 2 show that

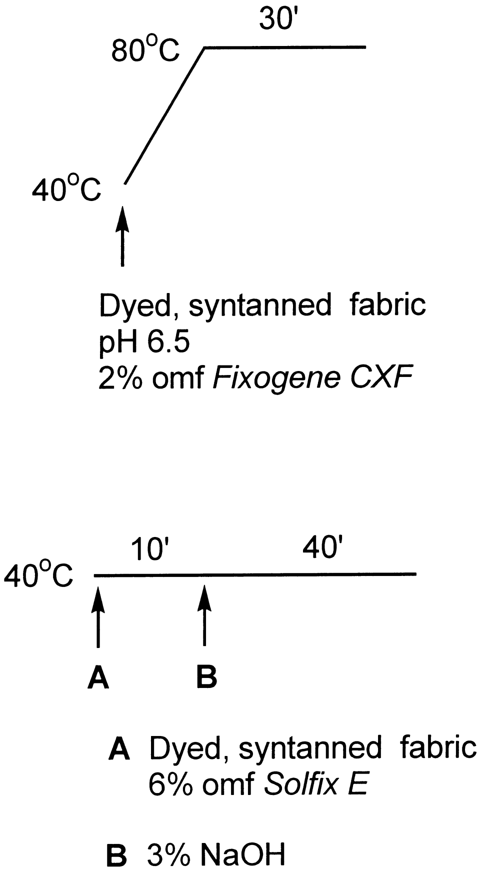

Fig. 3. Aftertreatment with cationic agents (Fixogene CXF and Solfix E).

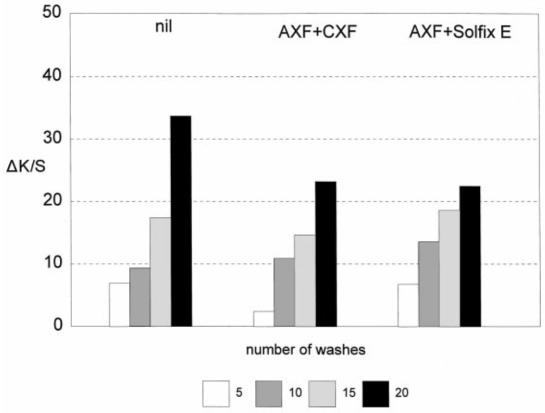

Fig. 4. Effect of aftertreatment on shade change of C.I. Acid Red 182.

aftertreatment with the Fixogene AC system did not impart any colour change to the dyeing and, also, that the shade of the aftertreated dyeing remained unchanged throughout the 20 repeated wash tests.

The observed improvement in the fastness of the dyeings of C.I. Acid Red 182 to repeated washing imparted by the two-stage, syntan/cation aftertreatment process can be attributed [1,2] to the presence of a large molecular size complex formed between the anionic syntan, Fixogene AXF and the cationic polymer, Fixogene CXF, situated at the periphery of the dyed substrate. The purpose of the subsequent application of the cationic polymer to the syntanned, dyed fibre [1,4] is to enhance the effectiveness of the syntan, this being achieved not only by an increase in the effective molecular size of the syntan but also as a result of a lowering of its aqueous solubility, by means of which, the propensity of the syntan to desorb from the dyed fibre during washing. In this context, as mentioned, a modification was made to the Fixogene AC process insofar as the cationic component, Fixogene CXF, was replaced by the cationic fixing agent, Solfix E. This particular compound, which is intended for use as an aftertreatment of direct dyeing on cellulosic fibres, is reactive and undergoes self-crosslinking under aqueous, alkaline conditions, resulting in the formation of a large molecular size, cationic polymer in situ [18]. The reason for replacing the non-reactive cation Fixogene CXF with the reactive cation, Solfix E, was to determine whether the self-crosslinking nature of the latter product could enhance the effectiveness of the syntan in the Fixogene AC syntan/cation system.

Table 2 and Fig. 4 show that aftertreatment with the AXF/Solfix E system improved the fastness to repeated washing of the 1/1 standard depth dyeing of C.I. Acid Red 182 to an extent that was similar to that secured using the AXF/CXF system. Thus, the self-crosslinking nature of the cationic fixing agent appeared not to offer an advantage over the non-reactive cation in terms of dye loss during repeated washing. The colorimetric data in Table 2 reveal that aftertreatment with the AXF/Solfix E system caused very little colour change of the dyeings and that the shade of

Table 2
Colorimetric data for pre-metallised acid dyes

Aftertreatment	Washes	C.I. Acid Red 182					C.I. Acid Yellow 137					C.I. Acid Black 194				
		L^*	a^*	b^*	C	h°	L^*	a^*	b^*	C	h°	L^*	a^*	b^*	C	h°
Nil	0	38.3	35.2	−2.5	35.3	355.9	64.8	25.2	48.8	54.9	62.7	25.8	−1.8	−3.5	3.9	242.2
	5	39.1	35.2	−2.6	35.3	355.9	66.4	24.2	47.8	53.6	63.2	26.5	−1.6	−3.5	3.9	244.8
	10	39.7	35.2	−2.5	35.5	355.9	67.8	23.5	47.3	52.8	63.5	27.7	−1.6	−3.5	3.9	245.6
	15	40.2	34.8	−3.0	34.9	355.6	68.7	23.2	45.9	51.4	63.2	28.7	−1.6	−3.8	4.1	246.8
	20	41.7	35.2	−2.7	35.3	355.6	70.5	22.8	46.3	51.7	63.8	30.0	−1.7	−3.7	4.0	245.9
AXF/CXF	0	38.5	34.5	−2.8	34.6	355.5	63.5	25.4	48.4	54.7	62.3	26.7	−2.0	−3.8	4.2	242.5
	5	39.0	34.6	−2.8	34.7	355.4	64.3	25.2	48.3	54.4	62.5	27.3	−1.7	−3.6	4.0	244.3
	10	40.3	34.8	−2.7	35.0	355.5	65.7	24.5	48.0	53.9	62.9	28.3	−1.7	−3.6	4.0	245.1
	15	40.7	34.5	−3.0	34.6	355.6	66.2	24.3	47.2	53.1	62.8	28.7	−1.7	−3.7	4.1	245.3
	20	42.3	34.7	−2.9	34.8	355.3	68.4	23.8	47.2	52.9	63.2	30.2	−1.8	−3.7	4.1	244.9
AXF/Solfix E	0	37.4	35.1	−2.5	35.2	356.0	63.6	25.4	48.4	54.6	62.3	25.8	−1.8	−3.6	4.0	243.0
	5	38.2	35.1	−2.6	35.2	355.8	64.8	24.8	48.3	54.2	62.9	26.5	−1.7	−3.5	3.9	244.8
	10	38.2	35.3	−2.4	35.4	356.2	65.6	24.1	47.8	53.5	63.2	27.3	−1.6	−3.5	3.9	245.1
	15	38.3	34.9	−2.8	35.0	355.4	66.4	24.1	47.1	52.9	63.0	27.4	−1.6	−3.6	4.0	246.3
	20	39.7	35.3	−2.5	35.4	355.9	68.1	23.7	47.5	53.1	63.5	28.8	−1.7	−3.7	4.0	245.6

the aftertreated dyeings remained virtually unchanged throughout the 20 repeated wash tests.

The colorimetric data obtained for the repeated washing of the two other 1:2 pre-metallised acid dyes are also given in Table 2 and the corresponding $\Delta K/S$ values are displayed in Figs. 5 and 6. The results secured for both C.I. Acid Black 194 and C.I. Acid Yellow 137 were identical to those obtained for C.I. Acid Red 182 in that aftertreatment with both the syntan/Fixogene AC system and the syntan/Solfix E system improved the fastness of the dyeings to repeated washing. Furthermore, aftertreatment with both syntan/cation systems imparted very little colour change to the dyeings and the shade of the aftertreated dyeings was virtually unchanged throughout the 20 repeated wash tests (Table 2).

However, Figs. 4 and 5 also show that aftertreatment with the syntan/Solfix E system was more effective than the syntan/Fixogene AC system

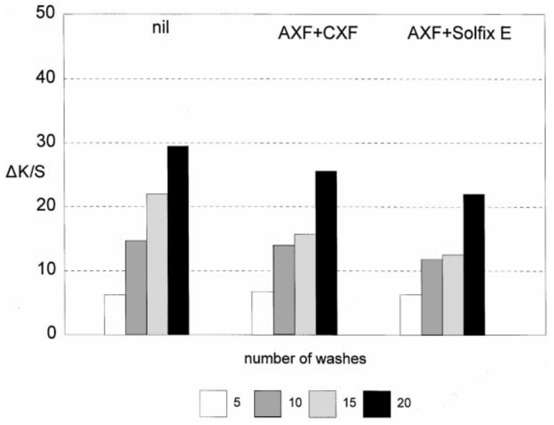

Fig. 5. Effect of aftertreatment on shade change of C.I. Acid Black 194.

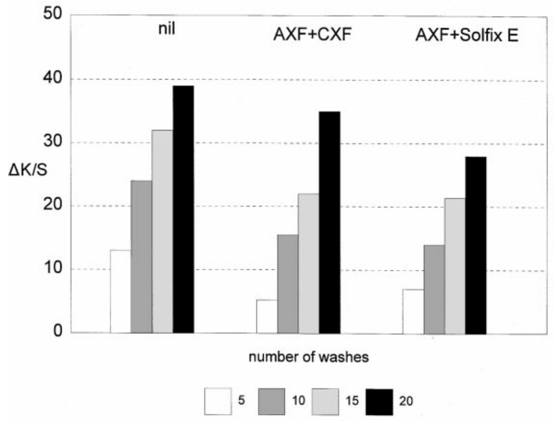

Fig. 6. Effect of aftertreatment on shade change of C.I. Acid Yellow 137.

in terms of improving the fastness of the dyeings to repeated washing. This may be due to the self-crosslinking nature of Solfix E which resulted in the formation of a complex between the anionic syntan and the cationic polymer that was larger and/or of lower water-solubility than that formed between the syntan and the non-reactive cation.

Table 3 shows the colorimetric data obtained for the standard depth dyeings of the three reactive dyes; the corresponding $\Delta K/S$ values are displayed in Fig. 7. It is evident that for each of the three reactive dyes, the extent of dye loss that occurred during repeated washing was low and the shade of the dyeings was little changed as a result of the 20 repeated wash tests. A comparison of the $\Delta K/S$ values obtained for the three reactive dyes (Fig. 7) with those secured for the three pre-metallised acid dyes (Figs. 4–6) reveals that considerably less dye desorbed from the reactive dyeings during repeated washing than from the pre-metallised acid dyeings. This finding is clearly evident in Figs. 4–7, as the same maximum abscissa value of 50 was used for all four plots. The marked difference in wash-down observed between the three pre-metallised acid dyeings and the three reactive dyeings can be attributed to the difference in the nature of dye-fibre interaction, namely covalent, in the case of the reactive dyes and non-covalent in the case of the pre-metallised acid dyes.

Table 3
Colorimetric data for reactive dyes

Dye	Washes	L^*	a^*	b^*	C	h°
C.I. Reactive Red 184	0	42.0	59.5	−2.4	59.6	357.7
	5	41.7	58.1	−2.7	58.2	357.3
	10	42.0	57.9	−3.1	58.0	357.0
	15	42.5	57.3	−3.9	57.5	356.1
	20	43.5	58.5	−3.4	58.6	356.7
C.I. Reactive Orange 91	0	72.8	22.2	72.5	75.8	73.0
	5	73.2	24.4	73.6	77.6	71.6
	10	73.5	24.6	74.0	78.0	71.6
	15	73.9	24.5	73.7	77.7	71.6
	20	74.1	24.4	73.7	77.7	71.6
Cibacron Black F-2B	0	25.4	−1.5	−5.9	6.1	255.6
	5	25.9	−2.4	−5.3	5.8	245.8
	10	26.4	−2.6	−5.1	5.8	243.0
	15	26.9	−2.7	−5.4	6.1	243.4
	20	27.6	−2.8	−5.3	6.0	242.2

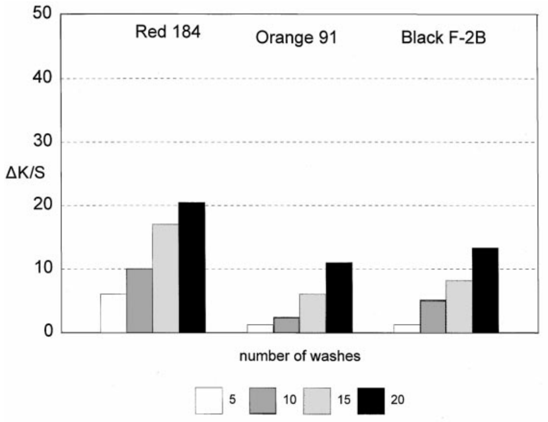

Fig. 7. Effect of aftertreatment on shade change of reactive dyeings.

4. Conclusions

Although in the case of the three unsulfonated, 1:2 pre-metallised acid dyes, aftertreatment with the commercial syntan/cation system as well as the modified syntan/cation system reduced both the rate and extent of dye loss during repeated washing, the extent of dye loss which occurred was not unsubstantial. In contrast, the dyeings obtained using the three commercial reactive dyes suffered considerably lower dye loss during repeated washing.

References

[1] Burkinshaw SM. Chemical principles of synthetic fibre dyeing. London: Chapman and Hall, 1995.

[2] Burkinshaw SM, Maseka KD. Dyes and Pigments 1996;30:21.

[3] Burkinshaw SM., Maseka KD. ICI Surfactants, US Patent 5 350 422, 1994.

[4] Blackburn RS, Burkinshaw SM. J Soc Dyers Col 1998;114:12.

[5] Blackburn RS, Burkinshaw SM. J Soc Dyers Col 1999;115:102.

[6] Burkinshaw SM, Collins GW. J Soc Dyers Col 1998;114:165.

[7] Koo B-C, Burkinshaw SM. Adv Col Sci Tech 1996;1:76.

[8] Burkinshaw SM, Gandhi K. Dyes and Pigments 1996;32:101.
[9] Burkinshaw SM, Maseka KD. Dyes and Pigments 1997;33:259.
[10] Burkinshaw SM, Wills AE. Proc. 1996 AATCC IC & E, Nashville. p. 520.
[11] Burkinshaw SM, Wills AE. Dyes and Pigments 1997;34:243.
[12] Burkinshaw SM, Collins GW, Gotsopoulos A, Wills AE. Proc. 1997 AATCCIC & E, Atlanta. p. 421.
[13] Blackburn RS, Burkinshaw SM, Collins GW, Gandhi K, Gotsopoulos A, Wills AE. Proc. Confluences: Fashioning Inter-cultural Perspectives, University de Mode, Lyon, 1996.
[14] Burkinshaw SM. AATCC Int. dyeing Symp., Greenville, 1998. p. 30.
[15] Vogel A. A textbook of quantitative inorganic analysis. London: Longmans, 1994.
[16] Standard Depths: Matt, ISO 105 A01:1989. Bradford: Society of Dyers and Colourists.
[17] Anon. Methods of test for colour fastness of textiles and leather. 5th ed. Bradford: Society of Dyers and Colourists, 1990.
[18] Collins GW. Ph.D. thesis, Leeds University, 1998.