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Some Wet Processing Factors Influencing the Yellowing of Mohair

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ABSTRACT

Good quality Kid's hair was treated for increasing periods of time in various buffer solutions at various pH levels and at temperatures varying between 50° and 95°C. Yellowing was found to be dependent on time and temperature, and to a lesser extent on pH. Subsequently dyeings were performed on the mohair with three acid milling dyes at both 100°C and at 85°C. Dyebath exhaustion was found to depend on temperature. An economic dyeing formulation utilizing the lower temperature (85°C) was found to require a chemical auxiliary to promote dyestuff absorption, as well as a lowering of the bath pH to increase the affinity of the dyestuffs for the mohair.

KEY WORDS

Mohair — acid dyes — auxiliaries — buffers — dulling — yellowing.

INTRODUCTION

Good quality mohair is a luxury fibre and is primarily used in very specialised end-commodities only, such as quality mohair rugs and men's suitings. It is also an expensive fibre and both the price and the demand vary according to fashion changes from season to season.

Chemically, wool and mohair are identical fibres since they are both keratinous. However, the two types of fibre are physically quite different due to various factors, the main one being the uncrimped, smooth fibre surface of mohair compared with that of wool. The epicutical scales, common to all animal fibres, are only faintly visible and hardly overlap [1]. This gives a smooth lustrous appearance to the mohair fibre, which adds greatly to its inherent appeal [2,3].

During the processing of mohair, any operation which detracts from the natural aesthetic properties of the fibre will logically have an effect on the ultimate demand and price of the manufactured article. Such processes should be avoided, but in many cases this is not possible and the best that can be done is to find optimum conditions for such processes so as to retain the good properties of the fibre after processing. One such a process is dyeing.

Being chemically similar to wool, mohair is dyed with the same dyestuffs as wool. Because of the lustrous nature of the mohair, however, the latter appears to be significantly brighter than equivalent dyeings on wool. It appears, however, that mohair is inclined to lose its lustre when dyed for prolonged periods at the boil. Physical, and possibly also chemical, damage to the fibre therefore appears to manifest itself by a loss of lustre. This phenomenon is much more pronounced in mohair than is the case in wool.

It is known from practical experience that bright shades cannot be obtained from hair that has been yellowed previously or from hair that yellows during the dyeing process.

The present investigation is concerned with some wet processing conditions which accompany the loss in lustre and possible remedies for this problem in terms of optimising the processing variables such as time, temperature and pH of the dyebath, in particular. A number of recommended dyeing auxiliary products specifically designed for the low temperature dyeing of wool were compared in terms of their effects on the dyebath exhaustion at two pH levels, viz. pH 4 and pH 6, and under such conditions of time and temperature where yellowing and/or dulling appeared to be at a minimum.

EXPERIMENTAL

1. Preliminary experiments

Preliminary work on the effects of dyeing mohair which has been yellowed prior to dyeing was done on carbonised and uncarbonised hair. The processing details and the physical properties of this hair have been published elsehwere [4]. The yellowness of the hair was assessed subjectively by ranking the carbonised and uncarbonised tops. These tops were subsequently dyed to a 0,25 *per cent* depth of shade with the main classes of wool dyes, i.e. the premetallised, chrome, acid levelling, acid milling and reactive types. These dyes were applied by conventional methods as prescribed by various manufacturers. The dyed tops were subsequently assessed for brightness/dullness by subjective evaluation, and these rankings were then correlated with the yellowness ranking of the corresponding undyed tops.

2. Blank dyeings and treatment with buffered solutions

Super quality Kid's hair of 23,8 μ average fibre diameter and 69,3 mm average fibre length was used throughout for all further experiments. The top was prepared by conventional scouring, carding and combing at SAWTRI and was not prescoured prior to any given wet treatment to prevent additional factors from possibly influencing the yellowing tendencies of the hair other than dyebath conditions alone. Random samples (5 g each) were drawn from the top and treated in buffered solutions of which the pH was varied from 2,0 – 6,0 in an Ahiba Laboratory Dyeing apparatus. The buffered solutions were made up from varying amounts of HC1 and KC1 (for pH 2,0), and citric acid and Na_2HPO_4 (for pH 3,0 – 6,0) according to standard formulations listed by Britton[5]. The liquor-to-goods ratio was maintained at 40:1 and the temperature was varied between 50°C and 95°C. The treated samples were rinsed in cold running water and air-dried overnight.

The effect of treating the mohair in blank dyebaths was studied by dyeing for increasing periods of time (up to 180 min.) at 100°C from the following blank baths:

(a) Reactive dyeings

3% CH_3COOH (60%)
4% $(NH_4)_2SO_4$
pH 5,0 with CH_3COOH or aqueous ammonia, as required.

(b) Neutral dyeings

2% CH_3COOH (60%)
5% Na_2SO_4
pH 4,5 with CH_3COOH or aqueous ammonia, as required.

(c) 1:1 Premetallised dyeings

9,0% H_2SO_4
10% Na_2SO_4
pH 1,9 – 2,0

In all cases, the liquor-to-goods ratio was maintained at 40:1. The treated samples were rinsed in cold running water and air-dried overnight.

The effect of dyeing in the cold on the yellowing tendency of mohair was also studied by blank dyeing 100g of mohair top according to the I.W.S. Pad-Batch method[6]. A blank padding solution was prepared as follows:

Urea	300 g/l
Cellofas B (ICI)	5 g/l
Irgapadol P (Ciba-Geigy)	10 g/l
CH_3COOH	1 g/l
$NaHSO_3$	10 g/l

The top was padded to approximately 80 *per cent* pickup on a Benz Laboratory padder and batched for 24 hours in a sealed plastic bag. Excess urea, thickener and wetting agent were subsequently washed off in cold running water and the top was air-dried overnight.

3. Colour measurement

All colour measurements of the untreated mohair, blank-dyed mohair and the mohair treated in buffered solutions were performed on a Zeiss Elrepho Photoelectric Reflection Photometer. All reflectance measurements were performed relative to magnesium oxide (= 100% reflectance). The mohair samples were placed in a specially designed brass sample cell which was constructed according to a basic design by Hoare and Thompson[7,8]. This design was modified somewhat because of the needless complexity of the cell for routine measurement. A diagrammatic cross-section of the cell used in this study is shown in Fig. 1. It consists of a threaded retaining ring which supports the cell window which is cut from ordinary pane-glass. This ring is screwed down onto the cell body to provide a fixed volume for containing the mohair fibres. The back of the sample compartment is coated with a matt-black spray paint to prevent any stray reflection from the brass cell wall from influencing the measured reflectance values. The mohair samples were divided into 2 g portions and placed in the cell compartment in such a way that the fibres were as parallel as possible. This amounted to a packing density of approximately 0,3 g/cm^3, the value which Hoare and Thompson recommend for wool[7]. During the wet treatments, the fibres were restrained within the wire mesh sample holders of the Ahiba apparatus,

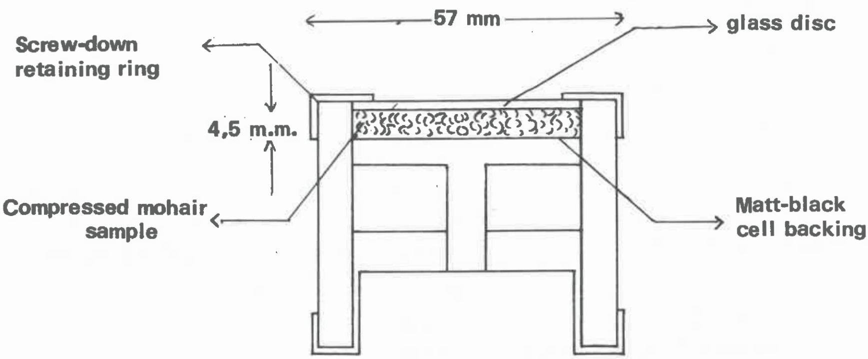

Fig 1 Cross section of the cell used for reflectance measurements

so that very little fibre disturbance took place so that no undue difficulty arose in placing the fibres parallel to one another in the reflectance cell. Four measurements were recorded for each sample, the cell being rotated through 90° between successive measurements.

A number of formulae have been suggested for the description of whiteness[9]. All these formulae are based on the measurement of the tristimulus values X, Y and Z. For the sake of simplicity and because conclusions were drawn from comparisons between samples, the Hunter formula[10] for the Yellowness Index was used:

Yellowness Index (YI) $= \frac{R_x - R_z}{R_y} \times \frac{100}{1}$, where R_x, R_y and R_z are the reflectance values determined by using the FMX/C (red), FMY/C (green) and FMZ (blue) Elrepho tristimulus filters.

4. Evaluation of dyebath auxiliaries

Dyeing experiments were carried out on the Ahiba apparatus using the same wire mesh sample holders as used earlier. Samples of mohair (5 g each) were dyed according to standard prescribed methods using the following dyestuffs:

C.I. Acid Yellow 71
C.I. Acid Red 111
C.I. Acid Blue 92

The dyebath was set containing the following (all percentages expressed o.m.f.):

2% dye
3% ammonium acetate
Liquor-to-goods ratio 40:1

The pH of the dyebath was adjusted to the predetermined values with acetic acid. The goods were thoroughly wetted out in the dye liquor at 40°C for ± 5 min. before raising the temperature to the predetermined values at a rate of 0,5 – 1°C per minute. Exhaustion figures were determined by analysing the dyebath liquor at various intervals of time and temperature. Aliquots were drawn from the baths, diluted appropriately and the optical density measured on a Zeiss PM2 DL Spectrophotometer. These figures were converted to bath exhaustion values by comparing them with the absorption values of the cold dyebath prior to entering the mohair. All readings were carried out at the wavelength of maximum absorption of each dyestuff.

The effect of the following commercially available dyebath auxiliaries on dyebath exhaustion was investigated:

Albegal B	(Ciba-Geigy)
Unisol BT	(Ugine Kuhlmann)
Lissapol N	(ICI)
Tinosol CLW	(Ciba-Geigy)
Keriolan W	(Tübingen)

Unless otherwise stated, 1,5 *per cent* (o.m.f.) of each auxiliary was used throughout. The goods were again thoroughly wetted out in the dye liquor at 40°C before raising the dyebath temperature at a rate of 0,5 – 1°C per minute.

RESULT AND DISCUSSIONS

A. The Effect of Dyebath Conditions on the Yellowness Index

The preliminary experiments performed on the carbonised and uncarbonised mohair confirmed that mohair which has been yellowed prior to dyeing cannot be dyed to a bright shade. The ranking of the carbonised and uncarbonised hair corresponded to an increase in the Yellowness Index from 19,7 (uncarbonised) to 20,8 (carbonised). This difference between samples was found to be significant at the 95 *per cent* confidence level. The samples subsequently dyed were ranked consistently as dull (for the carbonised hair) to bright (for the uncarbonised hair) for all the classes of dyes which had been used. From this it was deduced that since a yellowed fibre cannot be dyed to a bright shade, it would appear that a loss of lustre in the dyed goods is related to the yellowness of the undyed hair. If this is true, it may be assumed further that if yellowing takes place *during* the dyeing process, it would be accompanied also by a loss of lustre in the dyed top stage. There is, of course, the possibility that lustre is more sensitive than yellowing to dyeing conditions.

The determination of lustre with an instrument such as the Zeiss Photogoniometer[11] is only applicable to solid, smooth and regular surfaces, and in fact the use of this instrument or similar instruments using the same principle is not recommended due mainly to the problem of surface unevenness of fibrous samples[12]. Further observations in this work were based therefore on yellowness determinations rather than on lustre determination. It is not claimed however that the yellowness of the fibre is the sole consequence of the diminish in lustre or vice versa. Lustre is a surface phenomenon and a diminish in lustre is normally associated with a physical degradation of the fibre surface, whereas yellowing is normally associated with chemical damage. It can be said however that there is a possibility that both may occur simultaneously during the dyeing process.

Laboratory trials were then performed on the super quality Kid's hair which had a lower YI than the mohair used in the preliminary experiments. The average value for this quality was found to be 17,9 (25 samples, 3 readings per sample). In Table I, the combined effect of pH and temperature on the YI is shown.

TABLE I

THE EFFECT OF pH AND TEMPERATURE ON THE Y.I. OF KID MOHAIR (Y.I. OF UNTREATED SAMPLE = 17,9; 2 hr treatment time).

pH	YELLOWNESS INDEX		
	50°C	75°C	95°C
2,0	19,8	22,5	24,4
3,0	20,1	23,3	24,8
4,0	21,6	22,6	24,4
5,0	20,6	22,5	22,3
6,0	20,5	22,3	22,7

For this particular experiment, statistical analyses show that only differences between any two values which are equal to, or greater than, 1,3 are real, i.e. have statistical significance. From this the following observations were made:

(a) There was a real increase in the degree of yellowing of the hair as the temperature increased. Apparently this was more significant for the lower pH regions (i.e. 2,0 – 4,0) than was the case in the neutral to slightly acid conditions (pH 5,0 – 6,0). Peryman[13] and Hine and McPhee[14] have shown that boiling in strongly acid solutions increases the susceptability of wool to physical damage and this physical damage therefore appears to be manifested by a yellowing effect on the appearance of the fibre.

(b) The effect of pH at a given temperature was found to be less marked than the overall effect of an increase in temperature. No significant trend was found with an increase in pH at a given temperature, except at temperatures approaching the boil where it appeared that the critical conditions, i.e. low pH values tended to promote yellowing. Very alkaline conditions were not employed as mohair is very rarely dyed above pH 6,0.

In commercial practice however the carefully controlled conditions of pH used in this experiment by treating the mohair in standard buffer solutions are, generally speaking, not possible. The dyebath is normally set with prescribed amounts of auxiliaries, such as salt, acids and possibly synthetic wetting and levelling agents. The pH conditions thus may vary considerably during the dyeing cycle.

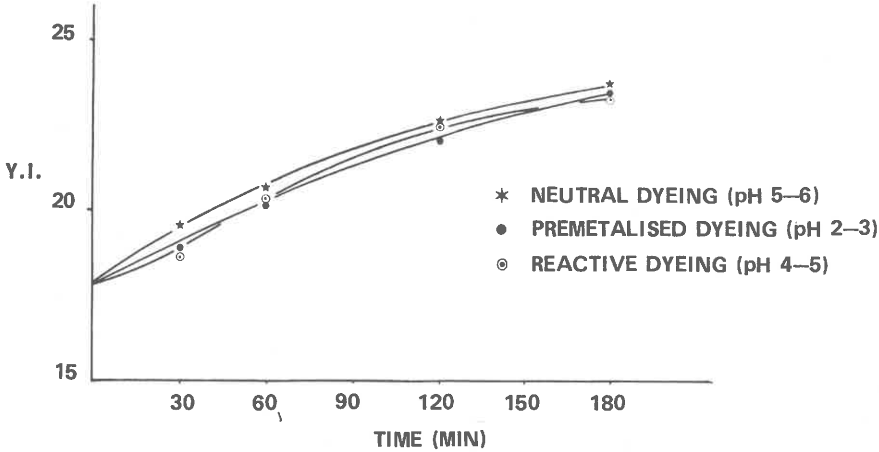

Fig 2 The effect of time of dyeing at 100°C on the Y.I. of Mohair treated in various blank dyebaths

In Fig 2, the effect of time of treatment in various blank dyebaths is illustrated. It can be seen that a gradual increase in the extent of yellowing occurred with increasing times of treatment. As a first approximation it can be seen from Fig 2 that although the initial dyebath pH-values varied considerably, no significant difference in the degree of yellowing was found at any given time of treatment for different initial pH conditions. It does seem, however, that the degree of yellowing was, on the average, slightly less than when the pH of the liquor remained constant for the duration of the treatment, as it is depicted in Table I. The samples were not treated for longer than 3 hours, as such a lengthy duration of boiling rarely would occur in practice.

The lower the temperature of dyeing, however, the less the degree of damage and subsequent yellowing and dulling of the shade will be. As a reference value, the Y.I. of blank dyed mohair dyed according to the IWS Pad Batch (cold) technique[6] was determined. The treated top appeared whiter than the untreated control (Y.I. = 15,9 compared with 17,9) due to a possible reductive bleaching action of the sodium bisulphite during the batching period. This technique, therefore, offers the possibility of producing bright shades on mohair with a minimum of fibre damaging, yellowing and loss of lustre.

Summarising, the following conclusions have been arrived at:

1. For long liquor dyeing systems time and temperature of dyeing apparently play a more important role in respect of yellowing than does a variation in the initial bath pH.

2. To retain the lustre of the hair as best as possible, it would seem necessary to reduce to a minimum the time and temperature of dyeing, irrespective of the class of dyestuff being employed.

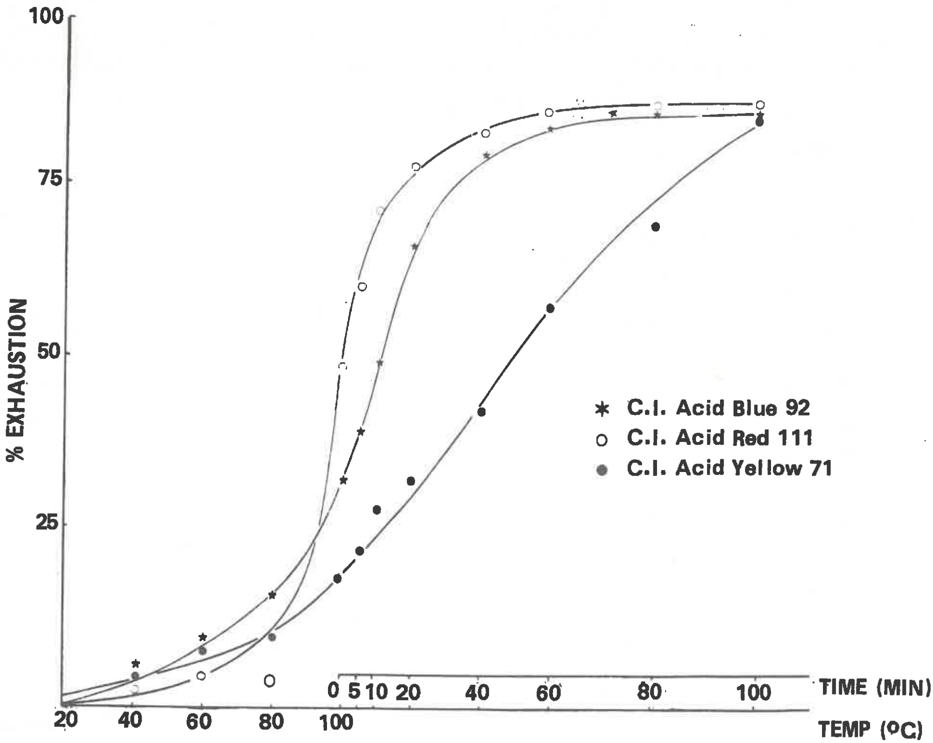

Fig 3 Sorption curves for 3 Acid Milling Dyes

B. The Dyeing of Mohair Below the Boil with Various Recommended Auxiliaries

Having made these observations, the exhaustion characteristics of three acid milling colours were studied. The sorption curves for the three colours are illustrated in Fig 3, where the dyeing temperature was increased to 100°C and the dyeing then continued for 120 min. In Fig 4 the isotherms for the three dyestuffs at 85°C, without auxiliaries, are given. These curves illustrate that at 85°C, the equilibrium exhaustion of C.I. Acid Red 111 was approximately 85 *per cent* after 2 hours, whereas the other two dyestuffs had not reached equilibrium values and the exhaustion may be considered generally poor and uneconomic. To dye at lower temperatures to reduce the extent of yellowing of the mohair to a minimum, one must increase, therefore, the swelling of the fibres and the rate of diffusion of the dyestuff into the fibre to increase the degree of exhaustion to an economic level. On the other hand, the strike should not be so high as to deteriorate the level dyeing properties of the dye. Several auxiliaries to fulfil these

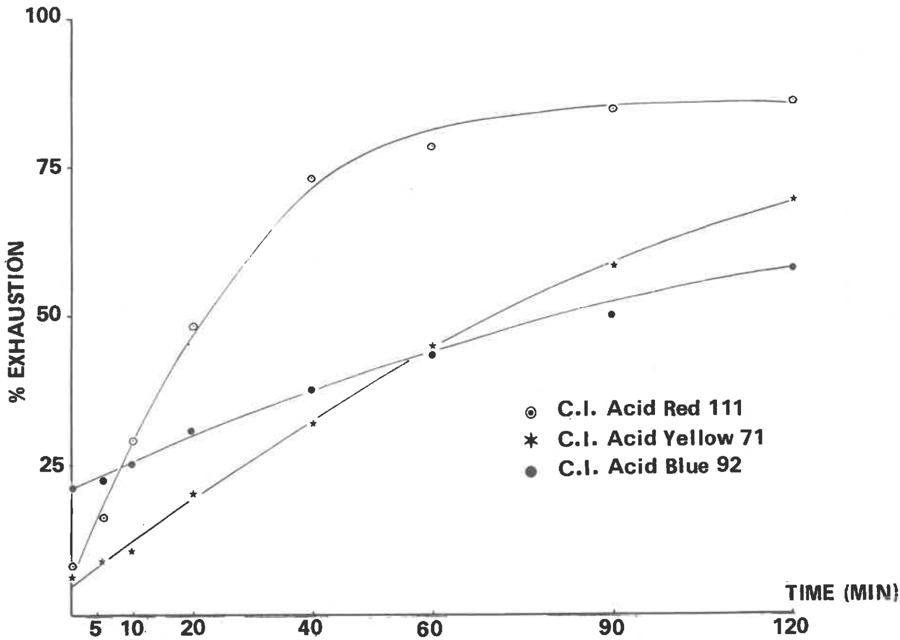

Fig 4 Sorption Isotherms at 85°C for 3 Acid Milling Dyes without Auxiliaries

requirements are at present on the market for application to wool at 80 – 85°C, which is approximately the lowest dyeing temperature which has to be maintained to give adequate exhaustion in the presence of these chemicals under one hour of dyeing in long liquor systems. The kinetic energy of the dye molecules at lower temperatures is not sufficient to allow diffusion of the dye from the dye liquor to the fibre surface and consequently into the fibre. Although temperatures below 80°C are more beneficial for a minimum of fibre damage and yellowing, such temperatures are too low for an economic dye yield. Batchwise exhaustion dyeing systems, therefore, must be replaced by either semi-continuous techniques such as the IWS Pad-batch method, or other continuous and batch techniques involving high concentrations of formic acid, urea, etc. which have been devised for wool [15]. None of these processes, except perhaps the IWS pad-batch system has been developed, as yet, into a commercial reality.

In Figs 5, 6 and 7 the effect of 1,5 *per cent* of auxiliary at pH 6,0 on the exhaustion of the three selected acid colours is shown. The dyeing tempe-

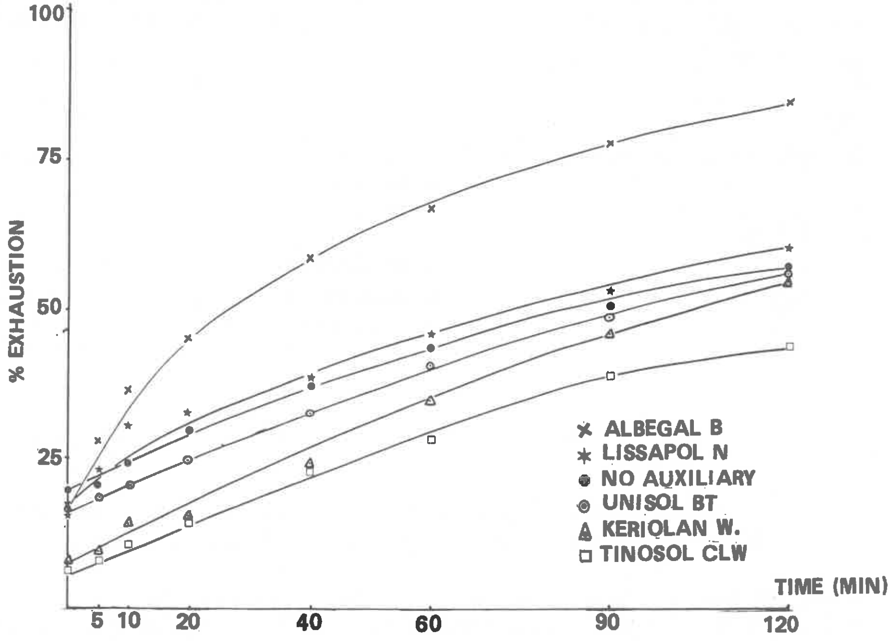

Fig 5 The effect of various dyeing Auxiliaries on the Exhaustion of C.I. Acid Blue 92, on Mohair at 85°C (pH 6,0, 1,5% auxiliary o.m.f.)

rature was maintained at 85°C. It can be seen from the various curves that no set trend could be established, as some auxiliaries tended to increase the exhaustion and others to decrease the exhaustion, depending on the dyestuff. From the overall picture, however, one may assume that Albegal B was the most efficient of the five auxiliary products screened. In all three cases an exhaustion of ± 80 *per cent* was achieved in less than 1½ hours at 85°C. The dyeings all appeared very bright without obviously being detrimental to the lustre. Further experiments carried out indicated that 1,5 – 2,0 *per cent* Albegal B is the optimum amount to be used.

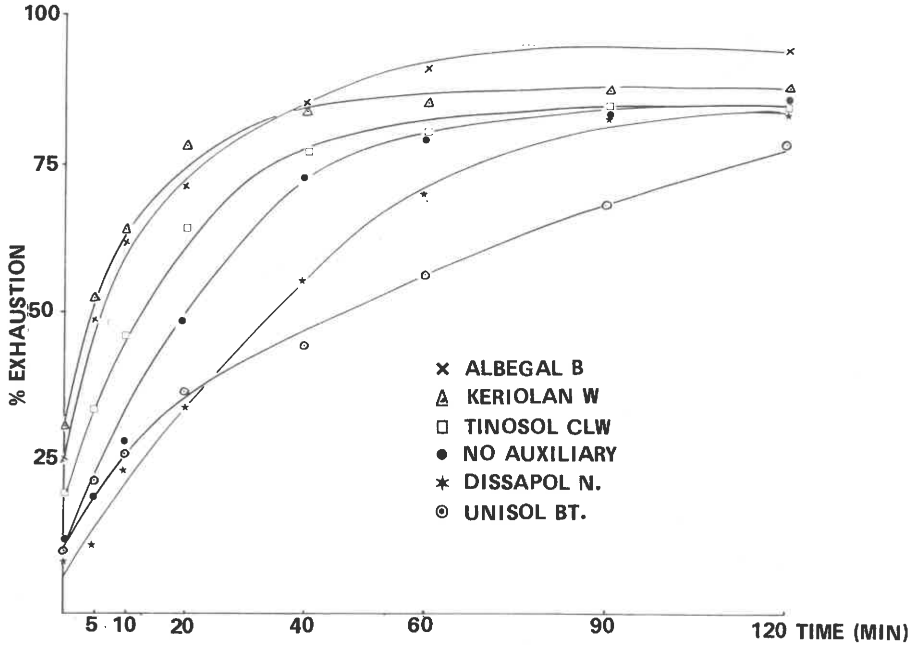

Fig 6 The effect of various Dyeing Auxiliaries on the Exhaustion of C.I. Acid Red 111 on Mohair at 85°C (pH 6,0; 1,5% auxiliary o.m.f.)

Above 2,0 *per cent* o.m.f. the auxiliary starts blocking the dyestuff and thus decreases the equilibrium exhaustion at 85°C. Albegal B being both dyestuff and fibre affinative, obviously caused this phenomenon to become predominant at levels above 2 *per cent* (o.m.f.) to such an extent that economy, i.e. dyestuff yield, suffered considerably.

To reduce the dyeing time to less than 1½ hours, it was decided to decrease the pH of the dye liquor from 6,0 to 4,0. Table II gives the dyebath

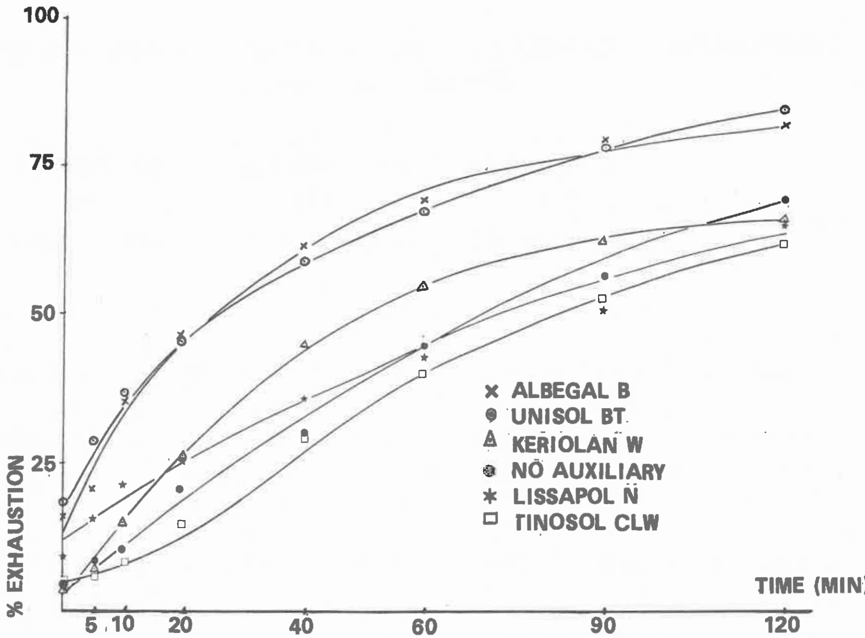

Fig 7 The effect of various Dyeing Auxiliaries on the Exhaustion of C.I. Acid Yellow 71 on Mohair at 85°C (pH 6,0; 1,5% auxiliary o.m.f.)

exhaustion values after 1 hour at 85°C at pH 4,0 and 6,0. Without the auxiliaries, which in this case act as levelling agents, the dyeings would be extremely unlevel due to the high affinity of the acid milling dyes for the mohair at pH-values below 5,0.

It can be seen from the Figures in Table II that, in most cases, the marked differences in the effect of the various auxiliaries on the dyestuff affinity at pH 6,0 was absent when dyeing at pH 4,0. Provided the rate of increase in temperature was sufficiently low (0,5 – 1°C/min), levelness was not found to suffer significantly, and economic degrees of bath exhaustion were obtained with all five auxiliaries. These results agree with those of Hine and McPhee[16] who suggest dyeing wool at 90°C for 30 minutes at pH 4,0 with 1 *per cent* Lissapol N (o.m.f.). The actual choice of method will depend, however, on whether time or energy requirements are the more important to the dyer.

TABLE II

COMPARATIVE EXHAUSTION VALUES AT pH 4,0 AND 6,0 USING VARIOUS AUXILIARIES

AUXILIARY	C.I. ACID RED 111		C.I. ACID BLUE 92		C.I. ACID YELLOW 72	
	pH 4,0	pH 6,0	pH 4,0	pH 6,0	pH 4,0	pH 6,0
Albegal B	70,0	67,5	100,0	91,5	80,9	70,0
Tinosol CLW	96,2	31,0	90,6	82,5	80,9	40,0
Keriolan W	92,8	36,5	90,9	87,5	78,1	55,0
Unisol BT	97,6	41,0	100,0	57,0	79.4	67,5
Lissapol N	92,3	70,0	97,6	45,0	81,4	42,0

(1,5% o.m.f., 2% dye, 3% ammonium acetate, liquor-to-goods 40:1, 1 hour at 85°C)

SUMMARY AND CONCLUSIONS

It was established that the dulling of mohair during long liquor dyeing might partially be due to a yellowing of the fibre which accompanies fibre degradation. Of the three independent dyeing variables, viz. pH, time and temperature, it appears that the latter two factors have the greater effect on the degree of yellowing in long liquor systems. Thus, the shorter the time of dyeing and the lower the temperature of dyeing, the less will be the tendency of the mohair to yellow during the dyeing cycle. It was established subsequently that the pH of an acid milling dyebath could be decreased from pH 6,0 to pH 4,0 and a chemical auxiliary, such as Albegal B or Unisol BT, amongst others, can be used effectively to prevent unlevel dyeings and to increase the dyebath exhaustion at 80 – 85°C. Dyeing at 85°C for 1 hour produced bright dyeings of good colour yield. If unlevel dyeings occur even when using the recommended 1,5 – 2 *per cent* auxiliary at pH 4,0, it is suggested that the dyeing is carried out at pH 6,0 for 60 – 90 min using 1,5 – 2 *per cent* Albegal B as dyebath auxiliary.

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THE USE OF PROPRIETARY NAMES

Various trade names have been used in this publication. This does not imply that other brands are not suitable or even better than those referred to in the text.

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