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The Characterisation of Treated and Dyed Hair

J. T. Guthrie,* A. Kazlauciunas, L. Rongong & S. Rush

The Department of Colour Chemistry and Dyeing, The University of Leeds, Leeds LS2 9JT, UK

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ABSTRACT

Studies have been undertaken to evaluate some of the factors that influence the dyeing of hair with dyes from the Arianor series. Dyed, bleached and untreated hair was examined by differential thermal analysis, optical microscopy, scanning electron microscopy, X-ray diffractometry and surface potential assessment. It has been found that marked changes in surface potentials arise on relatively mild treatment of human hair. Also clear are changes in the accessibility of the hair to dyes on treatment with various cosmetic systems. These changes have a marked influence on the nature of the dyeing process and on the hair/dye composite.

1 INTRODUCTION

The Arianor range of hair colours, manufactured by the Williams Division of Morton Thiokol Limited, may be classified as semi-permanent hair dyes. The Arianors are small, coloured molecules that are basic (or cationic), i.e. they carry a positive charge which is mainly associated with a quaternary ammonium group within the chromophoric systems. It has been suggested that the inherent affinity between hair and the Arianor colours lies in the inter-relationship between the anionic sites on hair and the cationic centres in the dye molecules.

Successful utilisation of a hair dye relies on various factors, many of which relate to questions of accessibility to sites of attachment, and to factors which influence diffusion characteristics. The process of hair coloration can be considered in terms of preferential adsorption and

* To whom correspondence should be addressed.

appreciated by considering those factors which influence preferential adsorption and the events which follow the development of adsorption. Such events could be physical or chemical in nature.

The dyeing of human hair presents various problems. These include:

(i) problems of penetrating the outer sheath of the hair;
(ii) the strong, natural colour of hair (particularly in younger people);
(iii) limitations associated with the requirement that the conditions employed in the dyeing process should be mild;
(iv) the social/psychological aspects of the reason for dyeing hair;
(v) requirements for uniformity of dyeing;
(vi) the condition of the hair;
(vii) the duration/fastness of the hair/dye composite.

Problems in diffusion may be reduced somewhat by use of small dye molecules, by use of swelling agents for hair and use of solvent-assisted processes. Where surface dyeing is the dominant, desired effect, those factors which enhance adsorption and limit diffusion are of significance. In this way, pretreatment of the hair using selected coatings may be of importance.

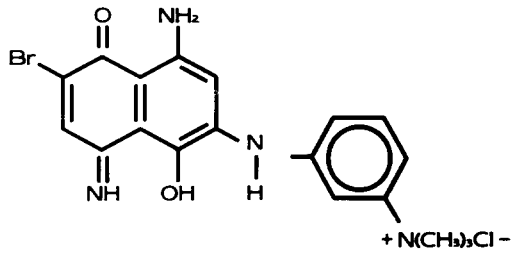
For the purpose of this investigation, evaluations were limited initially to Arianor Steel Blue (CI Basic Blue 99) although some data were verified by considering Arianor Mahogany (CI Basic Brown 16). These Arianor colours are compatible with amphoteric surfactants, nonionic surfactants and cationic surfactants. The dyes are not suitable for use with anionic surfactants because of charge neutralisation which leads to physical instability.

2 EXPERIMENTAL

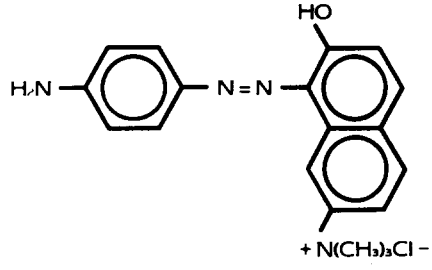
2.1 Reagents

The reagents used in this study were supplied by (or through) the Williams Division of Morton Thiokol Limited, Greville House, Hibernia Road, Hounslow, Middlesex, TW3 3RX, UK. These include:

(i) The Arianor hair colours—306004 Arianor Steel Blue (CI Basic Blue 99, CI 56059) and 306002 Arianor Mahogany (CI Basic Brown 16, CI 12550);
(ii) Gafquat 755N—a quaternised copolymer of vinyl pyrrolidone and dimethylaminoethyl methacrylate ($\bar{M}_w$ = approximately 1000000 g mol^{-1}), supplied as a 20% active solution in water, by GAF, Tilson Road, Roundthorn, Wynthenshawe, Manchester, UK;



Arianor Steel Blue



Arianor Mahogany

(iii) Genamin CTAC—a quaternary alkyl trimethyl ammonium chloride in which the alkyl component is predominantly a C_{16} aliphatic system. This cationic surfactant is supplied as a 29% active solution by Hoechst UK Limited, Stainland Works, Holywell Green, Halifax, UK;

(iv) Empigen OB—this surfactant is based on a mixture of the *n*-lauryl myristyl dimethylamine oxide, and is supplied as a 30% active solution by Albright and Wilson Ltd, Marchon Division, PO Box 15, Whitehaven, Cumbria, UK;

(v) bleaching agent—a commercial system supplied by Clairol (Born Blond) was used as the bleaching medium;

(vi) hair—tresses of untreated caucasian, natural blond hair supplied by the Williams Division of Morton Thiokol Limited were used in the pretreatment and/or the dyeing operations.

All other reagents were supplied by BDH, Poole, Dorset, UK, in analytical quality.

2.2 Experimental procedures

2.2.1 Pre-dyeing treatments

Each hair piece was obtained as a 20 cm long tress. During sample preparation, 3 cm of hair at the tip end was discarded as being

unrepresentative. The tress was then cut into three equal lengths to give swatches of approximately 5·5 cm in length, having a mass of approximately 0·5 g.

The dye solutions were designed to provide strengths of 0·5% (w/w) of dye in the aqueous solution. Deionised water was used as the starting point in solution formulation. The pH of the dye solution was adjusted to pH 7 using standard buffers. At the pH of unbuffered solution (pH 3·0), considerable damage was found to develop in the hair during the coloration process. Hence, buffering was shown to be a requirement during preliminary experimentation.

2.2.2 Dyeing procedures

Dyeings were carried out using sealable, plastic-capped sample vials. These were heated in a water-bath (40 ± 0·1°C) under conditions in which the hair swatches were immersed in 20 cm^3 of liquid which contained an excess of dye, together with the surfactant/finishing aid. Unless otherwise stated, dyeings were carried out over 20 min. Controls were used at each stage to monitor any changes arising as a result of the presence of each component of the total system. All treated swatches were suspended and carefully dried using a domestic hair drier. The hair swatches were free to move in the warm air-stream.

Coloured styling products were presented (in gel/mousse form) by a 7·5% (w/w) solution of Gafquat 755N. Colouring rinses and conditioners were represented by a 4% (w/w) solution of Genamin CTAC. Colouring shampoos were represented by a 14% (w/w) solution of Empigen OB. The dye concentration was maintained at the 0·5% (w/w) level (with or without additives), in an excess dye-availability mode. Table 1 lists the options assessed in both dyeing and hair treatment operations. Also included in Table 1 are the experimental techniques used in attempts at characterising the hair/dye and hair/additive composites.

2.2.3 Bleaching procedures

The bleaching system 'Born Blond' by Clairol is a hydrogen peroxide-based formulation. The bleaching system was applied according to a well documented protocol. All bleachings were carried out at 18°C (indicative of room temperature).

2.2.4 Assessment method

The methods of assessment of the bleached hair are based mainly on scanning electron microscopy and surface potential measurements.

TABLE 1
Hair Coloration Systems Evaluated

Hair sample	*Assessment methods*			
	Reflectance spectroscopy	*SEM*	*XRD*	*DSC*
Untreated	*	*	*	*
Wetted	*	*	*	
4% Genamin treated	*	*		
Dyed with Steel Blue	*	*	*	*
Dyed with Steel Blue + 4% Genamin	*	*		*
Dyed with Mahogany	*	*		
Dyed with Mahogany + 4% Genamin				
7·5% Gafquat treated	*	*	*	
Dyed with Steel Blue + 7·5% Gafquat	*	*	*	
Dyed with Mahogany + 7·5% Gafquat	*	*	*	
14% Empigen OB treated	*	*		
Dyed with Steel Blue + 14% Empigen OB	*	*		
Dyed with Mahogany + 14% Empigen OB	*	*		

2.2.4.1 Differential scanning calorimetry. Samples (2 mg) of the undyed hair and dyed hair were heated at 10°C min^{-1}. The thermal profile of the samples was assessed over a range of temperatures from 18 to 320°C in a nitrogen environment. The nitrogen flow rate (0·2 dm^3 min^{-1}) was designed to reduce oxidative decomposition reactions and to ensure effective removal of gaseous decomposition products.

2.2.4.2 Optical microscopy of hair cross-sections. Cross-sections of selected hair samples were obtained using a microtome assembly. Prior to examination, the hair was embedded in a solution containing cellulose nitrate and acetone. The acetone was carefully removed by evaporation. A Vickers optical microscope, equipped with conventional photographic capabilities and video-recording facilities was used in the microscopic examinations. Micrographs of representative zones of relevant hair samples were taken as required. Some emphasis was placed on the use of this technique to assess the influences of additives and bleaching conditions on dye penetration.

2.2.4.3 X-Ray diffraction studies. A Siemens X-ray diffractometer was used in attempts to evaluate any developments towards order in the dyed hair samples. Assessments were carried out on:

(i) undyed hair;
(ii) hair which had been pre-wetted for 24 h in deionised water and carefully air dried;
(iii) hair which had been previously dyed with Arianor Steel Blue under the aforementioned conditions;
(iv) hair dyed with Arianor Steel Blue in 4% (w/w) Genamin;
(v) hair which was wetted with a 7·5% (w/w) Gafquat solution before careful air drying;
(vi) hair which had been dyed with Arianor Steel Blue in 7·5% (w/w) Gafquat solution before careful air drying.

The treated samples were mounted on a pre-designed frame and presented to the X-ray source vertically.

2.2.4.4 Spectroscopic evaluations. Calibration procedures for all relevant analyses were established prior to assessments of dyeing procedures, residual dye analysis and wash-rinse out phenomena. Emphasis was placed on Arianor Steel Blue in this section of the global study. Measurements were made on a Perkin-Elmer SP200 spectrophotometer.

In a typical evaluation, each swatch of hair was dyed under predetermined conditions, after specific pretreatment had been carried out as required. Dyeing took place over 20 min before samples were removed, freed from excess dye solution and carfully air-dried. All residual liquors were collected in such a way as to ensure their accurate analytical evaluation for dye content.

The normalised solutions were then subjected to quantitative spectroscopic analysis. The procedures were repeated to establish the levels of reproducibility of data.

2.2.4.5 Reflectance spectroscopic evaluations. The spectral reflectance characteristics of dyed and treated hair samples were monitored to provide an indication, if possible, of the amount of dye located on the surface of the hair fibres. Thus, swatches of treated hair, dyed hair, treated–dyed hair and unmodified hair were taped to standard white card. The hairs were assembled in such a way that the fibres were aligned and maximum overall smoothness ensured.

Measurements were taken on a Macbeth Colour Eye (an abridged spectrophotometer) over 16 wavelengths. The data were software processed and printed in a standardised format. The measurement conditions were

such that small aperture viewing was used with a 10° observer angle, under illuminant D (artificial daylight, black body temperature 6504 K) and illuminant A (tungsten light, 2856 K). Spectral reflectance was included in measurements in attempts to compensate for the orientation of the hair. Reproducibility of data was assessed by carrying out each dyeing, treatment and assessment four times.

2.2.4.6 Scanning electron microscopic evaluation (SEM). Scanning electron microscopy was used to assess visually the effect of the various treatments on the condition of the hair. Untreated hair was also examined. The pretreatment conditions were outlined earlier.

Samples of hair (untreated, treated, dyed, treated–dyed) were securely fixed to metal stubs using double sided contact adhesive tape. The samples were then vacuum sputter coated with gold to a depth of 30 nm. Examinations were also carried out on the initial dye, after purification of the dye by membrane filtration and controlled solution.

SEM examinations were also performed on samples of hair which had been subjected to standardised, controlled bleaching.

2.2.4.7 Measurement of surface potentials. Streaming potential measurements were carried out on untreated hair and hair which had been previously treated in various ways and dried under controlled conditions. The cell assembly was that developed by Iyer and Jayaram,[1] and modified by Hao,[2] and consists of the cell housing containing two Ag/AgCl electrodes permanently fixed to ground-glass cones. The cell was linked to a microprocessor ionalyser (Orion Research, Model 901) for measurements of potentials. Conductance measurements were carried out on a standard conductivity meter.

The samples examined were:

(i) untreated hair;
(ii) bleached hair where bleaching was carried out for different times at a constant temperature (18°C);
(iii) hair which had been bleached at higher temperatures;
(iv) dyed hair;
(v) bleached and dried hair;
(vi) hair which had been previously treated with the three application additions, Gafquat 755N, Genamin CTAC and Empigen OB.

For measurement, each hair sample was chopped into 0·5 cm lengths and then soaked in a 10^{-3}-potassium chloride solution (24 h). Care was taken to avoid physical skin contact or other contamination of the hair during its preparation for assessment.

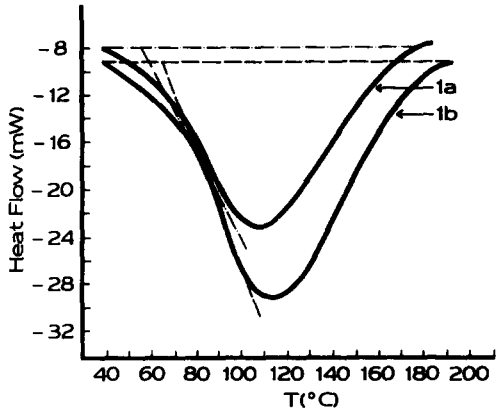


Fig. 1. Differential scanning calorimetric evaluation of (a) undyed hair and (b) hair dyed with Arianor Steel Blue.

3 RESULTS AND DISCUSSION

3.1 Differential scanning calorimetry

Differential scanning calorimetry was used on undyed hair and hair which had been dyed with Arianor Steel Blue for 24 h under ambient conditions. Figure 1 gives the thermographs for two typical situations: 1(a) from undyed hair and 1(b) for the corresponding dyed hair. Endotherms associated with the removal of loosely bound water in the region of 100°C are shown, and it can be seen that decomposition of the hair begins to be significant in the region from 160°C. Since the concentration of dye in the hair/dye composite is invariably very low, no changes associated directly with the dye are detectable by differential scanning calorimetry. However, the indirect consequences are clear.

It was generally observed that the dyed hair has a greater tendency to absorb water/moisture than the undyed hair (cf. Fig. 1(b) with Fig. 1(a)). It is also apparent that the dyed hair has a significantly greater tendency to bind this absorbed water more tightly. This is seen in the values of the desorption energy (J g^{-1} of hair/dye composite) and also in the temperature at which the endothermic minimum arises (111°C relative to 104°C for dyed and undyed hair, respectively).

3.2 Optical microscopy of hair cross-sections

It is clear from studies of Fig. 2 that the hair is ring-dyed. This was a general observation. Penetration occurs only near the surface of the hair

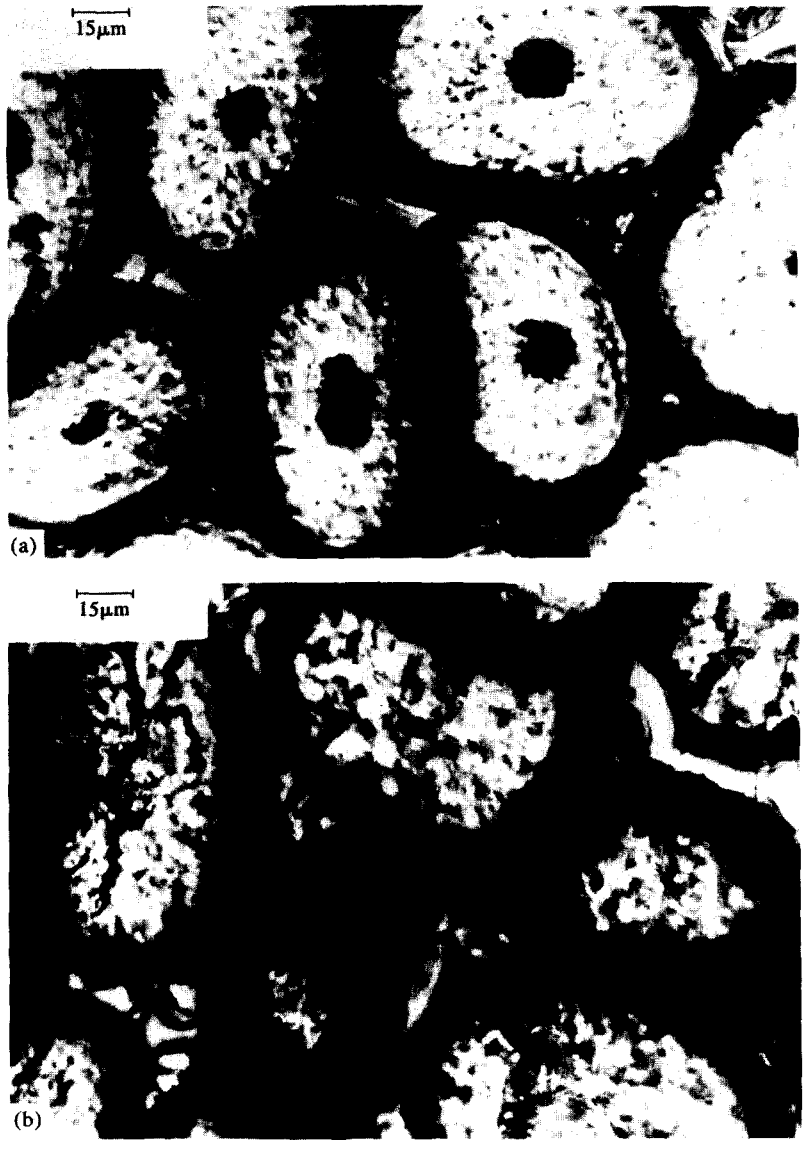


Fig. 2. Optical micrographs of (a) dyed untreated hair and (b) bleached/dyed hair.

and penetration through the fibre does not arise. The extent of ring-dye formation varies depending on the nature of the pretreatment given to the hair. Some hair samples, notably those dyed in the presence of Gafquat 755N, show dye build-up around the fibre, whereas others (especially the bleached–dyed samples), possess thicker rings with more penetration into the hair.

Those treatments which damaged the hair, or made the hair more penetrable with damage, did indeed allow much greater penetration of the dye. Conversely, treatments based on the coating of the hair fibre surface were effective in that they increased the resistance of the hair to penetration. In relatively isolated instances, some dye penetration occurred through fissures in the cuticle of the hair.

Examples of the various cross-sections observed are shown in Figs 2(a) and 2(b). Figure 2(a) relates to the dyeing of untreated hair under the standard conditions outlined earlier. A 40× magnification was employed in the microscopy. Figure 2(b) relates to hair (the same type as that used in 2(a)) which had been bleached at 30°C in the commercial bleaching system for 2 h before dyeing in the standard manner (magnification ×40).

3.3 X-Ray diffraction studies

X-Ray diffraction patterns were taken of untreated hair and of hair treated in each of the dyeing processes outlined earlier. All the diffraction patterns were similar, showing two broad peaks, one at a rotation angle of approximately 10° and the other centred on approximately 20°. It is possible that the dyed hair samples have the dye present in a very finely dispersed form and hence are incapable of resolution by the procedures used in this study. A typical example is given in Figs 3(a) and 3(b) which relate to undyed hair measured at $\Gamma = 2$ s and resolution $4 \times 10^2\ \rho\ s^{-1}$, and undyed hair measured at $\Gamma = 1$ s and resolution $1 \times 10^3\ \rho\ s^{-1}$, respectively.

Wetting the undyed hair with Gafquat (7·5% w/w) at pH 7·0, for 20 min at 40°C, before careful air drying, provides samples which give the diffraction behaviour indicated by Fig. 3(c). It is clear that such pretreatment causes the hair to be significantly more disordered, indicating that the coating agent fulfils its purpose by providing a smoother, amorphous surface to the hair than would otherwise be the case. Gafquat is a copolymer, designed to provide binding protection to hair.

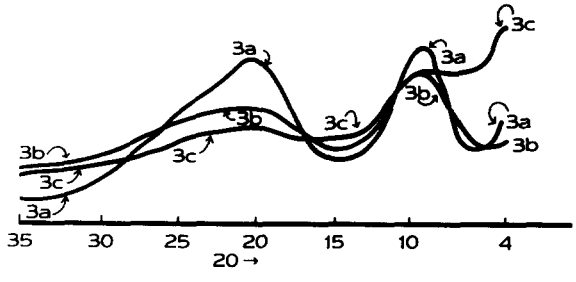


Fig. 3. X-Ray crystallographic representations of (a and b) undyed hair and (c) Gafquat-treated undyed hair. Conditions are as given in the text.

The diffuseness of the diffraction pattern makes it unsafe to attempt quantitative treatments of acquired data.

3.4 Spectral reflectance assessments

The spectral reflectance character of various samples was used as a guide to the effects of the dye and the application medium on the colour characteristics of the hair. To ensure that any change in the reflectance of the samples after treatment was not simply due to non-uniformity of the hair and the hair sample preparation assembly, duplicate assessments were provided. In addition, samples of hair dyed with two representative dyes were examined. The level of reproducibility was excellent. Any differences arising from variations in sample preparation were negligible when compared with those arising from the treatment given to the hair.

The colour differences were assessed using CIE, $L^*a^*b^*$ colour space. The Macbeth measurement system provides values of L^*, a^* and b^* for each sample which, in turn, are calculated from the reflectance spectrum. The measurement is of colour in isolation, unaffected by the background.

Table 2 provides spectral reflectance data for hair dyed with Arianor Steel Blue (0·5% dyeing) under standard conditions. Also given are the corresponding data for hair dyeing in the presence of Genamin CTAC, Gafquat 755N and Empigen OB, respectively. Data for Arianor Mahogany are also given for comparison purposes.

Table 2 shows an increase in the lightness of samples and also general increase in blueness, with various treatments. Gafquat dyed and treated hair, however, remains similar to the standard, dyed hair.

TABLE 2
Spectral Reflectance Data for Dyed Hair Samples

Arianor Steel Blue System				
	Standard 0·5% dye	*Genamin CTAC (4%) +0·5% dye*	*Gafquat 755 (7·5%) +0·5% dye*	*Empigen OB (14%) +0·5% dye*
L^*	22·33	35·09	22·7	23·92
a^*	−0·2	−6·9	−0·91	−4·9
b^*	−8·13	−10·69	−8·23	−11·93
Arianor Mahogany System				
	Standard 0·5% dye	*Genamin CTAC (4%) +0·5% dye*		
L^*	26·50	28·77		
a^*	8·76	19·69		
b^*	9·63	17·67		

The two surfactants, Genamin CTAC and Empigen OB, are intended for use in conditioner or shampoo colouring products. Gafquat 755N is designed as a styling product, remaining on the surface of the hair as a relatively hydrophilic coating. Thus, it is not surprising that dyeing is much less pronounced in the presence of the Gafquat.

There is an indication that the two surfactants increase the penetration of dye into the hair, less being left on the surface to absorb light. Thus, the lightness of the hair increases even when increased dye uptake occurs. The styling product, Gafquat, traps dye at the surface. Penetration of dye, therefore, is not a feature. Hence, the Gafquat treated hair behaves in a similar manner to the untreated, dyed hair.

The penetration of the Arianor Mahogany dye into the hair is enhanced by the use of the surfactant, as expected.

3.5 Scanning electron microscopy

This technique was used to examine the surface of hair fibres after they had been subjected to various specified treatments. Figure 4 indicates features of interest relevant to changes brought about on treatment of the hair.

The untreated, undyed hair (Fig. 4(a)) and the Arianor Steel Blue pure dye (Fig. 4(b)) were examined in order to provide a standard for comparison. The cuticle nature of the surface of the hair is seen and the fibre diameter easily appreciated. The dyes are seen as an assembly of aggregates, likely to form clusters. Figure 4(c) shows that control over the pH of dyebaths is an important factor in the avoidance of hair damage. The damage caused by treatment at pH 3 (the ambient pH of the unbuffered dye solution) is clearly seen in terms of breaking away of material from the surface. The resultant dyeing at pH 7 (Fig. 4(d)) shows the dye to be deposited as relatively well organised species on the surface, with evidence of significant disaggregation of the dye (Arianor Steel Blue).

Treatments given to the hair give the effects shown in Figs 4(e) to 4(g). The general appearance is one of increased contrast at cuticle edges, indicating perhaps the development of cuticle 'lifting' as a precursor to swelling (Figs 4(e) and 4(f)). Such contrast and lifting is not seen in Fig. 4(g), probably because the fibres carry the copolymer coating, 'styling' agent, Gafquat, which inhibits penetration.

Treated dyed samples are represented in Figs 4(h) to 4(m). In the absence of the wetting agent (Figs 4(h) and 4(j)), and in the presence of Gafquat (Fig. 4(m)), significant amounts of dye are seen on the surface of the fibres. Treatment with Genamin or Empigen allows greater diffusion of the dye into the hair fibre (Figs 4(i), 4(k) and 4(l)). This applies to both the

Arianor Steel Blue and the Arianor Mahogany. In addition, remnants of heterogeneously attached copolymer coatings are clearly seen in Fig. 4(m).

The consequences of bleaching the hair are shown in the micrographs depicted as in Figs 4(n) to 4(r). Such damage varies in magnitude and includes significant cuticle lifting, scalar damage and pronounced fissures or cracks which run across the orientation of the hair fibre (Fig. 4(n)) as

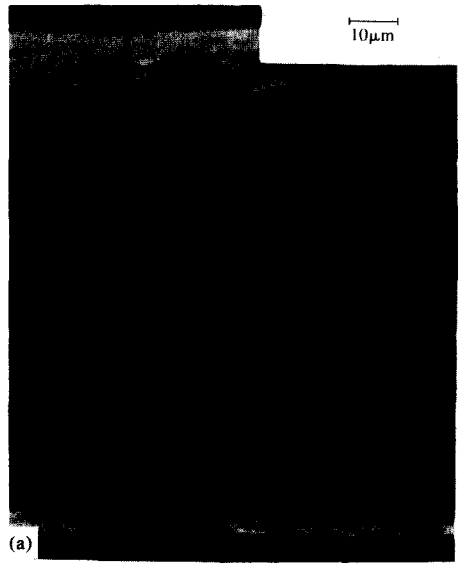


Fig. 4. Scanning electron micrographic representations of hair: (a) untreated hair, magnification 1×10^3; (b) Arianor Steel Blue (CI Basic Blue 99), solid dye, magnification 1×10^3; (c) dyed hair, pH 3 (ambient pH of dye solution), room temperature, magnification 2×10^3; (d) Arianor Steel Blue, pH 7, 1 h, particulate dye on surface, magnification 1×10^3; (e) hair wetted with Empigen OB (14%), pH 7·0, 40°C, 20 min, magnification 1×10^3; (f) hair wetted with Genamin, pH 7·0, 40°C, 20 min, magnification 1×10^3; (g) hair treated with Gafquat 755, pH 7·0, 40°C, 20 min, magnification 5×10^2; (h) Arianor Mahogany, no surfactant, pH 7·0, 40°C, 20 min, magnification 1×10^3; (i) Arianor Mahogany, Genamin treated, pH 7·0, 40°C, 20 min, magnification 1×10^3; (j) Arianor Steel Blue, no surfactant, pH 7·0, 40°C, 20 min, magnification 1×10^3; (k) Arianor Steel Blue, Genamin treated, pH 7·0, 40°C, magnification 1×10^3; (l) Arianor Steel Blue, Empigen OB treated, pH 7·0, 40°C, magnification 1×10^3; (m) Arianor Steel Blue, Gafquat 755 treated, pH 7·0, 40°C, magnification 1×10^3; (n) hair bleached for 135 min, standard bleaching treatment, magnification 1×10^3; (p) hair sample bleached twice, each time for 135 min, standard bleaching treatment, magnification 1×10^3; (q) hair bleached for 135 min, standard bleaching conditions, then dyed with Arianor Steel Blue, magnification 1×10^3; (r) hair bleached twice, each time for 135 min, standard bleaching conditions, dyed with Arianor Steel Blue, magnification 1×10^3.

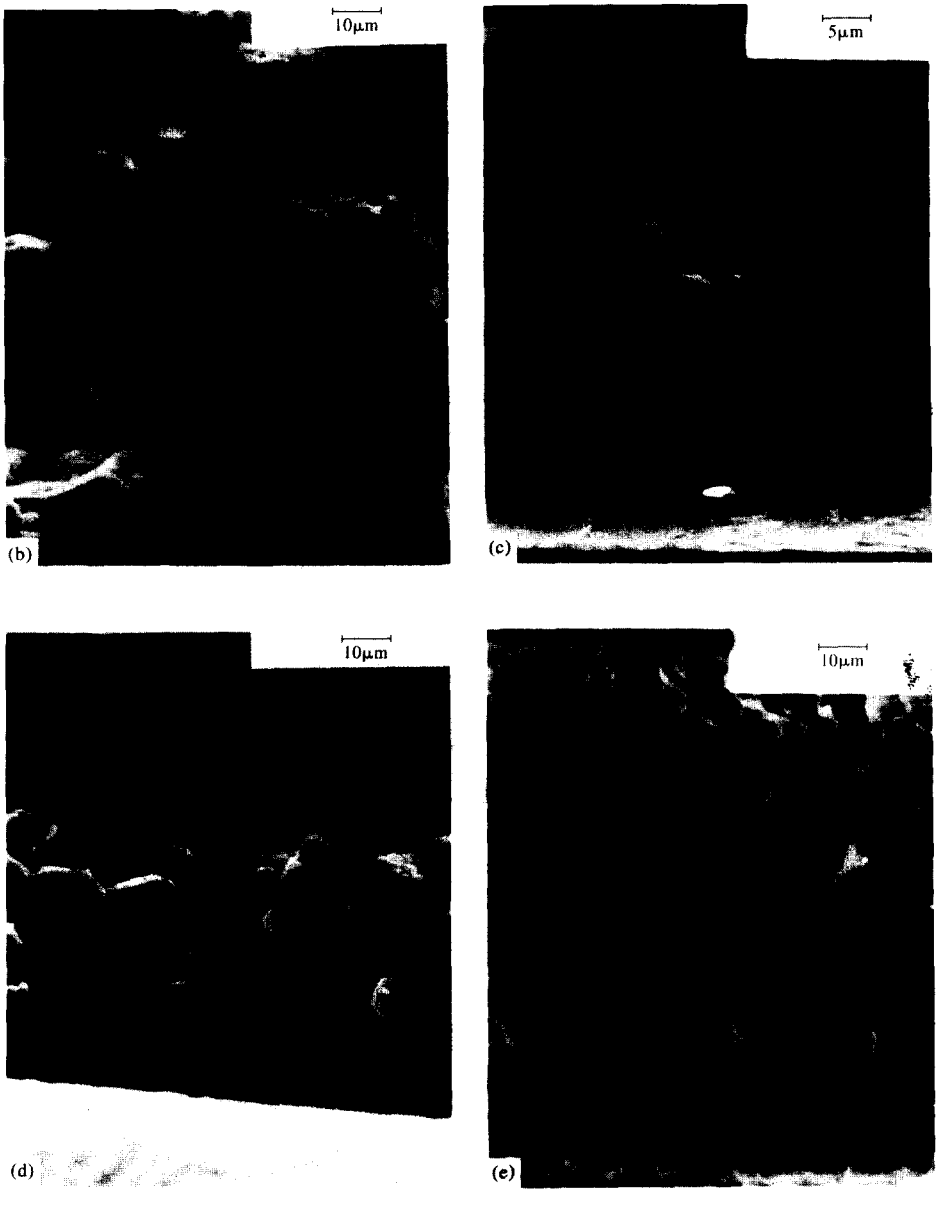
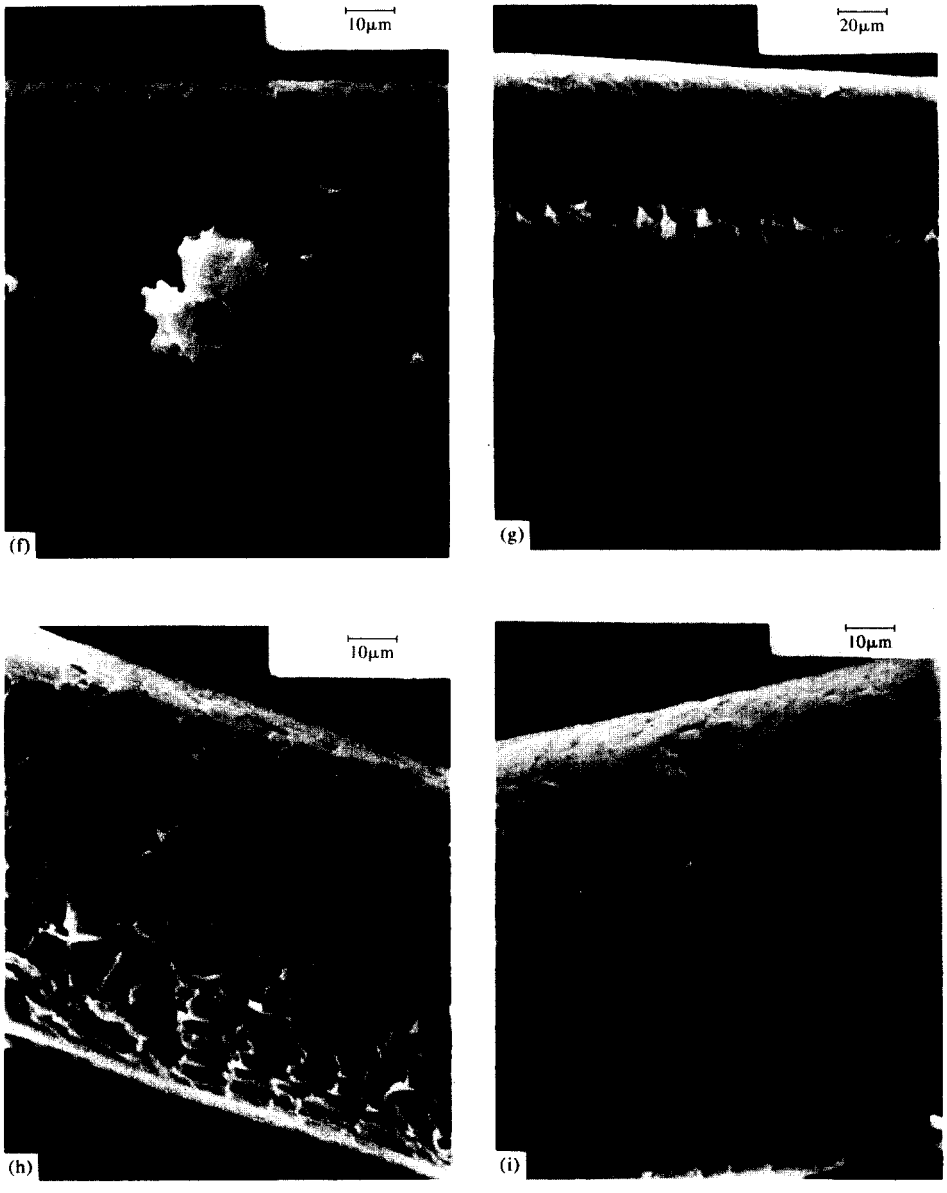


Fig. 4.—*contd.*



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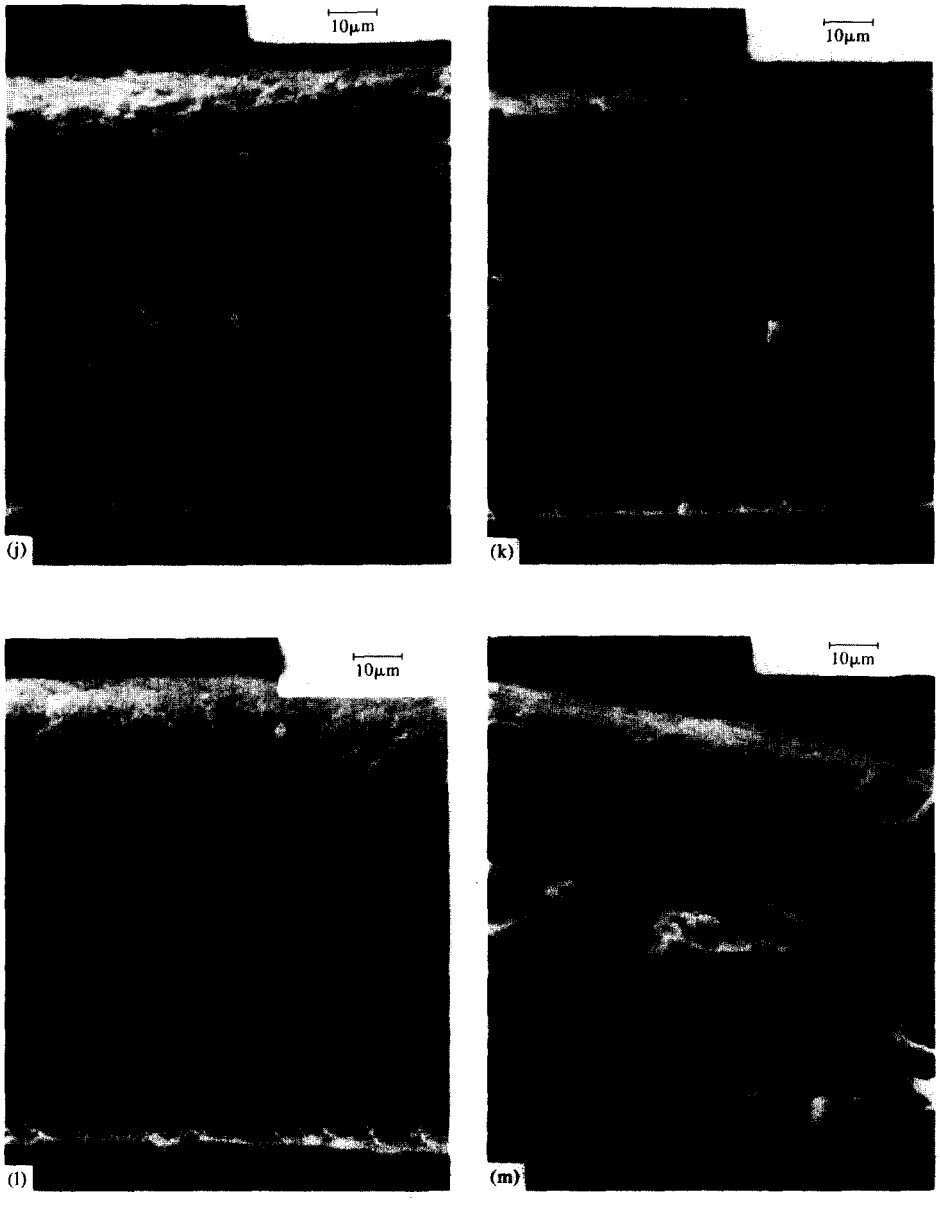

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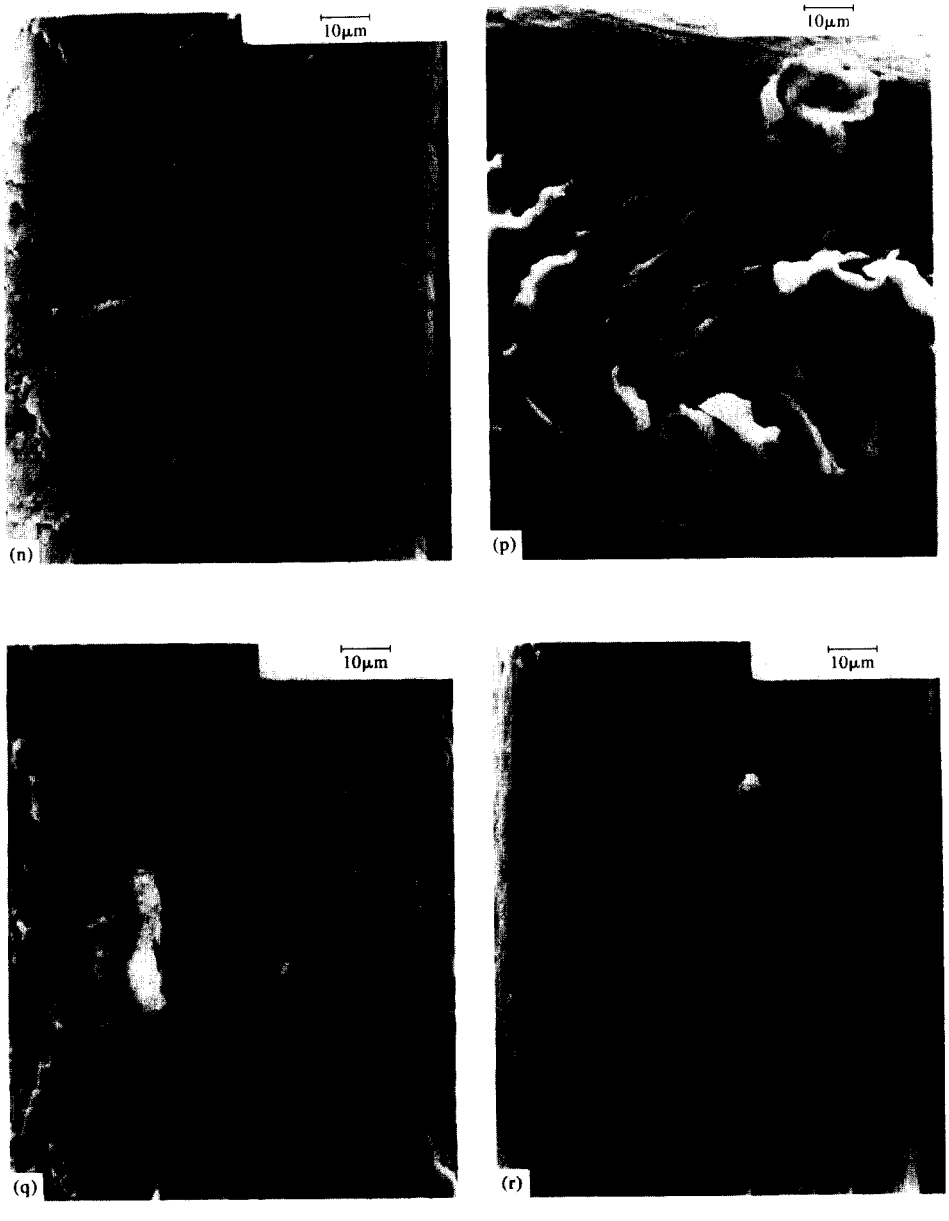

Fig. 4.—*contd.*

well as fissures which follow the orientation of the hair fibre (Fig. 4(p)). Extended bleaching causes greater damage than single bleaching (Fig. 4(q)).

There is some evidence that dyeing the bleached hair begins to repair the damage caused by bleaching (Fig. 4(r)). However, much more work is needed to establish this point.

3.6 Characterisation through streaming potential measurements

The surface charge of hair plays an important part in the success or otherwise of the coloration of the hair. It also influences the coloration protocol needed to achieve effectiveness.[3] This is true for all hair dyeing processes, whether they be dependent on adsorption phenomena or diffusion processes.[4] Adsorption is a prerequisite of diffusion. Controlled adsorption is of great significance to 'homogeneous' diffusion as seen in uniformity of coloration. It should be recognised that hair is a non-conductor in any significant sense. However, in theory, the surface charge properties of hair can be assessed indirectly through streaming potential measurements utilising double layer phenomena by creating a potential at the surface of shear, the zeta potential.

During measurement, each hair in the plug of hair fibres has a surface charge, and hence a double layer can be established. When the stream of electrolyte flows through the plug, a current is set up and a potential difference generated between the two ends of the plug. This potential was measured. Values obtained were then related to the condition of the hair used to provide the plug. Such treatments included the wetting, dyeing and bleaching programmes outlined earlier.

Owing to different degrees of packing in assembling the plugs of hair for assessment, variations in cell length arise. Hence, account of this is taken when establishing the constant of the streaming cell.

Table 3 contains data obtained from streaming potential measurements carried out on hair which had been previously bleached for various lengths of time, rinsed thoroughly and assembled in the cell. Table 3 also contains details of the conductance associated with the plug/electrolyte, the cell constant, the ratio of the potential to electrolyte pressure and the calculated value of the zeta potential.

The expression used to calculate the zeta potential is that proposed by Hao[2] who recognised that: (i) the plug used in such measurements is compressible and influenced by the electrolyte pressure; (ii) the flow of liquid past the fibres must not be turbulent; and (iii) the fibres must have no surface conductance. The last point is catered for by measuring the cell constant with a higher concentration of electrolyte. This compresses the double layer to nearly zero by providing enough opposite charges.

TABLE 3
Streaming Potential Measurement—Effect of Time of Bleaching

Air sample	*1/Conductance (10^6 mho)*[a]	*Streaming cell constant, C (cm^{-1})*[b]	*E/P ($mV\ cm^{-1}\ Hg^{-1}$)*[c]	*Zeta potential of hair (10^{-2} mV)*
Untreated	277·0	7·38	0·45	−0·88
Bleached for 45 min	46·9	6·56	2·05	−0·60
Bleached for 60 min	57·9	6·94	1·93	−0·74
Bleached for 90 min	76·0	7·38	1·68	−0·90
Bleached for 120 min	75·2	9·83	1·33	−0·94
Bleached for 135 min	69·2	9·08	1·20	−0·72

[a] Conductance of sample plug with experimental solution.
[b] Streaming cell constant, $C = K/L$ where K is specific conductivity of 0·1 M KCl and L is the conductance of the sample plug with 0·1 M KCl.
[c] The slope of the E/P relationship (linear). E is the measured streaming potential and P is the applied pressure.

The equation used in the current study takes the form:

$$\varepsilon = 9{\cdot}564 \times 10^4 \times E/Px\ C/R$$

where ε is the zeta potential, E is the streaming potential (mV), P is the electrolyte pressure (cm Hg), C is the cell constant (cm^{-1}) and R is the conductance (mho).

It is clear from Table 3 that bleaching has a marked effect on the zeta potential of the hair. The variation observed in the zeta potential, when the time allocated for bleaching is changed, shows that the situation is not straightforward. A hydrogen peroxide based bleaching system was used and bleachings were carried out at 18°C.

Neale and Peters[5] have shown that all fibres exhibit a negative electric charge on their surface in neutral media. In hair, the fibres could acquire this negative charge by dissociation of a proton, by ionisation of an acidic group, by the adsorption or anchoring of suitable anions, or simply by the acquisition of electrons from liquid water. Since wool fibres contain ionisable groups, the negative charge shown in the present study could be interpreted as arising from the ionisation of the carboxylic acid groups in the hair fibre surface.

Table 3 shows that oxidation of the hair fibres, generated by bleaching, leads to an initial significant reduction in the number of negatively charged centres. After this reduction, there is a gradual continuous increase in the value of the zeta potential until a maximum value is achieved. This suggests that complex oxidation processes are involved. Explanation of these phenomena would require further evaluations.

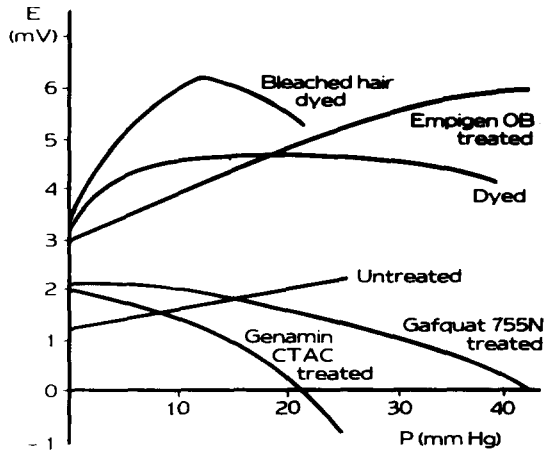

Fig. 5. Variation in streaming potential with variation in applied pressure, showing effects of different treatments on response at constant time.

Figure 5 graphs the effects of certain treatments on the variations of the streaming potentials with variations in applied pressure. This may be compared with the linear relationship observed for measurements on untreated and bleached hair (Fig. 5). Each of the treatments, dyeing, wetting and surface coating, leads to pronounced non-linearity: dyed hair produces maxima; the Empigen OB treated hair gives a continuously increasing *E/P* relationship; and when hair is treated with either Genamin CTAC or Gafquat 755N, both cationic materials, continuous decreases in the streaming potential are produced on increasing the pressure of electrolyte flow. It should also be noted that the various treatments produce hair

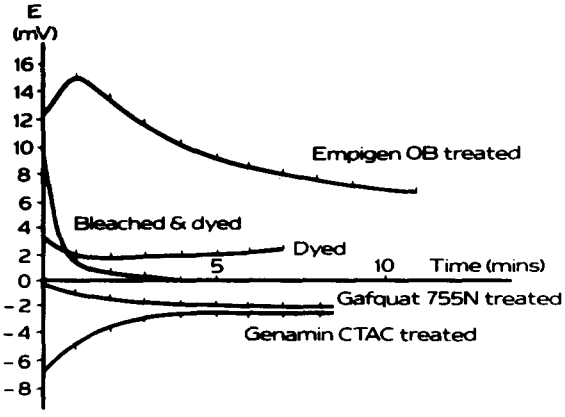

Fig. 6. Variation in streaming potential with time at constant pressure, showing effects of different treatments on the ε response.

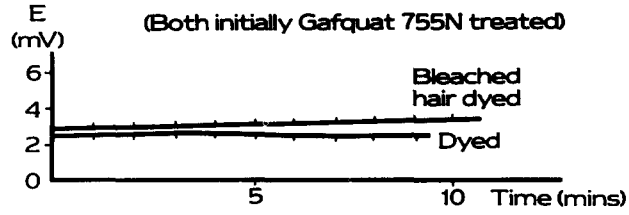

Fig. 7. Variation in streaming potential with time at constant pressure for Gafquat 755N treated hair followed by removal of excess coating.

which gives different values even at zero streaming pressures. Thus, the treated samples are different in their capacity for change, in their accessibility and in their inclination towards adsorption phenomena.

Figure 6 shows the changes in streaming potential with time at a constant streaming pressure, for various samples of treated hair. The data clearly show that the processing time is a vital feature of hair modification and that the optimum time varies from one treatment to another. If predictability of behaviour is a requirement, then the treatment time should be that indicated by the plateau region for each treatment.

Figure 7 gives information relating to dyed hair and bleached, dyed hair samples which were initially treated with Gafquat 755N. The coating was then removed by thorough washing and the samples carefully air dried. The streaming potential measurements were then carried out at constant pressure over 10 min. The distinct stability of streaming potential values is clearly seen.

4 CONCLUSIONS

The wetting of hair with various wetting agents produces swelling of unmodified hair and causes it to be more amenable to both physical and chemical changes. This is indicated by differences in the thermal characteristics of modified hair and in the extent of order in the surface of modified hair. Cross-sections of dyed hair, when examined by optical microscopy, provide a picture of ring-dyed fibres. However, in addition to penetration, scanning electron micrographic analysis shows that considerable amounts of dye remain deposited on the surface of the hair. Bleached hair shows greater tendencies towards penetration, as does pre-wetted hair.

Hair treated with styling formulations (Gafquat 755N) shows increased resistance to dyeing, as might be anticipated. The wetting treatments Empigen OB and Genamin CTAC give increased lightness to the hair, suggesting a significant degree of penetration and supporting the observations made in the microscopic analyses.

There is no doubt that bleaching conditions bring about marked changes to the hair and hence to the consequences of subsequent treatment of the hair. Also, reductions in pH bring about considerable damage to the hair during dyeing processes. The influence of bleaching on dyeing with Arianor Steel Blue is complex. Bleaching has been shown to reduce the zeta potential of the hair markedly, especially at shorter bleaching times. Prolonged bleaching gives zeta potentials which are equal to, or greater than, those of unmodified hair. However, bleaching clearly increases the degree of dye uptake even at short bleaching times.

It is important to note that at least two processes operate as a consequence of bleaching. Bleaching is seen to cause the hair to be much more accessible, as seen by dye uptake studies. However, the zeta potential measurements indicate that the binding between the Arianor dye series and the bleached hair will be weaker.

The surface potential measurements of treated (wetted and coated) hair (dyed and undyed) yield data which suggest that the dyeing processes are complex and likely to prove difficult to rationalise in any unambiguous sense. The reduction observed with Genamin CTAC and Gafquat 755N, both cationic materials, suggests that the number of available negative sites is reduced due to competition. Conversely, with Empigen OB, a non-ionic material, the number of negative sites increases. The traces obtained for the cationic Arianors suggest that initially the dyeing process may not involve charge association, but may be due to penetration.

The dyeing process is a complex dynamic system. Successful dyeing requires that the many variables involved be controlled as accurately as possible. Raw materials, pH conditions and dyeing times should be carefully selected and dyeing protocols adhered to. Deviations are likely to result in unsuccessful dyeings and non-uniform results.

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