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A REVIEW OF THE CHROME MORDANT DYEING OF WOOL WITH SPECIAL REFERENCE TO THE AFTERCHROME PROCESS

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INTRODUCTION

THE CHROME MORDANT DYEING OF WOOL — AN AGE-OLD TECHNIQUE

The Classical Age of the Greeks and the Romans saw the introduction of metal salts like ferrous sulphate and alum for use as mordants in the dyeing of fabric[1]. The sphere of influence of these two great Empires extended even to the remote districts of Western China where the technique still survives today[2]. The use of salts of other metals like lead, tin, copper, nickel, zinc, antimony, aluminium and bismuth as mordants, however, only became evident over the last three to four hundred years. England and Holland in the sixteenth century saw the introduction of tin salts as mordants to produce a bright scarlet with Cochineal[1]. It was two hundred years later, however, in 1824 when reference was again made to the use of metal salts, this time as mordants for Logwood[3]. In 1887, Kostanecki[4] first used the term "Mordant Dyestuffs" when referring to the use of aluminium and iron mordants which combined with the dye to form coloured complexes or "lakes". Until about the middle of the nineteenth century, iron and tin salts were the most popular mordants for wool, after which they were steadily displaced by chromium[5,6] which is now used almost exclusively.

CHAPTER 1

THE CHROME AZO DYE AND ITS APPLICATION TO WOOL

In general, dye molecules may be described as complex aromatic structures with extended π-electron systems, polar substituents and water solubilizing groups[7]. When dissolved in water, however, they tend to form "colloidal" solutions owing to aggregation. This places them in a large group of substances, including soaps and detergents, referred to as "colloidal electrolytes"[8].

The chrome mordant dyes are no exception and form a very important group which can be subdivided into several chemical classes. The relative importance of each class of chrome mordant dyestuffs can be gauged from Table I compiled from the Colour Index[9].

TABLE I

## THE NUMBER OF DYES IN EACH CLASS OF CHROME MORDANT DYESTUFF

Class	No. of Dyes	% of Total
Azo Dyes	296	75,5
Anthraquinone Dyes	22	6
Triarylmethane Dyes	42	11
Oxazine Dyes	21	5
Others	10	2,5

Because of the overwhelming majority of chrome azo dyes and their relative importance to this study, it was decided that they should be described in more detail.

In 1858, Peter Greiss, a chemist at a Burton-on-Trent brewery produced the first diazonium salts by treating primary aromatic amines with nitrous acid produced from hydrochloric acid and sodium nitrite[10]. A simple example is given in the following scheme:
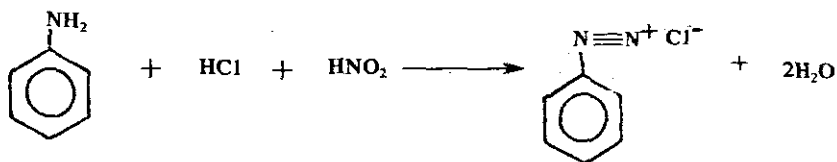
These diazonium salts undergo coupling reactions with aromatic amines and their phenolic derivatives to form highly coloured products, which, when sulphonated to render soluble in water, give rise to the azo dyes. Two of the earliest examples of dyes formed in this manner are Chrysoidine G and Orange II, both being produced in 1876[10]. Their structures together with the respective coupling reactions are as follows:

(Chrysoidine G)

(Orange II)
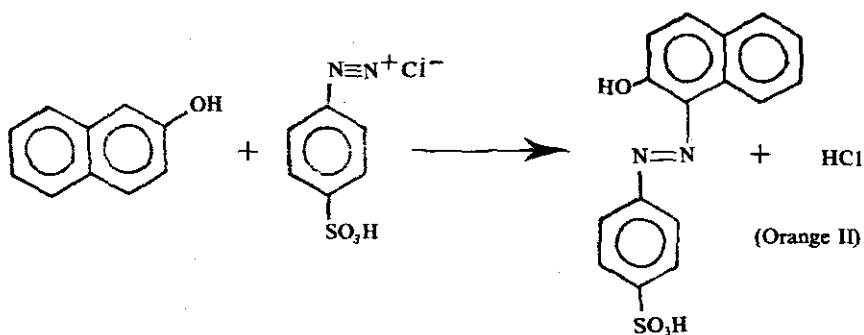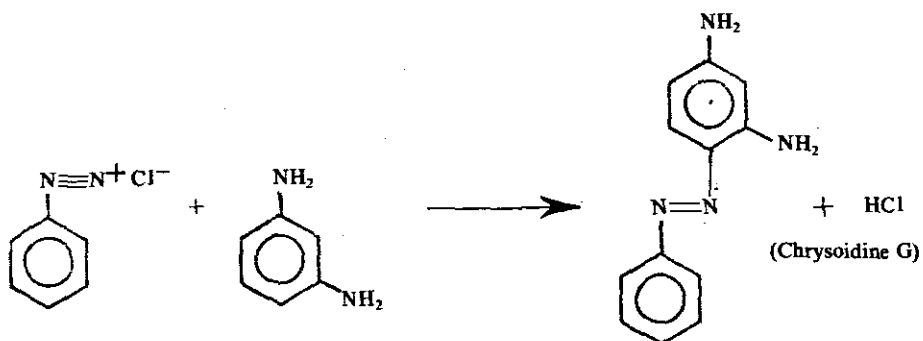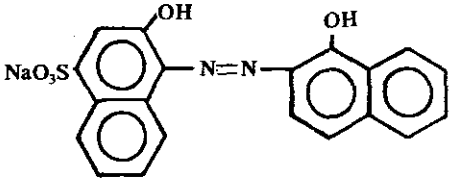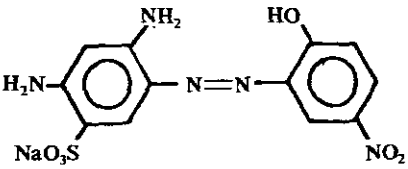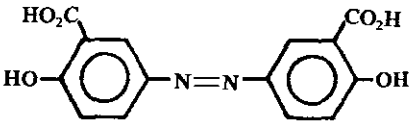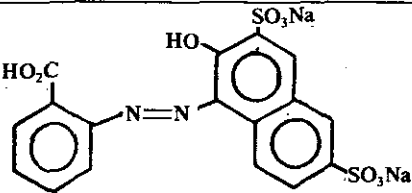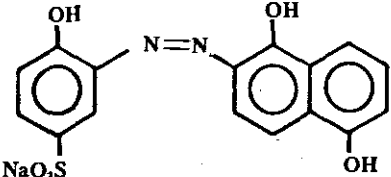
These dyes normally occur as the sodium salt, i.e. in the form $-SO_3^-$ Na^+

    The chrome azo dyes are closely related to acid dyes, chemically, except that their molecules contain additional groups which enable the dye to form a stable co-ordination compound with chromium. Certain combinations of these additional groups, further sub-divide the chrome azo dye into azo classes, the simplest of which appear with examples in Table II below[8]:

TABLE II

AZO DYES SUBDIVIDED INTO CLASSES ACCORDING TO CHEMICAL GROUPS

Azo Dye Classes	Example	
	Structure	Name
σ,σ'-Dihydroxyazo Dyes		® Eriochrome Blue Black B (C.I. Mordant Black 3)
σ-Amino-σ'-Hydroxyazo Dyes		® Chrome Fast Brown TV (C.I. Mordant Brown 33)
Salicylic Acid Dyes		® Eriochrome Flavine A (C.I. Mordant Yellow 5)
σ-Hydroxy-σ'-Carboxyazo Dyes		® Solochrome Red B (C.I. Mordant Red 9)
Azo dyes oxidised to Quinone form when complexed		® Diamond Black P.V. (C.I. Mordant Black 9)

The number of possible azo combinations is infinite and covers the whole colour spectrum, except for some bright blues, violets and greens[8]. Molecular masses range between 250 and 1080 and all azo dyes contain carbon, hydrogen, nitrogen and oxygen. A large proportion contain sulphonic acid groups, $(-SO_3^-)$ usually from one to four, mostly in the form of sodium salts. The great strength of the chrome azo dyes lies in blacks, browns, violets, dark blues and bordeaux[11].

Having introduced the chrome mordant dye in general, its azo constituent in particular with its chemical and physical attributes, and noted its similarity to the acid dyes, it is now convenient to discuss its application to the wool fibre.

The chrome azo dyes can be applied to wool in three ways, viz. after the chromium has been applied ("On-chrome", "Chrome mordant" or "Bottom chrome" method), at the same time as the chromium is applied ("Metachrome", "Monochrome", "Chromate", "Synchromate" or "Metomega Chrome" method) and before the chromium is applied ("Afterchrome" method)[9]. It is the latter method which is of relevance to this study so it will be dealt with in detail later.

Firstly, although most of the chrome azo dyes resemble acid dyes in dyeing behaviour, they are generally not suitable for use as acid dyes because under alkaline conditions in an unchromed state, salt forming reactions take place leading to a marked change in hue[12,13]. This is illustrated in the following reaction:

$$\text{HO-Dye-OH} \xrightarrow[\text{pH 7-8}]{} \text{HO-Dye-O}^+\text{Na}^+ \xrightarrow[\text{pH 9-10}]{} \text{Na}^+\text{O-Dye-O}^-\text{Na}^+$$
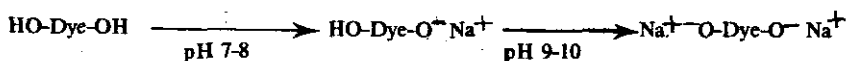
Secondly, acid dyes are also stable towards concentrations of acid considerably greater than those normally used in the dyebath, whereas this is not the case with many of the chrome azo dyes which are converted to fine dispersions, presumably of the free sulphonic acid derivative. Several of the chrome azo dyes are sensitive even towards normal acid concentrations and precipitate out of solution, e.g. ®Solochrome Black AS. (C.I. Mordant Black 1)[13].

Nevertheless, because of the chemical similarity between acid and chrome azo dyes and the fact that they are generally both applied from an acid dyebath onto wool (specifically by the "afterchrome" method for the chrome azo dye), research workers have found it convenient to compare their theories of application.
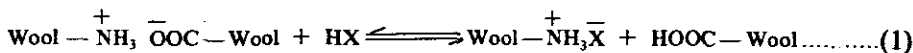
The degree of solubility of these dyes in water depends to a large extent on the number of solubilizing groups present on the molecule. The two most

commonly recognised solubilizing groups are — SO_3Na (there can be as many as five on certain dye molecules) and — CO_2Na, i.e. the sodium salts of the sulphonic and carboxylic acid residues attached to the dye molecules. It has been suggested that only single dye molecules or at the most aggregates of two to three molecules in solution can penetrate the wool fibre in a dyebath[8]. Anionic chrome azo dyes aggregate to a large extent with:

(a) Increasing dye molecular complexity

(b) Decreasing number of sulphonic acid groups

(c) Increasing dye concentration

(d) Decreasing dyebath temperature

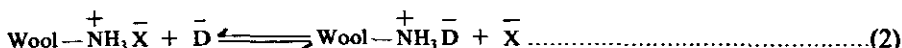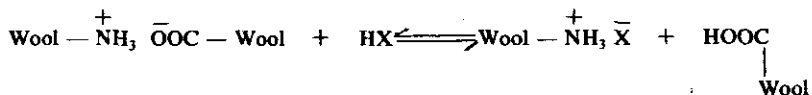(e) Presence of strong electrolytes, e.g. sodium chloride, sodium sulphate and sulphuric acid.

It is generally accepted, however, that when using simple acid or chrome azo dyes (at least two -SO_3Na groups present) at normal concentrations in the presence of the usual amounts of acid and salt for dyeing with a temperature at or near the boil, these dyes are not aggregated to any extent[8]. In fact, Valko[14] has shown that increasing dye bath temperatures decreases the degree of aggregation, while weak acids like acetic acid, which is only slightly dissociated, have a much smaller aggregating effect than strong acids, e.g. sulphuric acid[8].

In the presence of water the amino and carboxyl groups in the wool protein can be considered as "Zwitterionic" pairs[15]. Introduction of acid, HX (normally acetic or formic acid for chrome azo dyes) produces hydrogen ions in solution which rapidly diffuse into the fibre, combining with ionised carboxyl groups. The wool is thus afforded an overall positive charge which attracts the acid anions present in the bath, enabling them also to diffuse in as closely as possible to the protonated amino groups[16]. This simplistic approach is shown below[8,15]:

$$\text{Wool} - \overset{+}{N}H_3 \ \ \overset{-}{O}OC - \text{Wool} + HX \rightleftharpoons \text{Wool} - \overset{+}{N}H_3\overset{-}{X} + HOOC - \text{Wool} \dots\dots(1)$$

Suppression of the charge on the carboxyl groups in wool proteins upon addition of acid, not only increases the positive charge on the wool but also results in a decrease in pH of the dyebath[8]. As indicated above, the acid anions (X) diffuse into the wool and are found in the vicinity of the protonated amino groups ($-\overset{+}{N}H_3$). Upon introduction of azo dye to the water/acid/wool system,

however, there is an immediate anion competition, i.e. two different anions, acid ($\bar{X}$) and dye ($\bar{D}$) competing for the same basic sites in the wool. The dye anions, having the higher chemical affinity for these basic sites eventually displace the acid anions[16,17]. This competitive effect has been shown by Elöd[18] to be as follows:

$$\text{Wool} - \overset{+}{\text{NH}_3} \ \overset{-}{\text{OOC}} - \text{Wool} \ + \ \text{HX} \rightleftharpoons \text{Wool} - \overset{+}{\text{NH}_3} \ \overset{-}{\text{X}} \ + \ \text{HOOC} | \ \text{Wool}$$

$$\text{Wool} - \overset{+}{\text{NH}_3}\overset{-}{\text{X}} \ + \ \overset{-}{\text{D}} \rightleftharpoons \text{Wool} - \overset{+}{\text{NH}_3}\overset{-}{\text{D}} \ + \ \overset{-}{\text{X}} \quad\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(2)$$

The affinity which the azo dyes have for the wool fibre is associated with various types of bonds or linkages which result in their characteristic fastness properties. (The use of chromium in combination with the azo dyes, producing chromium-dye-wool links will be discussed later). These bonds are in the main as follows[8,15,19,20]:

(a) Covalent bonds — true homopolar covalent bonds formed with a shared electron pair. Found with reactive dyes.

(b) Ionic bonds — anionic dye molecules combining with the cationic groups in the wool forming ionic or salt links. According to Zollinger[21], this heteropolar salt mechanism is caused primarily by a guiding action.

(c) Hydrogen bonds.

(d) Van der Waals Forces — divided into polarisation forces (electrostatic) and dispersion forces (London forces) and occur when suitable juxtaposition of the dye molecule and peptide chain is found.

As early as 1924, Speakman[22,23], after having analysed figures obtained by other workers relating to the chemical combination of polybasic acids with wool, deduced that acid dyes in the presence of a mineral acid would therefore also combine chemically with wool. Later it was shown by Speakman and Stott[24] that wool, deaminated under fairly drastic conditions had a greatly diminished combining power with acid dyes. However, Gaunt[12] has shown that some chrome azo dyes which contain no sulpho groups ($-SO_3^-$) capable of reacting with

the basic groups of the wool are still rapidly absorbed by the fibre. The azo-salicylic yellow dyes, e.g. Solochrome Yellow 3G (C.I. Mordant Yellow 18) are typical examples where the only groups which could form salt linkages, are required for lake formation with the chromium. He concluded, therefore, that forces other than salt link formation come into operation.

Due to the stereochemistry of the molecule, it is sometimes not possible for all the sulphonic groups in polysulphonated dyes to be located close to positively charged sites in the wool fibre. Provided that neutralization of an equivalent number of positive and negative charges on the surface of the fibre crystallites occur, it is assumed that close approach of $- S\bar{O}_3$ to $- \overset{+}{N}H_3$ is not necessary[25-28]. Increasing the degree of sulphonation of a dye, decreases the rate of exhaustion of that dye, as well as its migration into the wool protein[29]. It is clear, therefore, that the presence of the sulpho groups in these dyes not only influences dye exhaustion at different pH values, but also the rate of dyeing and migration. More details relating to the rates of dyeing and dyeing kinetics will be furnished later in the discussion.

There are regions in the wool protein where the state of orientation of the main peptide chains is high, referred to as crystalline regions, as distinct from the rest of the fibre which is amorphous (less orientated chains). Originally, evidence was brought forward to suggest that molecules as large as those of dyes are unable to penetrate the crystalline regions, amounting to about 20% of the fibre[8, 30]. More recently, Baumann[31-35], with the help of wool protein fractionation methods, has shown that vinyl sulphone dye anions, reacted under all conditions preferentially with the insoluble residue of wool keratin. Much less reaction took place with the soluble fractions of low and high sulphur proteins. Zahn[36] refers to work done by Meckel[37] on wool proteins, who showed that it is the α and β keratose fractions which bind the chrome dye while the γ fraction contains very little. Further to this work Zahn himself[36] claims that it is the pronase soluble cell components, having a low cystine content and a high concentration of cationic and anionic side chain groups, which are penetrated first by dyes in aqueous liquors. Binding of the dye then occurs, preferentially on the microfibrils containing this high concentration of cationic and anionic sites. The matrix keratins on the other hand, are less reactive because of their high level of cystine cross-linking and relative low concentration of ionic side chain groups. Feughelman[38] has postulated that the opposite occurs, namely that dyestuffs preferentially react with the water swollen amorphous matrix and less with the orientated helically-crystalline microfibrils. Support for this idea has also come from Fraser et al [39], who based their conclusions on the volume swelling of the microfibril (11%) and matrix (53%) in porcupine quill upon being wetted. This pronounced increase in the matrix volume suggests that large molecules, such as dyes, would be accommodated there.

Taking all these theories into consideration, it is, however, still not clear whether the dye molecules actually penetrate these crystalline regions or merely accumulate on their surfaces in higher concentrations, or whether the amorphous matrix keratins are preferred. Obviously some more work will have to be carried out to elucidate this problem.

<div align="center">CHAPTER 2</div>

THE COMBINATION OF WOOL AND DYE WITH CHROMIUM VI

Potassium dichromate, or bichromate of potash as it was known in those days, was first manufactured on a commercial scale in 1830[40], but only introduced as a mordant for wool in about 1840[41]. In 1887, Nietzki[42], using the soluble azo acid dye ®Alizarine Yellow 2G (m-nitrophenyl-azosalicylic acid, C.I. Mordant Yellow 1), dyed wool from a normal acid dyebath and subsequently mordanted the dyed fibre by the addition of bichromate of potash to the exhausted dye liquor. This method was the forerunner to what is now generally understood to be the afterchrome process.

The use of potassium dichromate as a mordant for wool by the afterchrome process is the main theme of this study and as can be seen by the introductory paragraph, the idea was born almost a century ago. In order to best portray the chronological advances made towards the understanding of the exhaustion onto wool of chromium VI by the afterchrome process, it was decided to examine first the state of the chromium VI in the liquor and then its combination with the wool irrespective of whether it had been dyed or not.

In 1887 Kay and Bastow[41] postulated that potassium dichromate decomposed in the dyebath, forming potassium chromate and chromium *trioxide or chromic acid, according to the following scheme:*

$$K_2Cr_2O_7 \longrightarrow K_2CrO + CrO_3$$

or :

$$K_2Cr_2O_7 + H_2O \longrightarrow H_2CrO_4 + K_2CrO_4$$
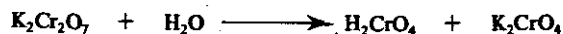
Their opinion was that chromium trioxide or chromic acid is taken up by the wool, while potassium chromate is left in solution. Kencht *et al*[43] supported *this theory in a paper published in 1889. Although in agreement with this theory* of chromic acid absorption by wool, Speakman *et al*[44] claimed that potassium dichromate in solution underwent ionisation and hydration in the following way:

$$K_2Cr_2O_7 \rightleftharpoons 2K^+ + Cr_2O_7^=$$

$$Cr_2O_7^= + H_2O \rightleftharpoons 2HCrO_4^-$$
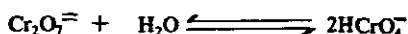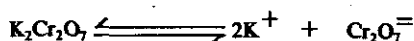
The concept, that it is the monobasic chromic acid anions which are primarily absorbed by wool from a mordant solution containing potassium dichromate, was adopted and for many years accepted by such workers as Gaunt[12], Fink[45], Peryman[46], Bichsel[47] and others. In the late nineteen sixties, however, Hartley[48] reported that he was in disagreement with this theory. He studied the equilibrium constants for the various chromium VI species in solution (Table III), and found that in the pH range normally used for mordanting, the only species present in any significant amounts were dichromate ($Cr_2O_7^=$), chromate ($CrO_4^=$) and bichromate ($HCrO_4^-$).

TABLE III

## EQUILIBRIUM CONSTANTS FOR CHROMIUM VI SPECIES IN SOLUTION

Equilibrium Equation	Equilibrium Constant	Ref.
$Cr_2O_7^= + H_2O \rightleftharpoons 2HCrO_4$	0,023	(49)
$HCrO_4^- \rightleftharpoons H^+ + CrO_4^=$	$3,20 \times 10^{-7}$	(49)
$H_2CrO_4 \rightleftharpoons H^+ + HCrO_4^-$	0,18	(49)
$H^+ + Cr_2O_7^= \rightleftharpoons HCr_2O_7^-$	1,175	(50)
$2H^+ + 2CrO_4^= \rightleftharpoons Cr_2O_7^= + H_2O$	$3,388 \times 10^{14}$	(51)

Infra-red spectrophotometric studies of wool treated at 25°C in the dark with chromium VI showed the presence of the dichromate anion when the wool was treated at pH 3 and the chromate anion when treated at pH 9. Following a critical examination of the solid and solution spectra of all three species, (dichromate, chromate and bichromate) Hartley concluded that neither the visible nor the infra-red spectra permitted any decision concerning the presence or absence of the bichromate anion on wool as was previously thought to be the case. Dobozy[52], in 1973, presented a different theory which in a sense agreed with that of Speakman. According to Dobozy, the chromate anions are in

equilibrium with dichromate anions, the dichromate with trichromate, and/or polychromates during mordanting. This is illustrated in the following scheme:

$$6HCrO_4^- \rightleftharpoons 3HCr_2O_7^- + 3OH^-$$

$$3HCR_2O_7^- + 3OH^- \rightleftharpoons 2HCr_3O_{10}^- + 4OH^-$$
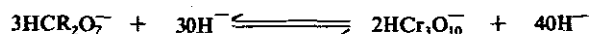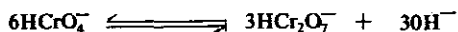
During mordanting there will always be chromate, dichromate, trichromate and/or polychromate present in the bath regardless of the concentration of the chromium VI, or the pH of the bath. The chromic acid anion ($HCrO_4^-$), acting as the oxidising agent, is re-formed from the dichromate species on the basis of the above equilibrium when its concentration in the dyebath decreases upon uptake by the wool.
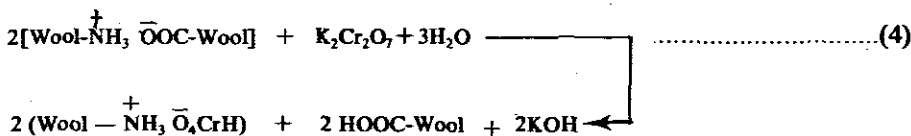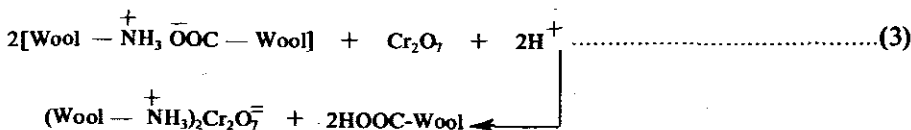
In dealing with the state of the chromium VI species in solution, no reference has so far been made to the very important role played by the acid species used in the mordant bath to assist the control of liquor pH. This aspect will now be discussed in more detail.

Jacquemin[53], in 1874, was one of the first to comment on the yellow colour acquired by wool when steeped in cold dichromate solutions with or without added acid. The idea that wool plays the part of a base which reacts with chromic acid to form an insoluble or sparingly soluble compound was put forward by Kay and Bastow[41], who showed that the exhaustion of the mordant bath improved in the presence of sulphuric acid. This view was also supported by Liechti and Hummel[54 - 56]. Hummel and Gardner[57] subsequently used hydrochloric and nitric acids and found them to be more effective than sulphuric acid. Although the use of mineral acids for improved exhaustion of chromium VI was well established, the possible use of organic acids as assistants in exhaustion was nevertheless also investigated at this very early stage. Amend[58,59] claimed that acetic acid damaged wool less when mordanting in the cold, while the use of the organic reducing acids like oxalic, tartaric and lactic became more and more prevalent as mordanting assistants[54 - 56, 60 - 65]. Knecht and Ward[43] observed that increased quantities of chromium were absorbed by wool when the mordanting temperature was raised or the time of treatment increased.

Initially, little was known about the chemical composition of wool keratins, and for this reason the pioneers in the field refrained from commenting on the chemistry of the wool-chromium interactions taking place during mordanting. In 1938, Speakman et al[66], however, ventured to suggest that when mordanting wool with potassium dichromate in the presence of acetic acid, there is competition between the acetic acid and chromic acid for certain sites on the wool. Because the chromic acid is the stronger acid, it is consequently absorbed.

When a strong acid like sulphuric acid is used, however, the competition from the acid for the sites on the wool becomes stronger and the absorption of the chromic acid is reduced. It was subsequently reported that a boiling potassium dichromate solution had a destructive effect upon wool owing to the disulphide bond attack which increases with decrease in pH of the dyebath[67].

By the time Giles[16] in 1944 had produced his paper on chrome mordanting, it was well known that wool consisted of proteins made up of long polypeptide chains, comprising amino acids linked together by the condensation of the carboxylic and amino groups. According to Giles, the first stage of mordanting consists of the diffusion of the hydrogen ions present in the acid dyebath into the wool, where they combine with the ionised carboxyl groups. This leaves the wool with an overall positive charge (resulting from the free protonated amino residues) which attracts the anions present in the dyebath. There is competition between the various anions for these basic sites, which is dependent upon their relative chemical affinities. From 1944 onwards till the present it became generally accepted that the chromium VI anion is attracted by the positively charged amino groups and arranges itself as closely as possible to them[12,13,20,44,45,47,48,68]. A number of schemes have been put forward in order to try and best describe the mechanism. Two of them are as shown below[8,29]:

$$2[\text{Wool} - \overset{+}{\text{NH}_3}\ \overset{-}{\text{OOC}} - \text{Wool}]\ +\ \text{Cr}_2\text{O}_7\ +\ 2\text{H}^+ \quad\text{.............................(3)}$$

$$(\text{Wool} - \overset{+}{\text{NH}_3})_2\text{Cr}_2\text{O}_7^=\ +\ 2\text{HOOC-Wool}$$

$$2[\text{Wool-}\overset{+}{\text{NH}_3}\ \overset{-}{\text{OOC-Wool}}]\ +\ \text{K}_2\text{Cr}_2\text{O}_7 + 3\text{H}_2\text{O} \quad\text{............................(4)}$$

$$2(\text{Wool} - \overset{+}{\text{NH}_3}\ \overset{-}{\text{O}_4\text{CrH}})\ +\ 2\ \text{HOOC-Wool}\ +\ 2\text{KOH}$$

Regardless of whether it is the chromic acid anions or the dichromate anions which are absorbed by the wool, according to the above schemes, the pH of the liquor should increase. This was in fact observed by a number of workers[8,44,45,48,69]. Further evidence in support of the above mechanism was put forward by Hartley[48], who showed that blocking most of the amino groups in wool by N-acetylation caused a reduction in chromium VI absorption, whereas esterification of most of the carboxyl groups resulted in an increase in the amount of chromium VI absorbed. It was obvious, therefore, that the chromium VI anions were associated with the positively charged amino groups, in particular the lysine, arginine and histidine groups. Esterification of the

carboxyl groups reduced the negative charge on the fibre and also decreased the formation of salt linkages between the carboxyl and amino groups, resulting in an increased chromium VI absorption.

Further to this salt link formation, it seems that once taken up by the wool, the chromium VI anion cannot be extracted by washing in water[66], but is in fact removed by rinsing in pH 8 buffer solution[44]. Although the oxidative properties of chromium VI are well known and in contrast to what was suggested by Speakman *et al*, a number of workers[37,46,70,71] have reported that there is little evidence to suggest a direct attack by chromic acid or chromate on the disulphide linkages in wool. It would also seem that the chromic acid absorption is independent of the presence of dye[44]. This aspect will be discussed in more detail later.

By 1944[16] it was also known that wool keratin consisted of regions where the main peptide chains were highly orientated (crystalline) and regions where less orientation of polypeptide chains occurred (amorphous). The crystalline regions were considered to be resistant to swelling in water and impenetrable by large molecules such as dyes[30]. Bischel[47] proposed in 1955 that chromic acid anions could form salt links with the protonated amino groups in the amorphous regions, but, because of their size could not penetrate the crystalline regions of the fibre. Instead, depending on the number of positive charges present, they could also become fairly strongly attached to the surfaces of the crystallites. It was further shown by Meckel[37] that treatment of wool with dichromate, increased the ß-keratose (insoluble) fraction and decreased the α-keratose fraction. This change was more pronounced when using acetic and formic acid than sulphuric acid. Because the increase in the insoluble portion of the wool was equivalent to the decrease in α-keratose fraction, Meckel concluded that the α-keratose was crosslinked during longer periods of chrome mordanting, thereby becoming insoluble. Interestingly enough, the bulk of the chrome was found to be situated in the insoluble fraction, in general twice as much or more than in the α-keratose, irrespective of whether the wool was dyed or not. Recently Kaplin and Kusch[72] studied chromium treated wool and have attempted to locate the metal within the fibre by means of electron microscopic techniques. The non-keratinous parts of the fibres, namely the nuclear remnants, intermicrofibrillar material, cell membrane complex and endocuticle, comprising 15% of the wool substance contain most of the chrome. The remainder is thought to be bound by the keratins in the microfibrils. According to Zahn and co-workers[36,73,74], this is not surprising, since the non-keratinous parts of the wool fibres are known to be rich in anionic (glutamic acid) and cationic (arginine) side chain groups and furthermore have a low cystine content. The matrix keratins, on the other hand, have a high sulphur content (more cross-linking) and relatively few cationic and anionic side chains and would therefore be expected to bind less chrome (see Fig. 1). This theory,

however, is not supported by Feughelman[38] and Fraser *et al* [39] who have predicted that chromium salts should preferentially react with the water swollen amorphous matrix (swollen by 53%) and less with the orientated helically crystalline microfibrils (swollen by only 11%).
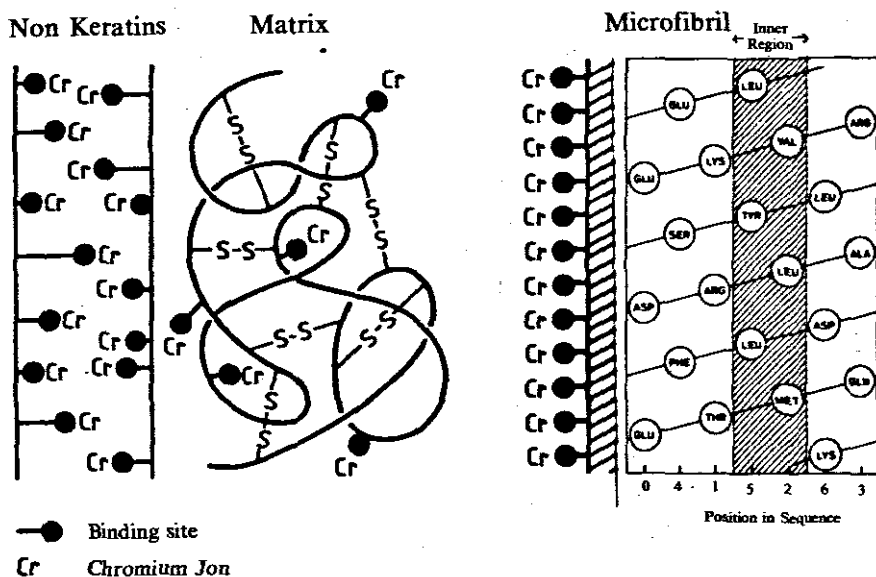

Non Keratins · Matrix · Microfibril

● Binding site

Cr Chromium Jon

Fig. 1 – Scheme visualising the anionic binding sites for chromium in the nonkeratins, the matrix and the microfibrils [36].

Recently, a scanning electron microscope and energy-dispersive X-ray system has been used by Maasdorp[75] to locate chromium in mordant dyed keratin fibres. The chromium was found to be evenly distributed in the keratin fibres and not preferentially absorbed by the orthocortical or paracortical regions which would tend to indicate that both the previous theories could be partially correct.

CHAPTER 3

THE REDUCTION OF CHROMIUM VI AND SUBSEQUENT FORMATION OF A CHROMIUM III WOOL BOND
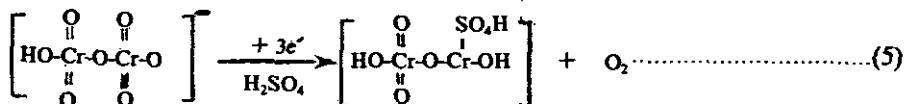
This concept, namely, that the chromium VI is reduced to chromium III

16

and subsequently fixed to the wool fibre, has been the subject of extensive investigations by many workers over the last century. In order to best portray the advances made over this period it was decided to deal first with the chromium VI reduction and the various groups involved in this reaction and then with the fixation of chromium III to the wool fibre.

As early as 1887[41], reference was made to the decomposition of bichromate to chromic hydrate by the reducing action of certain groups in the wool. Scurati-Manzoni[76] claimed that the sulphur in the wool was the responsible reducing agent, due to the fact that potassium sulphate was found in the bath in amounts proportional to the time of boiling, while the colour of the wool changed from yellow to greenish grey.

It was soon realised that the temperature of the mordant solution in which the wool was immersed largely controlled the degree of reduction which the potassium dichromate underwent. Hummel and Gardner[57] and later Iljinsky and Kodner[77] were among the first who showed that no matter how long the treatment of wool with dichromate solutions in the cold, the wool-chromic acid combination is stable and remains yellow. In 1932, Haller and von Hove[78] showed that wool treated with dichromate in the cold remained unchanged in shade for months when kept in the dry state in the dark, while only a slight degree of reduction was observed after a number of hours at 40° C. However, when the wool was immersed in the mordanting solution at 60° C, reduction proceeded steadily.

These earlier investigations[41, 54 − 57, 76 − 78] therefore concluded that chromium is reduced from the hexavalent to the trivalent state by certain groups (viz. sulphur) in the wool and that the change in colour of the wool from yellow to greenish grey begins at 60° C. It was also postulated that the reduction of chromium VI in the fibre takes place progressively through intermediate stages of chromic chromates to a final form of chromic oxide or hydroxide. Various possible structures have been proposed for these intermediate stages. Assuming a partial reduction of dichromate. La Fleur[79] suggests the structure of chromic chromates to be the following:

$$
\left[\begin{matrix} O & O \\ \| & \| \\ HO-Cr-O-Cr-O \\ \| & \| \\ O & O \end{matrix} \right]^- \xrightarrow[\mathrm{H_2SO_4}]{+\,3e^-} \left[\begin{matrix} O & SO_4H \\ \| & \| \\ HO-Cr-O-Cr-OH \\ \| & \\ O & \end{matrix} \right]^- + \; O_2 \qquad \text{(5)}
$$

Giles[16], however, proposed that during the reduction of chromium VI, high molecular mass chromium compounds are formed by olation and polymerisation, while a small portion of the reduced mordant may also be in a neutral non-ionised state as follows:

$$[Cr \, a_3 \, X_3]$$
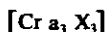
Where 'a' can be water or more probably groups such as $-NH_2$,-OH or -CONH- which form an integral part of the wool molecule and "X" being an ionic hydroxyl or sulphate radical.

A further alternative to the chromic chromate theory was that put forward by Fink[45]. He was of the opinion that the brown chromic chromate which forms on the fibre is in fact a green chromic salt which exists side by side with the yellow chromic acid salt. It was not until the late nineteen sixties when this aspect, namely, the intermediate stages in the reduction of chromium VI to chromium III was again brought into focus, this time by Hartley[9] who proceded to show that chromium VI had to pass through two intermediate oxidation states, i.e. chromium IV and chromium II before reaching chromium III. Because the mechanism and exact groups involved will be discussed a little later in this chapter it will now suffice to say that many of Hartley's theories still hold good today.

Originally it was thought to be the sulphur in the wool which facilitated the reduction of chromium VI to chromium III. Speakman *et al*[44,66] were of the first researchers to attempt to verify this. According to these authors combination of the chromic acid anions ($HCrO_4^-$) with the basic side chains of the wool and a corresponding number of hydrogen ions with the acid side-chains can cause the pH of the mordant solution to rise and at boiling point attack on the disulphide bonds via hydrolysis could be severe. In an earlier article Speakman[80] had already shown that disulphide bonds in wool could break down in water at 55°C and above in the absence of dichromate according to the following mechanism:

$$R-CH_2-S-S-CH_2-R \; + \; H_2O \longrightarrow RCH_2SH \; + \; RCH_2SOH$$
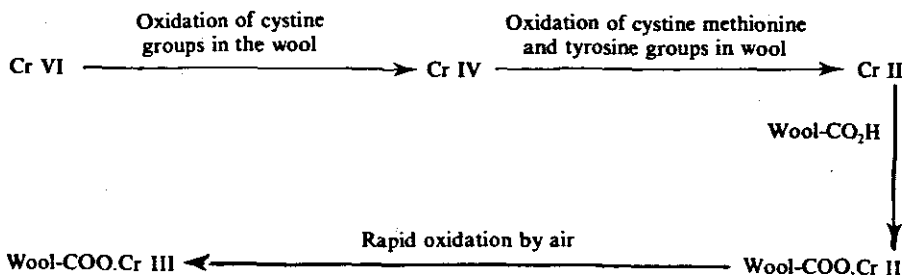
$$RCH_2SOH \longrightarrow RCHO \; + \; H_2S$$
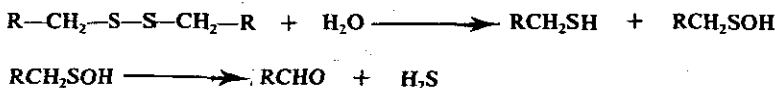
The reducing side-chains formed in the fibre with liberation of hydrogen sulphide rapidly reduced the chromium from the hexavalent to the trivalent state. This theory of Speakman, namely, that the disulphide bonds in the wool are fissioned when treated with a hot dichromate solution, producing thiols and other groups capable of reducing chromium VI to chromium III, was subsequently adopted by numerous researchers[12,44,45,46,66].

An important parameter, which could affect the cystine content and

hence the reduction of chromium VI to chromium III, was the pH of the liquor. Gaunt[13], in 1954 claimed that there was no significant change in the cystine content of wool when treated with boiling dichromate solutions at pH values higher than 4, whereas below 4 there was found to be a progressive reduction with time of treatment. The opposite theory was put forward by Peryman[46], in 1955. He stated that under acidic conditions (i.e. pH below 4) there was no change in the cystine content of the wool, whereas at pH values above 4 the chromium was reduced by the products of disulphide breakdown (viz. thiols, aldehydes, etc. c.f. Speakman[44,66]). This occurred independently of the chrome, except insofar as the latter behaved as a salt. Support for Peryman's theory came from Gianola *et al*[70] who stated that in acid medium chroming did not affect the disulphide bonds of the wool and reduction of dichromate was due to the tyrosine, tryptophane, methionine and probably the hystidine and serine groups of the wool. These authors claimed that the reactivity of the amino acids in the neighbourhood of the cystine in the keratin, as well as steric effects play a major role in disulphide breakdown. The importance of steric factors was also stressed by Campbell and Rushworth[19] who stated that the treatment of wool with a boiling dichromate solution could result in a breakage of the salt bridges with additional cross-link cleavage, due to the bulkiness of the chromate anion.

As mentioned before, Hartley[9] outlined the intermediate stages of chromium IV and chromium II which could be formed in the reduction of chromium VI to chromium III. He also found[81] that when wool was boiled in a chromium VI solution at a low pH, the disulphide bonds were oxidised directly, whereas at high pH values the hydrolysis products of the disulphide bonds, e.g. hydrogen sulphide, rather than the disulphide bonds themselves were oxidised. Apart from cystine, various other amino acids were attacked. For example, tyrosine was oxidised by chromium VI throughout the pH range investigated (pH 2-9), while lysine was only oxidised at high pH values (viz. 7 to 9). It was also possible that traces of serine could be oxidised at high and low pH values, but it was unlikely to occur under neutral conditions. In a later publication Hartley[82] forwarded the following reaction scheme for the reduction of chromium VI to chromium III by wool:

$$
\begin{array}{cccc}
 & \text{Oxidation of cystine} & & \text{Oxidation of cystine methionine} \\
 & \text{groups in the wool} & & \text{and tyrosine groups in wool} \\
\text{Cr VI} & \longrightarrow & \text{Cr IV} \longrightarrow & \text{Cr II} \\
& & & \Big| \quad \text{Wool-CO}_2\text{H} \\
& & & \Big\downarrow \\
\text{Wool-COO.Cr III} \longleftarrow & \text{Rapid oxidation by air} & & \text{Wool-COO.Cr II}
\end{array}
$$

Having discussed the reduction of chromium VI to chromium III in respect of intermediate species, e.g. chromic chromates, chromium IV and chromium II, as well as the amino groups in the wool which are possibly involved in the reduction reaction, e.g. cystine, tyrosine, methionine, etc., and the effect of temperature and pH on the above, it is obvious that in order for the chromium III to remain in the wool fibre it should be bound in some way or another. The next stage in the discussion will therefore be the mode of binding of chromium III to the wool fibre.

The earliest researchers[41] knew that the chromium III species (chromic hydrate) became attached to the fibre in some way. However, for many years the mode of binding of chromium III to wool was unclear. Speakman[44], in 1946, using results from supercontraction studies on chromed wool fibres concluded that there was no evidence that any chromium-containing cross-linkages were formed between the peptide chains of wool during mordanting. At that stage it was also known that chromium III could not be removed from wool by rinsing in buffer solutions, but that prolonged treatment with solutions of oxalic acid was effective in removing most of the chromium III. In contradiction to Speakman, however, Gaunt[12] postulated that it was probable that complexes could be formed between chromium III and the terminal carboxyl and amino groups of the wool.

Fink[45], in 1953 stated that, as the chromium finally found on the fibre was trivalent, the positive valencies could in part be attached to the negative groups found in the wool. He suggested that chromium III could also be bound to various other groups in the wool by secondary valences. Although cross-linkages between the chromium and the wool could also be formed the author suggested that chromium III was not directly involved, and rather assumed that - C = N - and - CH_2 - S - CH_2- bridges were formed in the wool by chroming. Finally, Fink proposed that the mode of binding involving the olation of two chrome atoms, in each case bound by a single secondary valent hydroxyl group, was as follows:
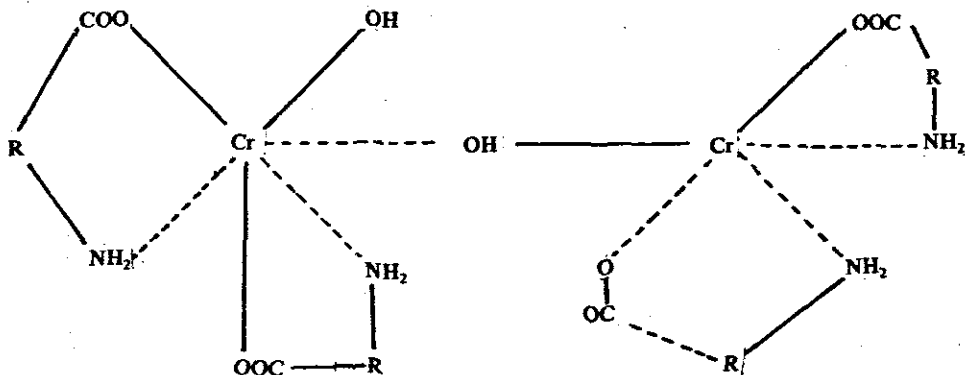
These cationic complexes are known to form readily with organic acids and are very stable[83].

Gaunt[13] in private communication with Lister claimed that although chromium in the form of the chromic acid anion could migrate readily in the wool fibre, once it was reduced and in trivalent state, it could not migrate at all. Bichsel[71] found that even prolonged extraction of normally chromed wool with ammonium oxalate solution did not remove all the chromium III and a small amount of chromium ($\sim 0,1\%$) remained in the wool. This chromium which was obviously very firmly bound, was termed 'active' chrome. Contrary to Gaunt, Gianola et al [70] have stated that chromium III present in the wool forms loose interchangeable bonds in which the -NH_2 functions of the keratin participate.

In 1965, Mikhailenko[84] put forward the theory that in the reduction of dichromate, a chromium cation bare of ligands is first formed, which, because of its high reactivity could form firm bonds with the wool keratin. This idea, however, was not further supported, because, in 1967, Meckel[85] published his findings relating to D.N.P.-amino acid analyses of chromed wool. These analyses indicated that there was no covalent binding of the chrome to the Σ-amino groups of lysine or to the other accessable dinitrophenylated side chain groups. Peracetic acid oxidation of wool and the subsequent fractionation into various keratose fractions showed that most of the chromium was held in the insoluble fraction. The carboxyl groups of the glutamic and aspartic acid moeities were probably responsible for the binding of the chromium III. In agreement with Bichsel[71], Meckel[37] also found a small constant portion of chromium ($\approx 0,1\%$) which was bound extremely fast to the wool. Neither author could forward any theories about the exact nature in which this 'active' chromium was bound to the wool.

Hartley[86], supported by Meckel[85], claimed that the chromium III is normally bound to wool by the carboxyl groups in the keratin. Infra-red and other evidence has shown that both oxygen atoms of the carboxyl group are involved in the complex formation. Hartley forwarded the following SN_1 process for the reaction between chromium III and the carboxyl groups in wool:
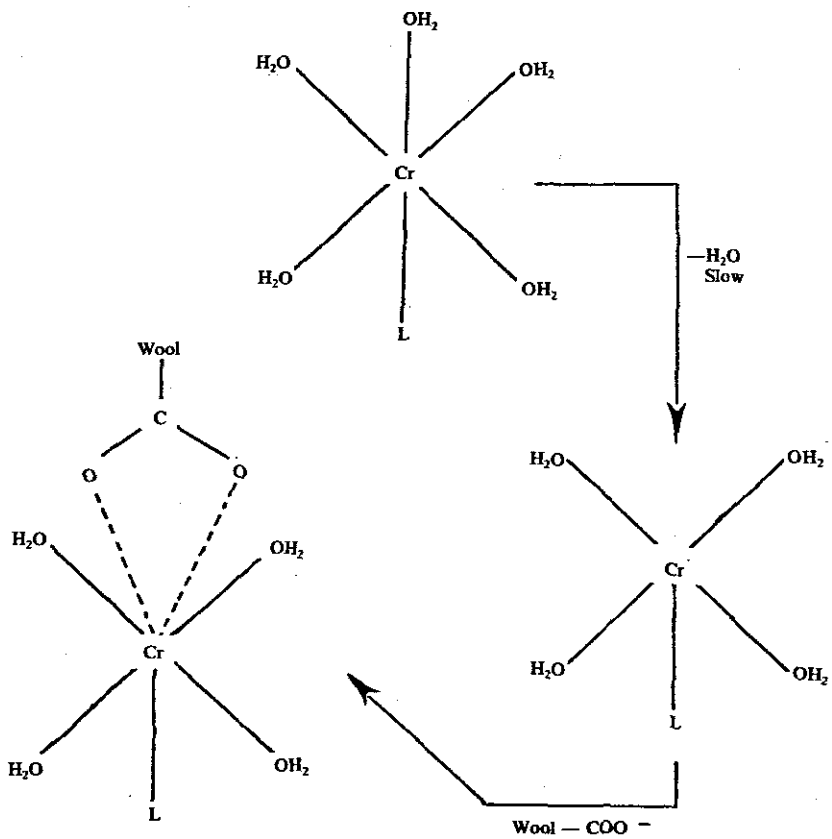
One of the most recent theories was that put forward by Dobozy[52], in 1973, which supported those of Gaunt[12] in that they claim that wool keratin forms chelates with chromium III through the terminal amino and carboxyl groups, wherever stric hindrances do not prevent it. A typical example of this reaction is the formation of the 1 : 3 chelate of chromium III with glycine according to the following mechanism:
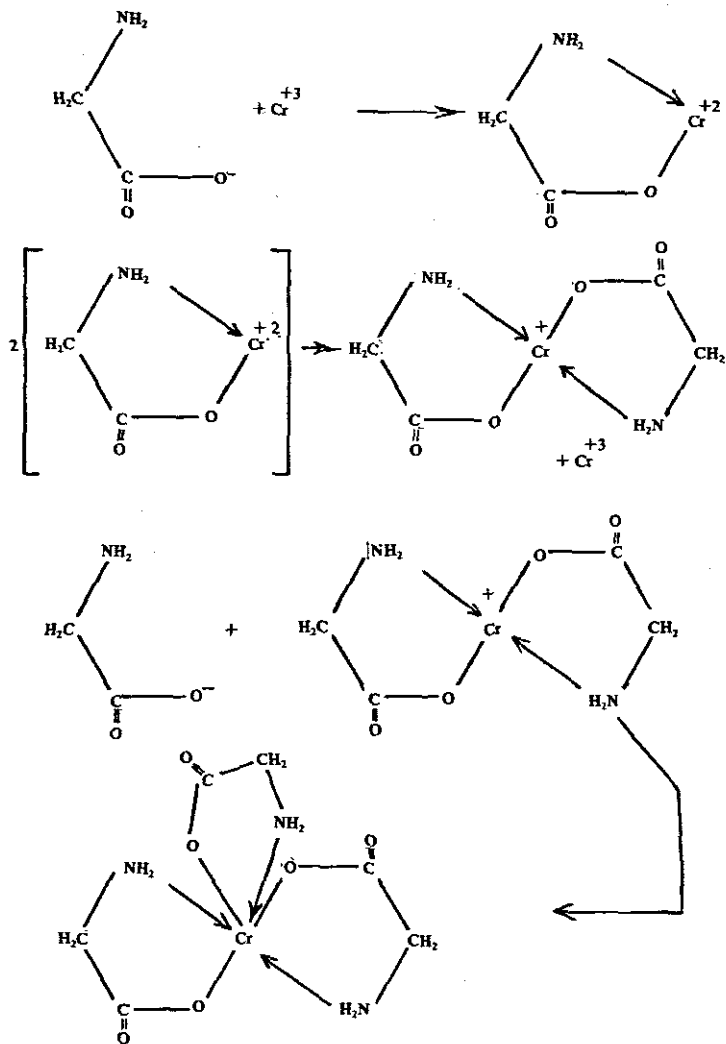
Further, according to Dobozy, some of the chromium III - kratin chelates so formed react with chromium VI as well, forming organochromic chromates. These were thought to form as intermediate species in the reduction of chromium VI to chromium III by many of the earliest investigators[41,54,55,56,79] introduced at the beginning of this chapter.

It is quite obvious that there is still a great deal of uncertainty as regards this very important step, viz. the reduction of chromium VI to chromium III and its fixation by the wool. The theories of Speakman and Hartley have been adopted to a large extent, but one should not disregard the important contributions made by the original research workers like Hummel and Liechti, some of whose ideas are still of consequence today.

<div align="center">CHAPTER 4</div>

THE CONSTITUTION OF THE CHROMIUM III — DYE COMPLEX AND ITS FIXATION BY THE WOOL

Having applied the azo dye to the wool and subsequently treated the dyed wool with dichromate which is consequently reduced, the final event in the afterchrome process is the formation of the chromium III-dye complex and its manner of fixation by the wool. In order to be able to simplify and better explain this last phenomenon it was decided to first discuss the formation of the chromium III-dye complex and then the various groups or forces involved in its fixation by the wool.

Originally it was known[42] that hydroxyl and/or carboxyl groups in the σ-position in an azobenzene dye molecule enabled the dye to be mordanted to wool with chromium salts. Morgan and co-workers[87-95] carried out a detailed investigation on the structures of the so-called lakes formed by the interaction of azo dyes with metals like chromium. They recognised the union of the metallic chromium atom with the azo nitrogen and with the hydroxyl group in the ortho (σ) position with respect to an azo group. After experiencing many difficulties in forming these chromium lakes, they eventually arrived at the conclusion that it is only after the conversion of the mono- σ-hydroxyazo dye to the σ, σ'-dihydroxyazo dye that a chromium lake can be formed.

This fact was recognised by Drew and Fairbairn[96], in 1939 when they undertook an investigation of the chromium lakes of σ, σ'-dihydroxy-, σ-hydroxy σ'-carboxy- and σ-hydroxy σ'-aminoazo dyes. Using the σ, σ'-dihydroxy- and σ-hydroxy σ'-carboxyazo dyes it was shown that the chief type of chromium lake formed, contained one azo dye molecule attached to each chromium atom. When the chromium atom interacted with a second molecule of the same or similar dye, however, a more complex type of lake, acidic in nature, was formed. Upon the introduction of a sulphonic acid group into the azo dye, Drew and Fairburn found they could produce water soluble lakes

retaining the same essentials of structure. The examples given by them of the primary (1:1) and acidic (1:2) chromium lakes formed from the substituted σ-hydroxybenzeneazo-ß-naphthol dye are as follows:
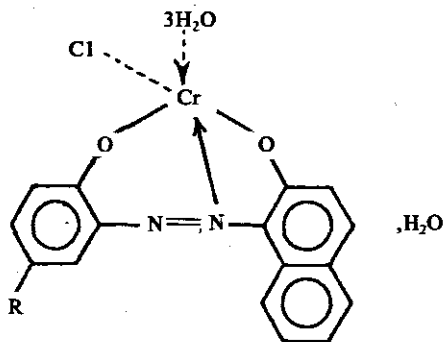

Primary or 1:1 chromium III – dye complex
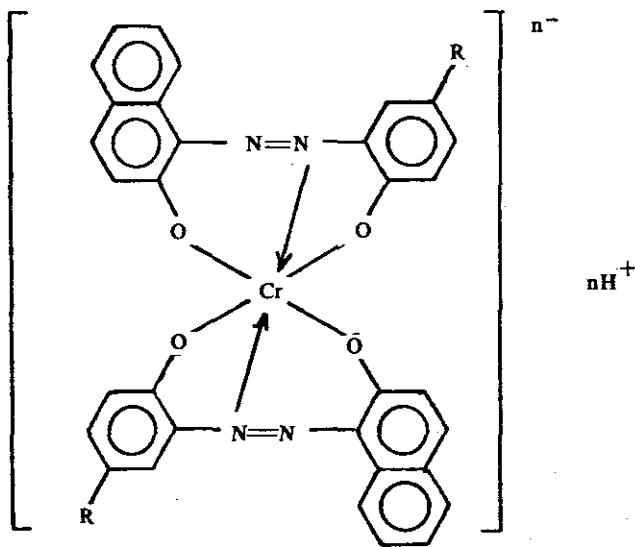
*Anhydrous salt forming acidic or 1:2 chromium III – dye complex*

$$(R = -H, -SO_3^-, -NO_2, \text{ etc.})$$

Finally they concluded that in all cases of σ,σ'-dihydroxyazo dyes, the chromium III atom is not only attached to the two hydroxyl groups, but is also probably co-ordinatively bound to one of the nitrogen atoms of the azo group.

Giles[16] also stated that the probable structure of the lakes corresponds to that of the primary complex which, when containing a sulphonic acid group, more than likely exists in the form of a 'zwitterion' as follows:
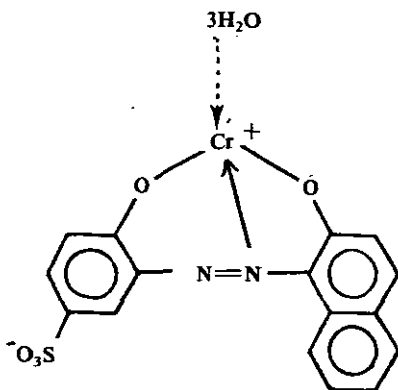

Since there is normally no shortage of chromium relative to dye in a mordant dyeing, the structure of the lake would be that of the primary complex and not the acid complex. This concept, namely that the primary complex is formed predominantly, was disputed soon afterwards by Speakman *et al* [97]. These authors, after dyeing wool with a limited known amount of dye, mordanted it with an excess of chromium. By extracting the excess of chromium with an oxalic acid solution and relating the residual chromium to the known amount of dye, they showed that the constitution of the dye-chromium complex formed was that of two molecules of dye for every one atom of chromium. (2:1 or acid complex). The following example was given, where two molecules of 3,4,6-trichloro-2-aminophenol → 1-benzoylamino-8-naphthol-4-sulphonic acid are coupled to one atom of chromium in the tribasic acid form:
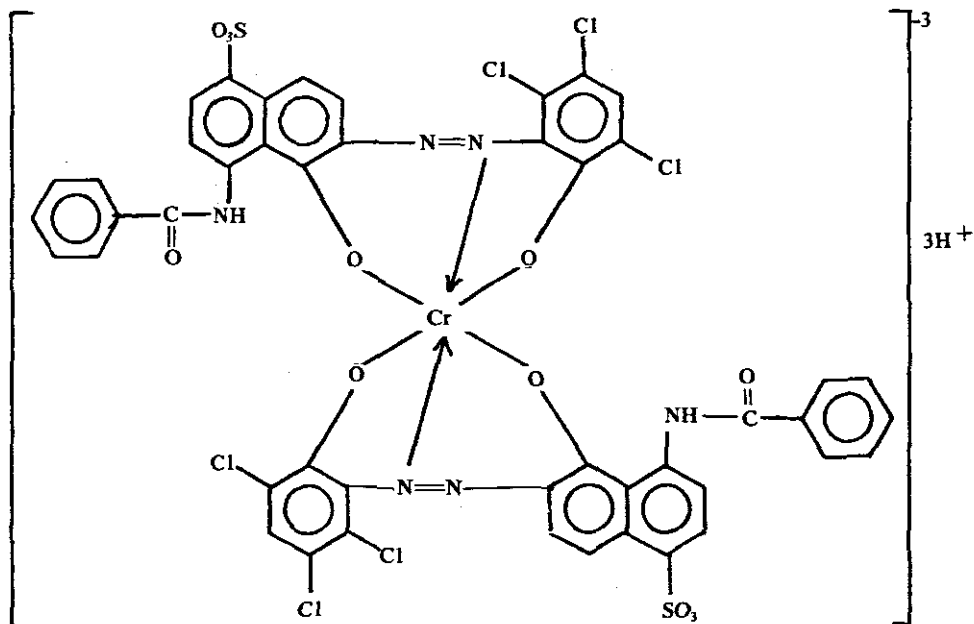
There followed a period of uncertainty as to whether the primary (1:1) or acidic complex (2:1) was formed. Gaunt[12] was of the opinion that with most of the chrome dyes, lake formation took place very slowly at temperatures below the boil either in the presence or absence of wool.

Race[98], however, in 1950 supported the original idea, viz. that it is the primary complex which is formed in which one molecule of dye is associated with one atom of chromium. Using a series of σ,σ'-dihydroxyazo dyes, he concluded that initially a 3:1 complex is formed in which three molecules of dye are attached to one atom of chromium. His analyses did not show, however, whether the 3:1 complex is converted directly to the 1:1 complex or whether the 2:1 acidic complex is formed as an intermediate product. The 1:1 and 2:1 complexes proposed by Race are similar in structure to those reported before and will not be given here. The 3:1 complex can be presented in the following two forms:
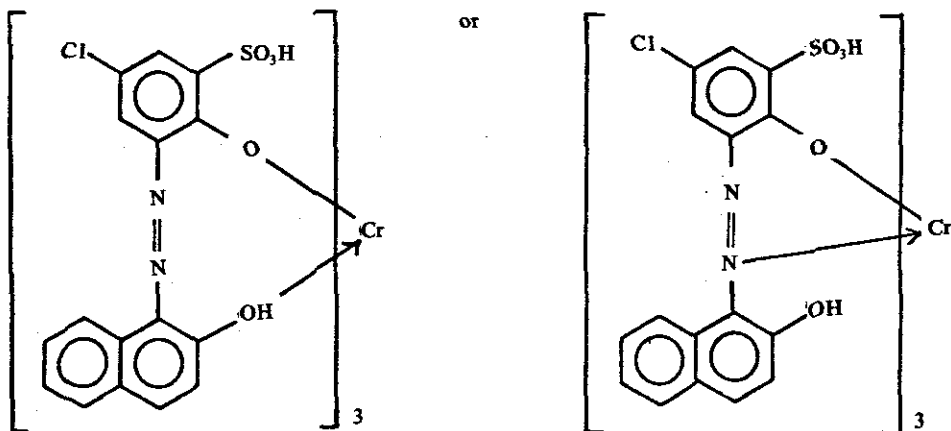
By now it had become generally accepted that, in order for complex formation to take place, the chromium must be in the trivalent state and the azo dye should have hydroxyl, carboxyl or amine groups in the ortho, peri or σ, σ'-position with respect to the azo nitrogen. These groups on the azo dye as well as the principal and secondary valencies available from chromium III can then form the cationic primary complex ('Zwitterion') or the anionic acid complex as shown.

With analytical techniques improving continuously, new theories relating to the formation of the 1:1 and 2:1 complexes were bound to be put forward. For the first time it was thought that perhaps the particular complex formed depended on the conditions of the reaction (e.g. temperature, pH, etc.) or the presence of certain donor groups in the inner co-ordination sphere (e.g. H_2O, NH_3, Cl, etc.). The chromatographic separation of the 1:1 and 1:2 complexes became possible and showed the 1:1 complex to be apparently homogeneous, whereas the 1:2 complex could be separated into two fractions both of which had identical absorption spectra[99].

Pfeiffer[100] claimed that a 2:1 complex of azo dye with chromium could be resolved into dextro and laevo forms. The dextro form apparently had nearly twice the rotation of the laevo form and they were considered to be optical enantiomorphs of different optical purity. Martell and Calvin[101], however, introduced a different view. They proposed that the two fractions obtained were two stereochemically different configurations, the one being a trans form (having a centre of symmetry, no dipole moment) and the other being one in which the bonds about each nitrogen atom are coplanar (showing polar characteristics). These two stereochemical configurations were called Pfeiffer ("sandwich") and Drew-Pfitzner structures respectively and are shown by Schetty[102] to be as follows:
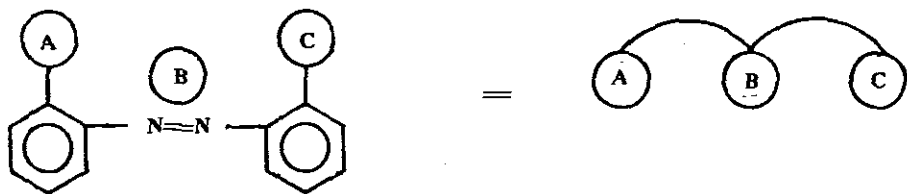
The five different Pfeiffer or 'sandwich' arrangements are given below:
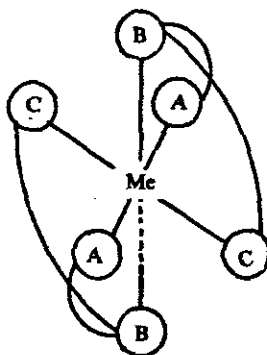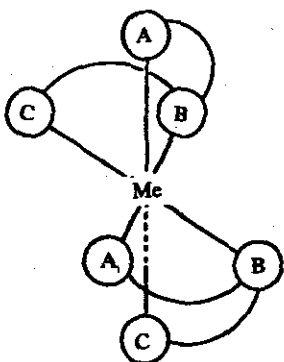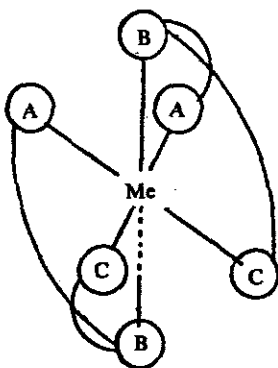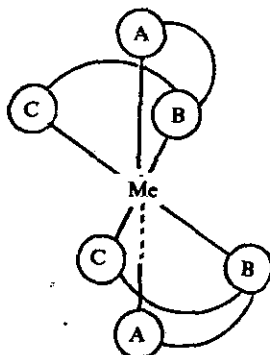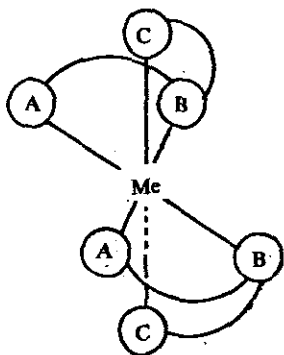
The Drew-Pfitzner arrangement is shown below:
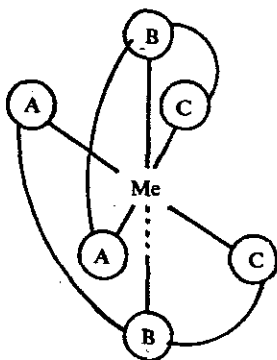
* Me = Cr

Further, for the tridentate azo dyes it was shown that: (i) The 'sandwich' arrangement forms with all diarylazo dyes having two annelated six membered rings when co-ordinated to the chromium atom. (ii) The Drew-Pfitzner arrangement forms when five and six membered annelated rings are co-ordinating the azo dye to the chromium atom.

The following tables with structural examples have been reproduced from the publication of Schetty[102]:

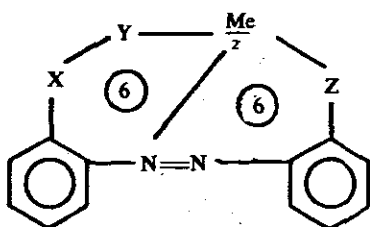| TABLE IV	TABLE V
'Sandwich' Complex	Drew-Pfitzner Complex

X-Y	Z
$-\overset{\overset{O}{\|}}{C}-O-$	$-O-$
$-\overset{\overset{O}{\|}}{C}-O-$	$-NH-$
$-SO_2-\underset{\underset{CO-\phi}{\|}}{N}-$	$-O-$
$-CO-\underset{\underset{SO_2-\phi}{\|}}{N}-$	$-O-$

Y	Z
$-O-$	$-O-$
$-O-$	$-NH-$
$-O-$	$-N\phi-$
$-O-$	$-N(SO_2R)-$

ϕ = Aryl group

It has been stated that the 1:1 chromium-dye complex exists predominantly in the Drew-Pfitzner arrangement[103]. Furthermore, the relative amounts of 1:1 and 1:2 chromium-dye complexes formed vary with the azo dye used and depend on:

(i) The degree of solubility of the 1:1 complex. Low solubility favours the formation of the 1:1 complex[104].

(ii) The pH of the solution. Low pH favours the formation of the 1:1 complex, being an internal 'Zwitterion' with no nett charge, while a higher pH favours the formation of the 1:2 complex which has an overall negative charge[103].

Finally, it was shown that when the dye co-ordinated with chromium III, the ultraviolet spectrum was hardly altered, whereas the visible spectrum exhibited a bathochromic shift which was ascribed to either the polarity of the chromium III-phenolic oxygen bond or the perterbation of the π electron system of the dye by d_π -p_π interaction[105].

Having examined the complex formation of chromium III with the azo dye in some detail, it is now necessary to look at the various groups or forces

involved in the fixation of the chromium III-dye complex to the wool. Most of the ideas relating to this subject were introduced many years ago, but it would seem that several are still valid today.

Giles[16] assumed that once the lake (1:1)was formed on the fibre, the water molecules co-ordinated with the chromium atom were replaced by co-ordinated linkages with oxygen and nitrogen atoms of the main protein chains in the fibre. He also felt that it was possible that the sulphonic acid groups of the dye and the remaining ionic valencies of the chromium atom could form salt links with the ammonium and carboxylic ions, respectively, in the protein side chains. These ideas were adopted by many subsequent researchers[19,37,45,52,106]. Speakman *et al* [97], considering only the 2:1 complex, have proposed that the anionic valencies of the chromium and sulphonic acid groups of the azo dye form salt linkages with the amino groups in the fibre. Once formed, these complexes remain in the wool in the same way as large acid dye molecules. The increased fastness properties of the chromed dyeings was attributed to (i) the 2:1 chromium III-dye complex, having a molecular size more than double that of the azo dye molecule, being bound to the fibre by van der Waals forces which are commensurate with its size, (ii) the 2:1 chromium III-dye complex having been formed inside the wool fibre, being too large to escape from spaces which were large enough to allow initial entry of individual dye molecules and chromium ions. These ideas were also adopted by other researchers[12,45].

Later, Giles and MacEwan[107] and others[19] proposed that some form of hydrogen bonding also occurs between nitrogen or hydrogen groups on the dye and hydrogen groups in the wool. Certain authors[19,45,52,108] believe that a fair amount of cross-linking takes place between the dye, the chromium and the fibre, whereas others[37,107] claim that no cross-linking takes place at all. In general it would seem that it is possible that cross-linking can occur with the 1:1 complex, while it is unlikely in the case of the 2:1 complex. Coates and Rigg[106] have stated that the mere proximity of another dye molecule to an already established 1:1 dye-chromium III complex with the wool could be more than sufficient to cause breakdown of this linkage and the formation of the 1:2 chromium III-dye complex. A schematic representation (see Fig 2) has been forwarded by Dobozy[52] for the 1:1 complex with wool. He quite clearly believes that the chrome plays the role of a bridge between the polypeptide chains and the dye.

Fig. 2:
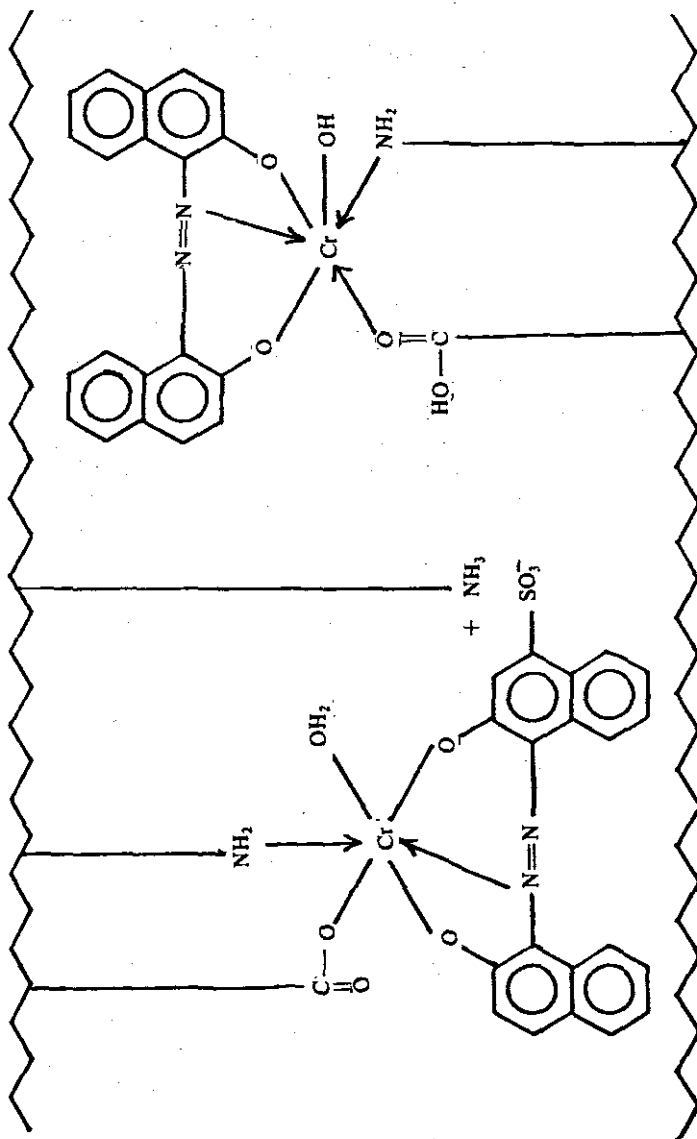
Finally, in summarising this chapter, it can be stated that many of the proposals put forward for the fixation of the chromium III-dye complex to wool (be it 1:1 or 1:2) by the original authors like Giles, Speakman, etc., are still acceptable today. There are, however, several more recent authors who have introduced new ideas.

THE KINETICS OF THE CHROMING PROCESS

In spite of the obvious importance of the kinetics of the chroming process, a study of the literature has shown that there are a number of controversies which still exist. The theories put forward by those authors who have contributed to the knowledge in this field will now be conveyed to the reader, and the anomalies which exist in this field will be highlighted.

Speakman *et al* [44] observed that the rate of absorption of chromium by wool at boiling point is initially very rapid but decreases steadily with time. In fact, they found that when the total amount of chromium absorbed by the wool is plotted against the square root of time, there is a linear relationship for the first 65 to 70% of the absorption. This observation prompted these workers to suggest that absorption of chromium is governed by a simple diffusion law. The Hill[109] equation was subsequently adopted and applied in the following form:

$$A = 2\,Y_{O}\sqrt{kt/\pi} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(6)$$

where A = Total amount of chromium diffusing across unit area of the fibre in time t.

Y_O = Initial concentration of chromium in the bath.

k = Diffusion coefficient.

Because the relationship mentioned above was observed for a wide range of initial chromium VI concentration, the authors believed Yo should remain constant in spite of the decreasing concentration of the dyebath.

Hence it was accepted that absorption into the fibres took place from a thin film on the surface of the fibres, the concentration of which remained constant regardless of the degree of circulation of dyebath liquors.

Confirmation of equation (6) came from Fink[45] who deduced the chromium uptake theoretically. Considering the heterogeneity of the reaction between chromium and wool (containing inaccessible crystallites and accessible

amorphous regions), the author introduced the following equations:

$$\text{Reaction rate} = \frac{\text{Driving Force}}{\text{Resistance to Reaction}} = \frac{dx}{dt}$$

The resistance to reaction was divided into chemical resistance (W_R) and diffusional resistance (W_D).

$$\frac{dx}{dt} = f \frac{C_s - C_f}{W_R + W_D}$$

where x = Converted amount of chromium from the liquor to the fibre.

t = Time

C_s = Total concentration of chromium in solution

C_f = Total concentration of chromium in the fibre

f = Unit combination factor.

The term W_D was computed from the well known physico-chemical relation with diffusion as follows:

$$W_D = D^{-1} \int \frac{dl}{Q}$$

where D = Diffusion constant

l = Width of the diffusion layer

Q = Diffusion cross-section.

For absorption Fink assumed $W_D \ggg W_r$ and Q to be constant. Therefore:

$$\frac{dx}{dt} = f \frac{C_s - C_f}{D^{-1} \int \frac{dl}{Q}} = \frac{fQD}{l} (C_s - C_f)$$

At the start of the reaction $C_f = 0$

$$\ell \; \alpha \; x$$

$$C_s = \text{constant}$$

Therefore: $\quad \dfrac{dx}{dt} = \dfrac{f' C_s Q' D}{x}$

Which reduces to:

$$x = \sqrt{2f' C_s \, Q' Dt} \quad = k\sqrt{t} \qquad \text{............(7)}$$

Subsequently C_f assumes greater proportions and $(C_s - C_f)$ is linked to the width of the diffusion layer (ℓ).

Consequently: $\quad \dfrac{dx}{dt} = f''QD$

or $\qquad\qquad \underline{x} = f''QDt + \text{constant}$

$$x = kt + \text{constant} \qquad \text{...........................(8)}$$

Relying on his own experimental measurements, Fink substituted his experimentally obtained values into the theoretically derived equations and obtained the following:

Initial absorption: $x = 3,01 \sqrt{t}$

Later absorption: $x = 11,4\,t + 96,5$.

Equation (7) has the same form as that of Speakman et al[44], equation (6), while equation (8) is similar to that compiled by Datar and Kulkarni[110] which refers to the formation of chromium complexes in general. According to Dobozy[52], the transition from the first to the second variant (i.e. equation (7) to

(8)) starts at the beginning of mordanting, so that chromium absorption is in fact a continuous transition between Fink's marginal cases.

Shozo-Bito[111] also studied the kinetics of wool mordanting with chromium VI, using an expression which has the following form:

$$\frac{\phi}{\phi - x}$$

where ϕ = Maximum available number of sites on the wool fibre for binding Chromium III

x = Total chromium concentration in solution.

Having examined mordanting as a function of chromium III affinity for the wool fibre, Shozo-Bito also observed Fink's breaking point and the fact that total chromium absorption is characterised by different equations, i.e. one for the initial stages and another for the later stages of mordanting. Therefore he too used two equations, one for the first 60 minutes of mordanting:

$$\frac{12,57}{12,57 - x} = 1,616 \, t^{0,1622} \quad\text{...(9)}$$

and the second one for mordanting after 60 minutes:

$$\frac{12,57}{12,57 - x} = 1,509 \, t^{0,2427} \quad\text{...(10)}$$

In general, Dobozy[52] was in agreement with Shozo-Bito[111], excepting that he queried whether it is correct for Shozo-Bito to have assumed ϕ as constant and equivalent to Meyer's[112] wool-cation equivalent weight.

Hartley[48] monitored the absorption of chromium VI by wool, but at $25°C$ in the dark, and plotted it against square root of time. He found that after an initial curvature, the points were linear (∓ 4 hours onwards) and equilibrium was attained after 144 hours. Further to this, he also derived an expression which describes the effect of chromium VI concentration in solution on the amount of chromium VI absorbed by the wool. (pH 4,5; $25°C$ in the dark for 144 hours). The resulting curve obeyed the Freundlich isotherm[113] and the expression has the following form:

$$[Cr\ VI\ (Wool)] = 0,43\,[Cr\ VI\ (Solution)]^{0,57} \quad\text{.....................................(11)}$$

In another publication, Hartley[81] also described the uptake of chromium III by wool when boiled in a chromium VI solution. Again the curve followed the Freundlich isotherm[113] which was found to give linear plots when the log of the chromium III concentration on the wool was plotted against the log of the chromium VI concentration in solution. The author obtained the following relationship:

$$[Cr\ III\ (Wool)] = a\ [Cr\ VI\ (Solution)]^b \quad\text{..(12)}$$

where for pH 2   a = 0,78   b = 0,84

     ·· 4   ··   0,99   ··   0,97

     ·· 7   ··   0,73   ··   0,72

On plotting the log of the chromium VI concentration against chroming time, Langman and Meier[114] found that the chroming of wool takes place in two stages (as was found by Fink[45] and Shozo-Bito[111]. With respect to the kinetics of the chroming process, it was shown that there is first a very rapid decrease followed by a slower decrease in the chromium VI concentration in the liquor. Furthermore, they have shown that for chroming times longer than five minutes, i.e. for the slower chromium VI absorption, the log of the chromium VI concentration is a linear function of time. The rate constant which describes this slower uptake has been presented by Langman and Meier as follows:

$$K = \frac{d\ C}{dt} \cdot \frac{1}{C}$$

where C = Chromium VI concentration.

The absorption of chromium from a normal dyebath under different chroming conditions, viz. temperature, acid concentration (pH) and type has recently been monitored by Maasdorp[115]. Because of the complexity of the system, a multi-regression analysis was performed on the results, yielding six significant regression equations, which, when presented graphically, facilitate interpretation of the rates of exhaustion of chromium from the dyebath under the different chroming conditions. The model selected for these equations was:

$$Y = f\ (X_1;\ X_2;\ X_3)$$

where:

Y = Total chromium concentration (mg/l)

X_1 = Temperature of chroming (°C)

X_2 = Amount of concentrated acid (ml)

X_3 = Time (minutes)

     The dependant variables, Y_1 to Y_6, differentiate between undyed wool using acetic, formic and lactic acid (Y_1, Y_3, Y_5) and dyed wool using acetic, formic and lactic acid (Y_2, Y_4, Y_6). These six regression equations together with their % fit have been reproduced in Table III. However, these regression equations could not differentiate between the initial very fast absorption of chromium and the slower absorption which occurs at a later stage.

     In a subsequent investigation, using specially selected chroming conditions, Maasdorp[116] was able to successfully monitor the initial very fast absorption of chromium by both dyed and undyed wool. Surprisingly, it was found that the Etters[117] diffusion equation for disperse dyeing systems had the best fit to the experimental data. From this equation analytical approximations can be made with a high level of accuracy. It has the following form:

$$M_t/M_\infty = \left[1 - \exp\left[-k\,(Dt/a^2)^x \right] \right]^{\frac{1}{y}} \qquad \text{...........................}(13)$$

or can be rearranged to give:

$$\left[\left\{ -ln[\, 1 - (M_t/M_\infty)^y\,] \right\} /k \right]^{\frac{1}{x}} = D/a^2 . t \qquad \text{...........................}(14)$$

and can reproduce with a high degree of accuracy, the functional relationships expressed by the conventional equations[44,45,109], where

M_t = Amount of material (chromium on the fibre at the time = t.

M_a = Amount of material (chromium) on the fibre at the time = ∞.

D = Approximate diffusion coefficient (cm²/sec).

a = Value for the average radius of the wool fibres (11×10^{-4} cm).

TABLE III

THE COEFFICIENT FOR THE REGRESSION EQUATIONS $(Y_1$-$Y_6)$ IN TERMS OF THE PRIMARY INDEPENDENT VARIABLES $(X_1X_2X_3)$

	Y_1	Y_2	Y_3	Y_4	Y_5	Y_6
X_2	- 1,691721	- 5,17418		- 2,72554	- 4,865637	-10,2645
X_3		-42,4101		-13,93008	-15,73649	-43,71527
X_1^2						- 0,00244
X_2^2	0,069350	0,203702	0,06935	0,1105040	0,162676	0,426677
X_3^2						22,16124
X_1X_2			- 0,030112		0,141285	0,113082
X_1X_3		0,48399	0,149470		0,925842	
X_2X_3			- 5,616164		2,910391	8,907316
$X_1^2X_2$	0,000038		0,000872	0,0002967	- 0,000395	
$X_1^2X_3$	- 0,002069	- 0,011886		- 0,00234	- 0,00556	
$X_2^2X_1$			- 0,002095		- 0,0029757	- 0,003517
$X_3^2X_1$	0,06094	0,65391	- 0,13448	0,14732	- 0,26820	0,05642
$X_2^2X_3$		0,093738	0,128324			
$X_2^2X_2$						- 4,38066
$X_1X_2X_3$	- 0,018517	0,029315	0,272724		0,051866	0,067304
$X_1^2X_2^2X_3$	0,000537	0,000597	- 0,001453	- 0,000268		
$X_1X_2^2X_3$		- 0,002819	- 0,004344	- 0,004151	- 0,004269	- 0,005942
$X_1X_2X_3^2$		- 0,02933	- 0,02022			
Constant	13,110	47,602	2,832	18,934	2,116	37,141
% Fit	87,2	92,0	98,7	87,0	97,2	85,0

The parameters, k, x and y are empirical approximations and are given as:

$$k = \exp \left[1,7824 \, (1\text{-}E_\infty)^{-0,0713} \right]$$

$$x = \left(0,2837 + 0,8133 \sqrt{1 - E_\infty} \right)^2$$

$$y = 2,6081 \, (1 - E_\infty)^{-0,0713}$$

where E is the equilibrium bath exhaustion, related to the intrinsic partition of the exhausting material (chromium) between the bath and the wool fabric and depends on the liquor ratio as follows:

$$E_{\infty} = K_{\infty} / K_{\infty} + r$$

where $k_{\infty} = C_{f_{\infty}} / C_{b_{\infty}}$

or the relative amount of material (chromium) in the fibre to the amount in the bath at equilibrium.

r = liquor ratio.

Using this equation Maasdorp was able to determine the approximate diffusion coefficients which were subsequently inserted into the Arrheunis equation[118], whereupon, he arrived at the apparent activation energy necessary for the initial fast absorption of chromium by both dyed and undyed wool. An interesting anomaly arose from this kinetic study, where it was found that, for undyed wool, an increase in chroming temperature caused a decrease in the rate of absorption of chromium by the wool. This reversal of normal reaction kinetics was ascribed to the rate of deposition of chromium III in the wool fibre, produced by the reduction of the exhausting chromium VI species. In the dyed wool species, however, an increase in chroming temperature caused an increase in the rate of absorption of chromium by the wool.

It is clear from the work already carried out on chroming kinetics that there is a real need to further understand this rather complex process. To date only certain specific aspects of the kinetics of the chroming of wool have been dealt with by the different research workers, and, because of the diverse nature of the reaction conditions employed by the different workers, it is not possible to relate the different results to one another in a meaningful way.

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THE USE OF PROPRIETARY NAMES

The names of proprietary products where they appear in this report are mentioned for information only. This does not imply that SAWTRI recommends them to the exclusion of other similar products.

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