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**A Method for the Removal of
Chromium from Chrome Dyeing
Effluent**

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A METHOD FOR THE REMOVAL OF CHROMIUM FROM CHROME DYEING EFFLUENT

BY M.B. ROBERTS

ABSTRACT

The minimum quantity of chromate necessary for the production of deep colours of high wet fastness on wool is shown for four chrome dyes. Determination of residual chromium content in the spent dye liquors suggest that levels of about 1 mg/l may be found although occasionally levels as high as 5 mg/l may exist.

A method for the removal of residual chromium based upon its reduction to the trivalent state and subsequent precipitation as the hydrated oxide, assisted by a primary coagulant and a polyelectrolyte is investigated. Laboratory results show that the use of a sedimentation system can reduce the level of chromium to about 25 µg/l while the use of a filter system may achieve complete removal.

The additional cost of the proposed treatment is negligible in terms of both chemicals and time.

The importance of avoiding excess sequestrants is stressed.

INTRODUCTION

In spite of the development of reactive dyes for wool and the improvements in structure and methods of application of other wool dyestuff classes, the old established chrome dyes remain a very attractive proposition, particularly at heavy depths. No other single class of dyestuff combines such high fastness potential together with low cost. The lack of brightness associated with chrome dyes is not a disadvantage when the objective shade is dark brown, blue, green, maroon or a black.

However, increasing concern with environmental pollution in general and industrial effluent in particular indicates the possible demise of chrome dyes on account of the toxicity of certain salts of this metal and the levels at which it is currently being discharged from dyehouses. The legislation with respect to the maximum permissible level of chromium in effluent is under review and current limits vary widely, both between countries and even within a single country. Some pertinent figures are shown in Table I.

It is currently predicted that forthcoming legislation will reduce these levels to below 1 mg/l.

Results obtained during the present work suggest that spent chrome dyeing liquors may contain up to 20 mg/l chromium using currently

TABLE I
MAXIMUM PERMISSIBLE CHROMIUM (HEXAVALENT) IN
EFFLUENT (mg/l)

South Africa¹	
Pretoria	20
Durban	50
Johannesburg	Total of Cd, Cr, Cu, Fe, Zn, Ni not to exceed 50
West Germany¹	
	4
United Kingdom²	
	(Limits variable but the following is a typical example.)
	Compounds containing Cr, Cu, Ni, Cd, Zn, Pb or Sn in soluble or insoluble form. Maximum 20, individually or in total.
	Above metals in soluble form.
	Maximum 10, individually or in total

recommended dyeing procedures. Thus it is obvious that there is an urgent need to develop a means of closing the gap.

Some work has already been undertaken to remedy the situation. Japanese workers³ have claimed the almost perfect removal of heavy metals using a chelating resin. Another approach was stimulated by the work of Funke¹ who found, in a study of metals in urban drainage systems and their effect upon the potential re-use of purified sewage, that the chromium content of the primary settlement tank inflow was reduced by 90 *per cent* by the time the water had passed through the sand filter and that primary settlement alone caused a drop of 60 *per cent*. This improvement was found to be caused by the reaction of soluble chromium salts with sulphides arising from the reduction of sulphates by organic waste resulting in the formation and subsequent settlement of insoluble chromium compounds.

Funke and Coombs⁴, while studying the removal of shock loads of metals from sewage concluded that the reduction of hexavalent chromium to the trivalent state was essential for its precipitation and successful removal. Funke¹ has also reported on the use of an alum flotation unit as a means of removing heavy metals from purified effluent. Using a chemical dosage of 70 — 75 mg/Al₂(SO₄)₃ · 14H₂O, 1,2 — 1,6 mg/l polyelectrolyte and careful pH control, the chrome content could be reduced from 0,02 mg/l to zero.

These results and conclusions drawn by Funke indicate that the reduction of residual chromium to the trivalent state followed by insolubilisation and sedimentation might provide a means of producing a chromium free effluent particularly when coupled with a dyeing routine designed to produce the minimum chromium in the spent liquor.

After an extensive study of the chroming process by Hartley⁵⁻⁷, the consensus of opinion is that no fundamental departure from the established process seems likely. The essential stages in the chroming process are the reaction of the dichromate anion with the basic side chains in wool followed by a reduction of the hexavalent chromium to the trivalent state by the wool. The trivalent chromium reacts with the carboxyl groups in the fibre. The final stage involves the formation of a 1 : 2 metal-dye complex.

Langmann and Meier⁸ have also studied the chroming process with the objective of reducing the chrome content of spent dye liquors. They concluded that the blocking of the cationic sites in wool by the addition of sodium sulphate prevented the dichromate anions from reacting with the fibre, thereby making more chromium available for dye-complex formation and consequently reducing the necessary quantity of chromium. It is felt that this argument may not be valid since if dichromate anions are prevented from reacting with the wool, there is no other species present capable of effecting the necessary reduction of the chromium with the possible exception of the dye. It is true that some dyes require oxidation in order to develop their characteristic shade, but the number of such dyes is small. There is, therefore, the additional risk of oxidative damage to the dye if the chromium exists in the hexavalent state for any length of time.

The chemistry of chromium suggests the optimum form for precipitation to be the hydroxide or, more accurately, the hydrated oxide. This is precipitated on addition of hydroxyl ions to solutions of trivalent chromium ions. It is amphoteric, dissolving in both acid and concentrated alkaline conditions. Some residual chromium in the dye liquor is likely to be in the hexavalent state since reduction to the trivalent form occurs primarily within the wool fibre with very slow subsequent release. Thus a chemical reduction followed by an adjustment of pH to neutrality appears a simple method of rendering the chromium in a form suitable for precipitation and subsequent removal.

Further potential advantages in this approach are that the liquor will have a neutral pH and not an acidity of pH 3 or 4 and that residual colour may well be adsorbed onto the surface of the hydrated aluminium oxide and thus removed from solution.

The approach in this investigation has been to establish the minimum quantity of the chromium required to retain the shade and fastness to potting and milling normally associated with those dyestuffs under examination, and to determine typical chromium residues in the spent liquor. The efficiency of the

aluminium sulphate-polyelectrolyte treatment of insolubilised chromium residues has then been assessed using sedimentation and filtration techniques.

One other aspect of significance which has been examined is the influence of ethylene diamine tetra-acetic acid (EDTA), a reagent commonly recommended for use in chrome dyeing recipes as a means of sequestering metallic ions which might otherwise chelate with the dye. Theoretical considerations suggest that the presence of EDTA in quantities in excess of that required to sequester metallic contaminants would result in the sequestration of chromium ions in a water soluble complex which is resistant to the insolubilisation treatments.

EXPERIMENTAL

The dyeing method employed in this investigation was the afterchrome process, since this is the most commonly used of the three available and it gives the best overall fastness properties. Since the afterchrome method may be a single or double bath process, depending upon the degree of exhaustion obtained at the conclusion of the dyeing stage, both procedures have been studied in this work. The dyes used were commercial samples of the ®Eriochrome range, namely:-

Eriochrome Flavine A (Mordant Yellow 5)
Eriochrome Orange R (Mordant Orange 44)
Eriochrome AzuroI BFF 250% (Mordant Blue 1)
Eriochrome Black T fin. disp. 200% (Mordant Black II)

The depth of shade employed was 3 *per cent* (o.m.f.), based on the standard strength dye and 8 *per cent* for the black.

The fabric used throughout the investigation was an all-wool worsted material of fabric density 140 g/m². Samples of 10 g were used for each dyeing. Dyeings were carried out in an Ahiba laboratory dyeing machine. The dyebaths were set at 50°C with the following (all percentages expressed o.m.f.):-

0,25% ®Albegal A
5,0% Anhydrous Glaubers salt
3,0% Dye (or 8% for the black)
Acetic acid to pH5
Liquor: goods 50:1
Demineralised water was used in all cases.

After entering the fabric samples the bath was run for 5 minutes and then heated to the boil in 30 minutes. After 30 minutes at the boil the pH was adjusted

to 4 with formic acid to complete the exhaustion. After a further 30 minutes at the boil the baths were either discarded and fresh chroming baths prepared if two-bath systems were under investigation or cooled to 80°C when the required amount of potassium dichromate solution was added and the pH checked. The temperature was raised to the boil and boiling was continued for 60 minutes. Fresh chroming baths were prepared with the auxiliaries indicated above save that the sodium sulphate was omitted. The pH was adjusted to 4 with formic acid and the required amount of potassium dichromate added. After removal of the dyed samples and rinsing, the liquors were retained for residual chromium determination.

The effect of ethylene diamine tetra-acetic acid upon the residual chromium content of spent dye liquors and in treated liquors was studied using various concentrations of ®Irgalon BT.

The experimental work relating to the treatment of spent dye liquor was carried out on water to which soluble hexavalent chromium was added at concentrations of 1 and 5 mg/l respectively, together with Irgalon BT when required. The temperature of the water was maintained at 95°C and the pH adjusted to 4 with formic acid to simulate commercial dyeing conditions. The reduction of the hexavalent chromium was effected with sodium metabisulphite and the optimum concentrations for total reduction and the time required for total reduction were determined by estimating residual hexavalent chromium. After raising the pH to 7 with ammonium hydroxide in order to precipitate the chromium as hydrated chromic oxide, the influence of various concentrations of a primary coagulant, aluminium sulphate, and an anionic polyelectrolyte, upon the sedimentation of the oxide, was studied.

Sedimentation trials were carried out in measuring cylinders containing 1 litre of hot liquor to which quantities of $Al_2(SO_4)_3 \cdot 14H_2O$ varying from 100 mg to 600 mg and of ®Magnafloc 155, the polyelectrolyte, varying from 0,5 to 2,5 mg had been added. Prior to the sedimentation period, the system was stirred at 250 r/min for 60 seconds after the addition of each auxiliary. Samples of liquor were withdrawn at the 500 ml mark after various time intervals and their chromium contents were determined.

The preparation of the liquors for filtration was carried out in precisely the same manner as for the sedimentation trials. The filter bed was prepared in a 125 mm diameter glass funnel using a twist of glass fibre as support upon which were overlaid glass beads of diameter 2,5 — 3,5 mm to a depth of 20 mm followed by glass beads of 40 mesh to a depth of 30 mm. The liquors were passed through the bed and the eluant collected for chromium determination, the first 150 ml of each eluant being discarded.

The method used for the determination of chromium was a well-established one⁹ based upon the spectrophotometric estimation of a coloured chromium complex. The method permitted the separate determination of total

chromium and hexavalent chromium.

Fastness to potting and to acid and alkaline milling was determined by standard methods¹⁰⁻¹².

RESULTS AND DISCUSSION

The first part of the experimental work set out to determine, for a number of colours, the minimum quantity of chromate necessary to achieve the fastness properties normally associated with them and to determine the level of chromium in the spent dye liquor.

From Table II, several conclusions may be drawn concerning residual chromium contents in relation to the quantity of chromate applied. The residual chromium content is not directly proportional to the quantity of applied chromate but rises sharply at levels in excess of about 1,2 *per cent*. The blocking effect of sodium sulphate is clearly shown, particularly at levels of applied chromate in excess of 1 *per cent*. There is no correlation between residual chrome content for different dyes when identical percentage shades and amounts of chromate are used.

Table III illustrates the effect of variation in applied chromate concentration upon fastness to potting and acid and alkaline milling. Figures in parentheses are typical values quoted by the dye manufacturer. From an overall standpoint it may be noted that the optimum fastness ratings obtained in this investigation are very similar to those quoted by the manufacturer. It is also apparent that there is a clearly defined level of applied chromate below which almost all the fastness ratings begin to deteriorate. From a combined inspection of Tables II and III it is possible to select the minimum level of chromate necessary to achieve the optimum fastness characteristics and to relate this information to the residual chrome content. The relevant figures are displayed in Table IV.

It will be noticed that even in the presence of sulphate, the residual chromium can be reduced to the order of 1 mg/ℓ while still attaining satisfactory fastness properties, the only exception being the Mordant Orange 44 which, in terms of fastness properties, is not a very attractive proposition even when applied with greater amounts of chromate than are suggested in Table IV. In the absence of sulphate, a situation likely to exist when chroming in a fresh bath, the residual chromium contents are further reduced.

Using the ratio of dye and chromate, shown in Table IV, for each dye system, the effect of depth of shade upon residual chromium content and potting fastness is shown in Table V. Depths of shade of up to 4,5 *per cent* (12 *per cent* for the black) were employed. It will be observed that this constant ratio of dye to chromium gives very satisfactory results at all but the heaviest depth. However, the heaviest depth applied exceeds that shown in the manufacturers pattern card

TABLE II
EFFECT OF VARIATION OF APPLIED CHROMATE
CONCENTRATION ON RESIDUAL CHROMIUM
CONCENTRATION IN THE PRESENCE AND ABSENCE OF
SULPHATE IONS

3% Depth of Shade Applied (8% in the case of the Black)

Applied Chromate Concentration (% omf)	Residual Chromium Concentration (mg/l)	
	Sulphate Present	Sulphate Absent
Mordant Black 11		
0,25	0,06	0,06
0,5	0,10	0,14
1,0	0,56	0,33
1,5	4,13	0,74
2,0	21,00	9,75
Mordant Orange 44		
0,2	0,15	0,09
0,4	0,40	0,15
0,75	1,13	0,38
1,2	5,13	1,85
1,5	12,13	8,25
Mordant Yellow 5		
0,2	0,08	0,05
0,4	0,20	0,13
0,75	1,30	0,38
1,2	11,25	1,00
1,5	20,00	2,23
Mordant Blue 1		
0,2	0,06	0,06
0,4	0,19	0,14
0,75	0,75	0,59
1,2	7,50	1,45
1,5	24,00	6,25

TABLE III
EFFECT OF VARIATION OF APPLIED CHROMATE
CONCENTRATION ON FASTNESS TO POTTING, ACID AND
ALKALINE MILLING

3% o.m.f. Depth of Shade Applied (8% in the case of black) Chroming carried out in the presence of Sulphate

Figures in parenthesis are typical values quoted by the manufacturer

Applied Chromate Concn. (% o.m.f.)	Potting Fastness		Acid Milling Fastness		Alkaline Milling Fastness			
	Change in Shade	Staining of Cotton	Staining of Wool	Change in Shade	Staining of Wool	Change in Shade	Staining of Cotton	Staining of Wool
Mordant Black 11								
0,25	5	4-5	3-4	5	3	4	4	3-4
0,5	5	4-5	4	5	3-4	4	4-5	4
1,0	5	5	4-5	5	4	5	5	4
1,5	5	5	4-5	5	4	5	5	4
2,0	5	5	4-5	5	4	5	5	4
	(5)	(5)	(4)	(5)	(4-5)	(5)	(5)	(4-5)
Mordant Orange 44								
0,2	3	4	2	2	2-3	3-4	3-4	2-3
0,4	3-4	4-5	2	2	2-3	4	3-4	2-3
0,75	4	5	3	2-3	3	4-5	4	3-4
1,2	4	5	3-4	3	4	4-5	4	4
1,5	4	5	3-4	3	4	4-5	4-5	4
	(4)	(5)	(3-4)	(2-3G)	(4)	(3-4)	(3-4)	(4-5)
Mordant Yellow 5								
0,2	2-3	4-5	3-4	2	2-3	3	4	3-4
0,4	3-4	4-5	4	3	2-3	3	4-5	3-4
0,75	4-5	5	4-5	3-4	3	3-4	5	4
1,2	4-5	5	4-5	3	3	4	5	4-5
1,5	4-5	5	4-5	2-3	3	4	5	4-5
	(4-5)	(5)	(4-5)	(2-3)	(4)	(4)	(5)	(5)
Mordant Blue 1								
0,2	4	4-5	4-5	3	3	4-5	5	4-5
0,4	4-5	5	5	3-4	3	4-5	5	4-5
0,75	5	5	5	4-5	4	4-5	5	4-5
1,2	5	5	5	4-5	4	4-5	5	5
1,5	5	5	5	4-5	4	5	5	5
	(5)	(5)	(5)	(4)	(5)	(4-5)	(5)	(5)

TABLE IV
MINIMUM QUANTITIES OF CHROMATE NECESSARY TO
ACHIEVE ADEQUATE FASTNESS AT 3 PER CENT DEPTH OF
SHADE (8 PER CENT FOR BLACKS) AND EXPECTED
RESIDUAL CHROMIUM CONTENT IN PRESENCE OF
SULPHATE IONS

Dye	Percentage Chromate Required	Residual Chromium Content (mg/l)
Mordant Black 11	1.0	0.6
Mordant Orange 44	1.0	4.4
Mordant Yellow 5	0.75	1.3
Mordant Blue 1	0.75	0.75

and is unlikely to be required for commercial purposes.

The levels of residual chromium used for the investigation into the effluent treatment process were dictated by the results obtained in the first part of the work. It has already been shown that satisfactory dyeings can be achieved with a level of residual chromium of the order of 1 mg/l. in most cases. However, in order to cover anomalous dyes, such as Mordant Orange 44, which consistently gave higher values and to provide a safety margin in situations when it might prove advisable to use slightly more chromate than the minimum determined in this work, a level of 5 mg/l. residual chromium was also employed.

The amount of sodium metabisulphite necessary to ensure reduction of the hexavalent chromium was found to be 0.1 g/l. Although this quantity is far in excess of that theoretically required to reduce even the upper level of chromium, it will be appreciated that other reducible species, such as fibre and dye, are also present. The rate of reduction of the chromium is extremely fast, if not instantaneous, since samples of liquor removed from the system immediately after stirring in the metabisulphite were shown to contain no hexavalent chromium.

It is important to make the adjustment to pH 7 accurately since the chromic oxide dissolves in both acids and alkalis. At the higher level of chromium residue the characteristic grey-green flocculant precipitate was observed to be precipitating even without the coagulant.

TABLE V
EFFECT OF VARIATION IN DEPTH OF SHADE ON RESIDUAL CHROMIUM CONTENT BEFORE SEDIMENTATION TREATMENT AND POTTING FASTNESS

Ratio of Chromate to Dye as indicated in Table IV in all cases

Depth of Shade (% o.m.f.)	Residual Chromium (mg/l)	Potting Fastness		
		Change in Shade	Staining of Cotton	Staining of Wool
Mordant Black 11				
4	0,24	5	5	4 -5
8	0,61	5	5	4 -5
12	1,93	5	5	4
Mordant Orange 44				
0,5	0,13	4	5	3 -4
1,5	0,59	4	5	3 -4
3	4,38	4	5	3 -4
4,5	18,75	4	5	3
Mordant Yellow 5				
0,5	0,10	4 -5	5	4 -5
1,5	0,31	4 -5	5	4 -5
3	0,98	4 5	5	4 -5
4,5	3,25	4 5	5	4 -5
Mordant Blue 1				
0,5	0,03	5	5	5
1,5	0,30	5	5	5
3	1,10	5	5	5
4,5	6,75	5	5	4 -5

The results of the sedimentation trials are shown in Figs 1 — 5, Figs 1 — 4 referring to the residual chromium level of 1 mg/l and Fig 5 to that of 5 mg/l. From Fig 1 it is apparent that using 0,5 mg/l polyelectrolyte, a dosage of aluminium sulphate of at least 400 mg/l is required to reduce the chromium content to below 50 $\mu\text{g/l}$. Fig 2 indicates that the use of 1 mg/l polyelectrolyte allows chromium levels of less than 50 $\mu\text{g/l}$ to be achieved with as little as 200 mg/l aluminium sulphate while Fig 3 suggests that no advantage is to be gained in using still higher levels of polyelectrolyte. From Fig 4, which shows the use of 200 mg/l and 400 mg/l aluminium sulphate with all three levels of polyelectrolyte, it will be observed that the optimum combination is the use of 1 mg/l polyelectrolyte and 200 — 400 mg/l aluminium sulphate. Under the

experimental conditions employed, the chromium content was reduced to about 25 $\mu\text{g}/\ell$ in 30 minutes.

Fig 5 shows the settlement characteristics for the 5 mg/ℓ residual chromium system. It will be noted that although a dosage of aluminium sulphate of 300 mg/ℓ produces a liquor containing less than 50 $\mu\text{g}/\ell$ chromium, a period of some 8 hours is necessary for its achievement. An increase in aluminium sulphate to 600 mg/ℓ produces the same result in only 1 hour.

Filtration of the combined precipitates of the hydrated oxides of chromium and aluminium through the bed of glass beads reduced the level of chromium to zero in both test liquors.

The influence of the presence of free EDTA is demonstrated in Table VI. There being no metals in the water used, the levels of EDTA illustrate the effects of either its unnecessary addition or addition in excess. Clearly the chromium reacts freely with the sequestrant and the complex so formed is resistant to the reactions designed to effect precipitation.

TABLE VI
EFFECT OF FREE EDTA (IRGALON BT) AT THE CHROMING
STAGE ON RESIDUAL CHROMIUM CONTENT BEFORE AND
AFTER THE SEDIMENTATION TREATMENT

Data for 3% o.m.f. Mordant Yellow 5 applied by Single Bath using 5%
Anhydrous Glaubers salt, 0,75% Chromate and Demineralised Water

Free Irgalon BT (g/l)	Residual Chromium Content (mg/l)	
	Before Treatment	After Treatment
0	0,30	0,02
0,05	1,25	0,80
0,1	2,66	1,97
0,15	4,35	3,20
0,2	5,65	4,38

Currently recommended rate of addition of Irgalon BT - 0,1 g/l

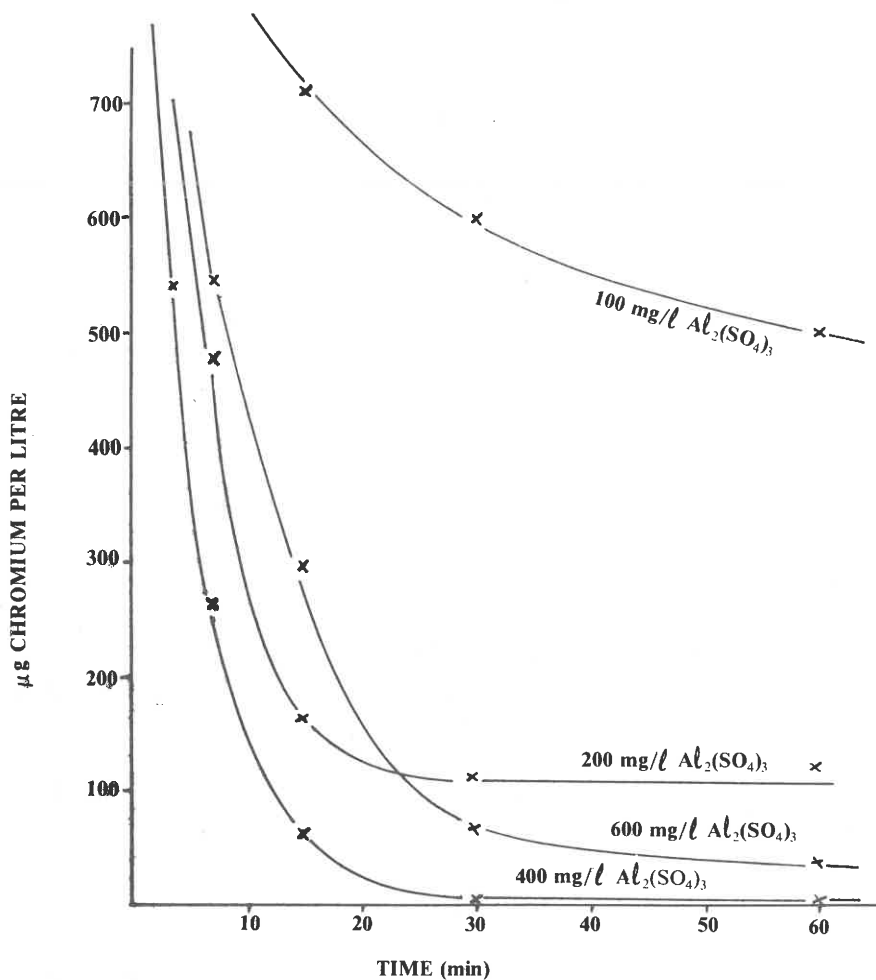


Fig 1 Effect of Aluminium Sulphate Concentration on Settlement Characteristics of Liquor Containing 1 mg/l Chromium in the Presence of 0,5 mg/l Magnafloc 155

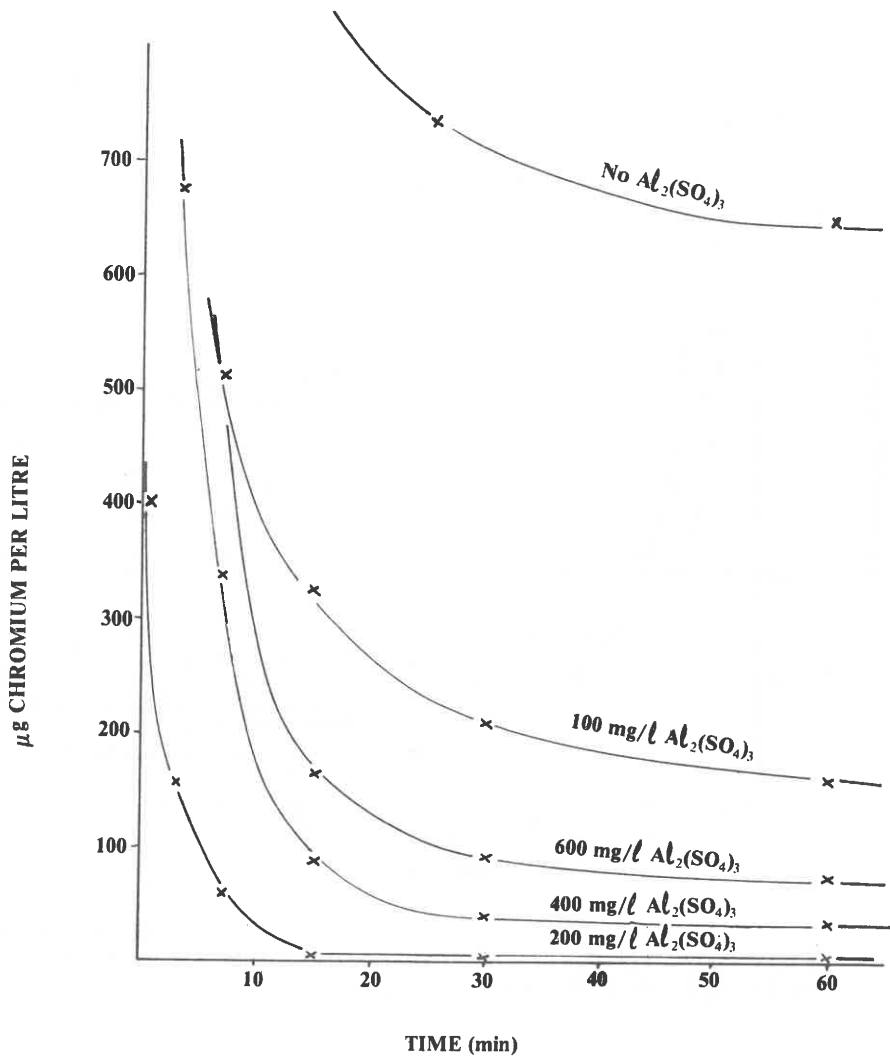


Fig 2 Effect of Aluminium Sulphate Concentration on Settlement Characteristics of Liquor Containing 1 mg/l Chromium in the Presence of 1.0 mg/l Magnafloc 155

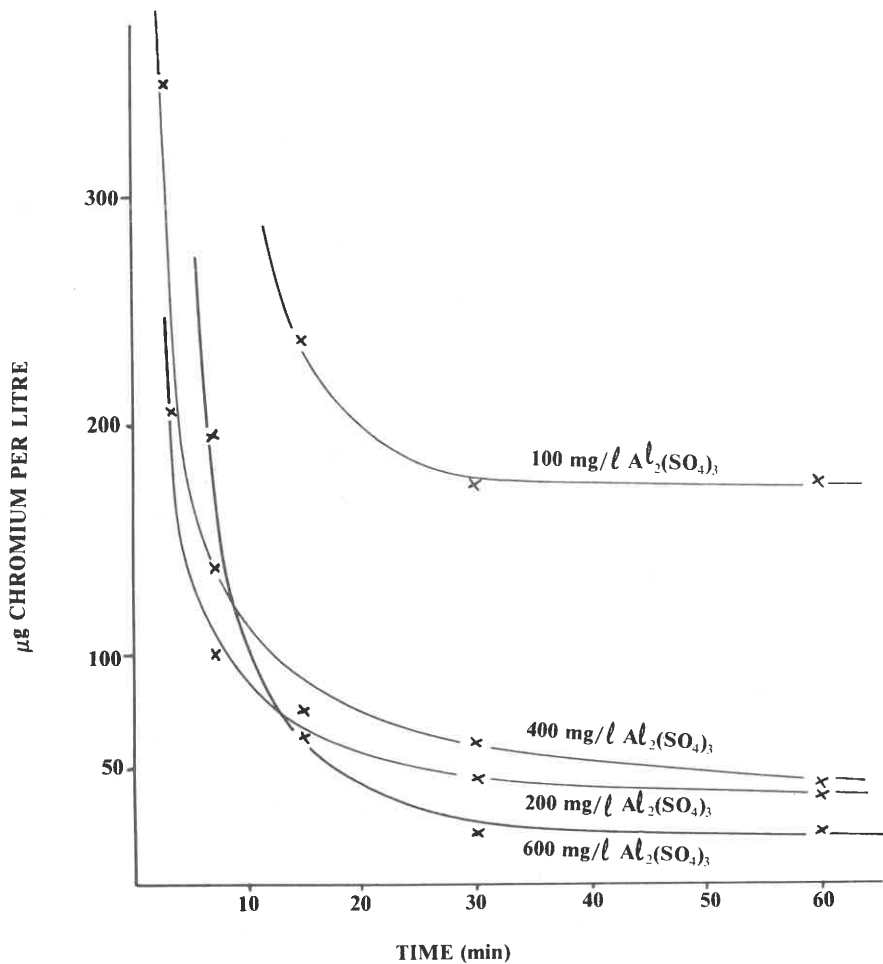


Fig 3 Effect of Aluminium Sulphate Concentration on Settlement Characteristics of Liquor Containing 1 mg/l Chromium in the Presence of 2,5 mg/l Magnafloc 155

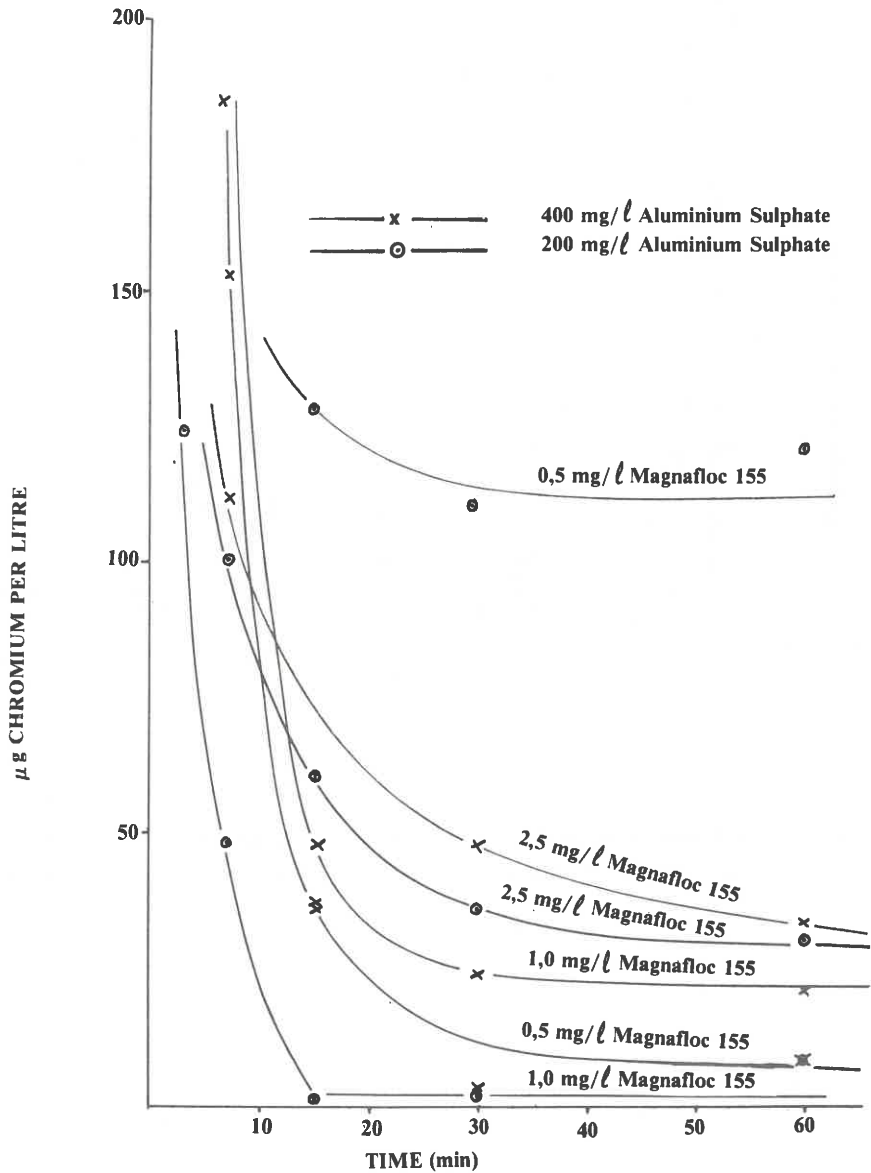


Fig 4 Relative Efficiencies of Some Aluminium Sulphate-Magnafloc 155 Settlement Systems on Liquor Containing 1 mg/l Chromium

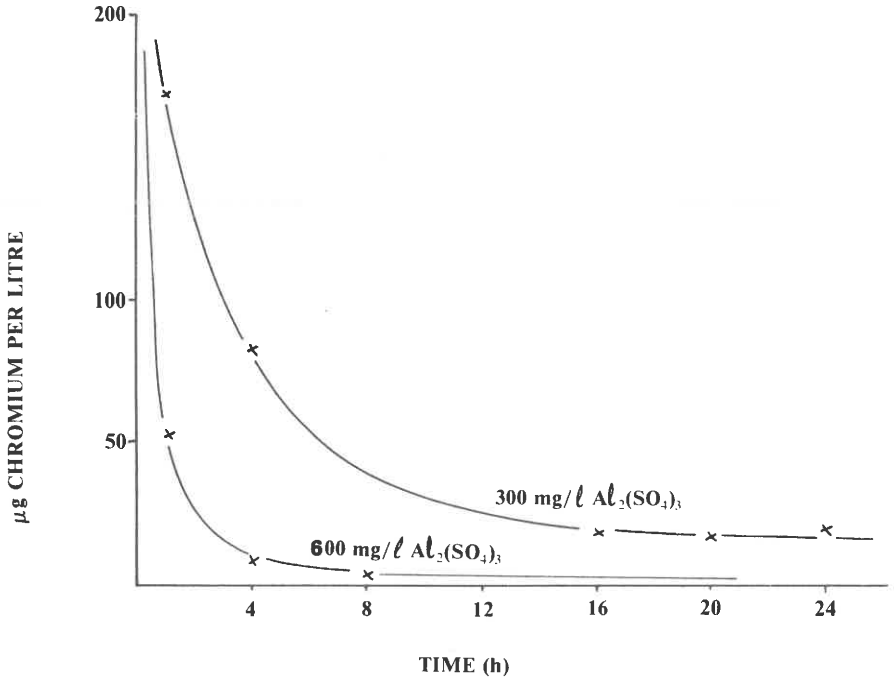


Fig 5 Settlement Characteristics of Liquor Containing 5 mg/l Chromium using 1 mg/l Magnafloc 155 and 300 mg/l and 600 mg/l Aluminium Sulphate

SUMMARY AND CONCLUSIONS

This investigation has shown that the problem of residual chromium in chrome dyeing effluent can be overcome and that this factor is not a valid argument for the discontinuation of the use of chrome dyes.

The early part of the work has shown that, by using the appropriate amount of chromate, it is possible to produce dyeings of similar wet fastness characteristics to those normally associated with the particular dyestuffs from dyeing systems which exhibit residual chromium contents of, in many cases, about 1 mg/l and, in all cases tested, not exceeding 5 mg/l. The blocking effect of sodium sulphate has been clearly demonstrated but is not considered critical at the levels of chromate recommended for use. The slight shade changes accompanying changes in the amount of applied chromate have been considered unimportant for several reasons. With some dyes there is little or no change whereas, with others, there is a steady change as the amount of chromate changes. It is considered that the mixing of dyes could overcome any discrepancies. In this respect the dye manufacturers could render a valuable service if, within each range of chrome dyes, the respective strengths were adjusted such that *x per cent* of each dye required *y per cent* of chromate.

The system of treatment of spent dye liquors containing not more than 5 mg/l residual chromium which has been developed has shown itself capable of removing all traces of chromium provided a filtration system is used and of reducing the residual chromium to about 25 $\mu\text{g/l}$ where sedimentation is employed. The essential steps are as follows:-

- (a) Adjust pH to 3 — 4 with formic acid, if necessary.
- (b) Add to the spent dye liquor 0.1 g/l sodium metabisulphite and circulate liquor
- (c) Raise pH to 7 with ammonium hydroxide
- (d) Add 300 mg/l or 600 mg/l aluminium sulphate, previously dissolved in the minimum quantity of water. Circulate liquor.
- (e) Add an appropriate quantity of a suitable polyelectrolyte. Circulate liquor for 5 minutes.
- (f) Pump liquor to sedimentation tank or through the filter.
- (g) The presence of excess reducing agent will give rise to an undesirably high B.O.D. in which case the effluent should be dosed with a suitable oxidising agent, e.g. hydrogen peroxide.

It is envisaged that this treatment will be carried out in the dyeing vessel at the completion of the chroming stage but prior to rinsing, the dyed fibre being removed from the spent liquor. This is easily achieved in most modern package and loose stock machinery but may not be practicable in winch-type equipment.

However, black chrome dyeings, agitated for 30 minutes in a bath in which the precipitation treatment was carried out and with no subsequent rinsing, showed no visible signs of a white precipitate in the wet state nor after final drying.

The mass of precipitated sludge is quite small. Assuming 1 000 kg dyed wool, a liquor ratio of 20:1, and a dosage of 600 mg/l aluminium sulphate, the sludge mass, calculated as Al_2O_3 , is 2 kg. Changes in dosage of aluminium sulphate and liquor ratio may be expected to alter this figure on a pro rata basis.

Using the above example, the current materials cost is about R0,01/kg wool and the extra plant time required should not exceed 15 minutes. The installation of sedimentation facilities and filtration plant as ancillary equipment in modern dyehouses is becoming obligatory in order to meet existing legislation.

The results concerning the use of EDTA indicate that a standard addition such as is recommended by many dyemakers is clearly inadequate. The removal of metals from water prior to its use for dyeing is to be preferred. Failing this, the regular determination of trace metals in water coupled with the appropriate addition of EDTA would do much to prevent the sequestration of chromium and its subsequent failure to precipitate. The local water authority is normally able to provide an up-to-date metals analysis of municipal water while dyehouses using their own water supplies might well invest in the necessary skills and equipment in order to make their own analyses.

Several significant factors remain to be investigated. The picture would be more complete if the whole gamut of chrome dyes was examined. While the effect of sodium sulphate is not critical its effect becomes more pronounced as the residual chromium increases. Mordant Orange 44 is a good example. It would be interesting to consider the use of alternative levelling and restraining agents based upon chemical systems of different ionic characteristics to sodium sulphate.

Perhaps the most important feature is the development of a system which sequestrates metals likely to chelate with the dye but which does not prevent the subsequent removal of chromium. It is possible that the use of a phosphate auxiliary might be beneficial in this respect. Theoretical considerations indicate that both iron and chromium phosphates are insoluble in water and organic acids and thus, provided that the dyeing and chroming process could be conducted in the absence of mineral acid, the iron would remain insolubilised together with chromium rendered insoluble by excess phosphate. Both these insoluble products ought to be removable by filtration or sedimentation techniques.

These outstanding factors will be the subject of a further investigation.

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THE USE OF PROPRIETARY NAMES

The product names ®Eriochrome, ®Albegal and ®Irgalon are registered trade marks of Ciba-Geigy Ltd., ®Magnafloc 155 is a registered trade mark of Allied Colloids. The fact that chemicals with proprietary names have been mentioned in this report in no way implies tht there are not others of equal or greater merit.

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