UNIVERSITY OF CINCINNATI

May 26 1953

I hereby recommend that the thesis prepared under my supervision by William K. Schweitzer, Jr.

entitled Studies on the Mechanism of Leather Dyeing

be accepted as fulfilling this part of the requirements for the degree of Doctor of Philosophy

Approved by:

Form 668—G.S. and T.C.—1M—4-51

STUDIES ON THE MECHANISM OF LEATHER DYEING

A dissertation submitted to the
Graduate School of Arts and Sciences
of the University of Cincinnati

in partial fulfillment of the
requirements for the degree of

DOCTOR OF PHILOSOPHY

1953

by

William Kenmore Schweitzer, Jr.

B.S.E. Princeton University 1949
M.S. University of Cincinnati 1951

ProQuest Information and Learning Company
300 North Zeeb Road
P.O. Box 1346
Ann Arbor, MI 48106-1346

Acknowledgements

The author wishes to express his thanks to the Foundation Tanners' Council of America and to the Hilton-Davis Chemical Company, whose support and cooperation made this work possible.

Thanks are also extended to Drs. Fred O'Flaherty and R. M. Lollar under whose direction this work was carried out, and to Mr. W. T. Roddy and Dr. S. S. Kremen of the Tanners' Council Research Laboratory staff for their valuable suggestions and advice.

Table of Contents

Introduction

Although dyeing is one of the more important processes in converting tanned skins into a saleable product, there has been relatively little experimental work attempted to elucidate the exact nature of the mechanism by which this is accomplished. Only recently, in the work of European investigators, has any attempt to define the nature of the forces involved been made. Yet, in the past few years, great strides have been made on this same problem in connection with other proteins and polyamide materials which, fundamentally, are very similar to collagen, the basic protein of skin and hide. With this background of work on similar proteins, and the more recent investigations of leather, this study was initiated in an attempt to more fully investigate the details of the dyeing mechanism.

This paper has confined its scope to chrome tanned leathers dyed with anionic dyes, particularly of the simple, monoazo type. These restrictions are still broad enough so that the principal tannage types and one of the more important class of dyes are included.

The earliest investigations of leather dyeing were primarily concerned with showing a stoichiometeric combination of the dye with the leather, and the formation of salt linkages was either recognized or inferred (3, 4, 5, 13, 17, 18, 30, 43). A rather similar view, but also postulating a Donnan membrane, was taken by Elod and Kohnlein (12). However, Vickerstaff points out that this view does not satisfactorily account for the differences in the affinities of similar dyes in the case of wool (43), and the same argument must necessarily hold with leather. Nevertheless, work on other proteins has also indicated that electrostatic forces may not be ignored.

The role of secondary binding forces between the dye and collagen has not received much attention, although Gustavson (16) suggested their importance in 1928. Cockbain has also speculated that hydrogen bonding must be a major factor (7), although he has offered no experimental evidence in this regard. More recently Otto (34) has shown that the pi, or mobile, electrons of conjugated double bond systems play a definite role in binding dyes to leather, leading to secondary forces which reinforce electrostatic bonds.

Studies on proteins other than collegen has given much more evidence of the importance of these secondary bonding forces (i.e. hydrogen bonding and van der Waal forces) (1, 9, 10, 19, 36, 38, 40, 41, 42). Klotz and his co-workers (22, 23, 24, 25, 26, 27) especially have amassed a large amount of evidence showing that these weak forces explain the differences in binding of dyes of similar structure. They have shown that dyes with the same number of polar groups, but differing in the size of their aromatic rings, have increased binding affinity for the protein with increased molecular weight, and conclude that these differences are due to van der Waal interactions, Teresi and Luck (45) have shown that increasing the length of side chains of aromatic carboxylic acids also increases the binding energy and this increase is probably due to the effect of additional van der Waal forces.

Gilbert (15) has also shown that replacement of the benzene ring of several dyes by a naphthalene ring increases the affinity of the dyes for wool, and concludes that secondary forces must be important.

Karush (19, 20, 21) and Cogin and Davis (8) indicate that there are also differences in the reactivity of the sites on the protein and that configurational differences of both the dye and the protein contribute toward differences in the binding. These conclusions are based on studies of competition between dyes and detergents for the protein sites at various concentrations. Teresi (44) has also shown, by modifying the e-amino groups of lysine and the guanidinal groups of arginine with formaldehyde, that methyl orange does not bind at the same sites as nitrophenolates. And with wool, Speakman and Elliott (39) indicate that deamination reduces dye affinity, but that combination with weak acids is not solely through the amino group.

There is also evidence from the investigations of nylon, a polyamide free of the confusing effects of varying side chain groups, that both electrostatic and hydrogen bonding to the peptide groups occur (6, 29, 49). This is due to the ability of nylon to bind amounts of dye far in excess of that accounted for by the free amino groups. However, Klotz (22) has demonstrated that dyes with phenolic groups para to the azo linkage are bound more strongly than those with the phenolic groups in the ortho position. He attributed this difference to the ability of the latter to form an intramolecular hydrogen bond and the stronger interaction of the para isomer with the solvent.

In the specific case of chrome tanned collagen, consideration must also be given to the possibility of reaction of the dye with the chrome complex. Elod and Hansel (11) stated that, in dyeing chrome leather, part of the dye is combined with the protein and part with the complex. Otto (33) has recently shown that anionic dyes will penetrate the basic chrome complexes in solution, and states that this also occurs on the leather, with the degree of such combination being determined by the ratio of the molecular weight to the number of sulfonic acid groups on the dye. Tewari and Ohosh (46) have also shown that both acid and basic dyes can be bound by hydrated chromic oxide (2).

Therefore, a study of the dye-leather system must consider four types of bonding forces: (1) electrostatic bonds or salt linkages between the free amino groups of the protein and the sulfonic acid groups of the dye, (2) hydrogen bonds between the active hydrogens of the dye and the centers of high electron density on the protein, or between active hydrogens on the protein and the azo linkage of the dye, (3) short range van der Waal forces between the dye and the protein, and (4) coordinate bonds between the dye and the chrome complex. From other investigations these types of forces have been shown to occur in dye-protein systems or dye-chrome systems. Strict covalent bonding has not been seriously considered for these systems in the past, and has not been investigated in this work.

Experimental Plan

The initial problem to be solved in this study was an adequate means of evaluating the dyeing of the leather. In order to answer this question, and to provide some additional information needed in the approach to the problem of the specific bonding forces involved, a survey experiment was carried out. Four types of chrome tannages and depickled, untanned stock were dyed with four different dyes at five pH levels to get an estimate of the effect of each of these sources of variance (See Figures 1 and 2). In addition one undyed set was carried as a control. This entire experiment was set up on a Latin Square plan and the dyeings were analyzed in terms of dye bound, surface coloration, and physical properties of the leather.

The preliminary experiment indicated that the rate of dyeing and the amount of dye bound in a given period were the most valuable means of evaluating the dyeing. It also provided some indications that secondary valence forces were

Figure 1

Design of Survey Experiment

	Tannages				
Dyes	**Depickled, Untanned**	**Unmasked**	**Tartrate Masked**	**Unmasked, Quebracho Mordanted**	**Two Bath**
Orange G	Aa2	Bb3	Dc4	Cd5	Ee1
Malachite Green	Cc3	Da1	Ed2	Be4	Ab5
Orange II	De5	Ad4	Cb1	Ea3	Bc2
Phenol Red	Eb4	Ce2	Ba5	Ac1	Dd3
Undyed	Bd1	Ec5	Ae3	Db2	Ca4

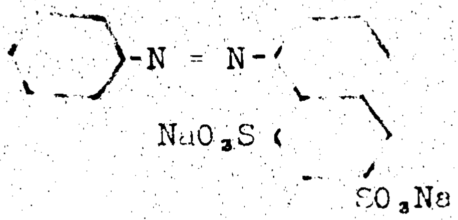
Key:

A = pH 3.5   a = Areas AG   1 = Skin 1
B = pH 4.1   b = Areas BH   2 = Skin 2
C = pH 4.7   c = Areas CI   3 = Skin 3
D = pH 5.3   d = Areas DF   4 = Skin 4
E = pH 5.9   e = Areas EJ   5 = Skin 5

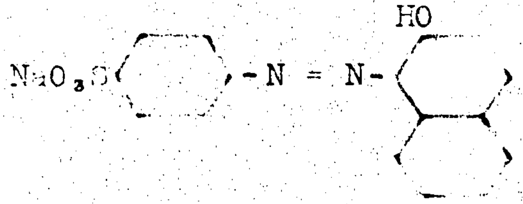
Figure 2

Dye Structures

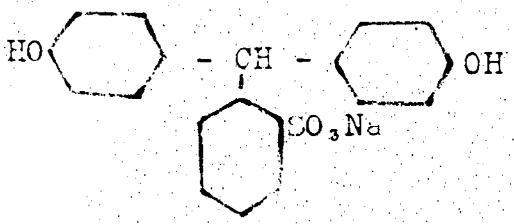
Orange G
C. I. 27



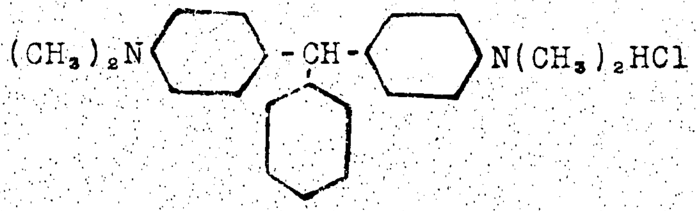
Orange II
C. I. 151



Phenol Red WS.



Malachite Green
C. I. 657



important, and that the effect of polar groups could not be ignored. In addition the initial experiment was deliberately designed to give information as to the effect of between skin and within skin variability on dyeing.

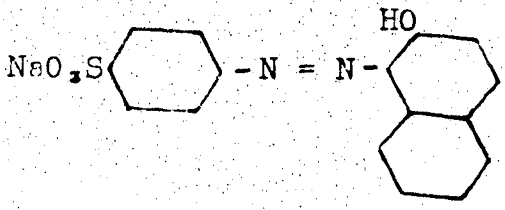
With this preliminary information at hand, work was designed to attack the problem of the specific forces involved. Four dyes of similar constitution were selected, so that their structural differences would enhance or inhibit various types of bonding (Figure 3). Orange II (C.I. 151) was chosen as the basis for comparison. Then Orange I (C.I. 150), which differs only in that the phenolic group is para instead of ortho to the azo linkage, would have a greater potential for hydrogen bonding to the substrate since the possibility of forming an intra-molecular bond to the azo link would not be present. Fast Red A (C.I. 176) was selected because the added aromatic ring would increase the molecular weight, and, consequently, its van der Waal attraction would be greater than that of Orange II. Finally Red II was chosen to show the effect of increased sulfonic acid groups and, therefore, greater salt formation potential.

Recalling that penetration of the chrome complex by the dye has been suggested as playing an important role in the dyeing, tannages were used that presented varying degrees of difficulty for the penetrant. An unmasked tannage was used as a basis of comparison, and formate masked and tartrate masked tannages were selected to give easily and

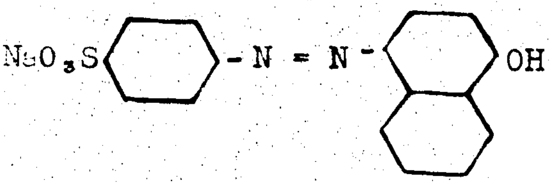
Figure 3

Dye Structures

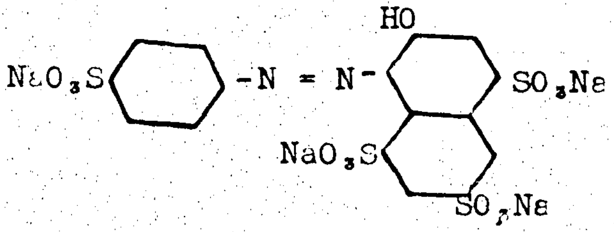
Orange II
C. I. 151



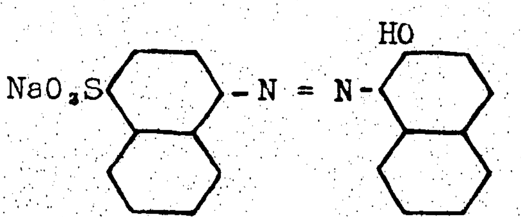
Orange I
C. I. 150



Red II



Fast Red A
C. I. 176



difficultly displaced anions respectively. In addition, the tartrate anion gave an increased possibility for hydrogen bonding through its hydroxyl groups. A fourth tannage, unmasked and retanned with formaldehyde was also included. It was felt that the formaldehyde would react with the free amino groups and thus inhibit salt formation at those sites.

Finally, the pH was varied to study its effect on these other variables. Dyeings were run both at a pH slightly above the isoelectric point of the tanned stock, and at a pH more nearly comparable to normal dyeing procedure.

This entire experiment was designed to be analyzed by the analysis of variance technique, thus giving a statistical basis to the information obtained. The dyeings were evaluated using the rate of dyebath exhaustion as the criterion.

To determine if the dyes were held in the same manner and by the same mechanism that was responsible for its takeup by the leather, an additional experiment was made on the dry, dyed leather. The leather samples were ground and subjected to continuous extraction with agents that are known to be specific bond breakers. Water was used as a basis for comparison and the samples were washed with various salts at a constant rate. Urea, specific for breaking hydrogen bonds, sodium sulfate, to break salt links, and sodium oxalate, which is a very strong complex penetrant, were used to wash out the dye held by these various types of forces. The wash liquors were then analyzed for their dye content and the percent dye removed by each could be calculated.

From the data obtained on the uptake of the dye by the leathers, the effect of the various factors on the dyeing could be determined. Thus, a basis for postulating the mechanism was obtained. Similarly, the effect of the various washing agents indicated the forces involved in holding the dyes on the dry leather.

Procedure

A. Survey Experiment -- An initial experiment was made to determine the important factors for further study and to determine the optimum tannage and dyeing conditions. Pickled calfskins were cut into four inch squares and conditioned in a standard pickle solution after marking for identification. The pickle liquor contained 12 per cent sodium chloride on the solution basis and was made acid with sulfuric acid, to an equilibrium pH of 2.6. The pieces were held in this liquor and withdrawn as needed.

A 31 per cent basic chrome liquor was prepared by the reduction of chromic acid with sulfur dioxide and subsequent neutralization with calcium hydroxide. Portions of this liquor were masked with sodium tartrate to give a molal ratio of one mole of tartrate to six moles of chromium.

Tannage was accomplished with the unmasked and tartrate masked chrome solutions on the pieces designated in the design (Figure 1) in the following manner: The pieces were placed in one quart glass jars containing five per cent sodium chloride and 1.48 per cent chrome (as the oxide) on the wet stock weight, and enough water to give a float of 3:1. The jars were placed in a launderometer and run for four hours at 90° F., after which the temperature was raised to 100° F. and the run continued for an additional 20 hours. The pieces were then neutralized to pH 3.5 by the addition of several feeds of borax solution at the same temperature, and again run for 24 hours. A small additional amount of borax was needed to bring the final pH to 3.4-3.5. The pieces were removed from the exhausted liquor and placed in the deep freeze (-10° F.) until needed for dyeing.

The pieces needed in the two bath tannage were placed in one quart glass jars containing two per cent hydrochloric acid and five per cent sodium dichromate (based on the wet, pickled weight of the skin) and sufficient water to give a float of 2.4:1. The jars were placed in the launderometer, and, after running for 24 hours at 75° F., then removed. They were placed grain-to-grain between two blotters, saturated with water, and wrapped in a damp towel for 24 hours. At the end of this period the pieces were placed in jars containing 30 per cent sodium thiosulfate (on the wet, pickled weight) and 300 per cent water, and run in the launderometer at 90° F. for 24 hours. During this time, dilute hydrochloric acid was added in several feeds so that the final pH of the system was 3.3-3.4.

The samples that were depickled were placed in 600 per cent 0.17N acetate buffer of pH 4.8 for two days with good agitation. They were then transferred to 500 per cent of 0.1N acetate buffer at pH 3.3 containing five per cent sodium chloride on the solution basis, and held in this solution for two days with agitation. The samples were then removed and frozen.

The frozen samples were prepared for dyeing by placing the appropriate pieces in 0.1N acetate buffers (700 per cent on the wet pickled weight) of the required pH for 2.5 hours. They were then removed and placed in their respective glass jars containing 100 per cent of the appropriate dye solution (0.1M), 170 per cent of 0.017N acetate buffer of the same pH as previously, and 3.4 per cent sodium chloride, all on the wet, pickled weight basis. The jars were placed in the launderometer for 2.5 hours at 120° F., removed, the samples washed with 600 per cent water twice, and the pieces tacked to dry.

One milliliter samples of the dyebath were removed before the skins were added, and every 30 minutes thereafter, and the dye concentrations at each of these intervals determined spectrophotometrically. The washings were also saved to determine the amount of dye removed under these conditions.

All of the samples were treated in this manner except those mordanted. In this case, two per cent of dry sumac extract in 300 per cent water was placed with the samples in jars after the initial buffer was added. The jars were then run in the launderometer for one hour at 120° F., the excess liquor discarded and the samples washed with 600 per cent water for 30 minutes. The samples were then blotted dry and dyed as above.

The above dyeings were evaluated for dye uptake before and after washing, surface coloration, and tensile strength. These results will be discussed below.

B. Dyeing Rate Study -- A more detailed study of the factors in leather dyeing was made by investigation of the rate of dyebath exhaustion. Pickled calfskins were cut into one inch squares, all taken from the area shown by previous work to give the most reproducible dye exhaustion results (37). These were placed in a pickle liquor containing 12 per cent sodium chloride and enough sulfuric acid to bring the pH to 2.5. After a minimum conditioning period of five days in the pickle, the pieces were removed and divided into four groups for the tanning.

Each group was tanned with 31 per cent basic chrome liquor -- unmasked (two groups), tartrate masked, or formate masked. The masking agents were prepared in the same ratio as in the previous experiment. Each group of pieces was placed in an empty glass jar with an amount of liquor equivalent to 0.0149 grams chrome (as the oxide) per gram of wet, drained pickled skin, and 0.05 grams sodium chloride per gram of skin. Enough water was added to give a 1.5:1 float, and the tannage was carried out in the launderometer at 90° F. for 24 hours. At the end of this period the tannages were neutralized with borate to pH 3.5 - 4.0 and allowed to set 48 hours. The pH was again checked and adjustments were made to bring the final pH to 3.5. One group of the unmasked, chrome tanned pieces was retanned by running them with 100 per cent water, two per cent borax, and one per cent formaldehyde (all based on the wet, tanned weight) in the launderometer at room temperature for 48 hours. As each of the tannages was completed, the pieces were placed in the deep freeze for storage.

The pieces were divided into groups of about 50 grams each for dyeing according to the experimental design. Each group was placed in 1000 per cent acetate buffer of pH 3.6 or 4.7 according to the plan, and held there 16 hours. The pieces were then removed and placed in a one quart jar containing 0.0001 moles of the appropriate dye per gram of the wet, tanned leather with enough water to give a float of 3:1 and having a buffer concentration of 0.2N acetate buffer at the correct pH. The dyeing was carried out in the launderometer at 120° F. One milliliter samples of the dye liquor were removed at time intervals of 0, 1/3, 2/3, 1, 1½, 2, 3, and 4 hours, by which time the dyeing rate had reached a fairly constant value. At the end of the dyeing time the exhaust liquor was drained off, and the leather rinsed with 500 per cent water. The washings and the exhaust liquor were combined for analysis.

After rinsing the leather was placed in the hydraulic press between two blotters and the uncombined dye pressed out at a pressure of 4000 psi. The samples were then air dried and weighed.

From the dye concentration at each time interval, which was determined spectrophotometrically, the dye take-up rate curve was plotted for each case.

C. Dye Removal Study: Each of the above dyeings was ground in the Wiley Mill and subdivided according to the experimental plan. Samples of 1.500 grams each, for all of the above dyeings done at pH 3.6, were washed with water, five per cent sodium sulfate, six molar urea, or one per cent sodium oxalate. The washing was carried out with a modified Wilson-Kern apparatus, described by Kremen and Lollar (28), and the wash solution collected at the rate of one liter per hour. The concentration of the dye in the wash liquors was determined spectrophotometrically at intervals of 0, ½, 1, 2, 3, 4, and 5 hours. From this data the relative amounts of dye removed from each sample for each washing solution could be determined.

Discussion of Results

Dye uptake was calculated as the difference between the amount of dye remaining in the bath at the end of the dyeing and the amount initially present for the survey experiment (Table 1). The statistical analysis of the Latin Square

Table 1

Survey Experiment
Moles Dye Bound x 10^3

Dye	Tannages Depickled, Untanned	Unmasked	Unmasked, Quebracho Mordanted	Tartrate Masked	Two Bath
Orange G	4.00	4.10	3.62	4.23	3.24
Malachite Green	1.84	1.69	2.84	1.37	3.61
Orange II	3.61	4.51	3.76	4.10	3.75
Phenol Red	2.27	3.51	3.35	3.69	2.93
Undyed	0.00	0.00	0.00	0.00	0.00

Statistical Analysis:

Source of Variance	Degrees of Freedom	Mean Squares	F	Significance Level
Dyes	4	131,343	40.83	0.001
Tannages	4	1,422	0.44	--
pH	4	4,807	1.49	--
Areas	4	2,131	0.66	--
Residual	8	3,217		
Total	24			

established a significant variation in the amount of dye taken up due to dyes, but there was no significant difference due to pH or substrate. It was felt that the reason for the failure of the method to show variations in these latter factors was due to the extremely large variations in the dyes used. In one case, no dye was added, and this certainly contributed to a large extent in the significant between dyes variance. Therefore, it was concluded that this source of variance would have to be much more rigidly controlled in order to pick up small differences due to variations in the pH and substrates.

When the moles of dye bound after washing (Table 2) was taken as the criterion, there was a significant variation due to tannage. Again, there was a significant difference due to dyes, and no difference due to pH. The substrate was then influencing the manner in which the dyes were held, and apparently tannage influenced the dyeing. However, the data were insufficient to prove this point with this experimental design.

One other conclusion could be drawn from the data obtained. The variations due to sample area used were insignificant, and the between skins difference also showed no significance.

Color difference, in terms of judds, was determined on each of the leathers with the Hunter Color Difference meter using a single white porcelain plate as the standard (See Table 3). It was determined that the dyes and type of tannage

Table 2

Survey Experiment
Moles Dye Bound After Wash x 10^3

Dye	Tannages Depickled, Untanned	Unmasked	Unmasked, Quebracho Mordanted	Tartrate Masked	Two Bath
Orange G	3.37	3.87	3.69	3.98	2.97
Malachite Green	0.93	1.29	2.48	0.96	2.46
Orange II	2.68	4.33	3.45	3.85	3.50
Phenol Red	1.67	3.13	2.91	3.29	2.42
Undyed	0.00	0.00	0.00	0.00	0.00

Statistical Analysis:

Source of Variance	Degrees of Freedom	Mean Squares	F	Significance Level
Dyes	4	113,933	59.34	0.001
Tannages	4	6,964	3.63	0.05
pH	4	3,076	1.60	--
Residual	12	1,920		
Total	24			

Table 3

Survey Experiment
Color Difference in Judds

	Tannages				
Dye	Depickled, Untanned	Unmasked	Unmasked, Quebracho Mordanted	Tartrate Masked	Two Bath
Orange G	79.34	72.24	64.01	71.48	67.01
Malachite Green	80.15	74.23	78.91	67.59	70.63
Orange II	75.05	72.72	65.16	64.87	62.37
Phenol Red	72.54	58.24	55.30	57.92	54.99
Undyed	63.89	21.95	32.64	18.70	18.96

Statistical Analysis:

Source of Variance	Degrees of Freedom	Mean Squares	F	Significance Level
Dyes	4	6,053	26.51	0.01
Tannages	4	1,199	5.25	0.05
pH	4	157	0.69	--
Residual	12	685		
Total	24			

have significant influence on the surface coloration, but that the pH of dyeing did not.

The physical tests, tensile strength (Table 4) showed no significant influence by the dyes or pH on these properties, but that the substrate (or tannage) influence was significant. This was at least in part due to the effect of the untanned pieces on the results.

The data from the dyeing rate study were calculated to determine the moles of dye remaining in the dyebath at the various time intervals. It was found that this data could then be best rectified to give an approximately linear relationship by plotting time against the reciprocal moles of dye in the dyebath per gram of dry leather. The slopes of these curves are tabulated in Table 5. The amount of dye remaining on the leather was determined from the difference between the amount of dye fed and dye remaining in the combined exhaust bath and washings. The moles of dye washed out of each sample by water, urea, oxalate and sulfate, were also calculated. Then assuming a linear relationship between the amount of dye on the leather and the amount washed out, the per cent of dye removed from each sample by each of the agents was determined and is listed in Table 7.

The data in Table 5 indicate a variation between the exhaustion rates of the dyebath for different types of leathers. Analysis of the data (Table 6) shows that this difference is real. It will be noted that the means of the

Table 4

Survey Experiment
Tensile Strength in Pounds per Square Inch

Dye	Tannages Depickled, Untanned	Unmasked	Unmasked, Quebracho Mordanted	Tartrate Masked	Two Bath
Orange G	222	126	102	121	176
Malachite Green	180	146	169	144	120
Orange II	202	108	160	140	166
Phenol Red	184	140	108	132	138
Undyed	156	121	156	151	115

Statistical Analysis:

Source of Variance	Degrees of Freedom	Mean Squares	F	Significance Level
Dyes	4	239	0.32	--
Tannages	4	2,836	3.80	0.05
pH	4	231	0.31	--
Residual	12	745		
Total	24			

Table 5

Rate of Dyebath Exhaustion Expressed in Units of 10^5/mole-hour

	Tannages								
Dye and pH	Unmasked		Formate Masked		Tartrate Masked		Formaldehyde Treated		Means
Orange II									
3.6	1.27	1.09	1.33	1.12	1.14	1.04	0.88	0.94	1.10
4.7	1.02	0.96	1.18	0.92	0.71	0.72	0.55	0.53	0.82
Orange I									
3.6	0.83	0.97	0.93	1.09	0.98	0.75	0.79	0.64	0.87
4.7	0.82	0.80	0.89	0.90	0.73	0.72	0.53	0.49	0.74
Fast Red A									
3.6	0.61	0.61	0.80	0.67	0.52	0.54	0.50	0.48	0.59
4.7	0.45	0.48	0.47	0.44	0.42	0.47	0.36	0.36	0.43
Red II									
3.6	0.21	0.22	0.20	0.21	0.21	0.22	0.13	0.15	0.19
4.7	0.18	0.18	0.18	0.16	0.14	0.16	0.10	0.08	0.15
Means	0.67		0.72		0.59		0.47		

Table 6

Dyebath Exhaustion Rate

1. Analysis of Variance

Source of Variance	Degrees of Freedom	Mean Squares	F	Significance Level[1]
Dyes	3	1.944	403.	0.001
Tannages	3	0.1879	39.0	0.001
pH	1	0.3859	80.1	0.001
Dye-Tannage	9	0.0205	4.25	0.001
Dye-pH	3	0.0362	7.51	0.001
Tannage-pH	3	0.00386	0.80	--
Dye-Tan-pH	9	0.00596	1.24	--
Duplicates	32	0.00482		
Total	63			

2. "t" Test Between Means[2]

Means Compared	Significance Level[1]
Unmasked and Formate Masked Tannages	--
Unmasked and Tartrate Masked Tannages	0.01
Unmasked and Formaldehyde Treated Tannages	0.01
Orange II and Orange I	0.01
Orange II and Fast Red A	0.01
Orange II and Red II	0.01

---

[1] Probabilities of less than 95% were not considered meaningful.

[2] The following formula was used for "t":

$$t = \frac{\bar{X}_1 - \bar{X}_2}{s} \quad \text{where} \quad s = \sqrt{\frac{2(\text{Mean Square for Duplicates})}{\text{no. in the mean}}}$$

Table 7

Percentage Dye Removed from the Leather
(Based on the Amount Bound)

Dyes and Washing Solutions	Tannages								
	Unmasked		Formate Masked		Tartrate Masked		Formaldehyde Treated		Means
Orange II									
Water	15	14	12	13	24	19	9	9	14
NaOx	77	74	75	72	77	71	77	82	76
Na_2SO_4	42	38	44	39	48	40	40	46	42
Urea	45	54	67	44	77	62	64	53	58
Orange I									
Water	11	15	9	9	13	12	7	8	10
NaOx	84	81	75	70	75	83	78	73	77
Na_2SO_4	50	61	48	66	44	53	52	65	55
Urea	61	64	57	56	65	69	51	73	62
Fast Red A									
Water	12	4	11	7	16	16	10	4	10
NaOx	41	24	31	25	35	47	33	51	36
Na_2SO_4	5	3	2	3	6	4	4	4	4
Urea	84	68	89	78	78	81	76	96	81
Red II									
Water	11	8	10	6	7	7	7	6	8
NaOx	67	68	72	69	73	72	64	64	69
Na_2SO_4	66	64	70	64	68	63	54	47	62
Urea	41	30	41	34	46	39	45	34	39
Means	43		43		47		43		

unmasked and formate masked leathers are only slightly different, and the statistical "t" test indicates that there is no significant variation between these factors. However, there is a real difference in the mean rate of exhaustion between both the tartrate masked and formaldehyde treated leather and the unmasked tannage.

Since the means of the formate masked and the unmasked leathers are not significantly different in regard to the ease of dye removal (Table 7), it is probable that the dye is taken up and deposited on the leather by the same forces in each case, and that there is no difference in the effect of the formate masked tannage and the unmasked tannage with regard to their influence on the dyeing. In other words, the dye seems to displace the formate and the sulfate groups from the chrome complex about equally.

The mean of the tartrate tannage shows a significant departure from that of the unmasked tannage in regards to its effect upon dyebath exhaustion. The former binds less dye, and the dye that is bound is more easily removed (Tables 5 and 7). Since the only difference in the two leathers is the presence of the tartrate group compared to the sulfate group, the different effect in dyeing rates must be assigned to the tartrate ion. The tartrate anion is much more tightly held than the sulfate, and the dye apparently displaces it with difficulty or not at all, thus limiting the number of sites available to it. Then the dyeing rate, or the rate of dyebath exhaustion, is reduced and the dye is more readily removed.

Formaldehyde treatment of chrome tanned leather reduces the number of free amino groups available for the formation of electrostatic bond formation with the sulfonic acid group of the dyes. Then the significantly lower exhaustion rate of the formaldehyde treated leather (Table 5) may be attributed to the reduction of the number of sites available, or to the decrease in charge of the leather. Since there is no difference in the means for dye removal (compared to unmasked leather), the second factor offers the most logical explanation. Thus, the charge on the leather is a factor in controlling the rate of exhaustion of the dye, but the dye is bound to the leather chiefly through linkages other than an electrostatic bond with the free amino groups.

It is apparent from examination of the means of the dyes in Tables 5 and 7 that the exhaustion rate and the ease of dye removal are influenced significantly by the constituent groups on the dyes. This is confirmed in the analyses of variance in Tables 6 and 8. In addition, the rate of exhaustion of the dyebath shows significant dye-pH and dye-tannage interactions, indicating that the rate of exhaustion of the dyes is influenced by both the pH and the type of tannage. Also, the significant dye-washing solution interaction for dye removal shows that these factors are not independent.

Table 8

Dye Removal

1. Analysis of Variance

Source of Variance	Degrees of Freedom	Mean Squares	F	Significance Level[1]
Dyes	3	2040.	55.1	0.001
Tannages	3	98.73	2.66	0.05
Wash Solution	3	19154.	516.8	0.001
Dye-Tannage	9	48.48	1.31	--
Tannage-Wash	9	46.34	1.25	--
Dye-Wash	9	2939.	79.3	0.001
Dye-Tan-Wash	27	32.79	0.88	--
Duplicates	64	37.06		
Total	127			

2. "t" Test Between Means

Means Compared	Significance Level[1]
Unmasked and Formate Masked Tannages	--
Unmasked and Tartrate Masked Tannages	0.05
Unmasked and Formaldehyde Treated Tannages	--
Orange II and Orange I	0.02
Orange II and Fast Red A	0.01
Orange II and Red II	0.05
Water and Sodium Oxalate	0.01
Water and Sodium Sulfate	0.01
Water and Urea	0.01
Sodium Oxalate and Sodium Sulfate	0.01
Sodium Oxalate and Urea	0.01
Sodium Sulfate and Urea	0.01
Orange II and Orange I (Sodium Oxalate Only)	--
Orange II and Orange I (Sodium Sulfate Only)	0.01
Orange II and Orange I (Urea Only)	--
Orange II and Fast Red A (Sodium Oxalate Only)	0.01
Orange II and Fast Red A (Sodium Sulfate Only)	0.01
Orange II and Fast Red A (Urea Only)	0.01
Orange II and Red II (Sodium Oxalate Only)	0.05
Orange II and Red II (Sodium Sulfate Only)	0.01
Orange II and Red II (Urea Only)	0.01

[1] Probabilities of less than 95% were not considered meaningful.

It is noted from Table 5 that Orange I exhausts more slowly than Orange II, although these dyes differ only in the position of the phenolic group (See Figure 3). This difference in rate may be attributed to the stronger interaction of the para phenolic group of Orange I with the solvent, as suggested by Klotz (22). Then, in the competition between the leather and the solution for the dye, the Orange II is more readily taken up by the leather because of its lower probability of interaction with the solvent than is Orange I. However, it was also noted that both of these dyes are removed with the same ease from the leather by urea (Table 7). The "t" test failed to indicate a significant difference between the means in this case (see Table 8). This may be due to the two dyes having the same hydrogen bonding potential when they are fixed on the leather, even though these potentials are different in solution. Then changes in the position of the phenolic groups (between ortho and para) influence the rate of dyebath exhaustion, but do not affect the manner in which the dyes were held.

The mean exhaustion rate of Fast Red A was also less than that of Orange II. In this case, the dyes differ in the substitution of a naphthalene ring for the benzene ring of Orange II. This leads to an increase in the molecular weight with the consequent increase in the residual, or van der Waal, valency forces in the Red A molecule, and a shift of the absorption maximum to a higher wave length. To explain the significant decrease in the rate of dye exhaustion, the steric effect of the added ring and the effect of the additional attractive forces to give aggregation may be theorized. The latter undoubtedly plays some role, and the lower solubility of Fast Red A (compared to Orange II) gives some evidence for this. Since the rate of diffusion of the dye into the leather effects the rate of exhaustion of the dyebath (48), the larger aggregates would be expected to exhaust more slowly than the smaller Orange II monomers. The extremely small amount of dye washed out of the leather by sodium sulfate also indicates that the dye binds only slightly through the formation of salt links (Table 7). Therefore, the steric factors may also be important.

The fourth dye, Red II, is also exhausted significantly more slowly than Orange II from the dyebath. This is undoubtedly due to the large number of solvating sulfonic acid groups on the molecule. Then the ability of the dye to interact strongly with the solvent lessens the rate of reaction with the leather. This effect of decreasing the dyeing rate by increased sulfonation has been demonstrated on wool by Ruggli (35) and Otto (34) has recently pointed out its importance in leather dyeing. However, Otto ascribes the effect of the sulfonic acid groups to screening the available sites for coordinative or secondary bonding by the mobile electrons of the sulfonic acid groups, and the subsequent reduction of this secondary bonding between the dye and the leather.

In the case of Red II it is also apparent from Table 7 that large numbers of anionic sites on the dye molecule favor electrostatic bonding, and the mean value for the amount of dye removed by sodium sulfate for Red II is significantly greater than the corresponding one for Orange II.

The two pH levels used in the dyebath exhaustion rate study showed a significant difference as may be noted in the data, and this effect of pH on the rate may be attributed to the charge on the leather. At the higher pH, the leather is slightly above its isoelectric point and, carrying a net negative charge, may be expected to bind fewer anions than it would with a net positive charge, as at the lower pH (31, 32). It was also determined that there was no shift of the spectral curve in the region of the absorption maxima for Orange II and Orange I at the concentrations used in dyeing between the two pH levels. Consequently, differences cannot be attributed to changes in aggregation of the dyes at these two levels.

The solvents used for effecting removal of the dyes show the expected variations in their means as may be observed in Table 7. Table 8 indicates that this is a real, or significant difference. The oxalate was the most active in this capacity, giving evidence that the dye anions did penetrate the complex. However, since sodium oxalate is ionic, part of the dye removed by this agent was probably due to the rupture of electrostatic bonds as well as part being removed by displacement of dyes from the chrome complex. In this connection it will be noted, however, that in every case the oxalate removed more dye from the leather than did sodium sulfate, even considering the latter's greater ionic strength. If the increased amount of dye removed from Red II by sulfate is considered to indicate that most of the dye in this same case removed by oxalate was due to the latter's ionic function, some validation is given to Otto's theory that the amount of dye penetrating the chrome complex is determined by the molecular weight/sulfonic acid group ratio of the dye (33).

Urea was also significantly active in removing dyes from the leather, as evidenced by its high mean value in Table 7. The dye removed in this manner was assumed to give an indication of the importance of hydrogen bonding of the dyes to the leather. Fast Red A showed an appreciably larger amount of dye removed by urea than did the other dyes. This was attributed to the increased conjugation (as evidenced by the spectral shift mentioned above) (47) increasing the hydrogen bonding potential of the dye. The mean for urea on Red II, on the other hand, was somewhat lower than that on Orange II. This was probably due to the greater possibility of salt link formation by Red II. Inspection of the data seems to indicate that there may be some hydrogen bonding on the tartrate group of that tannage, since urea apparently removes a slightly greater percent of each dye from this tannage than from the others. However, the absence of a significant tannage-wash interaction term in Table 8 prohibits the use of a "t" test on the data, and this point could not be substantiated.

The great effect of sodium sulfate on the removal of Red II indicates that this dye is held by electrostatic bonds to a greater extent than the others. This is readily explained by the presence of the large number of possibilities for such bond formation with this dye. However, the significantly small amount of Fast Red A removed by sulfate points to hydrogen bonding and penetration of the chrome complex as the principle bonding forces holding this dye on the leather. Also, in view of the apparent difficulty in removing Fast Red A by all of the solutions except urea, it is possible that the residual valency forces contributed by the added ring may also be more important with this dye than with the others.

Conclusions

The data presented above indicate that dyeing chrome tanned leather with anionic dyes of the simple monoazo type may be regarded in two steps: (1) The take-up of the dye, or the exhaustion of the dyebath, and (2) the fixation of the dye on the leather.

The exhaustion of the dyebath is influenced by the interactions of the dye and the solvent as well as by the relations between the dye and the substrate. Then there exists a competition between the leather and the solvent for the dye. The factors which tend to make the dye interact more strongly with the solvent, such as increasing the number of solubilizing groups, and those which decrease the affinity of the dye for the leather (reducing the number of sites available for reaction by reducing the negative charge on the leather, or increasing the difficulty of complex penetration) act together in reducing the rate of exhaustion of the bath. These same factors determine the amount of dye that will react with the leather in any given time.

Dyes are undoubtedly held to the leather by a number of different types of bonding forces. The evidence indicates that the penetration of the dyes into the chrome complex and hydrogen bonding between the dyes and the leather are extremely important in this role. Apparently electrostatic bonding, through the formation of salt links, also plays a part, although it does not seem to be necessary for this type of bond to be formed in all cases. It is strongly suspected, in view of the results of other investigators and from some of the indications in this work, that residual valency, or van der Waal, forces are also important in the total picture. However, complete evidence for this is not available at the present time.

Bibliography

1. Astbury, W. T., and Dawson, J. A., J. Soc. Dyers and Colourists 54 6 (1932).

2. Bailar, J. C., and Callis, C. F., J. Am. Chem. Soc. 74 6018 (1952).

3. Bravo, G. A., Collegium 772 (1932).

4. Bravo, G. A., and Baldracco, F., Boll. Uff. R. Staz. per l'Ind. dell Pelli 143 (1932); Ann. Chem. App. 21 355 (1931).

5. Bravo, G. A., and Baldracco, F., Collegium 338 (1932).

6. Carlene, P. W., Fern, A. S., and Vickerstaff, T., J. Soc. Dyers and Colourists 63 388 (1947).

7. Cockbain, E., J. Soc. Lea. Trades' Chem. 29 102 (1945).

8. Cogin, G. E., and Davis, B., J. Am. Chem. Soc. 73 3135 (1951).

9. Einbinder, J., and Schubert, M., J. Bio. Chem. 188 335 (1951).

10. Elod, E., Textil-Praxis 7 66 (1952).

11. Elod, E., and Hansel, H., Collegium 764 763 (1933).

12. Elod, E., and Kohnlein, A., Ibid 764 754 (1933).

13. Felzmann, C., Ibid 759 373 (1933).

14. Gerstner, H., Melliand Textilber. 32 307 (1951).

15. Gilbert, G. A., Proc. Roy. Soc. 183A 167 (1944).

16. Gustavson, K., Collegium 678 437 (1926).

17. Horsfall, J. D., Leeds University Thesis (1947).

18. Hsiao, C., and Wilson, E. O., J. Am. Lea. Chem. Ass'n. 27 500 (1932).

19. Karush, F., J. Am. Chem. Soc. 72 2705 (1950).

20. Karush, F., Ibid 72 2714 (1950).

21. Karush, F., and Sonenberg, M., Ibid 71 1369 (1949).

22. Klotz, I. M., Ibid 68 2299 (1946).

23. Klotz, I. M., Chem. Rev. 41 373 (1947).

24. Klotz, I. M., Burkhard, R. K., and Urquart, J. M., J. Am. Chem. Soc. 74 202 (1952).

25. Klotz, I. M., Triwush, H., and Walker, F. M., Ibid 70 2935 (1948).

26. Klotz, I. M., and Urquart, J. M., Ibid 71 1597 (1949).

27. Klotz, I. M., and Walker, F. M., Ibid 69 1609 (1947).

28. Kremen, S. S., and Lollar, R. M., J. Am. Lea. Chem. Ass'n. 43 542 (1948).

29. McGrew, F. C., and Schneider, A. K., J. Am. Chem. Soc. 72 2547 (1950).

30. Otto, G., Paper presented at 10th International Congress of Chem. in Rome, May (1938), through J. Soc. Lea. Trades' Chem. 22 473 (1938).

31. Otto, G., Das Leder 1 81 (1950).

32. Otto, G., Ibid 1 133 (1950).

33. Otto, G., Melliand Textilber. 32 311 (1951).

34. Otto, G., Das Leder 4 1 (1953).

35. Ruggli, P., and Fischli, A., Helvetica Chim. Acta 7 496 (1924).

36. Scatchard, G., 120th Meeting Am. Chem. Soc., Abstracts 16c No. 21 (1951).

37. Schweitzer, W. K., and Lollar, R. M., J. Am. Lea. Chem. Ass'n. 47 140 (1952).

38. Skinner, B. G., and Vickerstaff, T., J. Soc. Dyers and Colourists 61 193 (1945).

39. Speakman, J. B., and Elliott, G. H., Ibid 59 185 (1943).

40. Speakman, J. B., and Elliott, G. H., Soc. Dyers and Colourists Fibrous Proteins Symposium 116 (1946).

41. Speakman, J. B., and Stott, E., J. Soc. Dyers and Colourists 50 341 (1934).

42. Steinhardt, J., Annals N. Y. Acad. Sci. 41 287 (1941).

43. Strutt, C. R., J. Internat. Soc. Lea. Trades' Chem. 18 203 (1934).

44. Teresi, J. D., J. Am. Chem. Soc. 72 3972 (1950).

45. Teresi, J. D., and Luck, J. M., J. Bio. Chem. 174 653 (1948).

46. Tewari, S. N., and Ohosh, S., Kolloidzchr. 124 31 (1951).

47. Venkataramann, K., Synthetic Dyes 323 - 404, Academic Press, New York (1952).

48. Vickerstaff, T., The Physical Chemistry of Dyeing, Interscience Publishers, New York (1950).

49. Weber, F., Textilber. 32 865 (1951).