

STUDIES OF THE DIRECT DYEING OF CELLULOSE -
THE EFFECT OF INORGANIC SALTS

A THESIS

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by

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SUMMARY

The purpose of this work was to determine the effect of inorganic salts on dyebath exhaustion and on the stability of direct dyes to prolonged boiling. The effect of pH was also determined.

Nine selected commercial direct dyes were applied at the boil for from one to five hours in the presence of inorganic salts containing mono-, di-, tri- and tetra-valent cations at an initial dyebath pH of 3.0. The various inorganic salts were added to the dyebath on the basis of equivalent ionic strengths. Loss of dyestuffs from the dyebaths and/or uptake of dyestuffs by cotton cloth were determined with the aid of a spectrophotometer.

The decomposition of C. I. Direct Red 2 and C. I. Direct Blue 71 on prolonged boiling is prevented when dyeing is carried out in the presence of 0.01 M NaCl at an initial dyebath of pH 3.0; and adsorption of dye by cotton fiber is increased slightly when the dyeing is effected at this pH.

The variability of the effect of any one salt on the dyes used in this work is very marked. Magnesium chloride was similar in its action to sodium chloride except in the case of Direct Blue 71. Calcium chloride gave dyebath

exhaustions equal to or better than those obtained with sodium chloride with five of the dyes (C. I. Direct Red 4, Green 6, Yellow 50, Red 2 and Yellow 29) but apparently destroyed the Blue 71. Of the six salts used aluminum chloride gave the poorest dyeings with the largest number of dyes.

It is not possible, from this work, to make any general statements regarding the effect of inorganic salts on direct dyes. No correlations of the effect of the various salts with size, charge, or other physical characteristics have been possible. Apparently the results are determined by both the nature of the dye and the added salt as well as by other factors which have not yet been determined.

CHAPTER I

INTRODUCTION

Fifty years ago Knecht and Batey (1) stated: "It is well-known that many direct cotton dyes, such as Benzopurpurine, will only dye the cotton fiber in presence of an inorganic salt, such as sodium chloride, Glauber's salt, potassium chloride, etc.". Boulton, Delph, Fothergill and Morton (2), and Hanson, Neale and Stringfellow (3) have described work which confirmed this statement.

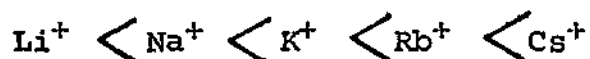
Because salt is generally added to aid exhaustion, the direct dyes are sometimes called "salt dyes". Direct dyestuffs ionize in solution to form colored anions, whereas cellulose acquires a negative surface charge when it is placed in an aqueous dyebath. Therefore, the first step in dyeing (approach of dyestuff molecules to the fiber surface) is hindered or, in extreme cases, prevented by natural forces of repulsion of like-charged ions. The main role of salt, in the application of direct dyes to cellulosic fibers, is to minimize this natural force of repulsion.

Background of the Problem.--Vickerstaff (4) states that:

"The effect of electrolytes other than sodium chloride or sodium sulfate on direct dyeing has been investigated to some

extent, although for economic reasons there is little likelihood of sodium chloride and sodium sulfate being displaced from practical usage." Most of this work has been summarized by this author.

Chun (5) has recently studied the effect of various monovalent inorganic ions on cotton dyeing, using Calcodour Resin Fast Grey 2G. His experimental results indicated that the effect of anions on cotton dyeing is of minor importance. From the results obtained after five hours of dyeing, using chlorides, he has found that the order of cations producing increasing adsorption of the dye under consideration was:



It has been known for many years that a variety of dyes decompose or are unstable in aqueous solutions at elevated temperatures (6, and references contained therein). Millson (6) has shown that some direct dyes decompose in the dyebath on prolonged boiling, resulting in a decrease in color intensity; others produce an increase in color intensity with prolonged boiling, this being referred to as "build-up". It was found (6) that decomposition could be prevented or retarded by the addition of certain ammonium salts to the dyebath at the start of the dyeing cycle. The rate of color build-up could be accelerated by the addition of the same

ammonium salts which inhibited dye decomposition. For example Millson (6) has shown that a dyeing which, boiled for six hours, decomposed to give a color value only 58 per cent of that obtained in a normal one hour dyeing, gave a color value of 160 per cent when boiled for six hours in the presence of five per cent ammonium thiocyanate. This same salt was also found (6) to be effective in increasing the exhaustion of a dyestuff, the exhaustion of which increased with time of boiling. Using a normal one-hour dyeing as a standard (100 per cent) Calcomine Yellow 2G (C. I. 40,000), boiled for one hour in the presence of ammonium thiocyanate, gave a color value of 160 per cent; after boiling for six hours in the presence of five per cent ammonium thiocyanate a value of 328 per cent was obtained.

It is obvious, therefore, that the behavior of an individual direct dye depends upon many factors, among which are: the chemical nature of the dyestuff, the fiber being dyed (both its chemical and physical state as well as the nature of various impurities which may be present), the pH of the dyebath, the time and temperature of dyeing, the kind and amount of salt added (both by the dyestuff manufacturer for purposes of standardization, and the dyer during the dyeing operation), as well as a method of adding the salt.

Purpose of Investigation.--An attempt was made to pursue further the effect of inorganic ions on cotton dyeing, which was begun by M. S. Chun in this laboratory. Since very little investigation of the effect of the pH on dyeing of cellulose is reported, the purpose of this investigation was to determine the effect of inorganic salts on the stability of direct dyes to prolonged boiling, and on dyebath exhaustion, as well as the effect of pH control.

Method of Attack.--Nine selected commercial direct dyes were dyed at the boil for from one to five hours in the presence of various inorganic salts in a dyebath the initial pH of which was adjusted to 3.0 using hydrochloric acid. The various inorganic salts were added to the dyebath on the basis of equal ionic strength (except for the tin salt) and the results were compared. Loss of dyestuffs from dyebath and/or uptake of dyestuffs by cotton cloth were determined with the aid of a spectrophotometer.

CHAPTER II

EXPERIMENTAL PROCEDURE

Materials

The materials used in this work were as follows:

Fabric.--Cotton, commercial 80 square plain weave, scoured and bleached.

Dyestuffs.--The nine commercial direct dyes selected for this work were chosen because metal ions were believed to have little or no effect on their shade and/or dyeing properties. Information about the dyestuffs used is given in Table 1; formulas for the dyes are included as Fig. 9.

Inorganic Salts.--The seven salts used were all reagent grade chlorides. Sodium as a monovalent cation, and the four divalent cations used differed in size; one chloride with a trivalent cation and one with a tetravalent cation were also used. Information regarding the salts is summarized in Table 2.

Magnesium Carbonate Block.--This was used in the reflectance measurements of the dyed cloth as a reference standard.

Experimental

Scoured and bleached cotton cloth (5.0 gram samples, weighed without previous conditioning, were used throughout

Table 1. Dyestuffs Used

C. I. Name	C. I. No.	duPont Name	Class (Millson) (6)
Direct Yellow 12	24895	Pontamine Yellow CH	Stable
Direct Yellow 50	29025	Pontamine Fast Yellow RL	Decompose
Direct Yellow 29	19556	Pontamine Fast Yellow BBL	Build-up
Direct Red 4	29165	Pontamine Scarlet G	Stable
Direct Red 2	23500	Purpurine 4B conc.	Decompose
Direct Red 37	22240	Pontamine Scarlet B	Build-up
Direct Green 6	30295	Pontamine Green BXN	Stable
Direct Blue 71	34140	Pontamine Fast Blue SFL	Decompose
Direct Blue 78	34200	Pontamine Fast Blue 4GL	Build-up

Table 2. Inorganic Salts Used in Dyebaths

Name	Formula	Formula Weight	Moles per liter	Relative Size of Hydrated Cation
Sodium Chloride	NaCl	58.5	0.010	4-4.5
Magnesium Chloride	MgCl ₂ .6H ₂ O	203	0.0033	8
Calcium Chloride	CaCl ₂	111	0.0033	6
Barium Chloride	BaCl ₂ .2H ₂ O	244	0.0033	5
Lead Chloride	PbCl ₂	278	0.0033	4.5
Aluminum Chloride	AlCl ₃ .6H ₂ O	241	0.00167	9
Tin Chloride	SnCl ₄ .5H ₂ O	351	0.00074*	11

*The concentration of this salt was equivalent to 0.0074 molar NaCl.

this work) were dyed at the boil for from one to five hours in 40:1 (200 ml.) baths containing one per cent dye on the weight of fabric (0.05 grams) and added salt at the concentration given in Table 2, at an initial pH of 3.0 adjusted with hydrochloric acid.

Preparation of Dyebath.--A concentrated dye solution was prepared by dissolving 5.000 grams of dyestuff, which was weighed accurately using an analytical balance, in deionized water, and adjusting the final volume to one liter in a volumetric flask. The desired amount of dye in this work was one per cent on the weight of fabric, therefore 0.05 grams of dye was transferred to 200 ml. volumetric flask by pipetting 10 ml. of the concentrated dye solution. The required amount of salt given in Table 2 was accurately weighed on the analytical balance, and in each case the weighed salt was dissolved and diluted in deionized water to approximately 170 ml. in the 200 ml. volumetric flask with the dye solution. The pH of each initial dyebath was adjusted to 3.0 with hydrochloric acid, and then the final volume was adjusted to 200 ml. with deionized water. This solution was transferred to a 500 ml. porcelain beaker and used as the prepared dyebath.

Effect of pH Control.--One hour and five hour dyeings for the

following six dyes, in the presence of 0.01 M NaCl, were carried out without pH control.

- C. I. Direct Yellow 50 (Pontamine Fast Yellow RL)
- C. I. Direct Yellow 29 (Pontamine Fast Yellow BBL)
- C. I. Direct Red 2 (Purpurine 4B Conc.)
- C. I. Direct Red 37 (Pontamine Scarlet B)
- C. I. Direct Blue 71 (Pontamine Fast Blue SFL)
- C. I. Direct Blue 78 (Pontamine Fast Blue 4GL)

The initial and final pH of each dyebath for the one hour and five hour dyeings were determined with Beckman Model H-2 pH meter and the change of pH during dyeing is given in Table 3. The overall effect of pH control is shown in Fig. 1 and Table 8.

Dyeing.--The 5.0 grams of cotton cloth was placed in the prepared dyebath (porcelain beaker) at room temperature and the bath was heated to the boil during 15 minutes on the steambath; a rolling boil was maintained throughout the dyeing cycle. Deionized water was added from time to time to replace water lost by evaporation to maintain the 40:1 (200 ml.) bath to fiber ratio; also the dyebath was agitated constantly by hand with a glass stirrer in order to obtain level dyeing. In the presence of various inorganic salts, other than sodium chloride, Direct Yellow 12, Direct Red 4

Table 3. Change of pH Values during Cotton Dyeings
in the Presence of 0.01 M NaCl

Dyestuff	No pH Initial	Control After 5 Hrs.	Initial Initial	pH3 After 5 Hrs.
Direct Yellow 50	7.5	6.6	3.0	2.9
Direct Yellow 29	9.1	7.1	3.0	3.1
Direct Red 2	6.9	6.6	3.0	3.1
Direct Red 37	5.7	5.8	3.0	3.0
Direct Blue 71	8.3	6.6	3.0	3.2
Direct Blue 78	6.6	6.6	3.0	2.9

and Direct Green 6 were dyed for five hours, and the other six dyes were dyed for one and five hours. The dyed samples were removed and rinsed carefully in warm water when dyeings were complete. They were then dried in a constant temperature oven at 230°F, and pressed between samples of white cloth.

Reflectance Measurements

Absorption spectra for six of the dyes were obtained with a Beckman Model DU Spectrophotometer, equipped with photomultiplier attachment over the wavelength range 380 to 700 millimicrons, using solutions of the indicated concentration, each at a pH of 3.0:

Direct Yellow 12, 0.05 grams per liter

Direct Yellow 29, 0.1 grams per liter

Direct Red 4, 0.0125 grams per liter

Direct Red 37, 0.0125 grams per liter

Direct Green 6, 0.0125 grams per liter

Direct Blue 78, 0.0125 grams per liter

Details are given in Table 4, 5 and 6 in the Appendix.

Reflectance data, versus the magnesium carbonate block for Direct Yellow 29, measured in both the warp and filling directions with the Beckman Spectrophotometer, are also included in Table 6.

Reflectance data for Direct Yellow 50, Direct Red 2

and Direct Blue 71 are given in Table 7.

The absorbance values obtained for each sample (versus the magnesium carbonate block) were compared with those obtained from a standard one-hour dyeing in the presence of 0.01 M NaCl either with no pH control or in a dyebath the initial pH of which was adjusted to 3.0 with hydrochloric acid.

The data for the effect of pH control on cotton dyeing (see Table 8 and Fig. 1) were obtained from a comparison with a one-hour dyeing in the presence of 0.01 M NaCl and no pH control.

For a comparison of the effects of the various inorganic salts on cotton dyeing, the per cent reflectance values were calculated as follows: The absorbance value of each 5 hour dyeing with a salt at an initial dyebath pH of 3.0, was divided by the absorbance value of the same dye for a one-hour dyeing in the presence of 0.01 M NaCl and at an initial dyebath pH of 3.0, and then multiplied by 100.

Results are shown in Fig. 2 through Fig. 8 and, also in Table 9 through Table 15 in the Appendix.

Attempts were made to determine the light absorption characteristics of samples of the original as well as of the exhausted dyebaths. This was found to be impractical because

of apparent dyestuff decomposition and the separation of insoluble substances from the samples.

CHAPTER III

RESULTS AND DISCUSSION

Five differences in the conditions between Millson's work and the present study should be noted:

1. Cotton cloth was used instead of spun viscose rayon fabric. It is known that various cellulosic fibers differ in their behavior toward direct dyes (7).

2. Dyeings in the present work were carried out for only five instead of six hours.

3. 0.01 M NaCl was used instead of 10 per cent (o. w. f.) NaCl; however, the difference is not great (0.58 grams versus 0.50 grams of NaCl).

4. Dyestuffs from different manufacturers were used in the two studies. The type of diluent used by each manufacturer may be different for dyestuffs of the same Colour Index Number.

5. The spectrophotometer used to measure reflectance was no doubt not of the same type in both investigations.

The impurities in dyes are of three types, namely (8):

A) Diluent such as sodium chloride, sodium sulfate, or soluble starch, which have been added to bring the dye to a standard tinctorial strength for convenience in use.

B) Substance other than the required dyes which have

been formed during manufacture.

C) Dyes of different constitution and color added for shading.

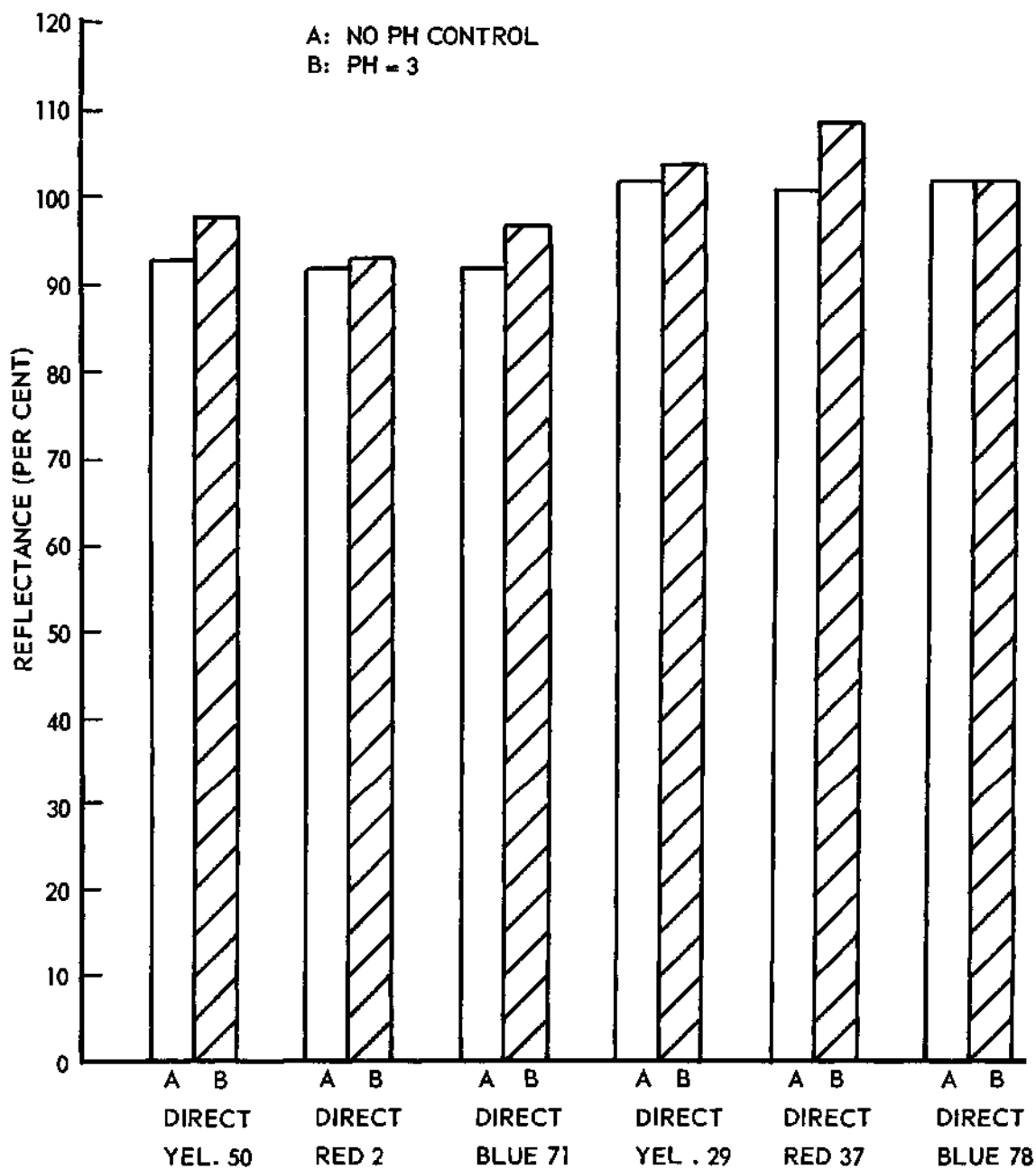
Since the actual amounts of coloring matter in each sample of dye are unknown, a comparison of the dyes one with another is impossible.

The dyestuffs applied under the conditions described in this work did not exhibit "decomposition" or "build-up" as described by Millson (6).

Figure 1 shows the effect of pH control; a pH of 3.0 is considerably lower than that normally used in commercial practice. With five of the six dyes examined in the presence of 0.01 M NaCl, the pH control (pH of the initial dyebath of 3.0) resulted in a slight increase in dyebath exhaustion.

Neale and Peters (9) measured the variation of the surface potentials of textile fibers with hydrogen ion concentration and found that chemically neutral fibers such as cotton and vinyon show potentials which are not markedly pH sensitive over the range pH 10-5, but which fall rapidly when the solution is more acid than a pH of 4. Therefore lowering the pH results in an increase in dyebath exhaustion due to a lowering of the negative surface potential of cellulose.

Vickerstaff (10) indicated that addition of acid increases the adsorption of direct dye on the oxycellulose much more



-Figure 1. Effect of Dyeing Conditions on Behavior of Direct Dyestuffs.

than it does on normal cellulose. The explanation of this effect is probably that the ionization of the carboxyl groups in the fiber is repressed in acid solutions, so that the electrical potential of the surface is reduced to the value shown by the unoxidized surface and dyeing is facilitated.

Acid is rarely added to a direct dyebath, as cellulose is very susceptible to acid hydrolysis. In particular mineral acid, which remains in the fiber when it is dried, can lead to serious degradation and loss of strength.

Cohen (11) studied the action of mineral acids on cotton and found that if cotton is boiled in hydrochloric acid for one hour, the cotton is affected when the acid is present in solutions which are 0.0007 normal or stronger. Sulfuric acid, under the same conditions of treatment, affects the cotton when it is in 0.0016 normal solution and upwards. If any solution of acid is used which is weaker than the above strengths, the cotton is not affected. Since the pH of 0.0007 N hydrochloric acid solution is approximately 3, it is believed that cotton fabric may be dyed under acidic conditions as long as the pH of the dyebath does not become lower than 3.

The data plotted in Figure 2 through Figure 8 show the effectiveness of the salts used, compared with sodium chloride and the same pH. It must be emphasized that the salt content

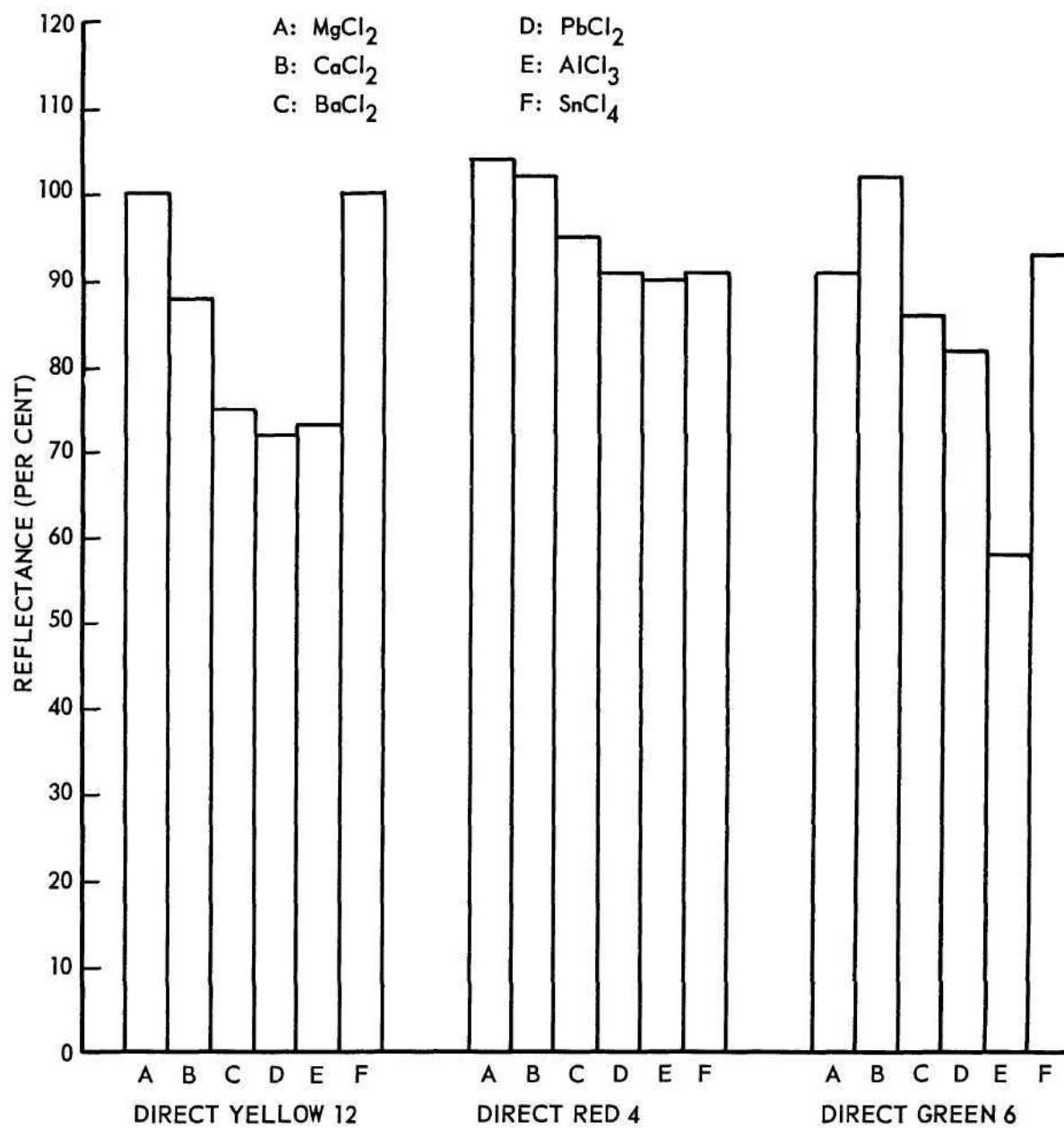


Figure 2. Effect of Inorganic Salts on Direct Yellow 12, Direct Red 4 and Direct Green 6 (PH = 3).

of each dyebath was not known because commercial dyes were used. However, for any one dye, a comparison of the effect of the added salts is valid because the total salt content (salt added as an inert diluent by the manufacturer as well as salt added in this work) of each bath was the same. All of the dyebaths prepared with any one dye contained the following anions: chloride ions from the hydrochloric acid and added salt, dye anions, and anions of the salt used by the manufacturer as a diluent. In addition these baths contained positive ions from the dye and diluent salt (usually sodium ions), and positive ions from the added salt. The ions added as dye diluent salt were of course the same for one dye; because the added salts were used at equal ionic strengths (except for the tin salt) each bath, with any one dye, contained the same concentrations of ions, and differed only in the nature of the added cation.

The effects of the six added salts on three of the stable dyes (Direct Yellow 12, Red 4 and Green 6) are shown in Figure 2. The barium and lead chlorides were detrimental to Yellow 12 dyeings. Aluminum chloride adversely affected both Yellow 12 and Green 6. None of the salts showed a marked effect on Red 4.

Chun (5) showed that monovalent inorganic cations

were effective in inverse proportion to the size of the hydrated ion in their ability to exhaust one dye (Calcodour Resin Fast Grey 2G). The relative sizes of the hydrated cations (in aqueous solution) of the six salts are given in Table 2. For the three "stable" dyes used in this work (see Fig. 2), it is seen that there is no correlation between the size of the hydrated ion and the extent of dyebath exhaustion for the polyvalent ions studied in this work.

Figure 3 shows that none of the ions was as effective as sodium in exhausting the Direct Yellow 50 dyebath. The results with tin chloride were significantly lower than those obtained with common salt.

The results with Direct Red 2 (Fig.4) were more variable. Calcium chloride and barium chloride gave exhaustions equal to or slightly better than sodium chloride. The lead and aluminum salts, however, gave only very weak dyeings.

Direct Blue 71 (Figure 5) was apparently partially destroyed by the calcium and aluminum ions, as evidenced by the marked shade change in the five-hour dyeings. The fact that the shade of many direct dyes is affected by certain metal ions is well known. Traces of the ions of aluminum, calcium, copper, iron, magnesium or manganese can change the shade of direct dyes (12). Of course metal ions are also used as after-

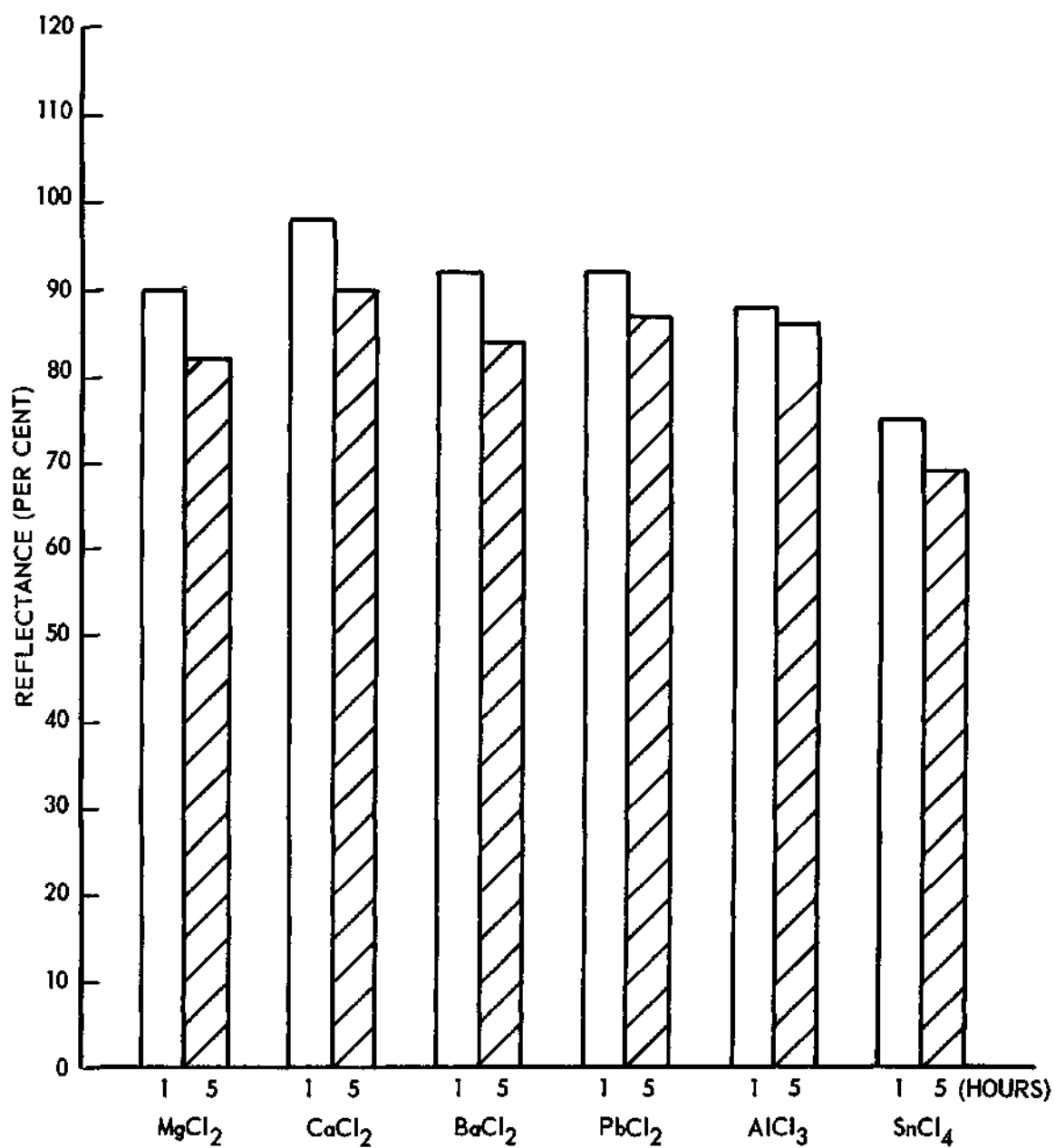


Figure 3. Effect of Inorganic Salts on Direct Yellow 50 (PH = 3).

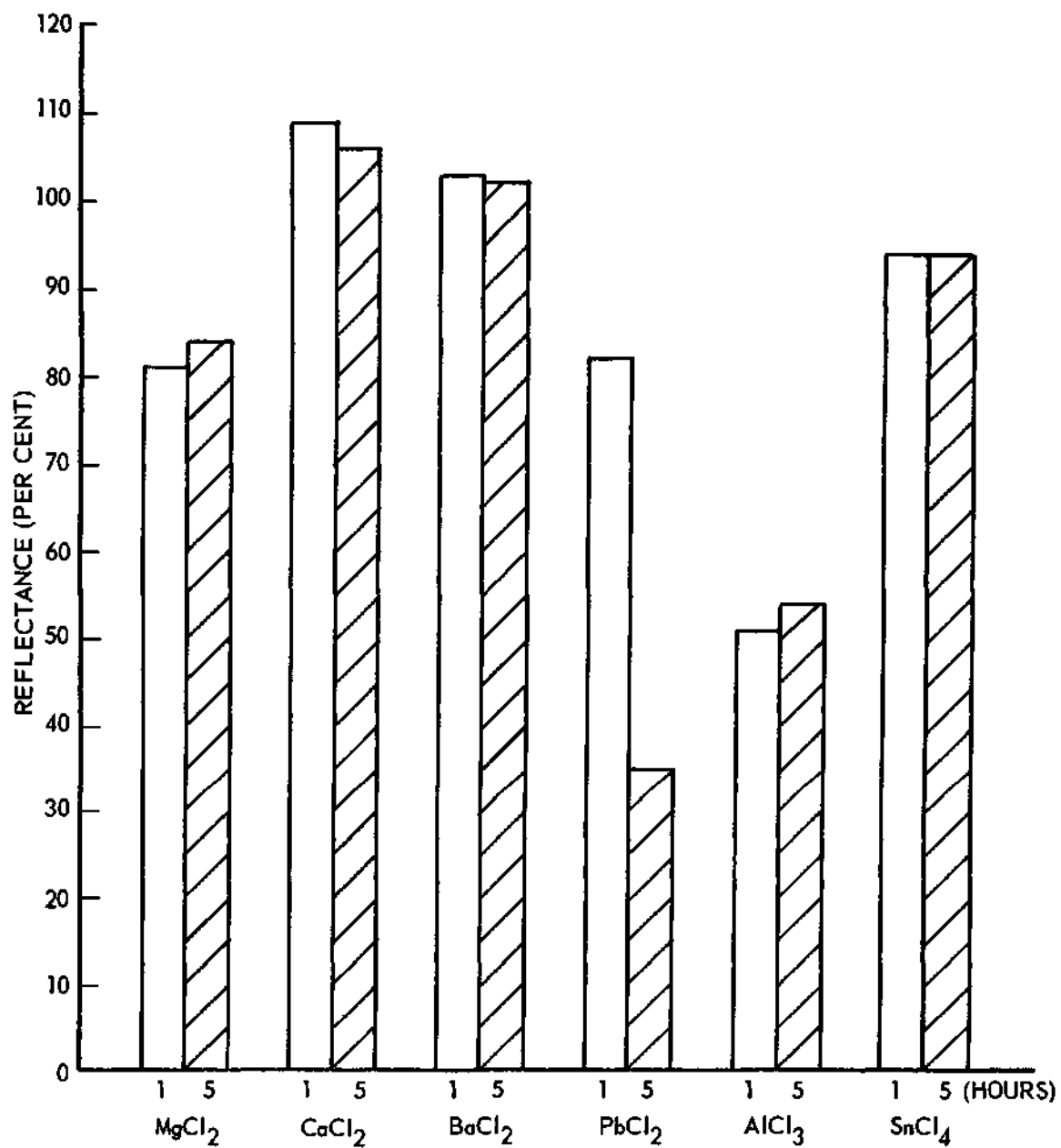


Figure 4. Effect of Inorganic Salts on Direct Red 2 (PH = 3).

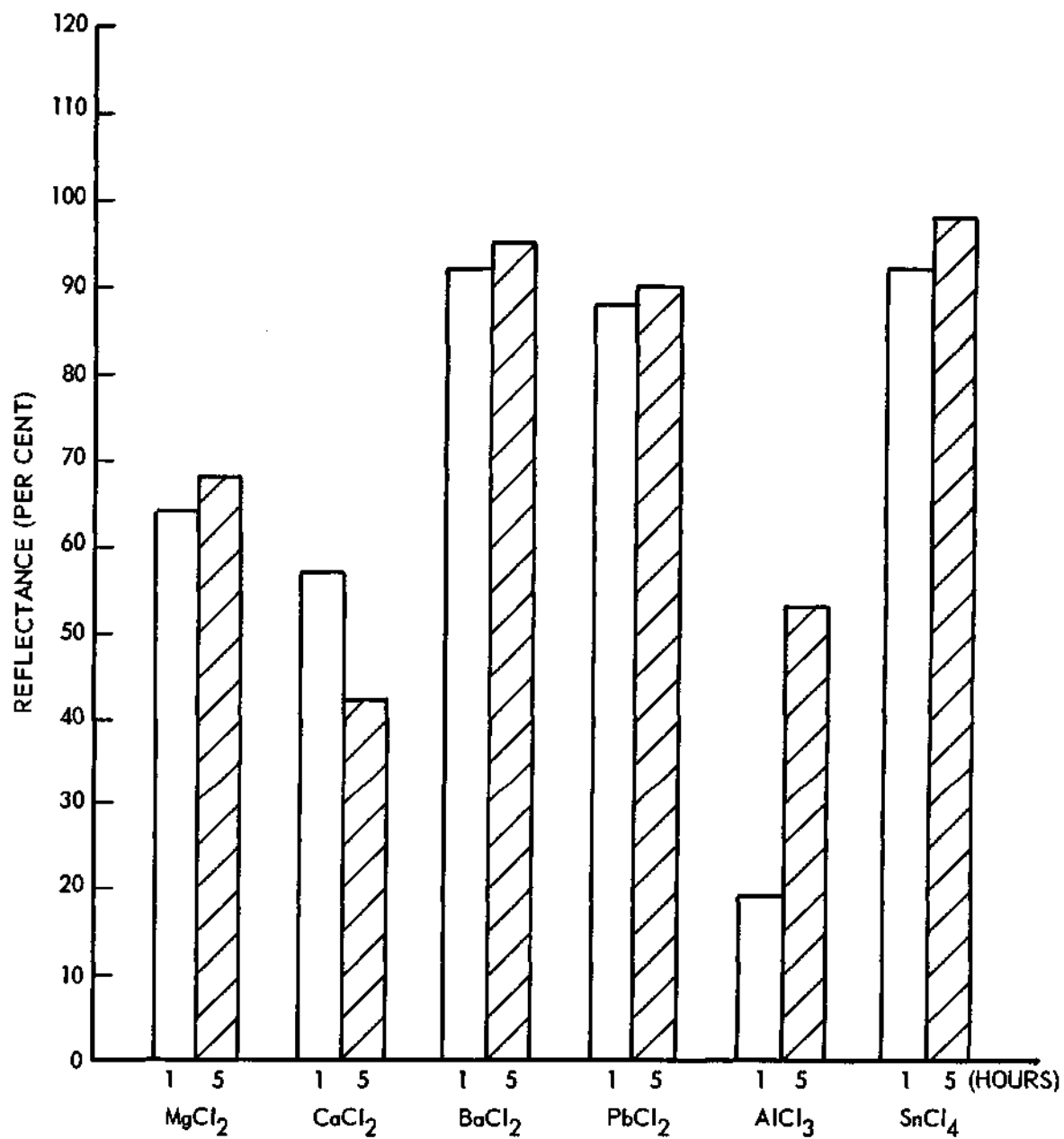


Figure 5. Effect of Inorganic Salts on Direct Blue 71 (PH = 3).

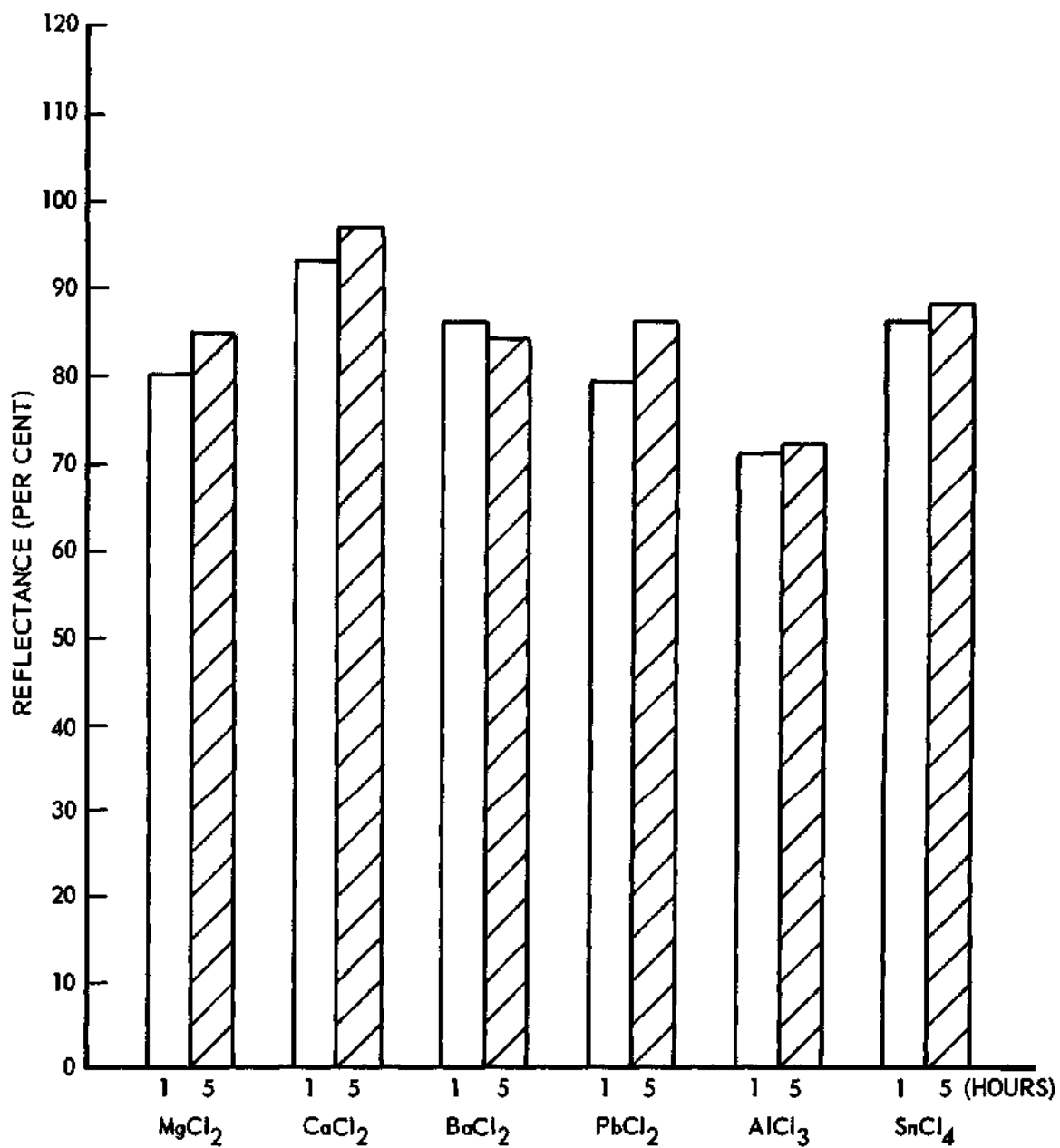


Figure 6. Effect of Inorganic Salts on Direct Yellow 29 (PH = 3).

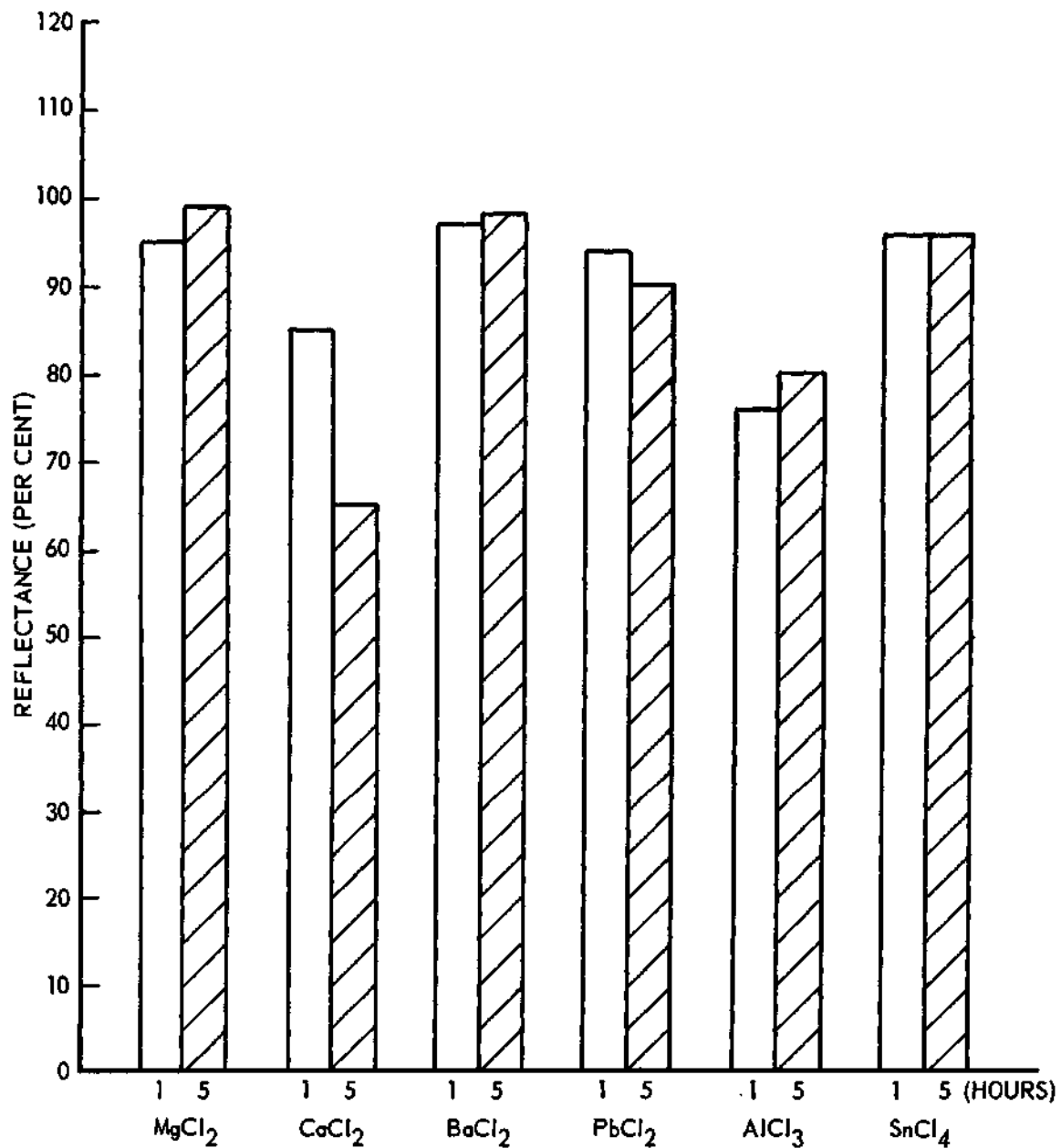


Figure 7. Effect of Inorganic Salts on Direct Red 37 (PH = 3).

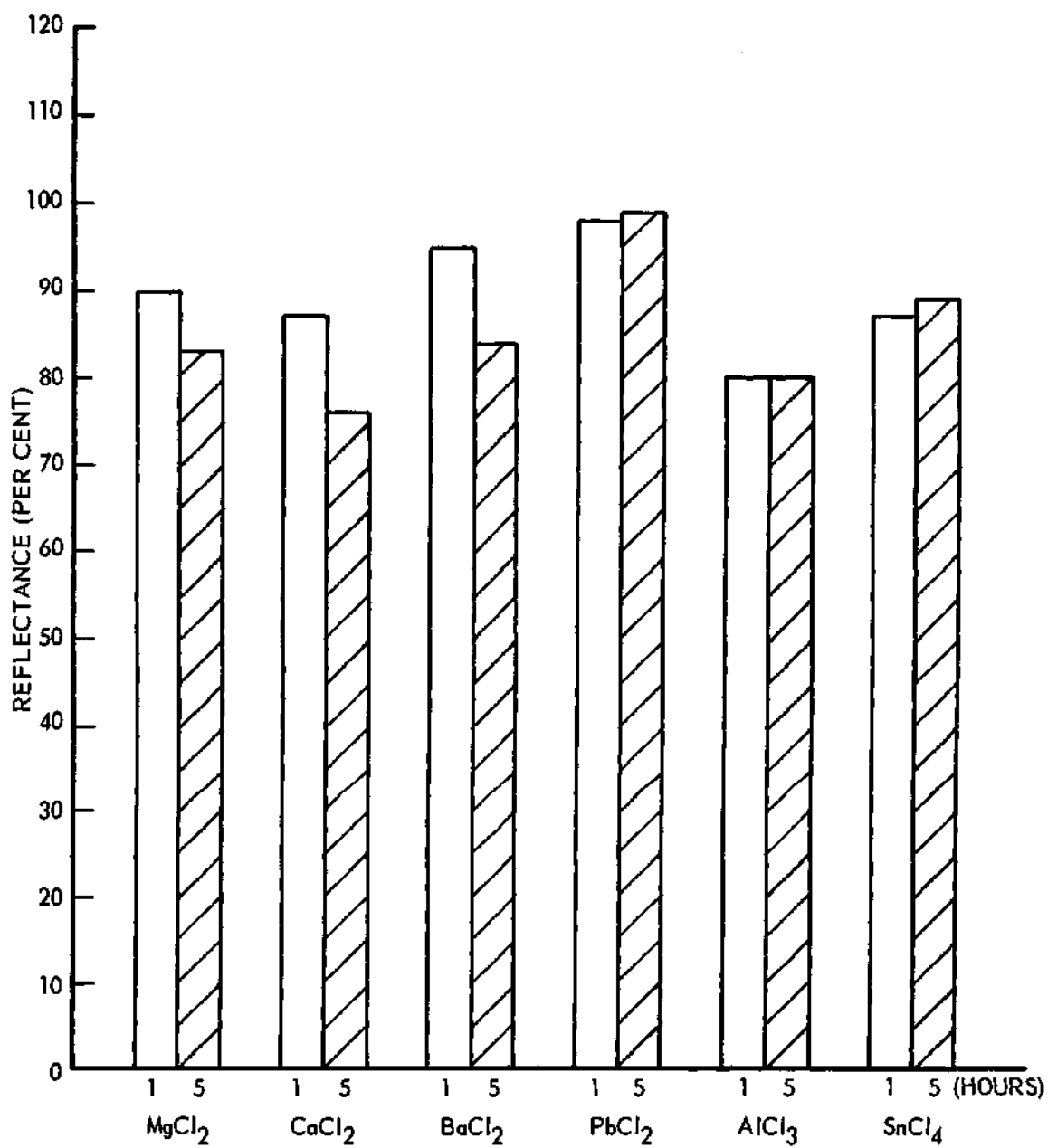


Figure 8. Effect of Inorganic Salts on Direct Blue 78 (PH = 3).

treatments to improve the fastness properties of some direct dyeings.

Figure 6 shows that none of the ions was as effective as sodium in exhausting the Direct Yellow 29 dyebath; and the results with aluminum chloride were also lower than these obtained with sodium chloride.

Calcium chloride also gave very poor exhaustion (compared with sodium chloride) of Direct Red 37 (Fig. 7) and Direct Blue 78 (Fig. 8). In these cases the marked shade change observed with Blue 71 was not noted.

The variability of the effect of any one salt on the dyes used in this work is very marked. Magnesium chloride was similar in its action to sodium chloride except in the case of Blue 71. Calcium chloride gave dyebath exhaustions equal to or better than those obtained with sodium chloride with five of the dyes (Red 4, Green 6, Yellow 50, Red 2 and Yellow 29) but apparently destroyed Blue 71. The barium salt gave significantly poor results only with Yellow 12. Lead chloride affected Red 2 and Yellow 12 adversely but had no marked effect on other dyestuffs. Of the six salts used aluminum chloride gave the poorest dyeings on the largest number of dyes. Tetravalent tin ions gave dyeings of significantly lower strengths than those obtained with common salt only in the case of Yellow 50.

McBain (13), and further Robinson and Mills (14) have shown that direct dyes exist in the form of colloidal electrolytes having negatively charged ionic micelles. The stability of micelles is determined by a balance between attractive (van der Waals) forces and repulsive forces between like-charges. An acidic salt would cause a greater adsorption than an alkaline one on account of the destabilising effect of the hydrogen ions and the stabilising effect of the hydroxyl ions. Neale and Patel (15) concluded that the effect of the various inorganic cations upon the direct dyestuff adsorption is shown to be analogous to the behavior in the destabilization of colloids.

Wiktoroff (16), who studied the effect of various electrolytes (mono-, di- and tri-valent cations) on the amount of dye absorbed in an arbitrarily fixed time, came to the conclusion that, in general, the greater the valency of the cation, the greater is absorption. Boulton, Delph, Fothergill and Morton (2) also found that adsorption is approximately the same from dyebaths containing equal ionic concentration of different inorganic electrolytes containing a univalent cation, but is increased if the cation is divalent. However, the results of the present experiment show no correlation between them when the various divalent cations and sodium ions are compared.

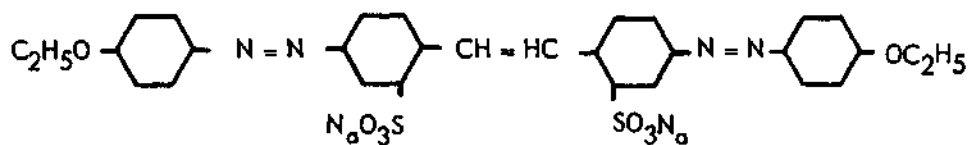
In the present study, as indicated before, aluminum chloride, with a trivalent cation, gave the least exhaustion with most dyes, lower than the exhaustions obtained with any of the divalent cations or with sodium ion.

Neale and Patel (15) observed that in the presence of aluminum sulfate, the dye solution, even at the boil, was slightly turbid, showing that an incipient coagulation probably due to the formation of an insoluble salt of aluminum with Chlorazol Sky Blue FF (C. I. 24,410) - acid set in. This shows that when discussing the effect of polyvalent cations on dye adsorption, their actual effect in precipitating the dye should also be taken into account.

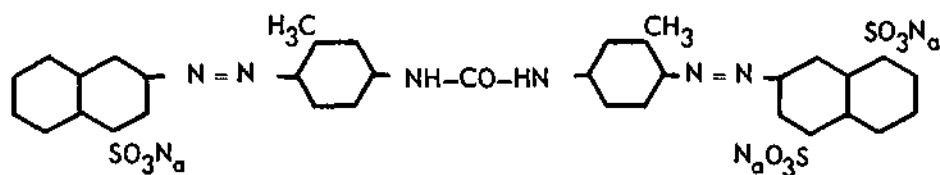
From a study of dye structures (see Fig. 9), it is noted that one of the dyes, Direct Yellow 50, which decomposes has a substituted diphenyl urea. Vickerstaff (17) has shown that many direct dyes containing the diphenyl urea structure undergo hydrolysis on prolonged boiling in water; the urea structure breaks down, releasing carbon dioxide.

It is not possible, from this work, to make any general statements regarding the effect of inorganic salts on direct dyes. No correlations of the effect of the various salts with size, charge, or other physical characteristics have been possible. Apparently the results are determined by

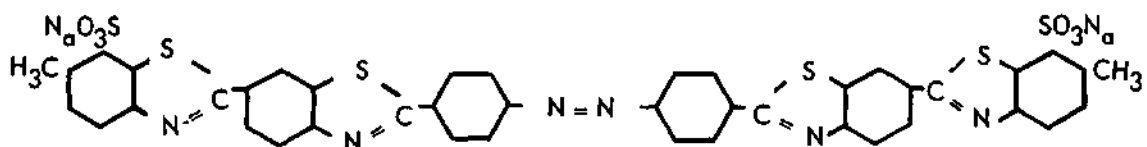
both the nature of the dye and the added salt as well as by other factors which have not yet been determined.



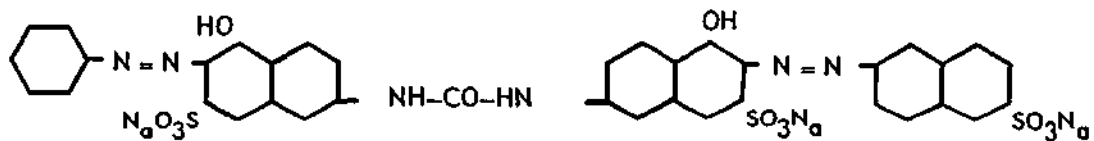
C.I. DIRECT YELLOW 12



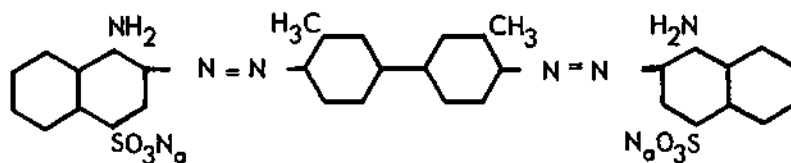
C.I. DIRECT YELLOW 50



C.I. DIRECT YELLOW 29

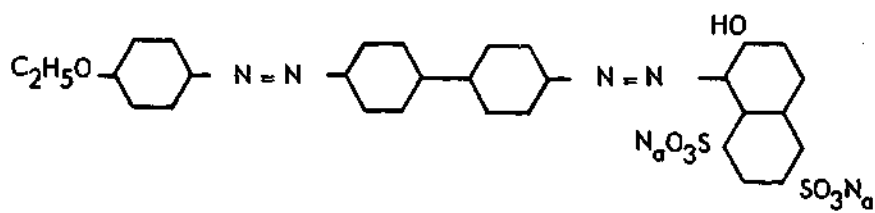


C.I. DIRECT RED 4

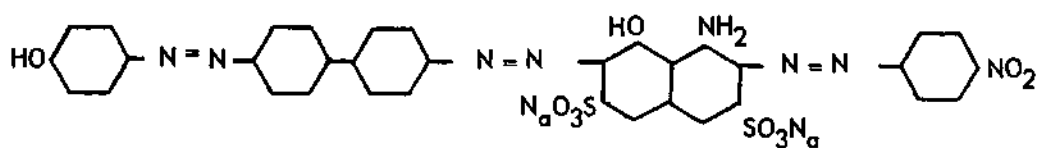


C.I. DIRECT RED 2

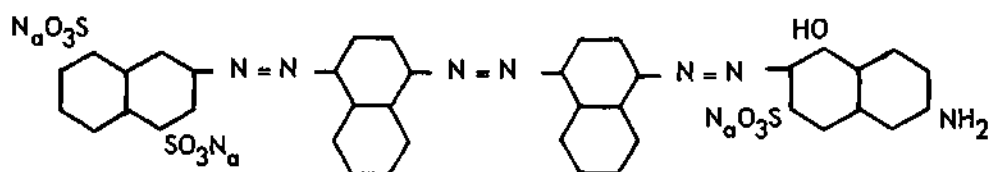
Figure 9. Dye Structures.



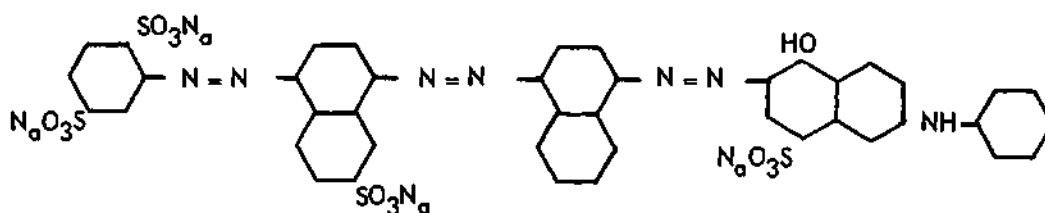
C.I. DIRECT RED 37



C.I. DIRECT GREEN 6



C.I. DIRECT BLUE 71



C.I. DIRECT BLUE 78

Figure 9 (Continued). Dye Structures.

CHAPTER IV

CONCLUSIONS

On the basis of the data obtained in this work, the following conclusions may be drawn:

1. The "build-up" phenomenon exhibited by some direct dyes on prolonged boiling is dependent upon the conditions of dyeing.

2. In the presence of 0.01 M NaCl, lowering the pH of the original dyebath to 3.0 results in a slight increase in adsorption of direct dye by cotton fiber. This may be due to a lowering of the negative surface potential of the cellulose.

3. Aluminum chloride produces low adsorption of direct dyestuffs by cotton fiber.

4. From this work, no correlations of the effect of the various salts with size, charge, or their physical characteristics have been possible.

CHAPTER V

RECOMMENDATIONS

It is recommended that investigations into the anomalous behavior of direct dyes be pursued further. Working with purified dyestuffs, the causes of "decomposition" and "build-up" should be determined. These are no doubt two separate problems and should be attacked on that basis. For dyes which decompose, the nature of the decomposition products should be determined in these cases where this work has not already been done. The effect of various substituent groups in the dye molecule (and their position) on dyestuff stability should also be investigated.

Armfield (18) has reported that many direct dyes are decomposed by boiling in slightly alkaline solution and attributes the effect to reduction, since it is accentuated in closed vessels and diminished by bubbling oxygen through the dyeliquor. Therefore it is recommended that the effect of various mild oxidizing agents, added to prevent the decomposition of dyes, be investigated.

It is also suggested that an investigation of other classes of dyes, especially those which are used in the high temperature dyeing of the new synthetic fibers such as Dacron

be pursued.

Investigation of the effect of various inorganic salts on cotton dyeing at various concentrations should be carried out in order to determine their effect on maximum exhaustion of dyeings and degree of coagulations, etc. Since it has been stated (16) that insoluble salts of aluminum and dye cause low adsorption in direct cotton dyeing, the actual effect, of polyvalent cations, in precipitating the dyes should be thoroughly observed.

The effect of various salts on the Zeta potential of cellulose has been determined by Briggs (19). It is recommended that attempts be made to correlate these results with the behavior of direct dyes in the presence of these salts.

APPENDIX

Table 4. Transmittance Percentages
for Direct Yellow 12

Wave Length (Millimicron)	Transmittance (per cent)	Slit (Millimeter)
380	0.4	0.250
390	0.3	0.217
400	0.3	0.185
410	0.3	0.161
420	0.5	0.145
430	0.9	0.130
440	1.5	0.112
450	2.5	0.101
460	4.8	0.093
470	9.6	0.088
480	18.6	0.082
490	33.8	0.078
500	53.1	0.071
510	69.9	0.069
520	82.9	0.065
530	90.0	0.064
540	94.2	0.063
550	95.8	0.065
560	97.5	0.067
570	98.1	0.068
580	98.3	0.070
590	98.6	0.075
600	98.8	0.091
610	98.8	0.126
620	98.9	0.160
630	99.2	0.051
640	99.2	0.047
650	99.3	0.045
660	99.3	0.043
670	99.4	0.040
680	99.4	0.036
690	99.4	0.035
700	99.5	0.033

Concentration of Dye Solution: 0.05 g/l at pH=3

Absorption Cell: Beckman Corex.

Standard: Deionized Water

Table 5. Transmittance Percentages for
Direct Red 4, Direct Green 6,
Direct Red 37 and Direct Blue 78

Wave Length (Millimicron)	Transmittance (per cent)			
	Red 4	Green 6	Red 37	Blue 78
380	76.8	60.0	45.2	86.4
390	73.1	59.9	48.0	86.2
400	69.7	61.2	51.2	86.1
410	67.4	63.7	54.3	86.2
420	65.7	66.8	57.0	86.7
430	64.0	69.8	59.5	86.9
440	61.7	72.2	59.3	86.8
450	58.2	73.7	55.9	86.4
460	53.3	74.6	48.6	85.6
470	48.0	75.5	41.0	84.6
480	43.0	76.4	43.3	83.4
490	39.3	77.5	29.5	81.9
500	38.8	78.4	26.7	79.9
510	40.0	78.7	26.4	77.8
520	41.5	78.5	28.1	74.8
530	45.4	77.7	32.2	71.5
540	52.8	76.0	41.1	67.9
550	64.4	73.9	55.6	64.0
560	76.5	71.1	72.0	60.6
570	87.3	67.7	85.0	57.2
580	94.0	64.2	92.8	54.5
590	97.1	60.0	96.5	52.5
600	98.3	56.3	98.0	51.4
610	98.8	53.1	98.7	51.8
620	99.2	50.8	98.9	53.9
630	99.4	49.7	99.1	57.0
640	99.5	49.5	99.3	60.8
650	99.5	50.3	99.4	65.1
660	99.5	51.9	99.5	69.6
670	99.6	56.0	99.5	74.4
680	99.7	60.6	99.5	78.3
690	99.7	66.2	99.6	82.3
700	99.8	71.9	99.7	85.5

Concentration of the Four Dye Solutions: 0.0125 g/l at pH=3.
Absorption Cell: Beckman Corex. Standard: Deionized Water.

Table 6. Transmittance and Reflectance
 Percentages for Direct Yellow 29
 and Comparison of the Cloth Positions

Wave Length (Millimicrons)	Transmittance (per cent)	Reflectance (per cent)	
		Filling Direction	Warp Direction
380	0.9	8.2	7.3
390	0.9	7.9	6.8
400	1.1	7.8	6.6
410	1.6	7.9	6.8
420	2.8	8.1	7.1
430	4.9	8.3	7.3
440	8.3	9.0	8.4
450	13.1	10.3	9.8
460	19.8	12.5	11.9
470	27.9	14.7	14.0
480	36.4	18.0	17.1
490	46.2	21.2	20.8
500	57.0	25.9	25.5
510	67.1	30.6	30.2
520	76.0	36.6	36.3
530	82.8	42.0	42.1
540	87.3	48.0	48.9
550	90.5	53.8	54.5
560	92.5	57.7	59.2
570	93.7	61.3	63.0
580	94.6	64.0	64.6
590	95.3	66.5	66.5
600	95.8	67.6	68.8
610	91.1	68.5	69.5
620	96.5	69.0	70.9
630	97.1	69.1	69.7
640	97.6	71.8	72.5
650	97.8	72.2	74.0
660	97.9	72.2	74.2
670	98.2	72.2	74.4
680	98.5	72.1	74.4
690	98.6	72.1	74.3

Table 6. (Con'td) Transmittance and Reflectance
 Percentages for Direct Yellow 29
 and Comparison of the Cloth Positions

Wave Length (Millimicrons)	Transmittance (per cent)	Reflectance Filling Direction	(per cent) Warp Direction
700	98.7	72.2	74.1

For Transmittance Measurements

Concentration of Dye Solution: 0.1 g/l (pH=3)

Absorption Cell: Beckman Corex. Standard: Deionized Water

For Reflectance Measurements

Sample: 1% Dyed Plain Woven Cotton Cloth

Standard: MgCO₃ Block

Table 7. Reflectance Percentages for Direct
Yellow 50, Direct Red 2 and
Direct Blue 71

Wave Length (Millimicrons)	Reflectance (per cent)		
	Yellow 50	Red 2	Blue 71
380	16.5	8.3	22.4
390	13.8	9.1	22.7
400	12.5	9.9	22.7
410	10.9	9.7	22.8
420	10.2	8.7	22.8
430	9.5	7.7	22.0
440	10.1	6.8	21.1
450	11.2	6.6	19.8
460	13.3	6.3	18.5
470	16.5	6.0	17.0
480	20.8	6.0	15.9
490	26.5	6.1	14.5
500	33.2	6.0	13.0
510	39.3	5.7	12.0
520	47.5	5.5	10.5
530	54.1	5.5	9.7
540	60.2	5.6	8.7
550	65.0	6.2	8.0
560	68.1	6.8	7.4
570	70.0	8.1	7.2
580	71.3	12.0	7.2
590	72.1	18.3	7.2
600	72.5	25.8	7.2
610	72.9	33.3	7.1
620	73.2	49.4	7.3
630	73.1	55.2	7.8
640	74.0	58.5	8.0
650	74.2	61.3	8.5
660	74.7	63.0	8.9
670	74.7	64.0	10.0
680	74.7	63.8	11.3
690	74.9	65.9	13.0
700	75.0	66.8	15.2

Samples: 1% Dyed Plain Woven Cotton Cloth
Standard: MgCO₃ block

Table 8. Absorbance and Reflectance Values
in the Presence of NaCl (0.01 M)

C. I. Name	Selected Wave Length (Millimicrons)	Absorbance				Reflectances (%)	
		PH=3 1 Hr. 5 Hr.	No pH Control 1 Hr. 5 Hr.	=(B) =(C)	=(D) =(D)	$\frac{(D)}{(C)} \times 100$	$\frac{(B)}{(C)} \times 100$
Direct Yellow 12	410	1.000	1.050				
Direct Yellow 50	430	1.024	0.948	0.970	0.905	93	98
Direct Yellow 29	400	1.181	1.136	1.091	1.113	102	104
Direct Red 4	500	1.237	1.200				
Direct Red 2	520	1.260	1.212	1.302	1.203	92	93
Direct Red 37	500	1.125	1.158	1.058	1.067	101	109
Direct Green 6	630	1.276	1.234				
Direct Blue 71	600	1.143	1.151	1.187	1.102	92	97
Direct Blue 78	600	1.149	1.132	1.112	1.141	102	102

Table 9. Effect of Inorganic Salts on Direct Yellow 12,
Direct Red 4 and Direct Green 6 (pH=3)

Description of Dyeings	Inorganic Salts	Yellow 12		Red 4		Green 6	
		Absorb. (At 410 ^{mu})	Reflect.	Absorb. (At 500 ^{mu})	Reflect.	Absorb. (At 630 ^{mu})	Reflect.
Standard Dyeing	NaCl	1.000	100%	1.237	100%	1.276	100%
5 Hours Dyeing	MgCl ₂	1.000	100	1.284	104	1.161	91
"	CaCl ₂	0.881	88	1.257	102	1.301	102
"	BaCl ₂	0.748	75*	1.175	95	1.093	86*
"	PbCl ₂	0.722	72	1.122	91	1.044	82
"	AlCl ₃	0.733	73*	1.112	90	0.737	58*
"	SnCl ₄	1.000	100	1.121	91	1.180	93

*Visible Shade Change

Table 10. Effect of Inorganic Salts
on Direct Yellow 50 (pH=3)

Inorganic Salts		Dyeing Hours				
		1	2	3	4	5
MgCl ₂	Absorb.	0.927	0.876	0.900	0.878	0.844
	Reflect. (%)	90	85	88	86	82
CaCl ₂	Absorb.	1.012	0.961	0.903	0.911	0.919
	Reflect. (%)	98	94	88	89	90
BaCl ₂	Absorb.	0.950	1.012	0.922	0.952	0.860
	Reflect. (%)	92	98	90	93	84
PbCl ₂	Absorb.	0.942	0.910	0.857	0.903	0.890
	Reflect. (%)	92	89	84	88	87
AlCl ₃	Absorb.	0.903	0.823	0.912	0.882	0.879
	Reflect. (%)	88	80	89	86	86
SnCl ₄	Absorb.	0.765	0.739	0.773	0.711	0.704
	Reflect. (%)	75	72	76	69	69

Selected Wave Length: 430 Millimicrons
Absorbance for Standard Dyeing: 1.024

Table 11. Effect of Inorganic Salts
on Direct Red 2 (pH=3)

Inorganic Salts		Dyeing Hours				
		1	2	3	4	5
MgCl ₂	Absorb.	1.026	1.026	1.044	1.042	1.055
	Reflect. (%)	81	81	83	83	84
CaCl ₂	Absorb.	1.375	1.360	1.360	1.327	1.339
	Reflect. (%)	109	108	108	106	106
BaCl ₂	Absorb.	1.293	1.320	1.264	1.312	1.288
	Reflect. (%)	103	105	100	104	102
PbCl ₂	Absorb.	1.031	0.839	0.585	0.441	0.438*
	Reflect. (%)	82	67	46	35	35
AlCl ₃	Absorb.	0.642*	0.683*	0.621*	0.683*	0.674*
	Reflect. (%)	51	54	49	54	54
SnCl ₄	Absorb.	1.181	1.171	1.169	1.186	1.186
	Reflect. (%)	94	93	93	94	94

Selected Wave Length: 520 Millimicrons
Absorbance for Standard Dyeing: 1.260

* Shade Changed

Table 12. Effect of Inorganic Salts
on Direct Blue 71 (pH=3)

Inorganic Salts		Dyeing Hours				
		1	2	3	4	5
MgCl ₂	Absorb.	0.735*	0.790	0.792	0.802	0.778
	Reflect. (%)	64	69	69	70	68
CaCl ₂	Absorb.	0.655	0.650	0.494	0.487	0.479*
	Reflect. (%)	57	57	43	43	42
BaCl ₂	Absorb.	1.049	1.192	1.231	1.191	1.087
	Reflect. (%)	92	102	108	104	95
PbCl ₂	Absorb.	1.013	1.044	1.042	0.993	1.026
	Reflect. (%)	88	91	91	87	90
AlCl ₃	Absorb.	0.329	0.366	0.360	0.384	0.668*
	Reflect. (%)	29	32	31	34	53
SnCl ₄	Absorb.	1.057	1.036	1.044	1.047	1.125
	Reflect. (%)	92	90	91	92	98

Selected Wave Length: 600 Millimicrons
Absorbance for Standard Dyeing: 1.143

*Shade Changed

Table 13. Effect of Inorganic Salts
on Direct Yellow 29 (pH=3)

Inorganic Salts		Dyeing Hours				
		1	2	3	4	5
MgCl ₂	Absorb.	0.940	0.940	1.000	0.980	1.000
	Reflect. (%)	80	80	85	83	85
CaCl ₂	Absorb.	1.103	1.078	1.064	1.101	1.144
	Reflect. (%)	93	91	90	93	97
BaCl ₂	Absorb.	1.020	1.000	1.046	1.029	0.990
	Reflect. (%)	86	85	88	87	84
PbCl ₂	Absorb.	0.938	1.005	1.011	1.022	1.014
	Reflect. (%)	79	85	86	86	86
AlCl ₃	Absorb.	0.838	0.860	0.840	0.817	0.850*
	Reflect. (%)	71	73	71	69	72
SnCl ₄	Absorb.	1.019	1.015	1.015	1.015	1.041
	Reflect. (%)	86	86	86	86	88

Selected Wave Length: 400 Millimicrons
Absorbance for Standard Dyeing: 1.181

*Shade Changed

Table 14. Effect of Inorganic Salts
on Direct Red 37 (pH=3)

Inorganic Salts		Dyeing Hours				
		1	2	3	4	5
MgCl ₂	Absorb.	1.069	1.150	1.095	1.070	1.117
	Reflect. (%)	95	101	97	95	99
CaCl ₂	Absorb.	0.960	0.888	0.810	0.752	0.732
	Reflect. (%)	85	79	72	67	65
BaCl ₂	Absorb.	1.098	1.103	1.025	1.089	1.110
	Reflect. (%)	97	98	91	97	98
PbCl ₂	Absorb.	1.054	1.043	1.048	1.012	1.012
	Reflect. (%)	94	93	93	90	90
AlCl ₃	Absorb.	0.860	0.862	0.820	0.812	0.899
	Reflect. (%)	76	77	73	72	80
SnCl ₄	Absorb.	1.078	1.023	1.112	1.080	1.083
	Reflect. (%)	96	91	98	96	96

Selected Wave Length: 500 Millimicrons
Absorbance for Standard Dyeing: 1.125

Table 15. Effect of Inorganic Salts
on Direct Blue 78 (pH=3)

Inorganic Salts		Dyeing Hours				
		1	2	3	4	5
MgCl ₂	Absorb.	1.039	1.013	1.000	1.007	0.950
	Reflect. (%)	90	88	87	87	83
CaCl ₂	Absorb.	1.001	0.940	0.932	0.907	0.870*
	Reflect. (%)	87	82	81	79	76
BaCl ₂	Absorb.	1.092	1.063	1.015	0.918	0.970
	Reflect. (%)	95	92	88	80	84
PbCl ₂	Absorb.	1.132	1.130	1.134	1.135	1.137
	Reflect. (%)	98	98	98	99	99
AlCl ₃	Absorb.	0.923	1.011	0.964	0.962	0.923
	Reflect. (%)	80	88	84	84	80
SnCl ₄	Absorb.	1.010	0.960	1.011	1.033	1.026
	Reflect. (%)	87	84	88	90	89

Selected Wave Length: 600 Millimicrons
Absorbance for Standard Dyeing: 1.149

*Shade Changed

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