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A SURVEY OF THE EFFECT
OF MINERAL SALTS
ON
DIRECT DYEINGS)

LAWRENCE R.
BORTOLOTTI
//
MAY, 28 1956.

INDEX

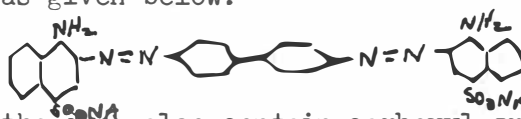
PAGE A	ABSTRACT
PAGES 1-12	LITERARY SURVEY
PAGES 13-17	EXPERIMENTAL OUTLINE
PAGES 18-19	SUPPLEMENTAL INFORMATION
PAGES 20-22	EXPERIMENTAL RESULTS
PAGES 22-26	DISCUSSION OF RESULTS
PAGE 27	CONCLUSIONS

ABSTRACT

A study of the effect of various minerals salts on dyeings made with direct dyes. Dyes were chosen for their frequency of usage in the paper industry; the salts were chosen for several reasons, the prime one being that they form a floc at approximately the same pH as that of the stack run over the paper machine, also for its cost and availability. Sheets were made with the various dyes and salts in several percentages of each, dried, cut up into test sheets for fading and bleeding. The test sheets were examined visually for evidence of fading and bleeding and the results accordingly were recorded. It was shown by this method that manganese chloride when used in connection with certain dyes improved the light fastness and bleeding resistance.

THE EFFECT OF MINERAL SALTS ON THE FASTNESS
PROPERTIES OF DIRECT DYES IN PAPER

Direct dyes are water-soluble dyes that exhaust on to cellulosic fibers such as cotton, linen and rayon without mordanting the fibre. Because of this property, these dyes are called "substantive". Chemically, the water solubility is due to the presence of sulfonic radicals. A typical dye molecule can be represented by the empirical formula, as given below:



A few of the dyes also contain carboxyl groups ortho to the hydroxyl. A configuration of this sort makes it possible for the dyer to add mineral salts to the dye solution as an after treatment, bringing about a complex dye compound which is insoluble in the dye solution. This complex dye compound is responsible for the improved fastness properties.

The process of dyeing is accomplished in two stages: adsorption and fixation.¹ The first is the simple diffusion of the dye throughout the fibre. The second is the resulting action in which the dye becomes insoluble in the material of the dye bath.

A direct dye solution is not an actual solution, but rather a collidal suspension of the dye molecule. The colloidal suspensions are referred to as "aggregates". The size of the aggregate is dependent upon the temperature of the solution and also the nature of the salt additive. The salt in the dyeing process is to restrain the tendency of the sodium ions in the dye molecules adsorbed by the cellulose to escape into surrounding water, since a decrease in solubility tends to increase absorption of the dye.² The early investigations of Wiktoroff on the effect of equivalent concentrations of different electrolytes on the mass of dye absorbed by cotton in a definite time showed that the dye adsorption increased with the valency of the cation of the inorganic salt present.³ He also showed that each dye molecule is held to the cellulose molecule by two hydrogen bonds. The reaction between the dye and the cellulose is exothermic, and 14,000 calories per mole are released.

CELLULOSE STRUCTURE

In the study of the cellulose fibre we find that there are micellular crystalline areas which are important in the dyeing of the fibre. It is the intermolecular spaces that interest the dyer, for the dye aggregation has to be able to pass through the intermolecular space in order to insure complete dye diffusion in the fibre.⁴ If the aggregation size, which can be measured by various methods (osmotic pressure, ultra centrifuge to name a few) is larger than the intermolecular space, we get only a surface adsorption of the dye instead of a complete dye absorption throughout the fibre. The intermolecular space of the cellulose molecule is 10.3, 8.35, and 7.9 A on A, B, and C planes determinable by X-ray methods. Therefore, the size of the dye aggregations would have to be less than these numbers in order to allow the dye molecule to pass through the minute intercellular openings.

Rose's Theory

Monomolecular dyestuff at high temperature and high concentration of salt readily diffuse into intramicellar pores of cotton fibres where it becomes anchored. The high electrolyte concentration on the surface of the cellulose may be responsible in part for the aggregation of the dye molecules on the surface of the cellulose, and the added salt probably supplies the remaining electrolyte needed for aggregation. Lowering of the temperature causes the dyestuff to aggregate back into particles which are too large to migrate back through the pores of the fibre, and the dyestuff is said to be fixed.

DYEING

The size of the dye aggregation is not the only variable involved in the dyeing with direct dyes. We now have to find methods of fixing the dye in the fibre once we get it there. The sealing of the dye in and on the fibre takes place in two ways, (a) mechanical and, (b) chemical, the mechanical process being the sealing of the dyestuff in the fibre by reducing the micellular spaces and thereby making it impossible for the dye aggregate to migrate out of the pore. The chemical process is the chemical valence bonding of the dye on the fibre. It has been theorized that the dye is held to the fibre by means of two hydrogen bonds. There also is the theory that the salt solution presents an intermediary substance which holds attraction for both the dyestuff and the fibre.

Vickerstaff⁵ states that the kinetics of dyeing takes place in three stages:

- (1) Diffusion of the dye through the aqueous dyebath to the surface of the fibre
- (2) Adsorption of the dye on the outer surface of the fibre

- (3) Diffusion of the dye inside the fibre from the surface towards the centre

The second of these steps, the actual adsorption process, is generally assumed to be so much more rapid than either of the diffusion steps that it can be regarded as instantaneous. In the early stages of dyeing the dye is distributed non-uniformly through the fibre with a high concentration at the fibre surface and a low concentration inside the fibre. The existence of the concentration gradient causes dye to diffuse towards the centre of the fibre at a rate proportional to the gradient. This behaviour is expressed in Fick's equation:

$$\frac{ds}{dt} = -DA \frac{dc}{dx} \quad (6)$$

where ds/dt is the rate of diffusion of dye across an area "A" at any point in the fibre and dc/dx is the concentration gradient of dye at that point. The concentration gradient must be expressed in terms of the weight of dye per unit volume of the substrate. The diffusion co-efficient "D" is numerically equal to the amount of dye diffusing in unit time across unit area of the fibre under a unit concentration gradient. "D" is therefore a measure of the diffusing properties of the dye and the permeability of the fibre.

Methods of Dyeing

The dyeing of fibres is accomplished in four basic methods which have proved to be successful from the viewpoint of exhaustion, levelness and brightness of final shade. These methods are used in accordance with the type and color of dye used.

Method 1 .25 - .50% synthetic penetrating agent
 5 - 20% common salt or sodium sulfate
 This method is used on most direct dyes

Method 2 .25 - .50% synthetic penetrating agent
 1 - 2% soda ash
 5 - 20% common salt or anhydrous
 sodium sulfate

Applicable to red acid sensitive dyes, the soda aids in maintaining brightness.

Method 3 .25 - .50% synthetic penetrating agent
 2 - 3% disodium phosphate
 5 - 20% common salt or sodium sulfate

Used for yellows that suffer from brightness and solubility losses when dyed in hard water

Method 4 .25 - .50% synthetic penetrating agent
 1 - 2% acetic acid
 5 - 20% common salt or sodium sulfate

Used only on triphenylmethane yellows, blues, and greens.

Special Methods

Attempts which have been made in the dyeing of direct colors in the presence of metal salts, i.e. chromium sulfate or chrome alum, or also by an aftertreatment of dyeings with metallic salts have given results which show very good light fastness properties. The application of this process, although used extensively in the textile industry, is not too prevalent in the paper industry, but is still in the experimental stages. Ciba in their patents, numbers U.S.P. 2,148,659 and 2,092,429 describe methods for the treatment of cellulosic material while being dyed and also after the dyeing has been completed. These patents cover a two-stage treatment of (a) dyeing in the usual manner and (b) treatment with copper sulfate, soda ash and tartaric acid. It is their claim that the dyeings are brighter and faster to light, than dyeings made by the usual after treatment with copper salts. In their explanation of the chemistry of their dyeing process they claim that the disazo or triazo dyestuffs are transformed into new metal couplings and form what are known as cuprantine colors.^P This assumption is based on the observation that under certain conditions direct dyes combine with metallic salts to form more or less insoluble complexes which are actually formed in the dye bath itself.

Ciba defines the new group of suprantine colors as "a new group of direct dyeing colors which exhibit far greater fastness properties than dyeings made by the usual copper aftertreatment dyes. They are fast to washing, milling and sea water. The fastness to light is very good (excellent in the case of L.L. brands)." The properties exhibited are not destroyed by alkaline treatment. The cuprantine colors are capable of forming complex metallic compounds as with chromium, aluminum, iron, and particularly copper salts. The dyes are dissolved with soda ash and a dispersing agent such as triethanolamine.⁷ The actual dyeing is carried out with soda ash, glaubers salt and a leveling agent such as "abbatex P.O.". The characteristic feature of the method lies in the fact that the copper aftertreatment is performed in the dyebath itself, after a major part of the dyestuff has been adsorbed by the material. The correct shade results only after aftertreatment with the cuprantine salt.⁸

Direct dyes form colloidal solutions, the size of the aggregate of a given dye depending upon temperature and the nature of salt addition.⁹ The rate of dyeing is greatly dependent on temperature, increasing in all cases with increases in temperature. Experimental evidence of direct dyes on cellulose fibres leads to the conclusion that the effect of increasing temperature with all direct dyes is to increase the rate of dyeing or rate of diffusion and to decrease the equilibrium adsorption. It has been considered that the molecularly dissolved particles diffuse freely through the fibre and take no part in the dyeing operation unless the conditions were subsequently modified (by adding salt) in order to affect a change in the state of aggregation. Robinson¹⁰ has investigated structures of aqueous solutions of direct cotton dyes by several methods; such as osmotic pressure, diffusion, conductivity and transport number measurements.

His results have shown quite conclusively the presence of aggregates and also the formation of aggregates by salt additives. Evidence for the aggregation of Sky Blue F.F. has been obtained by conductivity measurements. The dye forms blue solutions in a solution of cationic soap and water above the critical concentration for micelle formation. Below the critical concentration the solution is reddish, and the end point is sharp enough to determine visually by this color change when the micellular formation is broken down by titrating the cationic soap dye solution with distilled water.

(15) Valka has assigned aggregation number of 3.7 to dye solutions of .002 to .02% concentration in the presence of .02 to .05 molar solutions of sodium chloride.

Kinetics

Cellulose is negatively charged with respect to water; the electroeffect of the zeta potential is to oppose the absorption of an anion, the addition of the salt overcomes this repulsion.

One function of salt in the dyeing process is to restrain the tendency of the sodium ions in the dye molecules adsorbed by the cellulose from escaping into the surrounding water, since decrease in solubility tends to decrease side reactions that may take place and increase the absorption of the dye.

The effect of the dye varies considerably from dye to dye and is dependent upon the aggregation characteristics of the dye. Thus Sky Blue F.F., if it is chemically pure and free from inorganic electrolytes is not adsorbed at all by the cellulose, which adsorbs water preferentially over the dye. Benzopurpurine on the other hand, when free from inorganic electrolytes is appreciably adsorbed from aqueous solution.

Neale¹¹ suggested a quantitative explanation of the adsorption of dyes by cellulose in terms of a Donnan membrane equilibrium, regarding direct dyeing as a process of diffusion in which an ultimate equilibrium between cellulose and dyebath is obtained, dependent upon conditions of dyeing. The diffusion of the dye anions from the dyebath to the surface of the fibre when the solution is in a state of ebullition or mechanical agitation is instantaneous and may be considered to be true of the final stage of attachment of the dye molecule to the cellulose molecule; the rate determining step in the dyeing process is the diffusion of the dye from the surface of the fibre into the interior of the water swollen cellulose.

Neale discovered a rough correlation between apparent diffusion so-efficient and the amount of adsorption, when salt was added to the dyebath the diffusion coefficient increased, reached a maximum and then fell, whereas adsorption at equilibrium steadily increased.

Direct affinity may be due to certain symmetry of molecular structure and an attraction between the hydroxyl group of the fibres and the Azo or other chromophor of the dyebath.

FIXING AGENTS

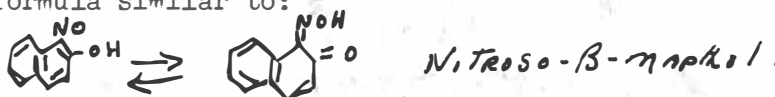
The compound that holds the dye molecule to the cellulose molecule is usually referred to as a fixing agent. The fixing agents have a dual effect on dyeing. We find that first it holds the dye to the cellulose molecule and secondly it gives a softening effect to the fibre. Unfortunately the dye fixers affect the light fastness to some degree and also change the shade of the dyeing to a small degree. These dye fixers act by virtue of their insolubilizing effect of a cation active substance on an anion active dye, the union being due to electrovalence.

The effect is easily removed by an alkali scour, to which even complex ammonium type compounds are not stable.

According to Wallis¹² formaldehyde can be used in conjunction with salt in dyeing with direct dyes. It is his opinion that the formaldehyde molecule links the dye molecule with the cellulose molecule. Although the interaction of formaldehyde with cellulose usually requires much higher temperatures and the presence of a mineral acid catalyst. This suggestion might be considered in the light of such facts as the slow combination of cellulose with formaldehyde to form a methyl ether to about .5% in the presence of lactic acid at 40 to 50 C and the curious effect of formaldehyde in promoting the solubility of cellulose in aqueous calcium thiocyanate in the colder temperature, while a temperature of 80 to 100 C is required in the presence of formaldehyde. Dyes used in conjunction with formaldehyde are found to be similar in that they contain a resorcinol group as an end component.

Listing of a few: Benzoform Orange G
 Benzoform blue BBL
 Benzoform Green FFG & FFL
 Benzoform Brown R

The above dyes contain the common resorcinol formula and exhibit a structural formula similar to:

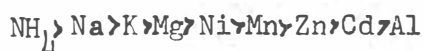


containing a terminal 3,5-dihydroxybenzamide group. These dyes when submitted to the formaldehyde treatment yield dyeings of greater brightness and light fastness than similar dyes containing an azoresorcinol terminal group.

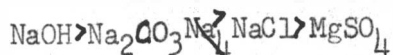
The effect of Different Electrolytes

The effect of electrolytes other than sodium chloride on dyeing has been studied to some extent although for economic reasons

there is little likelihood of sodium chloride or sodium sulphate being displaced from practical usage. From the discussion of the dyeing mechanism already given, it may be anticipated that the nature of the anion of the added electrolyte will have little effect on the adsorption and this is supported by the work of Neale and Patel¹³ on sodium chloride and sodium sulphate. Disodium hydrogen phosphate produced significantly less adsorption of chlorazol Sky Blue FF than did sodium chloride in normal solutions, but this may be due to the difference of pH of the solutions or the fact that the ionic concentration of sodium ions is less. Recently Willis, Warwicker, Standing, and Urquhart¹⁴ studied the adsorption of chrysophenine in the presence of sodium chloride, sodium bromide potassium chloride, potassium bromide and sodium sulphate. The interchange of chloride and bromide ions produced no detectable difference in adsorption, while the replacement of sodium chloride by the equivalent quantity of sodium sulfate produced only a very small reduction in adsorption. The nature of the cation and particularly its valence may be expected to have a much greater effect and this is found to be the case. The subject seems to have been first studied by Wicktoroff¹⁵, who measured the amount of dye adsorbed by the cellulose in an arbitrarily fixed time from solutions containing various electrolytes. The results have little significance, as no attempt was made to establish equilibrium, but using sulphates he found that the order of cation producing increasing adsorption of Benzo Pure Blue was



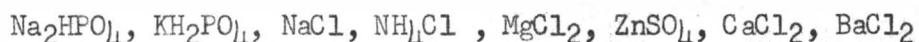
Similar experiments for three hours at 20 C (quite inadequate for equilibrium) were made by Schramek and Gotte¹⁶, who, using Dienil Blue R, arrived at the series



The series contains simultaneous variations of anions, cations and pH.

Boulton, Delph, Fathergill, and Morton found that adsorption is approximately the same from dyebaths containing equivalent quantities of different inorganic electrolytes containing a univalent cation, but is increased if the cation is divalent.

Neale and Patel⁽¹¹⁾ examined the effect of several cations on the rate and equilibrium adsorption of benzopurpurine 4B and Chlorazol Sky Blue FF. The order of effectiveness varies somewhat with concentration, but in n/10 solutions using Chlorazol Sky Blue FF the order was



In these experiments aluminum was also used but produced only low adsorption which Neale and Patel attribute to the formation of the insoluble aluminum salt of the dye. Insoluble salts were also formed with cerium, copper and thorium ions. The results being expressed mainly in graphical form are not available for quantitative treatment. The observations indicate that the nature of the cation of a salt and particularly its valency is of great importance in promoting adsorption of direct dyes on cellulose. The nature of the anions seems to be of secondary importance.

The pH of the Dyebath

Cellulose dyeing is almost invariably carried out in neutral solution, and very little investigation of the effect of pH on dyeing is recorded. In practice the dyebath is occasionally made alkaline by addition of a little sodium carbonate, which is alleged to improve levelling and may well do so, as increasing pH leads to decreased adsorption, as is shown in the extreme case of the addition of caustic soda.

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

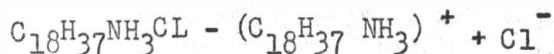
To consider the overall dyeing picture it would not be fair just to consider the adsorption and the absorption of the dye into the water-swollen molecule. Such a picture does not take into consideration the adsorption forces between the diffusing dye anions and the cellulose. The observed cellulosic diffusion coefficient of a dye must depend upon the adsorption of the dye by the cellulose occurring simultaneously with the diffusion process. When the dye anion diffuses in the water-swollen cellulose, the effective resistance to the diffusion of the dye anion is probably increased owing to the fine network of cellulose chains through which diffusion occurs, and on account of the adsorption forces tending to immobilize the dye anion.

From all the foregoing it can be concluded that a dye in order to be substantive to cellulose should fulfill the following requirements:

1. The molecule should be capable of assuming a linear configuration.
2. The aromatic nuclei should be capable of assuming coplanar arrangement.
3. The molecule should contain groups capable of forming hydrogen bonds.
4. Widely spread hydrogen bond-forming groups.
5. The presence of the minimum number of solubilising groups necessary for solubility.

Experimental Outline

The ultimate goal of this experiment is to discover the effect of various soluble salts on direct dyes in the dyeing of paper, in respect to light fastness and bleeding properties. The primary objective will be the binding of the dye to the fibre in such a manner (mechanical or chemical) that it will be relatively untouched by light from the Fade-ometer and will not exhibit bleeding characteristics when in contact with water. The above effects are hoped to be accomplished using soluble salts in conjunction with representative dyes chosen from dyes already in use in the paper industry. Since a cationic detergent is used in treating fibres prior to acid dyeing and there is a great similarity between acid dye and direct dye, one of our additives will be on a cationic detergent nature. A typical example of a cationic surface active agent is octadecyl ammonium chloride which dissociates in water according to the equation:



This salt was chosen for its high degree of dissociation and its solubility in solutions of low pH. Also, salts which form a floc when converted to hydroxides will be used. It is hoped that these salts will act in the same manner as the reaction between alum and rosin size in the affixing of the rosin to the paper.

The dyes selected are chosen from colors in predominant use in the paper industry today.

They are:

Violet	Orange
Sky Blue	Purpurine
Chenoline	Red
Yellow	Pink

A more complete list giving exact title and manufacturer's name will be supplied in the data provided with the "Description of Experiment". The colors chosen represent ones which are fair to poor in lightfastness and show some degree of bleeding.

General Procedure

The general procedure to follow will be to prepare dyeings using two different salt concentrations in conjunction with two different dye weights. A total of 128 different dyeings will be made. The handsheets will be made according to specification, dried and conditioned prior to cutting up into strips. The strips will be subjected to tests to check their lightfastness and bleeding properties.

Details of Procedure

A 100-gram sample of pulp is slurried up in a beater at a consistency of 1.56% based on bone dry pulp. Water used throughout experiment is "iron free" as the cellulose molecule has a great affinity for iron. The sample is stored in a stone crock for future use, with a .5% "Dowacide" preservative added to prevent any change in the color of the pulp through molding over a period of time.

Portions of 80 ml. of the slurry are measured out in 500 cc. beakers and diluted to 200 ml. The dye solution, previously made up in such a concentration that five ml. is equal to one pound, is added to the slurry to the extent of a five pound dyeing. The dye mixture is allowed to mix for 20-minutes to allow for good dye-fiber distribution. To four of the dyeings, four different salt solutions are added to the amount of .5% based on the fiber, and to the other four the salt

solution is added based on two percent of the fiber. Now we have four dyeings of two pounds with a .5% salt added and four dyeings of two pounds with a 2% salt added. The above process is repeated in the same manner except that the five-pound dyeings are now changed to a ten-pound dyeing.

After the addition of the salt we continue stirring for another 20-minutes. The times chosen for this experiment are arbitrary figures, but are set up to keep the time running smoothly and to allow intervals between dyeings for preparation of handsheets and material testing. The times chosen should be sufficient for complete dye-salt distribution throughout the fiber.

When the mixing is completed we begin to make handsheets. The dyeing is further diluted to 480 ml. and handsheets are made according to TAPPI T-205 M 53 and dried in accordance with T-402. After conditioning the sheet at a constant temperature of 70°F. and at a Relative Humidity of 50% to assure good dye fixation to the fiber for 48 hours, we cut the handsheet into one-inch strips in preparation for testing. The strips are all labelled according to the dye used, the weight of the dye and the salt and its concentration used, in order to be able to identify them later.

The strips are saved until a sufficient number have been accumulated to warrant the starting up of the Fade-ometer.

When sufficient strips for fading have been collected, they are placed on the rack of the Fade-ometer and allowed to expose to the light emitted for 24 hours. This time is comparable to the average light-life exposure time of a sheet of dyed paper.

Another batch of sheets, all marked accordingly, are placed between two white wet blotters and allowed to stand under a constant pressure of one pound for one hour.

Upon removal of the strip the blotter is examined for evidence of bleeding by the strip in contact with it. The results are graded visually and the noted gradings will be in accordance with the following scale:

- E - Excellent
- G - Good
- F - Fair
- P - Poor
- B - Bad

An "Excellent" rating means little or no fading due to light and little or no bleeding when in contact with water.

Materials Inventory

The following list will comprise materials necessary for the completion of this experiment:

A. Dyestuffs - Mfr. Calco.

- (1) Rheno Violet B
- (2) Rheno Sky Blue 6B x Conc.
- (3) Direct Chenoline
- (4) Phen Fast Yellow A.P. Conc.
- (5) Rheno Orange
- (6) Benzo Purpurine 4B Conc.
- (7) Congo Red 4B x Conc.
- (8) Phen Pink G x

B. Salts

- (1) Octodecyl Ammonium Chloride
- (2) Aluminum Hydroxide

C. Glass Materials

- (1) Two 1000 ml. Volumetric Flasks
- (2) Two dozen 500 ml. beakers
- (3) Pipettes 5 ml. and 25 ml.

D. Testing Materials

- (1) British Sheet Mold
- (2) Fade-ometer
- (3) Carbon Rods for light source

Time Inventory

From the present date to the prescribed date of completion (June 17, 1956) required for the submission of this report, we have

a total of 28 weeks. It must be noted however, that a series of holidays and recesses occur during this time which hamper the progress of our experiment. These holidays reduce out available time to 17 Mondays which would be available for the continuation of the experiment. There will also be a necessity to allow for time to accumulate and organize data for final incorporation into the report and also for presentation before the meeting of TAPPI members at the Hotel Harris on May 17, a total of two weeks are allowed for the aforementioned work and thus we have 15 weeks to accomplish our dyeings and testing.

A total of eight dyes are planned to be tested. We have eight dyes at two salt concentrations with four salts at two different dye strengths giving us a total of 128 dyeings.

The actual dyeing of eight is accomplished in one hour, it required another half hour to prepare the handsheets and 15-minutes to press the sheets dry and place them on drying rings. Considering a time period of one-and-a-half hours for the process and four different salts to be run, we find we can run one dye per week.

One hour of the six-hour laboratory period will be taken to attend a lecture on organic chemistry and will be made up at a later date.

When the eight dyes are completely investigated with the salts chosen, if any time remains, an experiment concerning the solubilization of the outer surface of the cellulose with potassium thio cyanate prior to dyeing will be conducted.

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SUPPLEMENTAL INFORMATION

Direct dyes are water soluble dyes that exhaust onto cellulosic fibres, such as cotton, linen, and rayon, from a salt bath without mordanting of the fiber. Because of this property these dyes are called substantive.

The first successful synthetic direct dye was Congo Red, a diazo derivative derived from benzidine by Boettiger in 1884, using the diazotization and coupling reaction discovered in 1858 by the German chemist Peter Griess, who became a Scotch brewer. The first direct dye made by Griess himself by coupling tetrazotized benzidinedisulfonic acid with 2-naphthylamine some years before the invention of Congo Red proved to be so fugitive that the product was never produced commercially. Even Congo Red, although still used because of its cheapness and brightness, is one of the more fugitive dyes. Chemically nearly all the direct dyes are azo products containing one or more sulfonic radicals, which impart water solubility. A few also contain carboxyl groups ortho to the hydroxyl; this configuration permits aftertreatment for improvement of fastness. In general they are easier to salt out from aqueous solutions than acid dyes. Most direct dyes contain two or three azo groups although monoazo and polyazo products are known.

According to the U.S. Tariff Commission the direct dyes are the second most important class in the U.S. in both tonnage and value, being second only to the vat dyes. They are also second in the number of products, being exceeded only by the acid dyes.

They find the most extensive use for coloring cotton and rayon textiles, on which they give a full range of colors from full rich blacks to bright shades of all hues. They are also used on leather, linen, jute, hemp, ramie, coir, silk, wool, glass, regenerated protein(soybean, casein and zein), and mixtures of other fibers, particularly when wool or silk is present. Direct dyes do not exhaust on cellulose acetate(estrone), although in some cases they stain it extensively.

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Experimentation began with the selection of typical dyes used in the paper industry, with special emphasis placed upon the lighter colors because of their greater fading properties. The salts were chosen for their ability to form a floc within the pH range similar to that necessary for good sheet manufacture and formation on the paper machine. The salts chosen were:

chromium nitrate
 Manganous chloride
 zinc chloride
 aluminium chloride
 copper sulfate

The first dye tested was direct chinoline. Dyeings of five and ten pound were made with salt additive of 0.5% and 2.0%. Observations of the change of color with the addition of salt to the dyeing were as follows:

Chromium	greenish yellow
Copper	greenish brown
Manganese	no change
aluminium	lighter yellow
zinc	no change

The next dye tested was Pheno Fast Yellow. The same color changes accompanied this dye as occurred with the Chinoline. Similar dyeings were made with Pheno Fast Orange. Color changes were noted only in the case of the addition of the copper salt, which gave a darker dyeing with a bluish tinge. Pheno Pink and Congo Red were next used for the investigation. Color changes noted were

Manganese	enhances red color
Aluminium	darkens red color
Chromium	darkens red color
copper	darkens red color
zinc	no appreciable change

After the dyeings were completed and the sheets were cut up into proper size for testing, the strips were faded for ten hours in the Fade-O-Meter, the faded strips were visually examined for degree of fading. This inspection seemed to indicate that the manganese chloride salt addition gave the best results in comparison to the salts tested.

Table 1 shows the dyeings made with the various salts on one of the dyes selected.

With the previous results indicating that manganese chloride was a possibility for our research, a more complete investigation of numerous dyes was conducted using manganese chloride as the sole additive, another set of dyeings using only the dye was made as a basis of comparison of the value of the salt. The dyes used were:

- 1 Pheno Orange R
- 2 Pheno Fast Yellow AP Conc.
- 3 Pheno Fast Orange 2RS
- 4 Pheno Orange O
- 5 Pheno Fast Yellow 95 Conc.
- 6 Pheno Fast Yellow B Conc. 125%
- 7 Pheno Fast Yellow 6G
- 8 Pheno Brilliant Violet KB Conc.
- 9 Direct Dark Green BG Conc.
- 10 Pheno Brown MRS
- 11 Pheno Blue PCN 2B Ex. Conc.
- 12 Pheno Sky Blue 6BX Conc.
- 13 Pheno Fast Scarlet 4BNC
- 14 Pheno Fast Pink G Conc.
- 15 Pheno Red 6BX 200%
- 16 Direct Fast Red 8BQ
- 17 Congo Red 4BX Conc.
- 18 Pheno Brown 3GXX

The blank dyeings and the dyeings containing the salt were faded for ten hours and the results again visually examined.

The Pheno Fast Yellow and the Pheno Orange R again gave the best results in respect to light fastness. The other dyeings varied from fair to poor.

Bleeding tests run on the samples were run by placing the strips of dyed paper between two wet blotters under a pressure of two pounds for a period of forty-eight hours.

Table two shows the dyeings made with various dyes and manganese chloride as the additive.

DISCUSSION OF RESULTS

The results obtained from this project indicate some value for the use of manganese chloride as an additive for dyeing. This is borne out by the results obtained with Pheno Fast Orange and Pheno Fast yellow.

In certain dyeings a complete change in color will be noted it may be thought that this is due to the salt additive, but examination of the salt free dyeings shows the same color change and therefore it might be concluded that the color change is due to the effect of the ultra violet rays from the Fade-O-Meter on the dye itself.

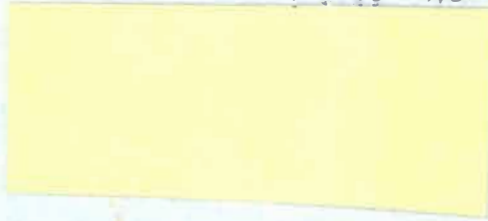
The results obtained certainly warrant a more complete investigation of the effect of mineral or organic salts on direct dyes, with the hope of finding a salt which acts as copper sulfate on Sky Blue 6BX.

TABLE II

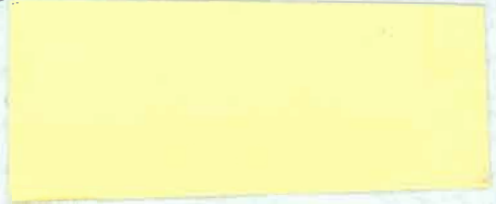
DYE

PLENO Fast Yellow

DYE + $MnCl_2$



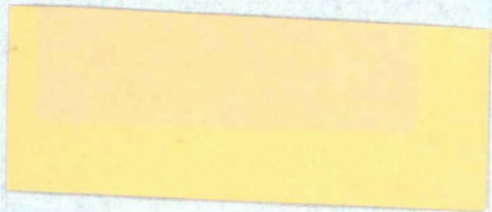
95
CONC



PLENO ORANGE O



PLENO ORANGE R



PLENO ORANGE 2RS



DIRECT FAST Red

8
BA



PLENO Red GBX 200%



Dye + Pulp

Dye + $mucL_2$
+
Pulp

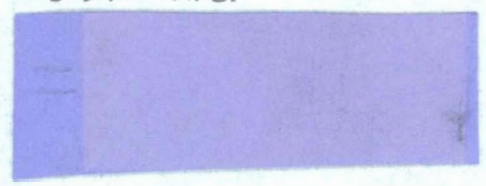
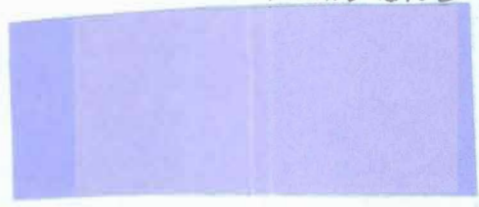
Pheno Brilliant Violet



KB
CONC.



Pheno Blue PCN 2B Ex. CONC.



Pheno Sky Blue 6BY



Pheno Brown MRS.



Pheno Fast Scarlet.



4
BNC.



Congo Red. 4BY CONC.



Dye + Pulp

Dye + mnc12
+
Pulp

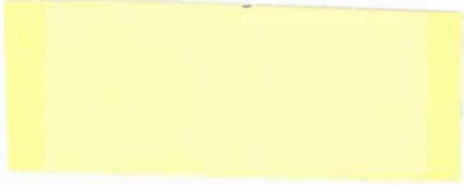
DIRECT DARK GREEN BG CONC.



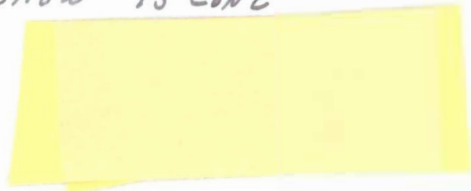
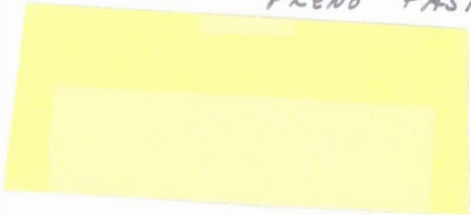
PLENO FAST PINK G. CONC.



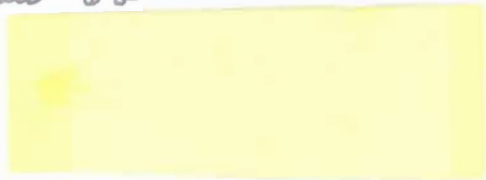
PLENO FAST Yellow Ap CONC.



PLENO FAST Yellow 95 CONC



PLENO FAST Yellow GG



PLENO BROWN 36XX



CONCLUSIONS

Examination of Tables one and two indicate some merit to the use of Manganese chloride as a salt additive to be used in conjunction with

Paper Fast orange
Paper Fast Yellow

In order to get more complete data on the subject, results must be obtained utilizing papermakers additives such as rosin size, alum and clay. It should be tested using the gamit of fillers in use in the paper industry.

Therefore it must be stated that the use of manganese chloride as a color stabilizer is by no means conclusive, but at present, results thus far obtained, do indicate that it may have some use and could someday have a commercial application.