TO: MEMBERS OF THE PROCESS SIMULATION AND CONTROL PROJECT ADVISORY COMMITTEE

Attached for your review are the Status Reports for the projects to be discussed at the Process Simulation and Control Project Advisory Committee meeting scheduled for April 26, 1993 in Atlanta.

We look forward to seeing you on April 26. Best regards.

Sincerely yours,

Gary Jones
Associate Professor of Engineering
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Attachment

GJ/mp

March 25, 1993
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PROCESS SIMULATION AND CONTROL
PROJECT ADVISORY COMMITTEE MEETING

April 26, 1993
Institute of Paper Science and Technology
Atlanta, Georgia

AGENDA

9:30 a.m. Process Simulation and Control Gary Jones
10:30 a.m. Water Reuse Gary Jones
12:00 - 1:00 p.m. Lunch
1:00 - 5:00 p.m. Committee Discussions Gary Jones
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Project</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3471</td>
<td>MAPPS Development</td>
<td>1</td>
</tr>
<tr>
<td>3725</td>
<td>Water Reuse</td>
<td>68</td>
</tr>
</tbody>
</table>
MAPPS DEVELOPMENT

STATUS REPORT

FOR

PROJECT 3576

April 26, 1993
Institute of Paper Science and Technology
Atlanta, Georgia
OBJECTIVE:

Develop new features for the MAPPS simulation program to extend the applicability of the program for industrial problem solving. These features include Performance Attribute Modeling, environmental chemistry and process dynamics and control.

CURRENT STATUS:

MAPPS Version 4.1 was released to subscribers in July, 1992. The new release included a new dynamic feature including a stirred tank (first order lay), plug flow vessel (time delay), a PID controller, a report writer based on the Summary block and a dynamic controller. Future releases will include modules to simulate dye addition and mixing and to predict color, reflectance and other optical properties (Jones and Chaturvedi 1993). The new release will also include dynamic signal generation modules such as a random, sinusoid, ramp and step to manipulate process inputs. A feedforward consistency controller and a logic element will round of the group of control elements available. In the area of separations, the 4.2 version of MAPPS will also include the improved screen model in the HYFRAC module.

MAPPS 5.0

The 5.0 version of MAPPS has been under development for some time. This version has been used extensively for research projects at the Institute and should be available for general use when testing and documentation are complete. Version 5.0 includes a number of important new features which are a departure from previous versions. Most important the stream structure has been revised by combining all the pulp stream types (pulping, recovery, bleaching, paper, and waste into one type. The number of components in the stream has been greatly expanded. All modules in the program were redesigned to handle the new stream structure. Chemical equilibrium calculations were added to compute changes in composition and adsorption/desorption from pulp fibers as well as interactions between gas and liquid. An important part of the new equilibrium chemistry are a series of databases. These include a databases of equilibrium constants, ionic constants, suspended solids data and files which contain
mappings between conventional MAPPS and equilibrium components. Performance attributes were also expanded to include carboxyl concentration and suspended solids attributes such as specific surface area, light scattering and absorption coefficients, specific gravity and diameter. Carboxyl concentration was needed to work with the surface change to determine surface adsorption. This new PAT variable fits naturally with the other composition variables such as YIELD, KAPPA and XHEMI (hemicellulose content).

In addition to the equilibrium block, several new modules have been developed to make use of these new structural improvements. These include a new screen model, hydrocyclone model and an aeration pond model (currently being developed). These new modules are either unfinished or require significant testing and validation before release.

One significant factor in version 5.0 which may affect user concerns is the requirement that Performance Attributes be used for pulping, bleaching and recovery simulations. The reason for this is that the old components "cellulose" and "lignin" are no longer present in the pulp stream definition. These components are defined instead in terms of the pulp "yield" and "Kappa number" attributes. The stream contains fibers only. This concept is more general since new components can be added to the system by adding attributes such as hemicellulose content. On the other hand, the simplification of the stream structures and the addition of many new components make it easier to specify streams. It is no longer a concern that modules work properly with user-defined stream types or unusual components.

One approach which may ease the burden of specifying PAT values would be to have a module to determine PAT values once given a set of sheet properties. For example, such a module would predict the PAT variables needed to predict the specified sheet density, breaking length, burst, tear, scattering coefficient and elastic properties. The number of PAT variables which are determined depends on the number of properties which are specified. The concept of 'properties' could be expanded to include the percent fines and shives in the stream. These additional data would allow the system to determine the standard deviations of the length and width distributions. The intention is to include this utility module in the new release of MAPPS.

Development and testing of MAPPS 5.0 is progressing well. Nearly all the existing models such as the kraft recovery model, paper machine model, bleach plant and steam and power system models have been run with the new system and the results are unchanged. Several applications using the new stream structure have been developed. Conversions of old to new data files is not a significant problem. None of the modules has been changed. Only the input streams must be changed. If any tear streams have been specified, these can simply be deleted. For chemical pulping or bleaching, in most cases, pulp streams are initialized in a WOOD block. It is a relatively simple matter to use the new WOOD02 block to create the input streams with PAT variables. Thus, conversion to the new version will not be a major task.
ACCOMPLISHMENTS SINCE LAST REPORT (MARCH 1992):

Activities since the past report have focused on two major areas:

- Environmental features of MAPPS (discussed in more detail under Project 3725)
- Testing of dynamic tanks and control in MAPPS 4.1
  - dynamic 2-ply papermachine application with control loops
- Technical report and paper on the color simulation work to be presented at the Oxford Fundamentals Symposium. The manuscript is included with this report.

Summary of the Dynamic Simulation and Control Development

The 4.1 version of MAPPS dynamic features have been extensively tested on a multi-ply paper machine application. This two-ply paper machine model was originally developed as a steady state model to determine the sensitivity of end-use performance such as burst and ring crush to process conditions. In the past year this model was been converted to a dynamic form by Steve Koepke as part of an A190 project. Control loops using combinations of PID and feedforward elements were added around each of the major tanks and the system was run successfully with constant level control. Over the course of the project, we found that dynamics and control of a complex multi-tank system was much more difficult than found previously with the continuous digester application. Numerous modifications were necessary to several of the dynamic modules, particularly the stirred tank. In order to make the tanks work properly, it was necessary to change the basic algorithm to solve the differential equations in the tank model.

This work will be presented at the 1993 TAPPI Engineering Conference (Simulation and Control Session). The manuscript is attached.

Color Simulation

New color matching algorithms were described in previous reports. Portions of this work were recast as an IPST Technical report which is attached. This report will also be presented at the Oxford Fundamentals Symposium in September, 1993.

Although nothing was fundamentally changed in the color matching models, it was necessary to recast many of the figures in the original report for easier interpretation of the results. In particular, a new approach was used to compare how well the L*a*b* values were predicted by the model. Rather than comparing the absolute values of the L, a and b values
separately, a combined variable, the color matching variable, was used to define how well the model predicted the color. The color matching function $\Delta C$ is normally defined as the square root of the sum of the squared differences for the L, a and b values respectively between the predicted and measured values.

$$\Delta C = \sqrt{(L_m - L_p)^2 + (a_m - a_p)^2 + (b_m - b_p)^2}$$ (1)

where subscripts m and p indicate measured and predicted values. Analysis of the results showed that most of the error in the predictions was due to error in predicting the L, a, b values of the base undyed sheet. Thus a new criteria was defined to compare the predictions and measurements by defining $\Delta C$ relative to the undyed sheet. After subtracting the base sheet value, the predictions of color change were very accurate. These results are shown for all the handsheets and machine papers used in the evaluation.

**Screening and Cleaning Simulation**

- Improved screening and cleaning models

A new cleaner model has been added to the HYFRAC block. This model, described previously, is based on empirical relationships developed by Bradley for conventional solid separation in hydrocyclones. Since separation is based on specific gravity differences between the solids and the liquid and also requires information on the diameter of the solids, the new algorithms require the new developmental stream structure and data bases in MAPPS 5.0.

A new screen model based on the work of Tirado has been added to the HYFRAC block to simulate fiber fractionation in the slotted screen. The new feature works in both MAPPS 4.1 and MAPPS 5.0. Fibers and shives are separated on the basis of screen slot size, fiber length distribution, fiber width distribution, stream consistency and flow and screen dimensions. Hank Wells as the University of Minnesota is testing the new program with screen room data.

**Fillers and Retention Aids**

A second related feature added recently is a polymer mixing and filler adsorption block. The purpose of the new feature is to model the retention mechanisms of fillers on the papermachine by mimicking the effects of polymers which influence the adsorption of fillers (i.e. carbonates, TiO2) to fibers. Adsorption takes place in a polymer mixing block. Adsorption is a function of polymer concentration (loading), filler surface area and fiber surface area. Fillers are preferentially adsorbed onto fines and the filler retention is therefore related strongly to fines.
A polyelectrolyte such as a polymer or cationic starch is modelled in terms of the concentration of the monomer. For dilute solutions, it is assumed that the monomer act independently.

These concepts require testing and development against data and realistic conditions. In particular fiber-fiber interactions need to be incorporated. Also electrostatic and other non-polymer interactions need to be included.
SIMULATION OF DYNAMICS AND CONTROL
OF A TWO-PLY PAPER MACHINE

GARY L. JONES
STEVEN A KOEPKE
TABLE OF CONTENTS

ABSTRACT 9
KEY WORDS 9
INTRODUCTION 10
OBJECTIVES 11
ELEMENTS OF THE DYNAMIC SYSTEM 11
  Dynamic Controller 12
  Stirred Tank and Plug Flow 12
  Control Algorithms 13
  Controller Logic 14
  Variable Computations 14
APPLICATIONS 14
  Single Stirred Tank -Consistency, Level and Fiber Flow Control 14
  Response to Set Point Change 17
  Multi-ply Liner Paper Machine Dynamics and Control 21
  Machine Break 24
CONCLUSIONS 27
REFERENCES 28
ACKNOWLEDGEMENTS 29

LIST OF FIGURES

1. Schematic of Single Tank Control 15
2. Load Fiber Flow vs. Time 16
3. Load and Level Control Consistency vs. Time 17
4. Tank Level vs. Time 18
5. Dilution Flow vs. Time 19
6. Tank Consistency vs. Time 19
7. Measured and Actual Outlet Fiber Flow vs. Time 20
8. Level Control Flow vs. Time 21
9. Tank Outlet Fiber Flow vs. Time 21
12. Couch Pit Consistency vs. Time 24
13. Broke Chest Volume vs. Time 25
14. Broke Chest Consistency vs. Time 25
15. Broke Chest Outlet Flow vs. Time 26
16. Approach Tank Volumes vs. Time 26
17. Reel Basis Weight vs. Time 27
ABSTRACT

Past efforts to use model-based controls in the paper industry have not been successful due to the sensitivity of the model control algorithms to sensor or model error and to noise. To better understand the reasons for this sensitivity and to develop more robust techniques, we have developed a series of dynamic models at various levels of control complexity. A single stirred tank model is used to illustrate the disturbance rejection and set point tracking of various control loops. A dynamic two-ply liner papermachine model is used to show the systems-wide effects of individual control loops during upsets such as sheet breaks and the response to changes in basis weight. Feedforward and selective control strategies proved to be essential for stable control of fiber flow to the machine and, therefore, to controlling basis weight. Improved numerical techniques were also needed for stable solutions of the dynamic equations. The models have been integrated with a real-time database making it possible to run the system faster than real-time with current input from the DCS. In this mode the model could provide optimal control to portions of the papermachine to minimize the effects of errors in consistency and the stability problems associated with feedback. The results shown here merely illustrate the variety of control concepts which could be evaluated.

KEY WORDS

Dynamics, process control, simulation, multi-ply papermachine, consistency control, basis weight control.
INTRODUCTION

The most significant applications of control hardware and sensor technology in the paper industry have been in the papermachine area particularly in machine direction and cross-machine basis weight, moisture and caliper control (Lindeborg, 1988). These applications rival those in other industries for sophistication and complexity. However, aside from the use of feedforward algorithms in the control of dry fiber flow, very little advanced control theory has been successfully applied in the paper industry. Most loops continue to use conventional feedback control. Aside from the headbox, slice and wire, papermachine wet end controls are comprised primarily of flow, level and consistency controls as well as refiner plate gap (Lavigne, 1977). Consistency measurement is perhaps the most crucial and the most prone to error. Headbox consistency usually cannot be reliably measured and must be adjusted by feedback from the basis weight sensors at the dry end of the machine.

Advanced adaptive control schemes have been most successfully applied to reduce the variance of moisture and basis weight (Åström, 1964, Åström and Bohlin, 1966, Cegrell and Hedqvist, 1973, Åström and Haggman, 1974, Borisson and Wittenmark, 1974, Fjeld and Grimmes, 1974, Al-Shaikh, 1978). However, most attempts to employ predictive and model-reference control commercially were abandoned due to sensitivity to model or signal error and to noise. The apparent failure of predictive algorithms has given way to the use of artificial intelligence tools such as expert systems and neural networks. These alternatives to predictive control allow typical noise and signal patterns to be "learned" and, once recognized to allow the appropriate control action to be taken. There is no conscious attempt to directly relate control action to specific signal components, however. Noise and signal error can result from errors in consistency sensors as well as vibrations and complex fluctuations in pumps, valves and pipe systems.

It is well accepted that steady state models represent typical process conditions quite accurately. For many years dynamic models have been used successfully (Beecher, 1963, Parker, 1981, Sullivan et al., 1965) to predict transient responses to process disturbances such as machine breaks (Bussiere et at, 1988) and grade changes (Miyanishi, 1988). It was somewhat easier to simulate dynamic behavior on a papermachine because most of the dynamics were caused by tank holdups while many other systems such as steam and power, pulping or recovery contained many different types of dynamic elements. The failure of predictive models to represent the detailed variability may lie in the failure to simulate and correct for noise and random disturbances. The recent work in robust model reference control may yet prove successful in overcoming these problems (Landau, 1979). A sequential modular system with the appropriate noise, sensor error and disturbance characteristics may be useful in interpreting actual machine data. It may be possible to reconcile the errors in consistency using the systems-wide model to more accurately control flows and basis weight.
OBJECTIVES

In this work our objectives are to develop improved and more robust control algorithms which could overcome some of the problems associated with "advanced control." Our short term objectives are to develop dynamic models of single tank control and then to apply these to more complex multi-tank control schemes. Our long term goal is to incorporate these models into existing control systems. Our control algorithms are based on simulation models which include the major dynamic elements of the papermachine. Although simpler systems could have been devised, the application which we will discuss is of a two-ply liner papermachine at a mill in the Southeastern US.

This application was first developed as a steady state model which included highly detailed calculations of the fourdriniers and multi-ply formers, the press sections, dryer section and white water system. The original work was used to investigate the sensitivity of multi-ply compressive strength to process variables such as OCC content, refiner power, press load, fiber orientation and MD restraint. The model used the performance attribute system developed at IPST to predict end-use performance and properties such as tensile, optical and elastic characteristics of paper (Jones, 1989). However, in order to control or optimize end-use performance, it is first necessary to control more fundamental factors such as fiber flow, sheet basis weight, and caliper. The control schemes developed so far are limited to the control of dry fiber flow, consistency and tank levels in the approach system of the papermachine. High frequency fluctuations due to manifold, headbox and slice dynamics are beyond the scope of the current sequential modular system.

The behavior of the single tank control system to set point changes and disturbances is discussed first. The single tank control scheme is then applied in a somewhat idealized and modified form to the multi-tank system of the two-ply machine. In each case the closed-loop response of the manipulated or control variables are shown after a load or set point change.

ELEMENTS OF THE DYNAMIC SYSTEM

The dynamics and control elements are a fairly new addition to the steady state process simulator (MAPPS, 1993) described many times in the past. The concept of dynamic simulation with a sequential modular simulator requires the following assumptions and simplifications:

1. The mass and energy balances are strictly converged only at the steady state. However, for small time steps and small perturbations, errors associated with non-converged tear streams are negligible.
Dynamic elements are represented in two ways. Truly dynamic elements such as plug flow vessels and stirred tanks are treated rigorously while many other potentially dynamic unit operations such as evaporators, heat exchangers, flash units etc. are currently treated with instantaneous i.e. steady state models followed by first order lags or time delay elements to lag the signals from the unit.

Elements such as piping systems which are both rapid and simultaneous are not handled. Signals are communicated at the rate at which the flowsheet is updated or scanned. This scanning frequency is related to the rate at which the computations are made (i.e. the hardware and software) rather than to the simulation time step. If the computer is sufficiently fast relative to the smallest time constants in the system, the approximation will not affect the results.

The order in which the signals are updated and passed in the flowsheet depends on the calculation order which is the order in which the process modules are listed.

The wire and headbox dynamics are not considered. The time delay between the thick stock flow and the dry end basis weight, which was found to be approximately of 70 seconds (Balchen, 1988), has no significant effect on the current dynamics but will be included in future versions.

Dynamic Controller

The dynamic system is controlled by means of a controller block (DCONTRTL) which is placed at the beginning and end of the calculation order. The first instance of the DCONTRTL block initializes the time step, the current time and the maximum time. A variety of modes can be specified. In one mode the dynamics are run continuously with no maximum time. The second instance of the DCONTRTL block checks for the current simulation time, updates the time and passes control back to the beginning of the sequence. This block is not an actual process operation but is needed to run the simulator much as the supervisor block used by Sullivan.

Stirred Tank and Plug Flow

The dynamic tank is similar to those described previously. However, this tank also incorporates the performance attribute variables in MAPPS such as fiber length and width distributions, CSF and many other fiber characteristics. These are mixed dynamically in a first order model similar to that of composition. The tank uses a pseudo-analytical integration method which is much more stable and accurate than the Euler methods and faster than predictor-corrector or multi-step techniques. The essential feature of the method is that the first order differential equation is treated as exact over each time step and is therefore integrated analytically assuming the coefficients are constant. Given the general form,

\[
\frac{dY}{dt} = A + BY
\]  

(1)
Rather than using the explicit finite difference approximation,

\[ Y^n = Y^0 + (A + B^0) \Delta t \]  \hspace{1cm} (2)

or the implicit finite difference approximation,

\[ Y^n = \frac{Y^0 + A \Delta t}{1 - B \Delta t} \]  \hspace{1cm} (3)

the "exact" solution is used instead,

\[ Y^n = -\frac{A}{B} + \left(\frac{A}{B} + Y^0\right)e^{B \Delta t} \]  \hspace{1cm} (4)

This same method is applied to all transient balances. In the case of coupled balances, the coupled linear system can be solved directly at each time step in terms of the eigenvalues of the matrix of coefficients.

The plug flow unit is used to simulate a true plug flow operation such as a batch, continuous digester or a bleach tower, or simply to delay a signal by a specified dead time. Dead time is neglected in these applications.

Four types of disturbances, random, sinusoidal, step and ramp, are modelled with four blocks which can be programmed to vary the disturbance parameters in a variety of ways. For example a random block can be used to randomly vary the frequency or phase lag of a sinusoidal block. The step and ramp can be programmed to occur at a series of specific simulation times. SINE and STEP are illustrated in examples. The step is designed to change 1 to N variables at independently specified times. The other modules are set up to change N variables in a specific way over a specified period of time.

Control Algorithms

The feedback controller (CONTRL) is based on a finite difference form of the standard PID algorithm. A feedforward control block (CCONSIS) based on a steady state mass balance (Stephanopoulos, 1984) performs feedforward control of consistency. This module "senses" the composition and flows of the feed streams to the stirred tank and adjusts a dilution flow of a given consistency to maintain a set point consistency. A secondary level control override feature may also be switched on. If the level drops below or rises above specified upper and lower limits, the dilution flow is adjusted to stay within the bound and the consistency control is
temporarily suspended. Given an exact value of the consistency, this module provides ideal disturbance rejection but is not sufficient for set point changes. Future versions will include a dynamic feedforward algorithm which "inverts" the dynamic mass balance thus allowing for set point tracking.

**Control Logic**

A logic block, called LOGIC, allows the specification of a logical IF - THEN condition which is tested as part of a control scheme. If the condition is true, the output of the module is one value; while if the condition is false, the output is a second value. In the future this feature can be generalized to allow the user to develop complex logical networks without having to perform any programming.

**Variable Computations**

Variables may be manipulated and new variables generated for use with the control schemes through use of the MATH block. This block performs elementary operations such as ratios, sums and differences, or multiplication by a constant thus allowing variables to be transformed for use by control modules. By combining LOGIC, MATH and CONTROL blocks, it is possible to construct realistic dynamics and control strategies.

**APPLICATIONS**

Basis weight control requires good control around each major tank in the approach system. The control of consistency, fiber flow and level are described first followed by an example of dynamics and control following a sheet break at the wet end of the top ply fourdrinier.

**Single Stirred Tank - Consistency, Level and Fiber Flow Control**

Dynamic simulation and control of a single stirred tank is shown in Figure 1. The tank shown in the center mixes three streams together: two stock streams generated by WOOD02 blocks and a dilution stream. By sensing the incoming consistencies and flows in the entering streams, feedforward consistency controller, CCONSIS, manipulates the dilution flow to control outlet consistency. Dry fiber flow is controlled through a feedback loop using a PID controller (CONTRL) to sense the outlet fiber flow computed by the MATH block and by manipulating the outlet flow from the tank. Level is controlled by adjusting one of the two fiber stock streams from one WOOD02 block by a feedback loop. Both feedback controllers use PI control where both proportional gain and reset time constant are set manually for rapid rise time and minimum overshoot. Set points are defined on tank level, discharge consistency and BD fiber flow rate. The loops are capable of both disturbance rejection and set point tracking with no permanent offset.
Disturbances are introduced in the form of oscillation in the consistencies of both the level control flow (average of 4%) and the load flow (average of 4.5%) from blocks WOOD02. The SINE block causes the fiber flowrate in the fiber source blocks (WOOD02) to oscillate according to a specified frequency and amplitude. A RANDOM block causes the frequency of the disturbances to vary randomly. As shown in Figure 2, the disturbance (load) fiber flow oscillates between 198 and 202 thousand lb/hr with a randomly varying frequency. Load and level control flow stream consistencies shown in Figure 3 oscillate between 4 and 5% and 3.5 to 4.5% respectively with randomly varying frequency. The time-smoothed period is 0.5 to 0.7 hours.

Figure 2. Load Fiber Flow vs. Time
Figure 3. Load and Level Control Consistency vs. Time

Under normal operation and before the set point change at 2 hours, the fiber-flow feedback controller maintained the fiber flow at the setpoint of 10 thousand lb/hr as shown in Figure 9. Tank volume remained near 3 thousand cu. ft. as shown in Figure 4. Tank and discharge stream consistencies were held constant by the feedforward controller with ideal sensor inputs as shown in Figure 6. Dilution flow varies as shown in Figure 5 in response to oscillations in tank inlet flows and consistencies.

Response to Set Point Change

At 2 hours the fiber flow set point was increased from 10 to 12 thousand lb/hr as shown in Figure 9. Tank volume dropped and then returned to the previous level as shown in Figure 4. Level control flow increased rapidly and then settled down to a new average level of 50 to 60 thousand lb/hr as shown in Figure 8. Dilution flow increased initially and then resumed a similar oscillation as shown in Figure 5.
As intended, the feedforward control adjusted dilution flow rapidly to the varying fiber flows into the tank. Tank and outlet stream consistencies remained at 3% (Fig. 6). This case is based on the assumption of accurate consistency measurements into and out of the tank which is rarely the case in actual practice. The effects of an error in the tank outlet consistency or fiber flow shown in Figure 7 caused the tank volume response to overshoot slightly and to lag behind the case where consistency is accurately measured (Fig. 4). The level control flow is lagged by the error in the outlet consistency but the effect is not significant (Fig. 8). The dilution flow is barely effected by the error in the outlet consistency measurement because it is manipulated by the feedforward controller which receives accurate inlet consistency values. Similarly, the outlet consistency is held constant (Fig. 6). The outlet fiber flow oscillated around the true value but the response to the set point change was not affected by the error as shown in Figure 9. The difference between the actual and the measured outlet fiber flow (based on the consistency) shown in Figure 7 indicated that the controller response to the step change was not adversely affected but that significant oscillations resulted. If similar random errors were applied to the inlet flow consistencies, the feedforward controller would not have responded with the same accuracy and the overall control would have been adversely affected.
Figure 5. Dilution Flow vs. Time

Figure 6. Tank Consistency vs. Time
The feedforward controller would in reality not be able to manipulate dilution flow as rapidly as shown due to the limitations of the control valves and capacity of the header system. Therefore, this feedforward system should have passed a signal to a control valve which is governed by a first or higher order response. Also the header itself could have been modelled as a first order lag plus deadtime system to mimic the actual header response.

Figure 7. Measured and Actual Outlet Fiber Flow vs. Time

Figure 8. Level Control Flow vs. Time
Multi-ply Liner Dynamic and Control

Applications were also developed to simulate dynamics and control on a two-ply liner papermachine model shown schematically in Figures 10 and 11. The unique feature of these models is the detailed retention and performance attribute models in the wire section and press sections. The attributes of each ply in the two-ply structure, generated in the multi-ply forming block, are altered as the stream passes through the press and dryer sections resulting in a multi-ply structure with unique properties at the dry end of the machine. Control loops are similar to those shown previously except that the feedback level control is maintained between upper and lower limits using an override feature of the feedforward controller. When level specifications are violated, the controller uses dilution flow to control level and temporarily suspends control of consistency.

In this application the high density flows and consistencies were constant with time. Basis weight was maintained by controlling total dry fiber flow along each fiber line to each headbox. The most stable control was obtained when total fiber flow is controlled at the discharge of each of the major tanks in the approach system on both fiber lines. By controlling dry fiber flow, it was possible to not only control final basis weight but also to adjust more rapidly and with greater stability to changes in dilution flow and consistency along the fiber line.
FIGURE 11

DYNAMIC TWO-PLY PAPERMACHINE

[Diagram of paper machine process]

- Stock
- Wire Pit
- Base Screens
- Base Stack
- Seal Pit
- Wire Chest
- REJECT CLEANER
- Secondary Cleaners
- Primary Cleaners
- Top Liner Thick Stock
- Top Liner Pulp Pum
Machine Break

A sheet break between the end of the multi-ply former and the press was initiated at 0.3 hours and the sheet was restrung at 0.7 hours. The break was simulated by a STEP block preset to change a split fraction in a SPLITTER block from 1 to 0 at the specified time. The resting operation was timed through the same STEP by resetting the SPLITTER from 0 to 1 at 0.7 hour. When the split occurred, the fiber flow dropped to zero at the wet end of the paper machine. As a result of the break and the small couch pit volume, the couch pit consistency, which is normally 0.025%, immediately increased to 0.11% and remains constant until the wire is restrung at which point the consistency dropped to the previous level as shown in Figure 12.

After the break, the flow increased from the couch-to-saveall system which led to increased flow to the broke chest. The broke chest volume was in a normal upswing which increases in response to the machine break as shown in Figure 13. The broke chest consistency also increases and then begins to decrease after the paper is restrung (Fig. 14). The feedback controller decreases the broke flow rate to maintain the proportion of broke in the base sheet when the machine is later restrung as shown in Figure 15. The base sheet refiner chest level and other approach tank volumes increase in a first order fashion as shown in Figure 16. Figure 17 shows the expected variation in the basis weight signal at the dry end.

Figure 12. Couch Pit Consistency vs. Time
Figure 13. Broke Chest Volume vs. Time

Figure 14. Broke Chest Consistency vs. Time
Figure 15. Broke Chest Outlet Flow vs. Time

Figure 16. Approach Tank Volumes vs. Time
CONCLUSIONS

These applications illustrate the use of dynamic simulations to develop more robust control schemes for the wet end of the papermachine. On-line use of a systems-wide simulation model of the wet end could provide a more reliable basis for robust adaptive and supervisory control which could overcome the deficiencies of previous efforts.

Feedforward control of dry fiber flow is superior to feedback control for stable MD basis weight control provided the errors in the consistencies can be minimized. Sensitivity to consistency errors will be studied further.

Many other scenarios can be investigated with this system. For example, the effects on drainage, retention and controller dynamics of variable CS freeness at the HD chests could be simulated. The effects of error in the upstream consistency meters on the feedforward control performance could be evaluated. Additional details such as control valves and machine delay should also be added. The step block could be used with other applications to simulate a set of discrete events.
REFERENCES


ACKNOWLEDGEMENTS

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ATTACHMENT II

PREDICTION OF PAPER COLOR:
A PROCESS SIMULATION APPROACH

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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Abstract</th>
<th>35</th>
</tr>
</thead>
<tbody>
<tr>
<td>Introduction</td>
<td>36</td>
</tr>
<tr>
<td>Objectives</td>
<td>37</td>
</tr>
<tr>
<td>Theoretical Background</td>
<td>37</td>
</tr>
<tr>
<td>Color and Its Measurement</td>
<td>37</td>
</tr>
<tr>
<td>The CIE L<em>a</em>b* Color Scale</td>
<td>38</td>
</tr>
<tr>
<td>Measurement of the Color Difference</td>
<td>40</td>
</tr>
<tr>
<td>Measuring Instruments</td>
<td>40</td>
</tr>
<tr>
<td>Reflectance of Paper</td>
<td>41</td>
</tr>
<tr>
<td>Light Absorption and Scattering</td>
<td>41</td>
</tr>
<tr>
<td>Kubelka-Munk Theory and the Color Prediction of Paper</td>
<td>41</td>
</tr>
<tr>
<td>Dye Characteristics</td>
<td>43</td>
</tr>
<tr>
<td>Dyeing Practice</td>
<td>44</td>
</tr>
<tr>
<td>Effects of Dyes on the Optical Properties of Paper</td>
<td>44</td>
</tr>
<tr>
<td>Performance Attributes and End-Use Performance Simulation</td>
<td>44</td>
</tr>
<tr>
<td>Experimental</td>
<td>45</td>
</tr>
<tr>
<td>Data Analysis and Model Development</td>
<td>45</td>
</tr>
<tr>
<td>Substrate Reflectance</td>
<td>46</td>
</tr>
<tr>
<td>Color Simulation</td>
<td>47</td>
</tr>
<tr>
<td>Dye Mixing</td>
<td>48</td>
</tr>
<tr>
<td>Optical Property Models</td>
<td>48</td>
</tr>
<tr>
<td>Dye K/S Data</td>
<td>49</td>
</tr>
<tr>
<td>Model Tuning</td>
<td>49</td>
</tr>
<tr>
<td>Model Validation</td>
<td>50</td>
</tr>
<tr>
<td>Reflectance of Calibration Paper</td>
<td>50</td>
</tr>
<tr>
<td>Color of Calibration Paper</td>
<td>52</td>
</tr>
<tr>
<td>Effect of Illuminant and Observer Angle</td>
<td>53</td>
</tr>
<tr>
<td>Effect of Dye Loading on Color Difference</td>
<td>55</td>
</tr>
<tr>
<td>Model Validation - Validation Papers</td>
<td>56</td>
</tr>
<tr>
<td>Color Change</td>
<td>58</td>
</tr>
<tr>
<td>Lab Values for the Validation Papers</td>
<td>59</td>
</tr>
<tr>
<td>Tinted Sheets</td>
<td>61</td>
</tr>
<tr>
<td>Conclusions and Recommendations</td>
<td>63</td>
</tr>
<tr>
<td>References</td>
<td>64</td>
</tr>
</tbody>
</table>
LIST OF TABLES
Table 1 Model Parameters for Substrate Reflectance 46
Table 2 Dye Mixture Combinations for Saturated Validation Papers 62
Table 3 Dye Mixture Combinations for Tinted Papers 64

LIST OF FIGURES
Figure 1 MAPPS Flow sheet for Property Model Validation 47
Figure 2 Effect of Pure Dyes on Reflectance Calibration Handsheets 51
Figure 3 L*a*b* Values for Calibration Handsheets-2 Degrees C Illuminant 52
Figure 4 Effect of Observer Angle and Illuminant on Color Change Cal Figures 52
Figure 5 Effect of Observer Angle and Illuminant on Color Change - Calibration Handsheets Measured and Predicted Values 54
Figure 6 Effect on Dye Loading on Color Difference - Calibration Handsheets Red, Blue, and Yellow Dyes 55
Figure 7 Effect on Dye Mixtures on Reflectance of Machine Paper 56
Figure 8 Effect of Dye Mixtures on L*a*b* Values Machine Papers, Red, Blue, and Yellow Dyes 57
Figure 9 Effect of Dye Mixtures on Color Change-Machine Paper, Couch and Validation Handsheets Red, Blue, and Yellow Dyes 58
Figure 10 Effect on Dye Mixtures on L*a*b* Values Validation Handsheets, Red, Blue, and Yellow Dyes 59
Figure 11 Effect of Dye Mixtures on L*a*b* Values Couch Handsheets, Red, Blue, and Yellow Dyes 60
Figure 12 Effect of Tints on Color Change Combined Calibration and Validation Handsheets Mixtures of Red, Blue, and Black Dyes 61
Figure 13 Effect of Tints on L*a*b* Values Combined Calibration and Validation Handsheets Mixtures of Red, Blue, and Black Dyes 63
ABSTRACT

A simulation system has been developed to predict the optical properties of dyed paper. The system is part of a papermaking process simulation program and is intended for use as part of an on-line color control system to reduce variations in color for dyed paper grades. The system calculates the effects of mixing of multiple primary dyes with fiber streams and the optical characteristics of the base paper. The optical properties predicted by the system include the reflectance at 20 nm intervals over the range of visible wavelengths (400 to 700 nm), CIE L*a*b values, and Tappi Brightness and opacity. The models were developed from handsheet data and validated with both handsheet and pilot paper machine data. Predictions are valid for a wide range of dye saturations (base sheet, tints to light saturated) and combinations of two observer angles (2 and 10 degree standard observers) and two illuminants (C and D65) and for combinations of red, blue, and black dyes at light loadings and red, yellow, and blue dyes for light to heavy loadings.

This paper describes color theory, modeling, and experimental methodology, and compares the results of the reflectance and CIE L*a*b* models with data for both pure dyes and mixtures of dyes applied to several different types of pilot papers.
INTRODUCTION

Color uniformity is a particularly important quality characteristic for fine paper manufacturers. Paper is colored by the addition of various dyes to paper stock in the stock preparation system just before sheet forming. Traditionally, dyes have been added in the stock blending chest, and sufficient mixing time is required for the uniform distribution and fixing of the dyes on the fibers. So-called direct dyes have a strong affinity for cellulose, making it possible to add them directly to the furnish. The development of liquid anionic and cationic direct dyes made possible the continuous addition of dyes in the stock.

The introduction of on-line spectrophotometers and microprocessor-based control systems has led to the closed loop control of color to any desired shade. However, on-line measurements are made in the wet state and, therefore, require adjustment to control final dry state color. Thus, it would be useful to have a model to predict color in the dry state as a way of improving control of final sheet color.

The coloring of paper is very sensitive to changing process conditions during paper making. Variations in the flow and retention of the dyes affect the final sheet color, its quality and uniformity. Considering the complex nature of color and its interactions with papermaking variables, a reliable simulation system would certainly be preferable to time-consuming and costly pilot-plant trials for design and troubleshooting. Color simulation can provide useful insights into effects of changing process conditions on color variations. Simulation can also be used to guide and interpret pilot experiments. In combination with experimental data, a process simulation model can be used to determine process parameters which may be difficult or impossible to measure directly. Process simulation makes it possible to perform 'what-if' analysis by quantifying the effects of changing process variables.

The development of a color simulation model is made easier by starting with an already available simulation package such as MAPPS (Modular Analysis of Pulp and Paper Systems). The unique features of MAPPS, particularly the Performance Attribute (PAT) modeling feature, provide the framework necessary to model dye mixing and color matching. The PAT system is currently used to simulate a wide variety of end-use performance properties (such as compressive, elastic, tensile, and optical) of various paper grades. In a later section, the connection between the PAT system and the color prediction program will be described in more detail.
OBJECTIVES

The specific objectives of this work were to measure the reflectance and color of both handsheets and machine papers under representative dying conditions and to develop and validate a modeling system to predict color and other optical properties from first principles. It was also desirable that the simulation system predict reflectance and CIE Lab values for combinations of 2 and 10 degree observer angles and C and D65 illuminants over a wide range of dye loadings and for a variety of colorant classes. The optical property system must also predict Tappi Brightness and Opacity at 457 nm and Tappi printing opacity at 572 nm.

THEORETICAL BACKGROUND

Color and Its Measurement

Color is a psychological response to a physical stimulus. The eye and central nervous system "see" color based on three components: the light source, the object, and the human observer (2). The light source defines an illumination condition which affects the way we see color. For example, color is perceived differently in natural light from artificial light. The International Commission on Illumination (Commission Internationale de L'Eclairage) or CIE has recommended various illuminants as light sources (3). These can be divided into tungsten light and artificial daylight.

The CIE established two different standard illuminants (B and C) to represent daylight. However, B and C have too little relative spectral power in the UV region which creates problems with fluorescent colors. D65 was designed to represent average daylight throughout the visible spectrum and into the UV region as far as 300 nm(3).

The appearance attributes of an object are related to the ways in which the object modifies the light that strikes it. Interactions of light with a object result in the specular reflection (related to gloss), scattering within the object (associated with diffuse reflection and diffuse transmission), absorption within the material (associated with color), and rectilinear transmission directly through the object (associated with clarity).

The perception of color is the result of how the human eye interprets the light reaching it from the object. In 1931, the CIE developed a standard observer to complete the description of the response to color of the normal human eye. The observer is defined in terms of color matching functions x(λ), y(λ), z(λ) (4). The 1931, CIE standard observer was based on a 2 degree field of view which was not sensitive to shortwave violet as observers tend to do when grading products with their eyes. In 1960, the CIE proposed a 10 degree standard observer which provides better correlation with commercial judgements (4). Standard observer and illuminant data are used to quantify color in terms or so-called tristimulus values of the color object.
The standard coordinates of the 1931 CIE system, the tristimulus values X, Y, and Z, are calculated from the spectral reflectance factors \( R(\lambda) \) over the visible range of 400-700 nm. These factors are the reflectance at each wavelength from an object as a decimal fraction of that reflected by a perfect reflecting diffuser (e.g., Magnesium Oxide or Barium Sulfate) identically illuminated. At each wavelength interval, \( R(\lambda) \) is multiplied by \( S(\lambda) \), the relative spectral power distribution of the illuminant, and by each of the three color matching functions \( x(\lambda) \), \( y(\lambda) \), and \( z(\lambda) \) and summed over a wavelength range.

\[
\begin{align*}
X &= k \sum \frac{R(\lambda)S(\lambda)x(\lambda)}{S(\lambda)y(\lambda)} \\
Y &= k \sum \frac{R(\lambda)S(\lambda)y(\lambda)}{S(\lambda)y(\lambda)} \\
Z &= k \sum \frac{R(\lambda)S(\lambda)z(\lambda)}{S(\lambda)y(\lambda)}
\end{align*}
\]

The scaling factor \( k \) is defined as

\[
k = \frac{100}{\sum S(\lambda)y(\lambda)}
\]

which means that Y of the perfect reflecting diffuser and therefore of the illuminant used in the calculation is always 100. The X, Y, and Z values for the illuminants C and D65 at a 2 degree and 10 degree field of view may be found in Re.f 1.

The CIE tristimulus values X, Y, and Z have limited use for specifying colors. The Y value correlates with lightness, but X and Z by themselves do not correlate with visual attributes such as hue, saturation, depth, vividness, redness-greenness, and yellowness-blueness (5). Over the years many color scales which correlate well with visual attributes have been developed, but only the CIE L*a*b* color scale has gained popularity among practitioners.

The CIE L*a*b* Color Scale

To achieve a uniformity of practice, the CIE in 1976 officially recommended an approximately uniform color space standard known as the CIE 1976 L*a*b* space (6).
The quantities are defined in terms of $X$, $Y$, and $Z$ as follows,

\[
L^* = 116 \left[ \frac{Y}{Y_n} \right]^{1/3} - 16 \quad \text{for} \quad \frac{Y}{Y_n} > 0.008856
\]

\[
L^* = 903.3 \frac{Y}{Y_n} \quad \text{for} \quad \frac{Y}{Y_n} \leq 0.008856
\]

(3)

\[
a^* = 500 \left[ f \left( \frac{X}{X_n} \right) - f \left( \frac{Y}{Y_n} \right) \right]
\]

(4)

\[
b^* = 200 \left[ f \left( \frac{Y}{Y_n} \right) - f \left( \frac{Z}{Z_n} \right) \right]
\]

(5)

where

\[
f \left( \frac{X}{X_n} \right) = \left( \frac{X}{X_n} \right)^{1/3} \quad \text{for} \quad \frac{X}{X_n} > 0.008856
\]

(6)

\[
f \left( \frac{X}{X_n} \right) = 7.787 \left( \frac{X}{X_n} \right) + \frac{16}{116} \quad \text{for} \quad \frac{X}{X_n} \leq 0.008856
\]

and

\[
f \left( \frac{Y}{Y_n} \right) = \left( \frac{Y}{Y_n} \right)^{1/3} \quad \text{for} \quad \frac{Y}{Y_n} > 0.008856
\]

(7)

\[
f \left( \frac{Y}{Y_n} \right) = 7.787 \left( \frac{Y}{Y_n} \right) + \frac{16}{116} \quad \text{for} \quad \frac{Y}{Y_n} \leq 0.008856
\]
Subscript "n" designates the reference white. The CIELAB space is used to compare differences between the object colors of the same size and shape, viewed in identical white to midgrey surroundings by an observer. For the illuminants C and D65 at the 2 and 10 degree viewing angles, the values of $X_n$, $Y_n$, and $Z_n$ for the perfect diffuser are given in Ref. 1.

**Measurement of the Color Difference**

The color difference between two papers as seen by the eye can be determined using the following color difference equation defined by the CIE in 1976 (7),

$$\Delta C = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (9)$$

where $\Delta L^*$, $\Delta a^*$, and $\Delta b^*$ are the differences in $L^*$, $a^*$ and $b^*$ values between two samples, and $\Delta C$ is the visual color difference between two samples. These differences quantify in a compact form the differences perceived by the eye. For example, the color difference between black and white samples is 100 $\Delta C$ units. The tolerance in commercial color matches is usually less than one $\Delta C$ unit. $\Delta C$ could also be defined in terms of the deviations between measured and predicted values of $L$, $a$, and $b$ (Eq. 10 top). $\Delta C$ could also be defined in terms of deviations from a reference such as the undyed sheet as defined in Eq. 10 (bottom). This definition is used in the following discussion to describe the so-called color change which occurs as various dyes are applied.

$$\Delta L = L^*_{\text{meas}} - L^*_{\text{pred}} \quad (10)$$

$$\Delta L = L^*_{\text{meas}} - L^*_{\text{ref}}$$

Similar definitions apply to $a^*$ and $b^*$.

**Measuring Instruments**

Two types of color measuring instruments commonly used are the colorimeter and the spectrophotometer. With each instrument the sample is illuminated with a standard
source and the reflected light passes through a filter or grating and then enters the
detector where the signal is converted into tristimulus values.

Reflectance of Paper

Light Absorption and Scattering

The interaction of light with paper can be explained by the scattering and absorption
properties of the paper. The absorption of light, described by an absorption coefficient,
K, is defined as the relative decrease of the flux in a collimated beam of light due to
absorption in a differential path length, divided by the differential path length (8,9).

To predict scattering coefficient, both the strength of scattering and the angular
distribution of the scattered light are required. The strength of scattering can be
described by a linear scattering coefficient, defined as a relative decrease of the flux in
a collimated beam of light due to scattering in a differential thickness, divided by the
differential path length (8). The angular distribution of light can be described by the angle
of deflection of the scattered light from its direction of travel before being scattered. For
approximately diffuse radiation, the ratio of scattering coefficient for diffuse light to
scattering coefficient for collimated light has a value of 1.0 for highly absorbing and 0.5
for negligibly absorbing materials (9).

Kubelka and Munk developed an approximate theory relating these coefficients to the
reflection and transmission in a turbid medium. This theory is approximate because light
is assumed to be moving upward and downward only. Multiflux theories have been
developed to account for light travel in all directions (10).

Kubelka-Munk Theory and the Color Prediction of Paper

This theory represents the exact solution to a specific problem of absorption and
scattering of electromagnetic radiation. The Kubelka-Munk theory rests on a substantial
number of assumptions:

1. The colorant layers such as paper consist of optically identical elementary layers
2. The light beam consists of two completely diffuse light fluxes, one proceeding
downward through the layer and the other one proceeding upward.
3. Light is not polarized, and both illumination and viewing use a diffuse light source.
4. Object has a plane, parallel surface, and no light losses occur at the edges.
5. The effects of large particles, agglomeration, or orientation of the particles in the layer
are neglected.
6. Optical contact is assumed with the next layer.
7. Scattering particles are assumed to be large in comparison to the wavelength of the
light but small compared to the thickness of the layer.
8. Reflections from the upper side of the boundary are ignored.
The relationship between $R_\omega$, the reflectivity of a sample, and the absorption and scattering coefficients, $K$ and $S$, was found by approximate exponential solutions by Kubelka and Munk (11) as

$$\frac{K}{S} = \frac{(1 - R_\omega)^2}{2R_\omega}$$  \hspace{1cm} (11)

or in terms of reflectance,

$$R_\omega = 1 + \frac{K}{S} - \sqrt{\frac{2K}{S} + \left(\frac{K}{S}\right)^2}$$  \hspace{1cm} (12)

The theory is applied to one wavelength of light at a time. The continuous reflectance curve is approximated by taking measurements for sixteen or thirty-two discrete wavelengths (12).

The Kubelka-Munk theory has been extensively used in the paper industry (13). The K-M theory has been applied to determine the mathematical relationship between basis weight, reflectance, contrast ratio, and other optical properties of a paper sheet (1). Given measurements of both $R_0$ and $R_\omega$, where $R_0$ is the reflectance of the single sheet of paper with black backing, the absorption and scattering coefficients $K$ and $S$ can be calculated using the following relationship (11).

$$K = \frac{1}{2W}[\frac{1-R_\omega}{1+R_\omega}] \ln \left[\frac{1-R_0R_\omega}{1-R_0}\right]$$  \hspace{1cm} (13)

and
\[ S = \frac{1}{2W} \left[ \frac{1}{1 - \frac{R}{R_\infty}} \right] \ln \left[ \frac{1 - R_0 R_\infty}{R_0} \frac{1 - R}{R_\infty} \right] \tag{14} \]

where \( W \) is the sheet basis weight.

The K-M theory has been applied to describe the effects of dyeing on the reflectance of the paper (15). It is assumed that dyes do not contribute to the scattering of the sheet and change only the specific absorption coefficient (16). The relationship between dye concentration and K/S ratio is given by the following mixture rule (15).

\[
\left( \frac{K}{S} \right)_{\text{mixture}} = \sum_{i=1}^{n} C_i \left( \frac{K}{S} \right)_{\text{dye } i} + \left( \frac{K}{S} \right)_{\text{substrate}} \tag{15}
\]

K/S for each dye is defined at concentration, \( C_i \), based on bone-dry fiber. The substrate refers to the undyed base sheet.

If the absorption coefficient of each dye is known and light scattering is caused only by the substrate, the above equation reduces to the following form (16).

\[
\left( \frac{K}{S} \right)_{\text{dyed sheet}} = \left( \frac{K}{S} \right)_{\text{substrate}} + \sum_{i=1}^{n} C_i K_i \tag{16}
\]

where \( K_i \) is the specific absorption coefficient of dye \( i \), and \( n \) is equal to the total number of dyes used.

Color can be predicted by first predicting the reflectivity of the paper sheet over the range of visible spectrum (400 to 700 nm) at discrete wavelengths. The tristimulus values are then calculated by numerical integration as described earlier.

**Dye Characteristics**

The paper industry has used four major colorant classes for dyeing paper to various shades. These are acid dyes, basic dyes, direct dyes, and colored pigments. Basic dyes are primarily used for unbleached grades (17). Acid dyes and pigments are used for special fine papers to provide certain effects such as brightness and light-fastness.
Direct dyes have either an anionic or cationic surface charge and are the most common dyes used in the production of bleached papers because they adsorb on cellulose without the need for mordants, fixatives, or alum.

**Dyeing Practice**

Dyeing of pulps is dependent on sorption processes, preceded by transport phenomena (mainly diffusion) and frequently accompanied by chemical reactions. The dyeing process can be described by dyeing kinetics (transport and reaction phenomena) and dyeing statics (sorption and desorption processes in the state of equilibrium). The kinetics of dyes is affected by processing conditions such as variation in contact time, temperature, and pH. Direct dyes have direct affinity for fibers and follow the Freundlich Isotherm when applied to cellulose (18). Cationic direct dyes have been shown to be 95% exhausted after about 30 seconds exposure to either bleached sulfite or bleached kraft pulp (19).

**Effects of Dyes on the Optical Properties of Paper**

The addition of dyes can affect all three important optical properties of paper: color, brightness, and opacity. Each dye has a characteristic absorption or reflectance curve. The shape and reflectance at the point of maximum absorption of light influence optical properties of the paper. The maximum absorption of light varies with the dye structure.

The opacity of paper is measured at 572 NM wavelength as defined by TAPPI standard tests T 425 om-86 and T 519 om-86. The opacifying power of dyes depends on the absorption of light in the wavelength region for which the human eye is most sensitive (approx. 555 NM). The opacifying effectiveness depends on the shade of the dye, depth of the shade, and the width of the absorption area (20). The most effective dyes for providing opacity are black, violets, and blues. The least effective dyes are yellows and oranges.

The brightness of paper is measured at a 457 NM light wavelength as defined by TAPPI T 452 om-87 and T 525 om-86. Except for the fluorescent dyes, colorants decrease brightness. The brightness of paper is least reduced by dyes which show maximum reflectance around 457 NM (20).

**Performance Attributes and End-use Performance Simulation**

The system to predict paper properties incorporated into MAPPS (Release 3.2 and higher) (21) is called the Performance Attribute or PAT system. Performance attribute simulation modeling has been applied to many areas of papermaking (22,23,24,25,26). An accurate prediction of the brightness and color of a dyed sheet is important for simulation of manufacture of fine papers. Therefore, the objective of this work was to
develop MAPPS modules to simulate dye mixing and optical properties of dyed paper.

**EXPERIMENTAL**

The experimental plan consisted of two phases, a model calibration phase and a model validation phase.

In part 1, handsheets were prepared with a series of pure dyes. Two sets of dyes were used to calibrate the model. For the saturated dyeing conditions, the primary color dyes were selected for their color and affinity for cellulose. A red, blue, and yellow dye were selected to cover the entire visible light spectrum. Calibration handsheets were prepared with each single dye at weight fractions of 0 (undyed), 0.5, 1.5, 2.5, 5.0, and $7.5 \times 10^3$, respectively. A second set of handsheets was prepared with three different direct dyes (red, blue, and black) at light tint loadings.

In part 2, both handsheets and pilot machine papers were prepared with mixtures of dyes with saturated and tinted shades. Loadings varied from 0 to $7.5 \times 10^3$ (wt. fraction) for the saturated samples and from 0 to $0.155 \times 10^3$ (equivalent to 5 oz./ton) for the tinted shades. The dye loading combinations are summarized in Tables 2 and 3.

Two handsheets were prepared for each optical test, and four samples were tested for each dye concentration condition. The nonglossy side of the sample was measured for reflectance. The recorded measurements included the reflectance curve of the sample and CIE $L^*$, $a^*$, and $b^*$ values for illuminants C and D65 for 2 degree and 10 degree observers. Each sample was measured once with a black backing and once with a backing of a thick pad of same sample. This provided reflectance with black backing, i.e., $R_\circ$, and reflectivity, i.e., $R_\infty$, measurements for each sample. The CIE $L^*$, $a^*$, and $b^*$ values for each sample were measured with a backing of a thick pad of the same sample. The color of the calibration handsheets varied from light to medium shade.

**DATA ANALYSIS AND MODEL DEVELOPMENT**

The average and standard deviation of the reflectivity were calculated at each measured wavelength. Using the data of reflectivity and reflectance with black backing and basis weight of each paper sample, $K$ and $S$ were then determined from Eqs. 13 and 14, respectively. The ratio of $K/S$ was then calculated.

The coefficients of Eq. 16 were determined by linear regression to represent the incremental effect of dye concentration on the $K/S$ value of each paper sample. The $K/S$ of the substrate was subtracted from the $K/S$ of the dyed sample.
Substrate Reflectance

To predict the reflectance curve of a dyed sheet, it is necessary to specify the reflectance curve of the substrate. This is a function of pulping and bleaching conditions and the wavelength of light. The effects of pulping yield and kappa number are reflected in both light absorption and scattering coefficient, while bleaching influences mainly absorption coefficient. The Performance Attribute system passes the absorption of all components at 457 nm. Scattering at 457 nm is derived from other attributes. Therefore, it is possible to compute K/S at 457 nm (brightness) for any stream containing fibers or other suspended material. Thus, the most convenient way to adjust or compensate for changes in papermaking or pulping conditions is to introduce (K/S)\textsubscript{457} as an index to adjust the K/S response. The resulting expression for K/S of the substrate (pulp) is shown in Eq. 17.

\[
\left( \frac{K}{S} \right)_{\text{undyed pulp}} = \beta_0 + \beta_1 \lambda + \beta_2 \left( \frac{K}{S} \right)_{\lambda=457} \lambda + \beta_3 \lambda^2 + \beta_4 \lambda^3 + \beta_5 \lambda^4 \left( \frac{K}{S} \right)_{\lambda=457}
\]

(17)

The coefficients and model fit statistics are shown in Table 1. The high R-squared value indicates the model fit is very good.

<table>
<thead>
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<td>\beta_0</td>
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Table 1. Model Parameters for Substrate Reflectance

The above model was developed with known values of K/S (brightness) at 457 nm (approximated by the value at 460 nm) for the calibration handsheets. The model was validated by predicting the reflectance and color of the validation sheets using the MAPPS PAT system.

Using Eqs. 16 and 17, \( R_L \) was predicted at discrete wavelengths from 400 to 700 nm for each of the calibration and validation conditions. The CIE L*a*b* values are then determined from Eqs. 3 through 8 for the validation conditions. Color error was
predicted from Eq. 9 based on differences between measured and predicted Lab values and relative color change was predicted from Eq. 9 based on differences between measured or predicted Lab values at a given level of dye loading and the undyed values.

Color Simulation

Two new computer modules were added to the MAPPS system to represent dye mixing and absorption and to compute optical properties. Referring to Figure 1, these were DYEMIX and OPTPROP. Figure 1 is a simplified three-step process flow sheet used to initialize the paper stream and PAT variables (WOOD02 block 1), to mix and adsorb dye (DYEMIX block 2), and to compute optical properties (OPTPROP block 3).

Figure 1 MAPPS Flow Sheet for Property Model Validation

The portion of the MAPPS PAT system relating to optical properties is summarized here. The first block (WOOD02) initializes both the flows of the stream components (fibers, water) and thermodynamic properties as well as performance attributes of fibers based in part on a species database. Previous pulping, bleaching, and refining operations are handled by overriding selected attributes with known values. For example, pulping yield, kappa number, and CS freeness are overridden with new values.
The light absorption at 457 nm is initialized in WOOD02 based on the weighted average of the specific absorptions of cellulose (3 cm²/g), lignin (338 cm²/g), and extractives (4 cm²/g), and the specific absorptions of any fillers which may be present.

\[ K_{457} = \sum_{i=1}^{4} K_i W_i \]  

(18)

Dye Mixing

The dye mixing block performs two simple functions. First the loadings of up to three dyes are specified. The model adjusts the mass flows of all the fiber components in the stream for mass balance assuming that all the dye is adsorbed uniformly on all fibers regardless of surface area or surface chemistry. These assumptions may be relaxed in future versions of the model. Next, the dye loadings are stored as PAT variables and passed to OPTPROP for optical property calculations.

Optical Property Models

The performance attribute stream at a given point in the process is "passed" to the Optical Property block. The PAT variables in the performance attribute stream include pulp variables such as fiber composition, fiber length and width distribution, cell wall thickness, tensile and elastic properties of the fibers, specific surface areas, contact areas and bonding areas if a sheet has been formed, formation levels, stretch and fiber orientation, as well as suspended solids attributes and dye loadings.

The optical property block determines the properties of both a hypothetical handsheet made from the pulp with fiber attributes provided or a machine paper with network attributes provided. The key property needed to determine the optical properties is light scattering at 457 nm. \( K_{457} \) may also be provided directly by the user if it is known, thus overriding the value predicted by the WOOD02 block.

Additional data needed to determine handsheet scattering are handsheet pressing pressure, formation, stretch, and fiber orientation. For a Tappi handsheet, these are defaulted to 60 psi, 1.0 (ideal formation), 0% net stretch, and 45 degrees (random handsheet). Different estimates of these values must be provided to "simulate" a machine paper in the absence of a direct calculation with the paper machine models.

Figure 1 is appropriate for handsheet calculations but is highly simplified for predicting machine paper properties. For handsheets, Block 3 automatically calculates handsheet properties based on standard Tappi handsheet conditions. These may be overridden by
the user. However, for machine paper the performance attributes are determined by paper machine models to represent dewatering and densification on the wire and in the press nips, etc. In the absence of these models, pilot machine papers were simulated by specifying an effective pressing pressure to represent the pilot machine conditions. The optical property block then determined the densification which would take place in the forming and pressing operation and the light scattering coefficient of the base sheet. The final light scattering coefficient of the base sheet is the weighted average of the intrinsic scattering coefficients of the fibers in the bonded sheet and the average contribution of the suspended solids,

\[ S_{\text{sheet} \ 457} = X_{\text{ susp}} S_{\text{susp}} + (1 - X_{\text{susp}}) S_{\text{fibers} \ 457} \]  \quad (19)

where the scattering of the fiber network is given in terms of sheet density, \( p \), adjusted for the average percent pulping yield, \( Y \).

\[ S_{\text{fibers} \ 457} = 50 + (24Y - 900)(1-p) \]  \quad (20)

Units are in \( \text{cm}^2/\text{g} \). Sheet density is based on other models defined in terms of fiber contact area, cell wall thickness, fiber stiffness, yield and average specific surface area. If the predicted scattering is not sufficiently accurate, an experimental value can be entered to predict a more accurate K/S at 457 nm of the base sheet.

K/S of the base sheet at 457 nm is then determined from the separate K and S models or a value provided by the user. K/S at 16 equally spaced wavelengths is then determined using Eq. 17.

**Dye K/S data**

The K/S data for each of three dyes are read in and stored in a database for use by the optical property blocks when needed. The data base was set up to read in one of several sets of dye data. The dye loadings are found from the performance attribute stream data. The mixture K/S is then determined over the visible range using Eq. 16 based on the base sheet K/S, the dye loadings, and the dye data.

\( R_\ast \) is then determined from K-B theory (Eq. 12). Tristimulus values and \( L^*a^*b^* \) values are then determined from Eqs. 1 and 2 and 3 through 8, respectively. Sheet brightness and opacity are obtained by interpolating \( R_\ast \) between 450 and 460 nm and 570 and 580, respectively.

**Model Tuning**

The scattering and absorption coefficients of the undyed stock were adjusted in the WOOD02 module to match the experimental data from the handsheet and paper machine
samples. In a more complete simulation model the pulp light absorption coefficient would be tuned through use of pulp composition data, particularly kappa number. The handsheet scattering coefficient would be one of several interrelated properties including density and tensile strength or elastic modulus which would be available to tune the predicted base sheet scattering coefficient. In a mill environment, fiber furnish data such as fiber length distribution and species information would also be available. The scattering coefficient of the machine paper would be the result of densification and bonding during paper forming, pressing, drying, and converting operations.

Nonideal dye retention could be simulated by reducing the dye loading on fibers parameters in the DYEMIX module. However, in the validation study, the dyes were assumed to be completely retained in the paper sheet.

MODEL VALIDATION

A complete discussion of the results of this work may be found in Ref. 1. For the purposes of this discussion, only selected and representative data will be discussed here.

Reflectance of Calibration Paper

Figure 2 shows the reflectance of the calibration handsheets for various dye loadings. Under the conditions investigated, the model accurately predicted the reflectance at all dye loadings.

The curves correspond to the following combinations of dyes: undyed; red, blue and yellow dyes at 5 and 15 lb/Am ton (0.25 and 0.75 wt. %); and additionally yellow at 10 lb/ton (0.5 wt. %). For the handsheets dyed with red dye, the maximum reflectance is in the range of 400 to 620 nm, while the maximum absorption is in the range of 400 to 620 nm, which is the red portion of the visible light spectrum. For the handsheets dyed with blue dye, the maximum reflection of light was in the wavelength range of 440 to 500 nm. giving the sheet its characteristic blue color. The maximum reflection of light for yellow-dyed handsheets was in the wavelength range of 520 to 700 nm. The maximum absorption of light was in the 400 to 520 nm wavelength range, resulting in the characteristic yellow color of the handsheets.

The change in the reflectance of the light is not linear with increasing concentration of dye in the sheet as can be predicted by Eq. 12. For this reason, the reflectance values were converted to the K/S values which show a linear relationship with increasing dye concentration from Eq. 16. The K/S coefficients of each dye can be found in the original reference (1, Tables 7 and 8).

With each pure dye, the reflectance curves in Fig. 2 are shifted downward as the loading increases. The effect of dye loading is accurately predicted, indicating that the linear mixing rule is justified.
Figure 2 Effect of Pure Dyes on Reflectance-Calibration Handsheets
Color of Calibration Paper

The $L^*a^*b^*$ values for various loadings of red dye are shown in Fig. 3. Again, the prediction of these values is very good over the entire loading range. The results are similar for the other individual dyes. $L^*$ decreases, while $a^*$ increases, and $b^*$ remains relatively constant with increasing levels of red dye. The response is different for the blue and yellow dyes. Since $a^*$ relates to redness-greenness, one would expect it to be sensitive to red dye.

![Figure 3 L* a* b* Values for Calibration Handsheets-2 Degrees C Illuminant](image-url)
Effect of Illuminant and Observer Angle

Figures 4 and 5 illustrate the effect of illuminant (C or D65) and observer angle (2 and 10 degrees) on the color difference, $\Delta C$. In all cases, as red dye loading increases, the color difference increases. These variables exert a subtle effect on color difference. $\Delta C$ decreases in the following order: 2 deg D 65 > 2 deg C > 10 deg D 65 > 10 deg C. Figure 5 shows that the model predicts the effect of angle and illuminant quite accurately. For better visualization, the data are separated by 10 units.

Figure 4 Effect of Observer Angle and Illuminant on Color Change-Calibration Handsheets
Figure 5 Effect of Observer Angle and Illuminant on Color Change—Calibration Handsheets
Measured and Predicted Values
Effect of Dye Loading on Color Difference

Figure 6 shows the effect of pure red, blue, and yellow dyes on color difference. Again, the model predictions are very accurate for all three dyes over the range in saturation. As expected, the color difference is greatest for red and least for yellow in qualitative agreement with our perception of these colors.

![Figure 6 Effect of Dye Loading on Color Difference-Calibration Handsheets Red, Blue, and Yellow Dyes](image-url)
Model Validation

Figure 7 shows the reflectance of pilot machine papers under three conditions: undyed - top curve, mixture 1 (.05, .05, and .15 wt. %, red, blue, and yellow respectively), middle curve and mixture 2 (.5, .5, and .25 wt % red, blue, and yellow), lower curve. The largest errors occur in the undyed sheet, and these are reflected in the deviations at the higher dye loadings for the mixtures. The deviations between the measured and predicted reflectance of the undyed sheets for the validation papers (machine, handsheets, and couch handsheets) led to similar differences in the predicted L*a*b* values. Figure 7 shows that reflectance decreases with increasing dye mixture loading.

Figure 7 Effect of Dye Mixtures on Reflectance of Machine Paper
The effect on $L^*a^*b^*$ of dye mixtures is shown in Fig. 8. $L^*$ values decrease generally with increased dye loading from left to right, while $a^*$ and $b^*$ values are much more sensitive to the combinations of dyes. $a^*$ is sensitive to red, while $b^*$ is most sensitive to blue. Again, the model predictions are quite good. The variations in $a^*$ and $b^*$ for each combination of dyes are accurately determined by the model, although the absolute value of the change may not always be predicted exactly.

![Figure 8: Effect of Dye Mixtures on $L^*a^*b^*$ Values - Machine Papers](image)

**Figure 8** Effect of Dye Mixtures on $L^*a^*b^*$ Values - Machine Papers
Red, Blue, and Yellow Dyes

57
Color Change

As pointed out previously, the error in the L*a*b* values comes about because of the error in the undyed base sheet reflectance curves. When the color differences relative to the undyed sheet are compared for the same set of dye mixtures, the agreement is remarkably good as shown in Fig. 9. The color difference increases with increased dye loading as observed earlier with the calibration handsheets. To better visualize each curve, the values were offset by 10 units. Generally, the response of each type of handsheet is similar for each dye mixture, although this is not always the case. For example, mixtures 5 and 7 show differences between the validation handsheets and the couch or machine papers. The model very accurately predicts the effect of dyes on each type of sheet after correcting the undyed values.

Figure 9 Effect of Dye Mixtures on Color Change
Machine Papers, Validation and Couch Handsheets
Red, Blue, and Yellow Dyes
Lab Values for the Validation Papers

The Lab values for the dye mixtures for the validation handsheets are shown in Fig. 10. For clarity, the L* values have been divided by 10. Correspondence between Dye Mixture ID and dye loadings can be found in Table 2. Again, the agreement is remarkably good. The observations made previously for the behavior of Lab for the machine papers also apply to the couch handsheets. However, the agreement for a* and b* is generally better than that for the machine papers.

![Figure 10 Effect of Dye Mixtures on L* a* b* Values-Validation Handsheets Red, Blue and Yellow Dyes](image-url)
The Lab values for the couch handsheets are shown in Fig. 11. The level of agreement between model and measurements is similar to that for the validation handsheets.

Figure 11  Effect of Dye Mixtures on L* a* b* Values - Couch Handsheets
Red, Blue, and Yellow Dyes
Tinted Sheets

The L*a*b* values for tinted handsheets for the undyed sheet and dye mixture cases are shown in Fig. 12. The correspondence between the Dye Mixture ID and dye loadings can be found in Table 3.

Figure 12  Effect of Tints on Color Change-
Combined Calibration and Validation Handsheets
Mixtures of Red, Blue, and Black Dyes
The color difference response to dye mixtures at tinted conditions is accurately predicted as shown in Fig. 13. The absolute color difference is, of course, much smaller due to the lower levels of dye used. The dye mixtures were not applied in the order shown. Instead, the mixtures were sorted in generally increasing saturation for presentation purposes.

![Graph showing the effect of tints on L*, a*, b* values](image)

**Figure 13** Effect of Tints on L*, a*, b* Values—Combined Calibration and Validation Handsheets
Mixtures of Red, Blue, and Black Dyes
CONCLUSIONS AND RECOMMENDATIONS

It is evident from the analysis that the models developed in this study are capable of predicting the optical properties of the handsheets as well as machine paper. The errors in the color coordinate values are due primarily to the reflectance curve of the undyed sheet. Therefore, given methods to more accurately predict the behavior of the undyed sheet, the system will accurately predict absolute color coordinates. The system can also predict changes in color quite accurately.

The effects of dye loadings, observer angle and illuminant type are also accurately predicted. This level of agreement indicates that the original assumptions of uniform loading and full saturation of the dyes were correct. Other assumptions particularly those regarding the applicability of linear mixing theory and Kubelka-Munk theory are also valid.

The system could be readily used for any combination or type of cationic dyes (not fluorescent dyes) by substituting the dye reflectance values into the system database. It is conceivable that the simulation system could form a part of an on-line control system to automatically adjust the addition of dyes in the papermaking system to control the final dry color of the sheet. This would constitute a significant application of paper physics principles and simulation technology in the improvement of optical quality of fine paper.

<table>
<thead>
<tr>
<th>Mixture I.D.</th>
<th>Dye Loading wt. fraction x 1000</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Red / Blue / Yellow</td>
</tr>
<tr>
<td>1</td>
<td>0 / 0 / 0</td>
</tr>
<tr>
<td>2</td>
<td>0.5 / 0.5 / 1.5</td>
</tr>
<tr>
<td>3</td>
<td>1.5 / 0.5 / 0.5</td>
</tr>
<tr>
<td>4</td>
<td>0.5 / 1.5 / 0.5</td>
</tr>
<tr>
<td>5</td>
<td>5.0 / 5.0 / 2.5</td>
</tr>
<tr>
<td>6</td>
<td>2.5 / 5.0 / 5.0</td>
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<tr>
<td>7</td>
<td>5.0 / 2.5 / 5.0</td>
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<tr>
<td>8</td>
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<tr>
<td>9</td>
<td>7.5 / 2.5 / 2.5</td>
</tr>
<tr>
<td>10</td>
<td>2.5 / 2.5 / 7.5</td>
</tr>
</tbody>
</table>

Table 2. Dye Mixture Combinations for Saturated Validation Papers
<table>
<thead>
<tr>
<th>Mixture I.D.</th>
<th>Dye Loading wt. fraction x 10^5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Blue  / Red  / Black</td>
</tr>
<tr>
<td>1</td>
<td>0 / 0 / 0</td>
</tr>
<tr>
<td>2</td>
<td>0 / 0 / 1.56</td>
</tr>
<tr>
<td>3</td>
<td>1.56 / 0 / 0</td>
</tr>
<tr>
<td>4</td>
<td>0 / 0.78 / 0</td>
</tr>
<tr>
<td>5</td>
<td>0 / 1.41 / 0</td>
</tr>
<tr>
<td>6</td>
<td>4.23 / 1.41 / 0</td>
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<tr>
<td>7</td>
<td>5.63 / 0 / 0</td>
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<tr>
<td>8</td>
<td>0 / 0 / 15.63</td>
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<tr>
<td>9</td>
<td>7.81 / 2.34 / 0</td>
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<tr>
<td>10</td>
<td>1.09 / 2.34 / 0</td>
</tr>
<tr>
<td>11</td>
<td>5.62 / 1.88 / 0</td>
</tr>
<tr>
<td>12</td>
<td>4.69 / 1.88 / 5.63</td>
</tr>
<tr>
<td>13</td>
<td>0 / 6.25 / 0</td>
</tr>
</tbody>
</table>

Table. 3 Dye Mixture Combinations for Tinted Papers

REFERENCES


12. ibid., 27-29.


WATER REUSE

STATUS REPORT

FOR

PROJECT 3725

April 26, 1993
Institute of Paper Science and Technology
Atlanta, Georgia
OBJECTIVE:

Develop and validate water chemistry and equilibrium features in MAPPS to analyze problems associated with water reuse, white water closure and changes in wet end chemistry.

ACCOMPLISHMENTS SINCE PREVIOUS REPORT:

The equilibrium system has been applied recently in a mill water closure study to determine the effects of reducing fresh water inflow on the compositions of streams in the paper machine area. The paper machine model included stock preparation, forming, bleaching and washing. All process input streams including additives were included. Samples of sixteen internal water and pulp streams were analyzed for bound and soluble forms of sodium, calcium, magnesium, iron, sulfate and chloride. The concentrations of the bound and free forms were matched by adjusting the absorption constants in the model. Four different pulp sources both hardwood and softwood including broke were included.

Approximately 95% of the calcium, 99% of the magnesium, and 50 to 70% of the iron is bound to the fibers while a much smaller percentage of the monovalent cations and anions are bound. A similar trend was seen with all fiber streams throughout the fiber lines. This behavior is consistent with observations in the literature. These three ions were more tightly bound and probably do not participate in equilibrium to the extent that the other ions do. To handle this situation, the fraction of irreversible binding was specified and these ions were not allowed to equilibrate with the pulp. This was accomplished by removing the equilibrium reactions between these ions and the pulp from the data base.

A conceptual flow diagram of a typical paper machine white water system is shown in Figure 1.
Figure 1. Typical Water and Fiber Flow Schematic in a Papermaking System
Pulps and additives including acids and bases serve as the main sources of trace metals and anions. An additional source of trace ions is through fresh water addition which contributes typical hard water components such as calcium, magnesium, sodium and chloride in proportion to the degree of hardness of the water.

Fresh water typically enters into the saveall system or as showers around the paper machine. In both cases this fresh water also ends up in the saveall system. Metals leave the system in a variety of ways. Bound forms leave primarily with the sheet or with the sludge from the save all. Dissolved forms leave with the sheet, with the spent wash liquor or with the various overflows and sewer streams. The sludge accounts for very little of either the free or bound forms. The so-called dissolved forms become associated with the pulp in the drier as water is removed and are not volatilized.

The primarily feedback loops in the process are created by use of treated water as stock dilution in the machine approach system and in the broke system. A major water loop can be defined as beginning with the various pulp dilution stages, passing to the white water downcomers and into the saveall and then into the dilution water system and back to the dilution stages.

Ion buildup will depend on the relative balance between the addition and the removal of ions from the system. Fresh water can be reduced to the extent that other high quality water is available and to the extent that the process can tolerate increased ion concentration. For example, excess treated water after dilution can be diverted to the showers or to the pulp seal system to replace fresh water. Also tank overflows which are sewered can be reduced. These diversions can be used to reduce the flow of fresh water to the system. After sewers and overflows have been reduced to zero and all excess treated water is used, no further decrease in fresh water can be made without increasing the consistencies of the various dilution stages. If fresh water is not used for washing the pulp and spent wash liquor is not reused, the opportunities to substitute for fresh water become quite limited.

The fiber line is actually quite open since fiber passes more or less directly from the high density chests to the dry end of the paper machine. Feedback occurs mainly through broke recycle. Addition of calcium will tend to increase the bound forms of calcium. Washing will not remove all of the tightly bound cations such as calcium, magnesium or iron. Extractable ions such as sodium will be more easily removed. Recirculation of wash liquor will tend to concentrate certain species in the water phase. The higher water phase concentrations will also lead to increased sorption. Simply diluting the feed with spent wash liquor and then thickening will not remove bound ions very effectively since sorption levels may increase rather than decrease.

The tolerance of the process to increased ion concentration will vary considerably. Chloride ions will affect corrosion rates and will play an important role in how closed the system
Status Report

Tolerance to increased salts in the sheet may also limit the degree of closure. Some of these implications are shown in Table 1.

Table 1

<table>
<thead>
<tr>
<th>Some Effects of Increased Water Closure</th>
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<tbody>
<tr>
<td>Effect</td>
</tr>
<tr>
<td>Increased Corrosion Rates</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Retention shifts</td>
</tr>
<tr>
<td>Sheet properties deteriorate</td>
</tr>
<tr>
<td>Deposits buildup</td>
</tr>
</tbody>
</table>

The conventional myth is that as the recycle ratio increases, the levels of ions in the process will increase. However, this may not always be the case. In the following sections, we will explore the notion of closure and try to sort out fact from fiction.

Effects of Reducing Fresh Water to the System

For illustrative purposes, two limiting cases are described. In one case equilibrium is not taken into account within the water system and no interactions between liquid phase components and pulp occur. All bound and free forms entering the system are based on the equilibrium composition on the entering pulps. Another way of stating this case is that there is no change in the degree of binding onto the pulps in the circulation system. In the second case equilibrium is assumed and the tightly bound ions are irreversibly bound while the more loosely bound ions adjust to the local conditions based on specified equilibrium constants.

There are three primary areas to consider: (1) the low consistency flows such as white water, saveall feed water and dilution water, (2) the stock streams such as the machine stocks to the paper machine, and (3) the flow into and out of the bleaching and washing area, the diluted feed, spent wash liquor and high consistency mat. The effects of reduced fresh water feed will be shown on the concentrations of key ions such as sodium and chloride as well as calcium and sulfate in each of these three areas.
Project 3725

Status Report

In-flow of Fresh water

As mentioned earlier, fresh water in-flow can be reduced to the extent that there is excess dilution water and overflows and other discharges to the sewer can be eliminated. In the present case, the excess dilution water is significant and there are other losses to the sewer. A new steady state is reached when the water flowing in as fresh water plus the water entering with the HD stocks equals the outflows from the saveall with the sludge and from the washer system with the spent bleach liquor. This amounts to a reduction of nearly 90% in the fresh water feed.

Case 1: Equilibrium is ignored

Effect on the levels of Bound Ions

When equilibrium is not considered, the levels of bound ions in all the streams are constant as fresh water flow decreases. Ash levels increase by only 20% as the fresh water is reduced. This increase is approximately the same as the dilution effect of the fresh water on the total dilution water.

The following figures show the relative changes in ion concentrations resulting from a reduction in fresh water feed to the system. For illustration purposes, the concentrations are normalized with respect to the initial concentration of that ion in the bleached broke mat stream which generally contains the highest concentrations. Values less than 1 indicate that the concentrations are less than that of the bleached broke mat and values greater than one indicate concentrations greater than the initial bleached broke mat.

Effect on Dilution Water Quality

Figures 2 through 5 show that in calcium, chloride, sodium and sulfate ion concentrations in the dilution or treated water from the saveall indicated by the "x" increase significantly. The calcium levels increase from 0.55 to 1.0. The chloride levels change very little while the sodium and sulfate levels increase by 100 to 300% respectively. It is interesting that the initial reduction in fresh water flow only leads to a relatively small increase while the large change results from the last 20% reduction. The chloride levels don’t change as much as the other ions because chloride is introduced primarily in the bleach which is washed out before entering the main water loop. On the other hand, acid and base introduce sulfate and sodium ions into the main water loop which tends to stay in the loop and become more concentrated as the fresh water flow is reduced.

Except for the sulfate ions, initially the ion concentrations in the diluted stocks and dilution water are 50 to 80% of the mat concentration. However, as fresh water is reduced, the concentrations in these more dilute streams approach that in the broke mat. In the case of chloride, all the concentrations increase slightly about the same amount and there is not much
effect. This is due to the removal of chloride ion in the washing stage which occurs immediately after bleaching. If chloride were bound to the pulp in the bleaching step, less chloride would be washed off and more would enter the main loop leading to a greater buildup.

Effects on the Diluted Stocks

Figures 2 through 5 show the effects of reduced fresh water on the ions in the two diluted stocks. In this case the change in ion concentrations reflect the changes in the dilution water. This is to be expected since the only way to introduce ions to the fiber stock is through dilution or through mixing of stocks such as the broke with the HO pulps.

Effect on the Streams Leaving the Bleaching and Washing

As with the diluted stocks, the mat and other streams leaving the washing stage increase dramatically in concentration as water flow is reduced from 70 to 90%. This is mainly attributed to the composition of the broke which is the mixture of all the stocks and thus reflects the change in the dilution water composition.

Effects on Ash Levels

Although not shown, the ash level in the dry sheet increases about 20% due to the increased ions remaining with the sheet at the dry end of the machine. If the sheet de-waters to 28% consistency and there is no pressing, then 72% of the total flow leaving the papermachine consists of water and associated dissolved ions. As the concentration in the diluted stocks increases, this change will show up as an increase in ash level.

Case 2: Equilibrium Considered

Effect on the levels of Bound Ions

When equilibrium is taken into account, the levels of bound ions in all the streams change significantly as fresh water flow decreases. In most cases, the level of bound ions increases while in a few situations the level decreases. In contrast to the previous example, the free forms of the ions do not change significantly as the fresh water flow is decreased. For this reason only bound forms of calcium, chloride, sodium and sulfate are shown in Figures 6 through 9.
Effect on Dilution Water Quality

As mentioned previously, the concentrations of free ions in this case do not change greatly as water flow increases. However, the sodium levels increase about 10% while the other ions change very little. Since there are no fiber present in the dilution water, the levels of bound ions are not relevant.

Effect on Diluted Stocks

About the only major change in bound ion concentrations in the broke and diluted stocks occurs in the sodium ion in the broke which increases by several hundred percent. In the case of sulfate ion, the concentrations actually decrease somewhat as the fresh water flow decreases. This is due to the reduction in the source of sulfate ions from the fresh water. Bound calcium increases about 20% in the broke while the changes in the diluted stocks is very slight. This is a result of the small change in the dilution water composition. For chloride, sodium and sulfate ions, the concentrations decrease very slightly due to the reduced contribution of fresh water. Calcium increases in the broke due to the contribution from bleaching chemicals.
Relative Change in Calcium Level
With Reduction in Fresh Water
- square = bleached broke mat
- x = treated water
- circle = first diluted stock
- triangle = second diluted stock

Figure 2
Relative Change in Chloride Level
With Reduction in Fresh Water
square = bleached broke mat
x = treated water
circle = first diluted stock
triangle = second diluted stock

Figure 3
Relative Change in Sodium Level

With Reduction in Fresh Water
square = bleached broke mat
x = treated water
circle = first diluted stock
triangle = second diluted stock

Figure 4
Relative Change in Sulfate Level

With Reduction in Fresh Water

square = bleached broke mat
x = treated water
circle = first diluted stock
triangle = second diluted stock

Figure 5
Relative Change in Bound and Free Calcium Levels
With Reduction in Fresh Water
square: bound form - bleached broke mat
circle: bound form - first diluted stock
triangle: bound form second diluted stock

Figure 6
Relative Change in Bound Chloride Levels

With Reduction in Fresh Water

square: bleached broke mat
circle: first diluted stock
triangle: second diluted stock

Figure 7
Relative Change in Sodium Levels

With Reduction in Fresh Water

square: bleached broke mat

circle: first diluted stock

triangle: second diluted stock

Figure 8
Relative Change in Sulfate Levels
With Reduction in Fresh Water
square: bleached broke mat
circle: first diluted stock
triangle: second diluted stock

Figure 9