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PAPER COATING CONSTITUENTS AND
THEIR INFLUENCE ON CHEMICAL GHOSTING

by

Craig R. Harmsen

A thesis submitted in partial fulfillment of the
requirements for the degree of Masters of Science
in the School of Printing
in the College of Graphic Arts and Photography
of the Rochester Institute of Technology

September, 1982

Thesis Advisor: Joseph E. Brown, Associate Professor

DEDICATION

Dedicated to my dear wife Patricia, without whose encouragement, this thesis would never have been completed

ACKNOWLEDGEMENTS

I would like to express my appreciation to my thesis advisor, Associate Professor Joseph E. Brown and to Mr. Chester J. Daniels for their assistance and support through every phase of this research.

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ABSTRACT

For many years the printing industry, specifically sheetfed offset and letterpress printers, have been dealing with the problem of chemical ghosting. Traditionally it has been a problem associated with drying oil inks. More recent research concludes that ghosting is also affected by the permeability of an adjacent substrate. This thesis examines paper coating constituents, their degree of concentration, and what influence they play with regards to ghosting.

A quickset drying oil ink has been found which when subjected to the proper laboratory conditions will display a high degree of colored ghosting. The thesis indicates the method of creating ghosting and a method of measurement. A procedure for making paper samples with various percentages of coating constituents is outlined.

Experimentation has shown ghosting to be affected by the absorbency and ink hold out of the paper coating. This effect is increased at low absorption levels but diminishes as absorption is increased.

In addition, comprehensive background information is included to assist the reader to become more enlightened

to the true nature of this problem. The list of subjects surveyed include the definition of ghosting, the mechanisms involved, associated variables, and a summary of all pertinent literature.

CHAPTER I

INTRODUCTION

The printing industry like any other industry, has its share of problems. Probably the most elusive problem the printer faces is that of chemical ghosting. There are very few problems which can show up so unexpectedly and yet be so devastating. One can well imagine the horror that a plant manager experiences when a finished job comes off the press, is stacked down for bindery operations, and the next day, discovers that ghosting has occurred. The manager generally has little choice but to print the job over.

Ghosting is a very misunderstood phenomenon. Many misconceptions exist within the industry regarding its origin and cause. The name it bears points out its mysterious nature. It is capable of appearing quite unexpectedly and sometimes even disappears as suddenly as it came. Unfortunately, the latter is not generally the case. Therefore, it was believed that further research needed to be conducted to gain a greater understanding of this relatively misunderstood subject.

The thesis deals exclusively with chemical ghosting and should therefore not be confused with mechanical or

press ghosting. Mechanical ghosting, as its name implies, is strictly a mechanical problem associated with the inability of the form rollers to become sufficiently inked up between impressions. Chemical ghosting, is a phenomenon believed to be primarily associated with variations in drying ink films.

Bender, defines chemical ghosting as "an area where a greater, or lesser, degree of gloss occurs with reference to the surrounding ink surface in a freshly printed solid area on the back-up side, opposite drying, printed ink on the first down side."¹ We can further divide this type of ghosting into gloss or dull ghosting. Other names associated with chemical ghosting are ink ghosting, and gas ghosting.

Changes in gloss are not the only problems which are encountered with chemical ghosting. Schlapfer and Kung have listed the following changes that could take place:

1. Increase or decrease in gloss.
2. Increase or decrease in density.
3. Changes in color.

According to their definition, "the term gloss ghosting is not only applied to gloss changes but to any changes in appearance."² The present work will be based on this latter definition.

To further illustrate, we can suppose that we are

printing a job that requires text on one side of the sheet and a large solid on the other. We choose to first run the side that consists of text material. We stack down the pile and let it dry overnight. The following day we print our solid on the back up side. The drying of the second down ink film, in contact with the already dried first down ink film will experience a different drying rate than areas which are not in contact. Figure 1 illustrates this point.

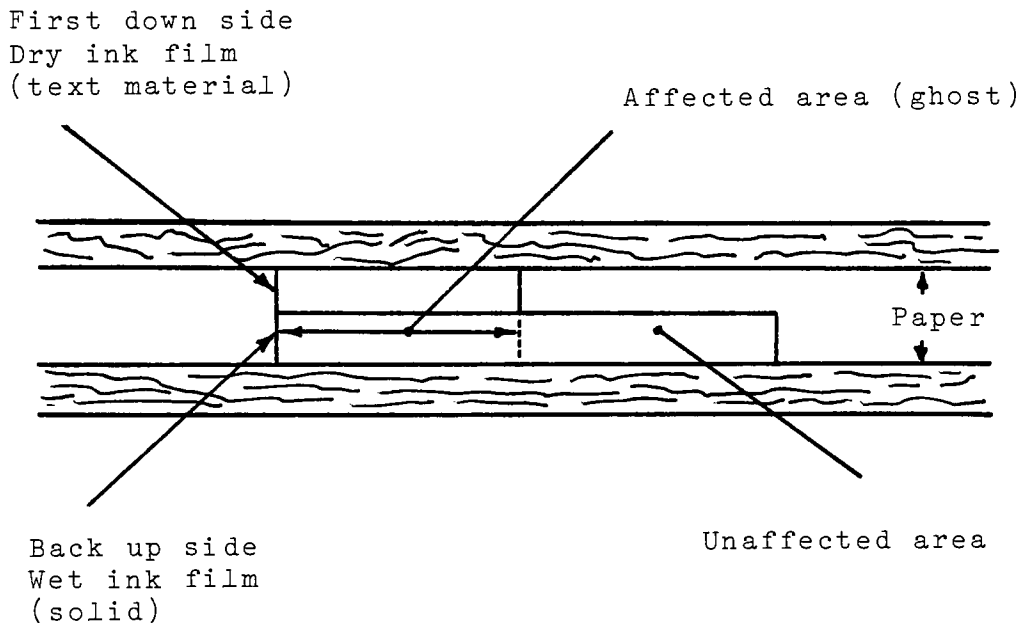


Figure 1. Relationship of ink films which result in ghosting.

The mechanism of this reaction at first glance may seem to be rather simple, however, its spontaneity and the number of variables involved make it a complex problem which is still not completely understood. To a greater or lesser degree, all of the following play a part in chemical ghosting.³

1. Thickness of ink film.
2. pH of the fountain solution.
3. Pressure imposed by stack.
4. pH of paper coating and paper body.
5. Quantity of cobalt drier in the ink.
6. Type of ink.
7. Type of paper.
8. Time interval between first and second printing.

Over the past 30 years, theories have developed as to how chemical ghosts occur. One theory indicated that the first ink film emits by-products that would be deposited on the adjacent sheet. These by-products would then selectively change the ink receptivity of the adjacent sheet. This in turn would effect the gloss characteristics of the ink film on the reverse side. Another theory indicated that the ink would fume through the sheet and hence, effect the reverse sides ink receptivity. Experimentation has been conducted to test these theories, and although they do hold some credence, their effect is

minimal.⁴

Another explanation which research has revealed is that of "phase separation." "Separation of ink components can occur in the presence of a previously printed ink film."⁵ Research has led to the proposal that the fluid components of the ink, separate during drying. Certain components of the ink along with various volatile by-products accumulate on the ink film surface. When in contact with an adjacent surface consisting of various absorbancies (ie. plain paper and dried ink film), the components can be adsorbed to varying degrees which will yield areas containing various degrees of gloss, density or hue. Drier can promote this type of separation.⁶

Research conducted by Schlapfer and Kung have revealed another variation. Their experimental conclusion was that "drying ink film itself seems to be altered by interaction with the overlaid image."⁷ This theory combines phase separation, but puts greater stress on the effect of varying absorbency of the adjacent sheet.

Another theory which attempts to explain the mechanism of ghosting, is that of "volatile by-product fuming off the dried ink film," containing ingredients which can accelerate the drying of adjacent wet ink films. Hartsuch refers to these agents as "volatile drying accelerators."⁸

It was also determined that aged ink emits a retarding material which was not volatile at room temperature.⁹ It is believed that during the period of acceleration, less vehicle is allowed to penetrate into the paper leaving the ink film with a higher gloss. Conversely, during the retardation stage, greater amounts of vehicle are able to leave the ink film and migrate into the paper, leaving a greater proportion of pigment to vehicle. This would result in a duller film.

A controversy exists as to the actual time limits of these phases. Hartsuch reported that the acceleration phase takes place immediately, and continues up to about three and one half days. At this point, the retardation phase will build up, reach a constant level and remain indefinitely.¹⁰ Bock reported acceleration up to 18 hours and then retardation.¹¹ Bender indicated that dull ghosting appeared within 3 to 4 hours and gloss ghosting from 18 to 24 hours.¹² These contradictions can probably be attributed to the varying varnishes and driers used for the different experiments conducted. Benders dull ghosting at 3 to 4 hours has not been attributed to vehicle drainage, but rather "to an ink solvent surface effect."¹³

These, in brief are the existing theories which explain this phenomenon. Some researchers claim that

only one mechanism is the ultimate cause, while others believe that different situations will encourage different mechanisms, and that perhaps several different mechanisms are taking place simultaneously. The Chapter entitled Background and Theory will examine each of these mechanisms in detail.

The purpose of much of the work carried out by organizations such as *GATF, has been to understand this problem so that the printer can avoid it, and at least correct the problem if it occurs. The following is a list of circumstances which can lead to ghosting.¹⁴

1. In glossy ink sheet-fed lithography or letterpress printing.
2. In large solid areas printed on the back up form.
3. In large heavy delivery piles.
4. On rush jobs, when the first side is backed up too soon after it is run.

It has been suggested that the printer should be on the lookout for these circumstances and try to avoid a combination of 2 or more of them. Unfortunately, these conditions are quite common and many times unavoidable. In the event that the potential for ghosting exists, GATF recommends the following:¹⁵

1. Wind sheets before printing back-up side. This replaces the stale air in the sheets with fresh air, and helps eliminate the gasses that are known to cause ghosting. When ink coverage is heavy, winding also offers protection against blocking, loss of gloss and chalking.

*Graphic Arts Technical Foundation

2. Run small lifts when backing up the sheets.
3. Keep piles in strict sequence for back-up.
4. Keep delivery piles away from sources of excessive heat or cold.
5. Hold delivery piles three days before printing the back-up side. Running the sheets through the press without printing does an excellent job of supplying fresh air before the back-up side is printed.
6. Print the heavy form first, and the light form on the back-up side.
7. In short, expensive runs, it has been suggested that the printer slip-sheet the stock while printing the second side.

Great effort was made to produce chemical ghosting in the laboratory. Various inks were tested, with varying amounts of drier. Samples have been subjected to varying pressures, differing time intervals between first and second impression, and emulsification of the ink with conventional and alcohol fountain solutions. Within this research, ghosting has only been made to occur by overprinting a fresh ink film over an already dried ink film or printing the sample on acetate. This experimental procedure is closely aligned with the one used by Schlapfer and Kung. As previously mentioned, they concluded that the mechanism involved is that of nonuniform absorbency of the overlay, causing a phase separation to occur.

Chemical ghosting is an occurrence which takes place in a closed environment. This being so, it is safe to

assume that each component of that environment effects every other component. This thesis concerns itself with those components which make up the experimental paper coating, namely water, clay, and latex (primarily latex). The objective will be to determine the effect that varying the amount of coating constituents has on ghosting. Correlations have been made to determine, what proportions of an ingredient will encourage ghosting and what proportions will minimize ghosting. It is felt that this information can be useful to papermakers, when formulating paper coatings for sheet-fed offset and letter-press printers.

Coatings containing varying proportions of ingredients have been tested. The results expected were that those proportions which increase the absorbency and porosity of the coating (of the overlay), will decrease the amount of ghosting. Further, it was expected that if (as in Figures 2A and 2B) a series of coated papers, ranging from low absorbency, low porosity to high absorbency, high porosity, were used in the ghosting procedure; it would demonstrate that ghosting increases as porosity and absorbency (of the overlay) decrease.

The previous statement is based on the following reasoning. The coated paper overlays will have some effect with regards to ghosting, however, the difference between those areas in 2A and 2B will be almost negligible. The

Low absorbency
low porosity
coating

10

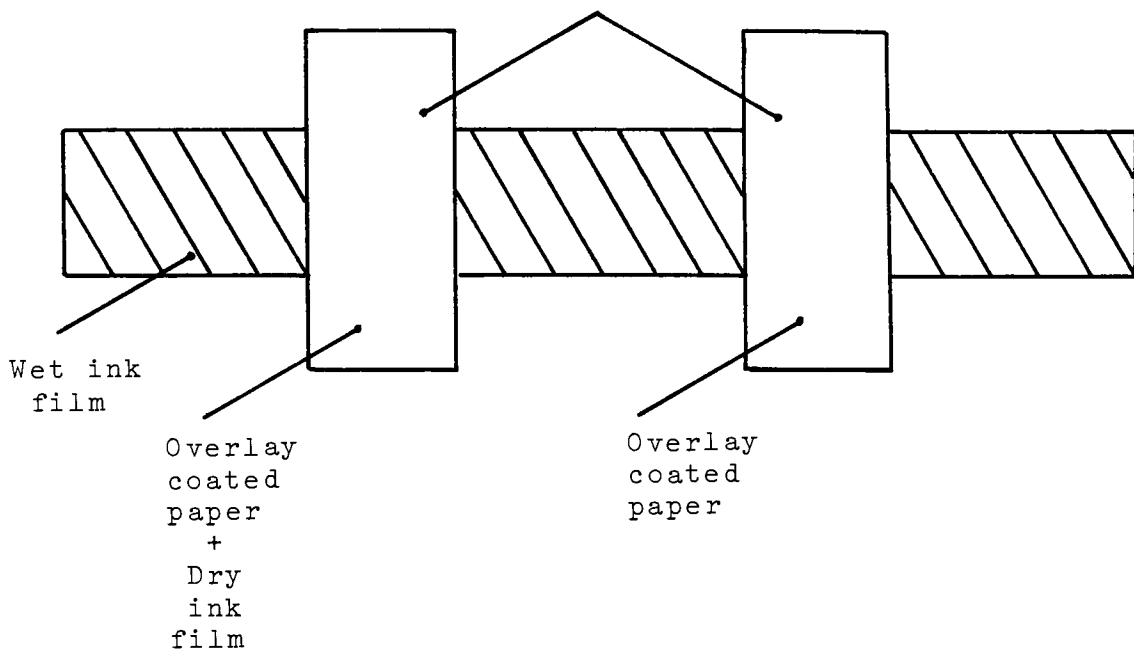


Figure 2A. High ghosting situation

High absorbency
high porosity
coating

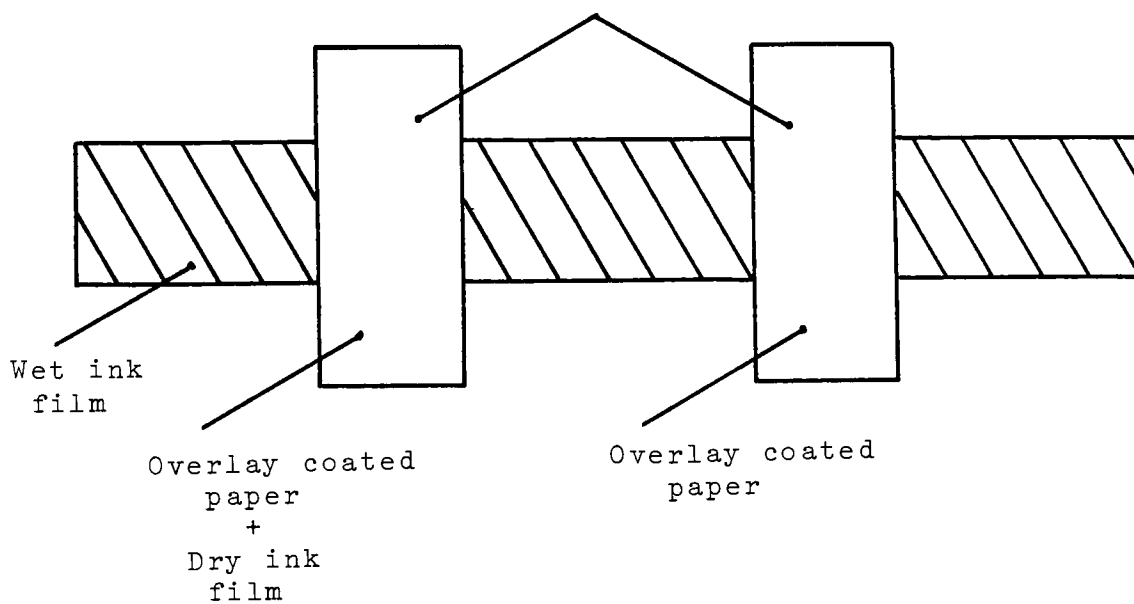


Figure 2B. Low ghosting situation

areas in 2A and 2B overlayed by coated paper plus ink will show a more dynamic optical difference. This is attributed to the difference in ink hold out that both overlays possess. The ink film on the overlay in 2A (coated paper plus ink) will more readily be held on the surface due to the ink's inability to penetrate the surface. This will create a uniform barrier, which will not allow the volatile by-products (evaporating solvents, aldehydes, etc.) of the adjacent wet ink film to freely disperse.

The overlay in figure 2B (coated paper plus ink) has however, allowed a much greater penetration of the ink's vehicle. The vehicle and associated nonviscous materials (solvent, etc.) are not only adsorbed into the coating, but the base stock fibers as well. The overlay in 2B is much less impervious than that of the overlay used in 2A, and will allow to a much greater extent the free flow of the by-products being emitted from the wet ink film.

CHAPTER II

HYPOTHESIS PROPER

Any manipulation of the coating constituents or physical treatment of the sheet that will increase the absorption and porosity, will decrease chemical ghosting. Conversely, any manipulation of the coating constituents or physical treatment (ie. calendering) of the sheet that will cause a decrease in absorption and porosity will increase chemical ghosting.

Note:

This hypothesis is based on the chemical ghosting mechanism of differential permeability inducing differential phase separation. It is this specific mechanism of this specific kind of ghosting that this thesis exclusively deals with.

CHAPTER III

BACKGROUND AND THEORY

The following is a more indepth look at some of the associated factors pertinent to this research. Ghosting inks, associated variables, mechanisms of ghosting and paper coating will be discussed.

Ghosting Inks

The problem of all types of chemical ghosting do have one common denominator. Ghosting has only been found to occur when using drying oil, linseed based inks. Ghosting tends to be a problem encountered by either sheetfed offset or sheetfed letterpress printers, since they are the major users of these inks. Drying oil inks undergo setting by absorption, and then oxidation polymerization. This process is slow and can take 24 to 48 hours. These inks pose several drawbacks. Because of their slow rate of polymerization they easily set off. Their gloss is usually not high because of their prolonged drainage. Chalking is frequent and rehandling time is longer.¹⁶

To overcome these problems ink manufacturers developed quick-set, high gloss inks. "Quick-set vehicles are composed of one phase of heavy linseed or synthetic

varnish and another phase of very thin, free flowing vehicle, a high boiling point solvent in which synthetic resin has been dissolved."¹⁷ The older drying oil inks are made up of less complex molecules and dry more slowly and hence give off smaller amounts of volatile by-products in a given time. The quick-set inks are more complex and emit gasses at a much higher rate. Therefore, quick-set inks have only stimulated the problem further. The "explosion" of ghosting occurrences correlated with the introduction of these inks.¹⁸

Throughout the literature there is general agreement in regards to the ink formulation. The following is a list of attributes possessed by those inks which have a tendency to ghost.

1. Drying oil vehicle.
2. High drier contents.
3. Combination of vehicles with different drying reactions.

Number 1 has previously been discussed and number 2 will be dealt with in the section on associated variables. Number 3 is a more recent finding. It appears that ghosting is more likely to take place if there exists in the formulation a combination of vehicles which possess different drying reactions. The following list shows the vehicle and its drying reaction.¹⁹

- . Linseed oil and soya bean oil, drying via isolated double bonds.
- . Tung oil, drying via conjugated double bonds.
- . Alkyd resins, drying by polycondensation.

Test Results

- | | |
|---------------------------------|-------------|
| . Linseed oil | no ghosting |
| . Bodied linseed oil | no ghosting |
| . Soya bean and linseed oil | no ghosting |
| . Tung oil and linseed oil | ghosting |
| . Linseed alkyd (several types) | ghosting |

These conclusions made by Schlapfer and Kung, regarding "combinations of vehicles with different drying reactions" have not been scientifically proven, rather, they are based on observation. Nevertheless, it is listed as one of the contributing factors.

Associated Variables

As previously mentioned, although the ink itself appears to be the origin of the phenomenon, there are other factors which cannot be ignored. Some of these variables may actually promote ghosting or merely serve to enhance it.

This catalog of variables and the points concerning them which will now be discussed, serve to illustrate

how little is really known about chemical ghosting. The number of contradictions will clearly support this statement.

Closely associated with the ink itself is the drying history. Drying history can be defined as the sequence of events that lead up to the actual dry ink film. The handling of the sheets refers to the method of drying (ie. air dried or pile dried).

From a perusal of the available literature it is clear that how the paper is handled and at what point the ink film comes in contact with one another is of importance to whether a ghost will appear and what form it will take. The importance of time between the first ink film and the second has been discussed in previous paragraphs. Bender concludes from his experimentation that ghosting was more apt to appear when sheets were dried separately. From this observation he proposes that an "optimum amount of oxygen between the sheets is necessary for the ghosting phenomenon to occur."²⁰ Gimbrone on the other hand claims "ghosting increased with more complete insulation of a dried sheet..."²¹ From these two diametrically opposed statements it can be assumed that it is either an unimportant variable or that the two researchers were experimenting with different kinds of ghosting.

Another factor which is influential is that of pH.

Tests have been performed to indicate the relationship between pH and how it effects ghosting. Higher pH of the body stock has been found to encourage ghosting.^{22,23} Strangely enough, it has been observed that lower pH of the fountain solution seems to be a promotional factor as well.²⁴

Researchers have made correlations between the ink film thickness and the tendency of the ink to ghost. The authors tended in each case to conclude that a relatively specific ink film thickness was necessary to promote ghosting, however, research has revealed these so-called specific ink film thicknesses to range anywhere from 2.5 microns, to an excess of 10 microns. From these findings an assumption will be made that the ink film thickness is not as important as researchers have tended to believe.

Of extreme importance has been the extent of drier used. Cobalt drier has been found in all cases to be a ghost inducing agent. Manganese, to a much lesser extent has also been found to amplify the problem. Schlapfer and Kung have found that although some inks received from the manufacturer were non-ghosting inks, they could be converted to ghosting inks by the addition of solvents. If, however, these inks "contained only additional solvent but not excessive drier, ghosting did not occur." They concluded that "ghosting is promoted primarily by

driers, but the driers seem only to be a catalyst and not the inducing ingredient."²⁵

Lastly, the paper used has been associated with the ghosting phenomenon. Ghosting has primarily been a problem found to occur with coated higher quality papers.²⁶ The printing job is generally one which requires high gloss characteristics. Hence, if a job printed on coated stock and uncoated stock were both found to possess the same amount of difference in gloss between affected and unaffected areas, the coated stock would be found to be more objectionable. The reason being that the coated paper and image esthetically requires a more consistent and uniform gloss. The job on coated stock generally has higher levels of gloss, and is therefore more noticeable. This then is a situation where the coating does not physically or chemically promote ghosting, but the optical characteristics merely exaggerates the effect.

Most work conducted to investigate ghosting has been confined to ink drier systems. The general consensus is that papers do not directly contribute to ghosting, however, it is generally agreed that further work must be carried out to either confirm or disprove these opinions. Some research has been conducted which reveals "that ghosting is caused by a reaction between the casein binder in the paper coating and certain aldehydes formed

during ink drying."²⁷ Furthermore, definite findings have not been established regarding the effect of coating components, sizing fillers, resins, etc.

Mechanisms of Ghosting

As previously mentioned, there appear to be several causes of chemical ghosting. This section will attempt to examine these mechanisms more closely. This will then give the reader a deeper understanding of ghosting and make clearer the mechanism which will be used throughout experimentation for this thesis.

In the Introduction, mention was made of two theories; fuming through the sheet and by-products depositing themselves on the adjacent sheet rendering nonuniform ink receptivity. Their effect is almost negligible and for this reason no further mention will be made of them, but rather we will discuss in more detail the two accepted theories of chemical ghosting.

1. The Effect of Volatile By-products From Dried Ink Film

This theory is based on the concept of volatile by-products fuming off the drying ink film, affecting the drying rate of an adjacent wet ink film. These by-products have been found to be capable of either accelerating or retarding the fresh ink film. The effect of acceleration or retardation has been found to be dependent on the time

interval between printing.

Although there is some dispute over the actual intervals necessary to either accelerate or retard drying, most references seem to indicate that initially there is an accelerating occurrence which will slowly decline, reach the drying rate of the surrounding unaffected areas and then begin to retard the drying.

The differential in gloss is then explained as follows. In areas of accelerated drying, very little vehicle has been allowed to leave the film. This would yield an area of high gloss. Areas which have experienced retarded drying will allow a larger amount of the vehicle to leave the film and travel into the paper, leaving a dull appearance.

Investigations have been made to determine which elements of the ink are responsible for this phenomenon. Thus far, fifteen oxidation by-products have been identified in one specific linseed-alkyd cobalt/dryer coated paper system.²⁸ Appendix 1 lists the by-products identified.²⁹

The two organic volatiles found in the greatest quantity were 2 carbon acetaldehyde and 3 carbon propionaldehyde.³⁰ The predominate inorganic volatile is water, which makes up approximately 90% of the total volume of volatiles which the ink film emits.³¹ Other suspected

by-products are carbon dioxide, carbon monoxide, formic acid, formaldehyde, acetic acid, valeric acid, and caproic acid.³²

The Graphic Arts Technical Foundation has done extensive research concerning this particular mechanism. They have suggested it to be the most common cause of chemical ghosting.

2. Differential Absorbency Encouraging Phase Separation

Work has been conducted to investigate another theory which involves differential absorbency which encourages a phase separation to take place.^{33,34} It is important to note that these studies have been conducted more recently than those which were associated with "volatile by-products from dried inks" (Bender, Gimbrone) and therefore must be considered more closely. The present mechanism under discussion partially includes the principle of the previous mechanism but gives it a lesser degree of importance.

Ghosting is "encouraged by the tendency of the fluid (non-viscous) components of an ink to separate out during drying (ie. phase separation)."³⁵ If a drying oil ink is printed on an impermeable surface, the fluid phase and volatile by-products will not be able to absorb into the substrate and will migrate to the surface.³⁶

Absorption of these volatile by-products is dependent then on the permeability of the adjacent overlay in

contact. Areas of high permeability will readily absorb and dissipate the volatiles. Conversely, a nonpermeable surface will cause retention of the volatiles. "For instance, a dried ink film is nonabsorbing and a coated paper has a considerable absorbency."³⁷ It must be emphasized again that the present research being conducted is employing this mechanism. It may now become clearer how important the role of the coatings becomes.

Paper Coatings

In order for a given paper to be considered coated it must meet 3 basic requirements:³⁸

1. Ten percent of its basis weight must consist of coating;
2. Fifty percent of the coating must be pigment, and
3. Its purpose must be to improve printability and/or appearance.

With this in mind our work will be conducted within the limitations of these three restraints:

Coating is made up of 3 components, namely:

1. Pigment
2. Binders or adhesives
3. Additives

The following paragraphs will examine these ingredients in detail. It is hoped that this examination will help to

better familiarize the reader with what is the focal point of our research.

Pigments

Regardless of the pigment used, certain qualities are necessary for it to be a useful pigment. Generally speaking, it is most desirable to have the coating held out on the surface. In order to coat all the surface fibers it is necessary to have a sufficient number of pigment particles.³⁹ Pigments which are characterized by small particle size and a low density will achieve this more readily than will a pigment with larger particles and higher density.

Satin white (calcium sulfo aluminate) which has a density of 1.81 grams per c.c. is considered a low density. It can be refined down to a very small particle size. These two attributes contained by satin white make it a desirable pigment. Titanium dioxide can be refined to about the same size but has a much higher density of 4.35 grams per c.c. Clay is also used as a pigment. Its average particle size is about two microns which is larger than the previous two pigments mentioned but has a uniform reflectance curve and a desirable shade. Clay is also cheaper than the aforementioned pigments.⁴⁰ Calcium carbonate, another pigment, "is often blended with clay

because of its ink trapping properties and whiteness."⁴¹

Other desirable qualities a pigment should possess are a high refractive index and high reflectance. The particles can vary in reflectance depending on the shape of the particle (ie. platelet, rhombus, needle, etc.) and its orientation.

The intended research will deal only with clay as a pigment. The reason for this choice is because of its dominant use in the paper industry. "Clay as a pigment is the backbone of the coating industry, and paper may be, and often is, coated with it as the sole pigment."⁴²

Adhesives

If a paper were coated with pigment only, which is the wholly desirable ingredient of the coating, the coating would quickly flake off. Coating without adhesives is analogous to chalk on a chalkboard. The chalk will stay on the board, but if touched it will wipe right off. Likewise, pigment has no adhesive power of itself. Not only do adhesives serve the purpose of bonding the pigment to the paper but they also impart other desirable and necessary qualities to the coating. Depending on the adhesive used these qualities may include protection, plasticity, water proofing qualities and good flow properties which make for easier and higher quality applications.⁴³

Libby has compiled a list of the necessary attributes which an adhesive must possess.⁴⁴

Specifications for Adhesives

The adhesive must possess some or all of the properties listed below:

1. High binding power proportional to the total costs of the adhesive (purchase price plus expense for preparation).
2. High barrier efficiency, again relative to costs.
3. Best properties to meet the end use of the surface-treated product.
 - a. Penetration and reinforcement of the base, or
 - b. Holdout of coating, fiber coverage, and controlled retention of water or liquid
 - c. Suitable rheological properties at high rates of shear for pumping
 - d. Good plasticity for calendering
 - e. Satisfactory resistance against wetting by liquids after the adhesives have been properly dried
 - f. Easy prevention of spoilage, foaming, and discoloration
 - g. Rapid conversion to a nonsticky surface to prevent deposits of adhesive or coatings at contact points

There are a number of different binders used, each possessing its own advantages and disadvantages. These adhesives can basically be broken down into 4 main groups; proteins, starches, latices and other synthetic types of adhesives.

Proteins have been in use the longest. A protein

type water soluble glue was used originally. This was then superseded by the other proteins. The most common protein in use is casein. This is a product derived from skim milk. "It is a strong adhesive and can readily be waterproofed."⁴⁵ Casein has increasingly been used less over the years. Because of increased demand for food, papermakers have had to compete for its use. This increased demand has made it an expensive binder material. Another protein used for binder is from the soya bean plant. "It is equal or similar to casein in all major properties and may be mixed with it in any proportion."⁴⁶ It too, like casein is a food product and is in competition with other markets.

The most commonly used adhesives today are the starches. It is estimated that 70% of all coated papers use a starch adhesive.⁴⁷ The most common starch is derived from the corn plant. It has a high binding power but has poor water resistance. Starch for the paper industry is also derived to a limited extent from potatoes, rice, wheat and tapioca.⁴⁸

After the Second World War, latices were incorporated into the coating ingredients with much success. Latices result in good flow properties of the coating mixture, good gloss, and some waterproofness. A common latex, styrene-butadiene, is made up of 30 to 50 parts butadiene

and 70 to 50 parts styrene.⁴⁹ The solution with the addition of emulsifiers and water are polymerized by "free radicals set free from a catalyst."⁵⁰ Latex is commonly combined with starch to improve water resistance and plasticity.

Polyvinyl alcohol is an example of the last type of binder. It is not in wide use presently; however, its use and the use of other synthetic adhesives may become more widespread as both proteins and starches may become more expensive due to the fact that they are derived from food products.⁵¹ Table I shows the physical properties and cost index for the various binders.

Table I: Adhesive Properties

	Price* index f.o.b. origin	Binding power, % on pigment	Water retention	Water resistance
Starch, untreated	24	14	Excellent	Very poor
Etherized starch	36	13-14	Good	Poor
Oxidized starch	34	14-15	Good	Very poor
Hide glue	92	13	Good	Fair
Casein	76-84	12	Very good	Good
Soy protein	84	12	Good	Good
Polyvinyl alcohol	200	4.5	Very good	Poor
Carboxymethyl cellulose	212	Fair
Sodium alginate	400	...	Excellent	Poor
Styrene-butadiene latex	112	12	Very poor	Good
Acrylic resin	208	11	Poor	Very good

*A no. 1 coating clay has a price index of 9.0 and titanium dioxide in anatase form one of 102.

Additives

In many cases it is desirable for a coating to possess certain qualities that cannot be achieved by the pigment and adhesive alone. This is when additives are employed. Some examples of additives are tinting dyes, defoamers, preservatives, dispersing agents and water proofing agents.⁵² No additives will be incorporated into the experimentation for this research project.

The Affect of Coating Formulation

Certainly the proportions of the coating constituents as well as the constituents themselves greatly affect the final qualities of the coating and how the ink interacts with that coating. This in itself is the motivating factor which has prompted this study. The Mead Corporation has published a list of results which will occur as starch or protein content is raised.⁵³

- 1 - The degree of bonding (surface strength) will be raised.
- 2 - If water resistance is a property of the particular adhesive being used, this will be increased.
- 3 - Brightness will be lowered, both because the adhesive very often has a lower brightness than the pigment it replaces, and because the adhesive is much less opaque than the pigment and permits light to enter more deeply into the coating layer and can be absorbed.
- 4 - Opacity will be lowered, not only because the adhesive is less opaque of itself than pigments, but primarily because the adhesive will fill

voids in the coating layer and permit a more continuous passage of light.

- 5 - The finished sheet will be rougher and lower in gloss since the extra adhesive makes a harder, less plastic coating which will not level out under the pressure of the supercalender.
- 6 - The finished sheet will be more brittle and will tend to crack more at the fold.
- 7 - Other effects such as poorer ink drying and reduced dimensional stability may be noted.

"On the other hand, if the adhesive used was one of the latices, which so often under heat are thermoplastic, then items 5 and 6 may actually be improved rather than worsened."

Tests were performed to determine what effect different starch and latex levels had on porosity and absorbency. In addition, observations were made concerning the effect of calendering. Four tests were performed:

1. Constant starch while varying the latex, uncalendered.
2. Constant starch while varying the latex, calendered.
3. Constant latex while varying the starch, uncalendered.
4. Constant latex while varying the starch, calendered.

Figures 3 to 8 show graphically the results of the experiment. It must be kept in mind that this experiment was not conducted under rigid scientific and statistical

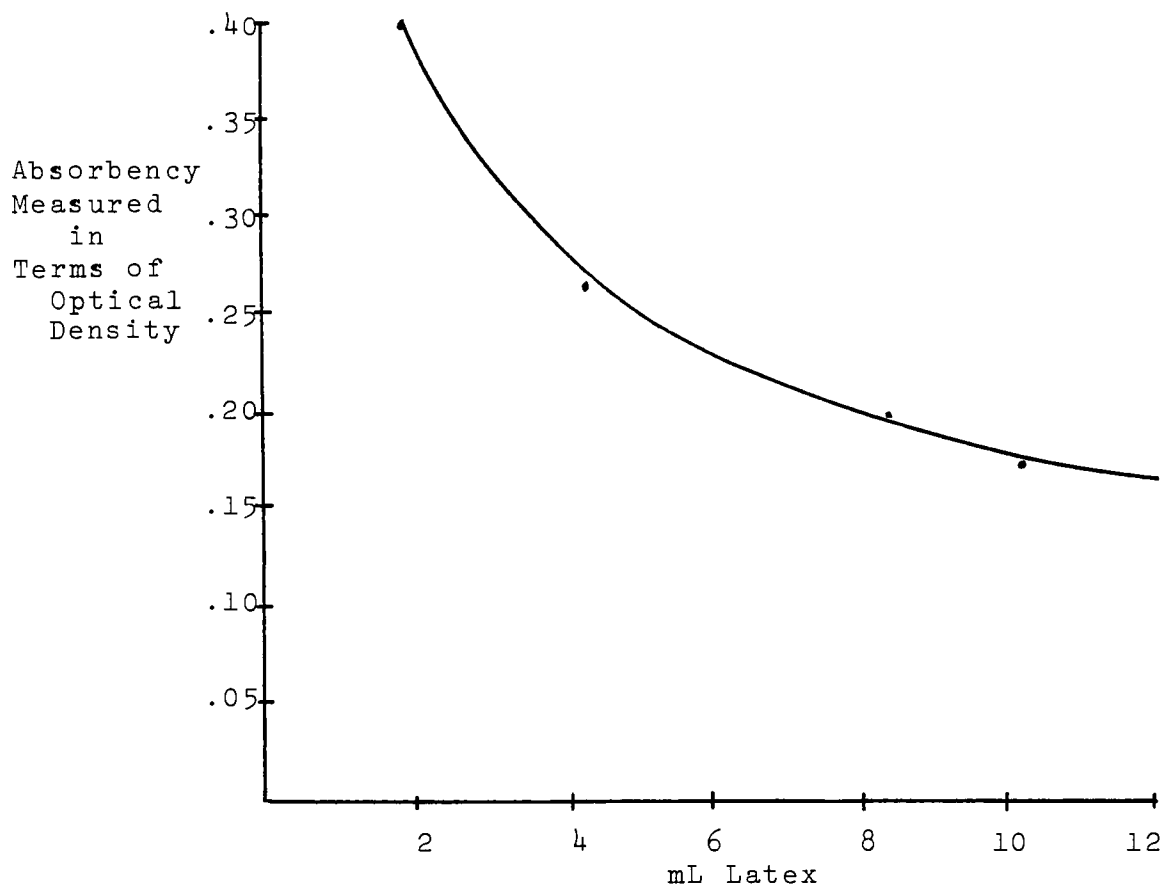


Figure 3. Absorption test, starch held constant while varying the latex, uncalendered.

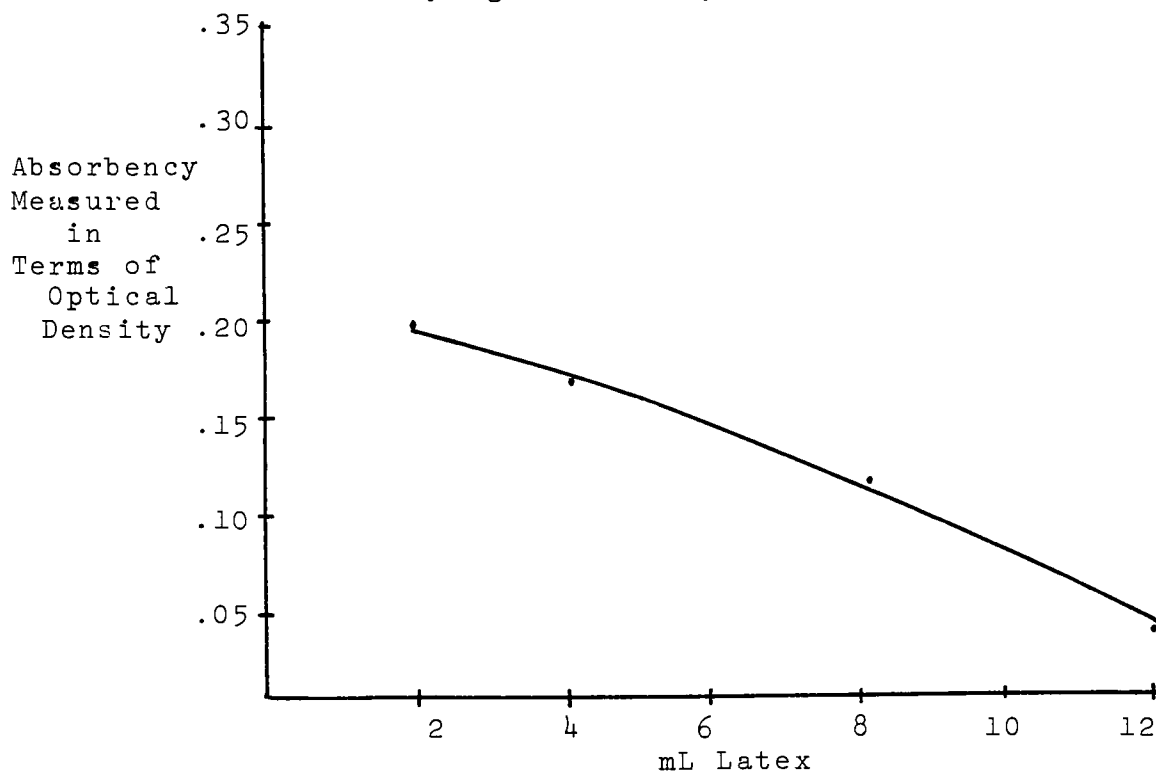


Figure 4. Absorption test, starch held constant while varying the latex, calendered

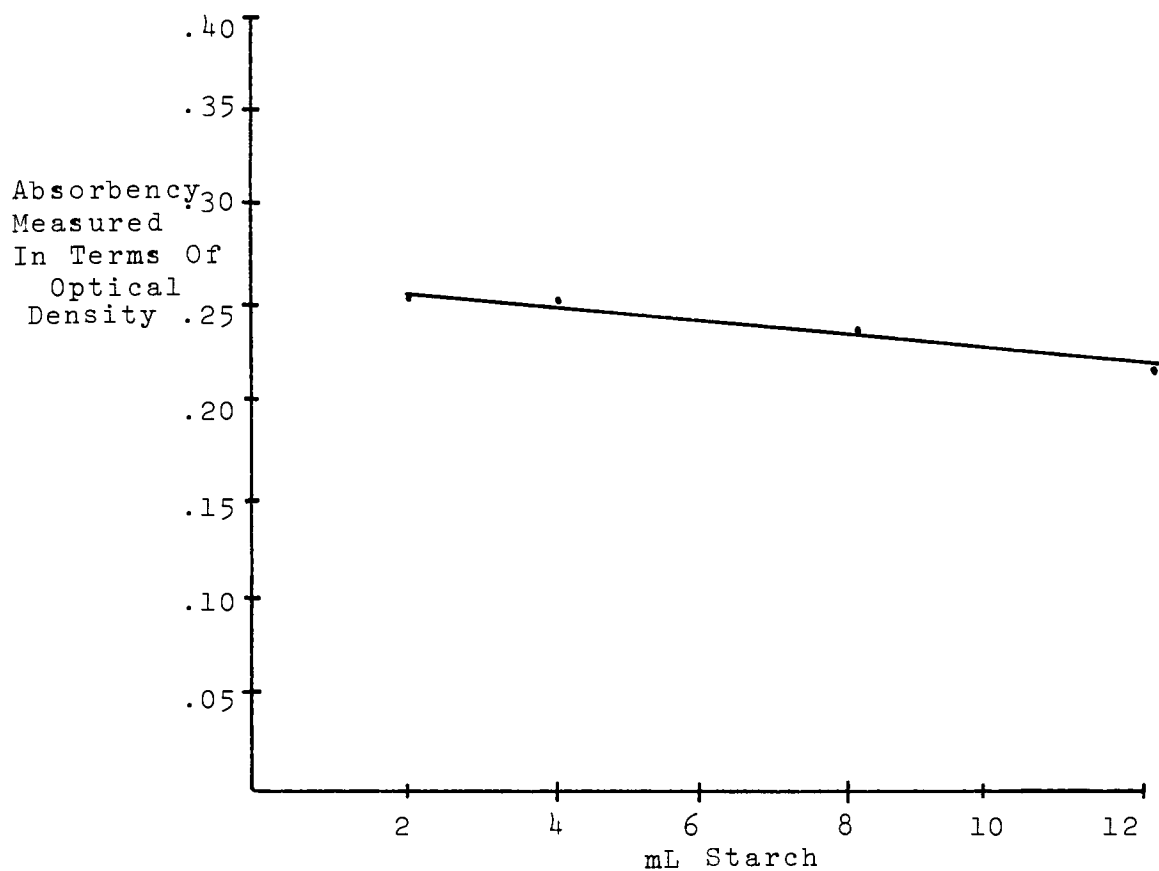


Figure 5. Absorption test, latex held constant while varying the starch, uncalendered

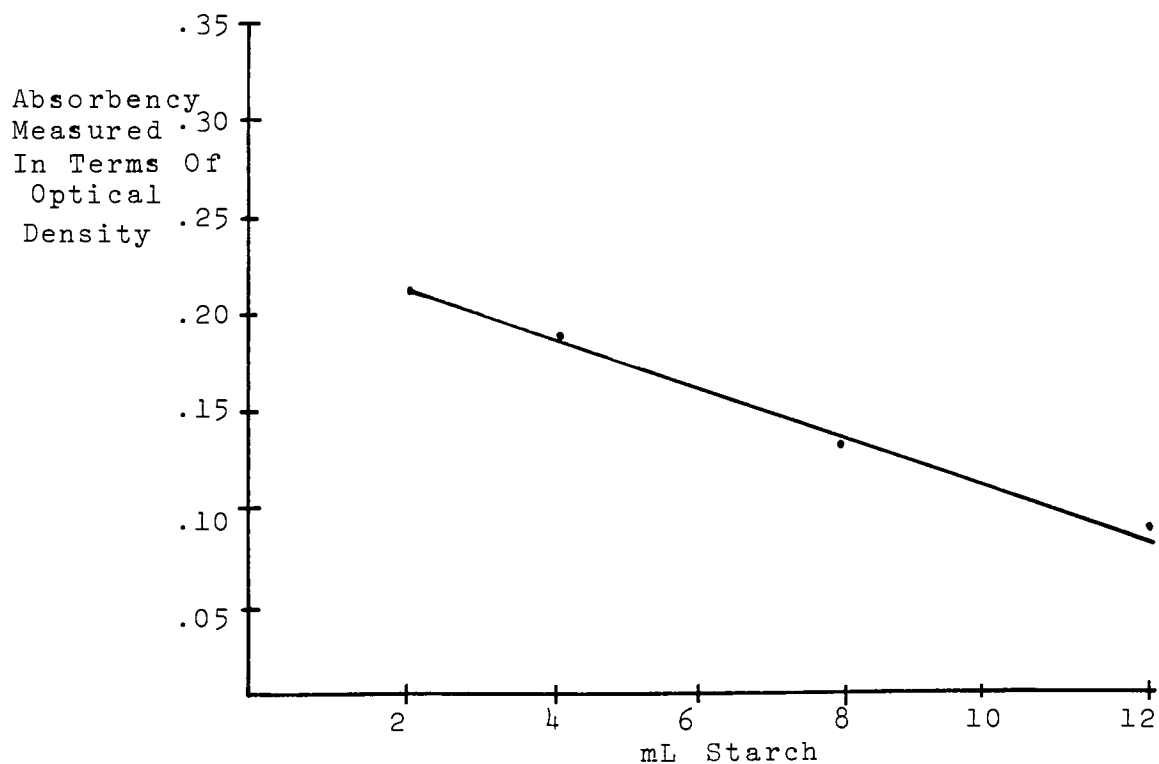


Figure 6. Absorption test, latex held constant while varying the starch, calendered

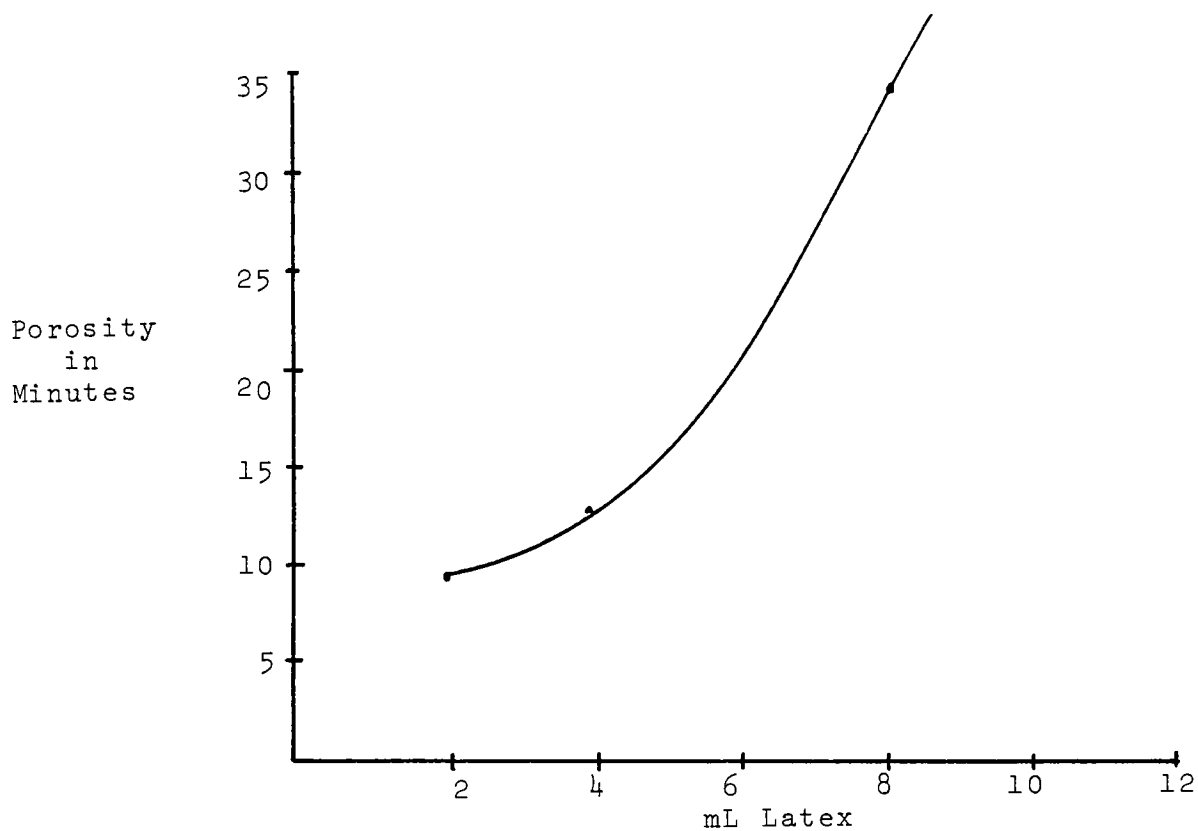


Figure 7. Porosity test, starch held constant while varying the latex

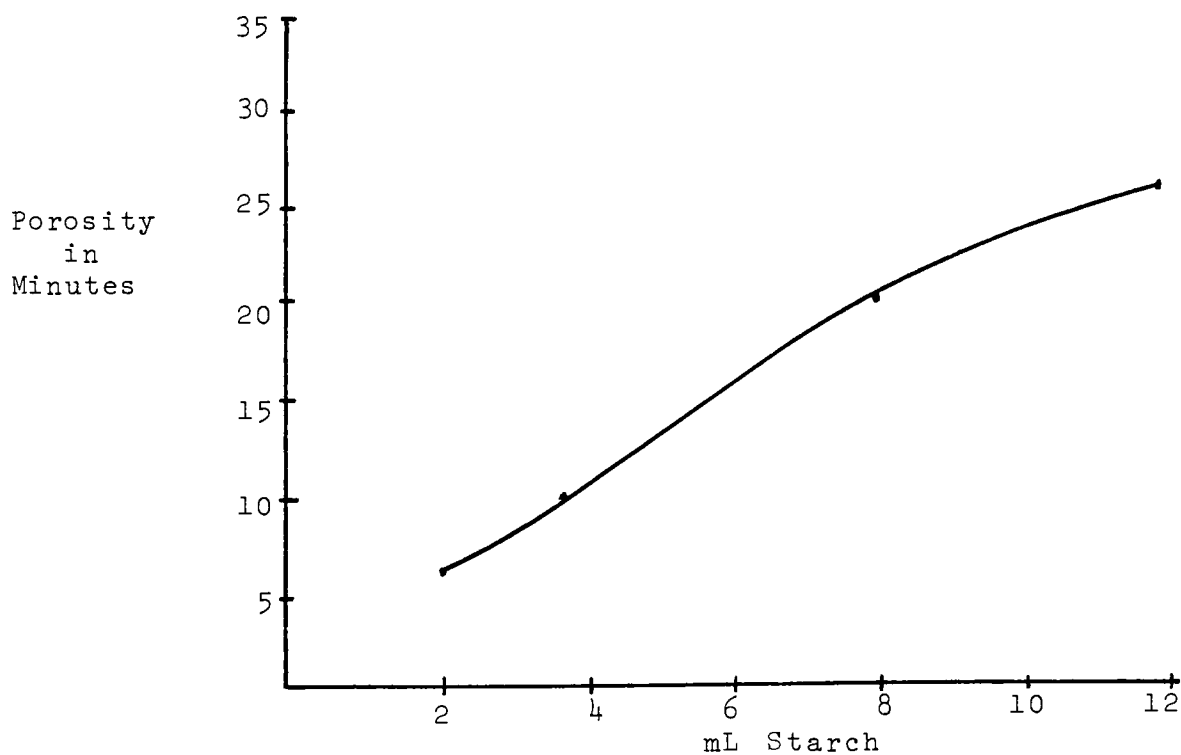


Figure 8. Porosity test, latex held constant while varying the starch

controls and it was necessary to redo the experiment (Chapter V: Results). Nevertheless, the tests do reveal some significant trends. The absorbency tests were done using K+N testing ink and measuring their relative densities using an optical densitometer. Porosity was measured with a Gurley Densometer which measures the time taken for 100 c.c. of air to pass through the sample.

Conclusions

1. Addition of latex will cause decreased absorption
2. Calendering lowers the overall absorption.
3. Addition of starch causes decreased absorption but to a lesser degree than with the addition of latex. (Test is not entirely conclusive.)
4. Addition of latex decreases porosity.
5. Addition of starch decreases porosity.
6. Addition of either starch or latex has no effect on caliper.

CHAPTER IV

METHODOLOGY

At a very early stage of research it was quickly realized why the phenomenon in question is called "ghosting". The name ghosting is derived for two reasons. First, it can give the appearance of a transparent but noticeable change in gloss, color or density. Secondly, it derives its name from its unpredictable behavior. The name ghost is quite appropriate as the affect can appear and then disappear. A thousand jobs may be run by a printer with no ghosting. Then, a rash of ghosting jobs may take place. Suddenly, the problem is resolved by itself, with the printer never finding out what caused it in the first place. GATF published a technical service report entitled "'Spooks in Print" haunt sheetfed printers."⁵⁴

The first objective of the research was to pinpoint a ghosting ink which could be used for experimentation. Through a close examination of the literature a list of characteristics that the ink should possess was compiled. Several inks were tested by varying the drier content, the drying history, and the intervals between impressions. Inks were also tested which were emulsified in conventional

and alcohol fountain solutions. All of these tests proved unsuccessful in producing gloss, dull, color or density ghosting.

Further steps were taken to obtain a ghosting ink. Anthony Gimbrone, a former ghosting researcher, GATF and three ink companies were contacted to employ their assistance. Finally, a black quickset ink was obtained that ghosted. This ink when tested at RIT was found to produce a very obvious colored ghost. Dull, gloss or density ghosts have not been obtained. With this information in mind, it will now be emphasized that the ghosting phenomenon studied throughout the duration of this research has been colored ghosting. This colored ghosting causes an obvious blue-green appearance in the affected areas, versus the plain rich black in the unaffected areas. The actual cause has not been substantiated, however, it is probably a phase separation, causing blue toner pigments and solvent to migrate to the film surface.

Measurement of Colored Ghosts

A number of methods were employed to measure the difference between affected and unaffected areas. The methods employed were:

1. Glossmeter
2. Optical Densitometer

3. The surface tension was measured via measuring the contact angle of linseed oil.
4. Colorimeter
5. Spectrophotometer

Numbers 1 - 4 were all unsuccessful in measuring any significant difference. It was hoped that a colorimeter could be used for convenience sake. The colorimeter has the advantage of computing a delta E value which is the sum total difference between the two samples. Unfortunately, it was found that the instrument exhibited a substantial amount of variability when measuring a black ink.

At an early stage an attempt was made to use a spectrophotometer to measure the samples. The Bausch and Lomb Model #505 spectrophotometer was used. At its normal sensitivity settings no intelligible differences were found between samples. The normal setting is 0 - 1 absorbance. It was found that at an absorbance of 1 - 2 photometric range (which is the instrument's highest sensitivity setting) a distinct difference existed between the two spectrophotometric curves. It was also found that the instrument at this high sensitivity exhibited variability and sporadic behavior. This could be due to slight changes in voltage, the extended age of the machine, and a number of other factors.

Finally, another spectrophotometer was tried and judged adequate for the experiment. The instrument is the Shimadzu Digital Double Beam Scanning Spectrophotometer UV-210. The machine has a wide range of sensitivity. It can give a digital read out of one wave length within a tolerance of one nanometer wide or it can print out the entire spectrophotometric curve of a sample from 190 to 900 nanometers.

For sample measurement, the highest sensitivity of 0 - 10% absorbency was chosen. At such a high sensitivity the curve would be out of the range of the printer, therefore the zero adjust was manipulated to put our curve approximately in the middle of the chart. With this in mind, the Y axis reflection values were ignored. It was decided to plot a curve from 200 to 800 nM. Figure 9 is a typical printout we received. These two curves are from the same sample. Curve A indicates where the sample was made to ghost. Curve B is the unghosted area. The ghosted area shows higher reflection throughout the entire range.

Now the problem remains; how to quantify a curve that is made up of an unlimited number of points? Ideally it was desired to come up with one value for the curve A and one for curve B. Four hundred nanometers was chosen as a suitable position from which to take readings. Now it was merely a matter of setting the spectrophotometer to digitally print out the reflection at 400 nM. Five

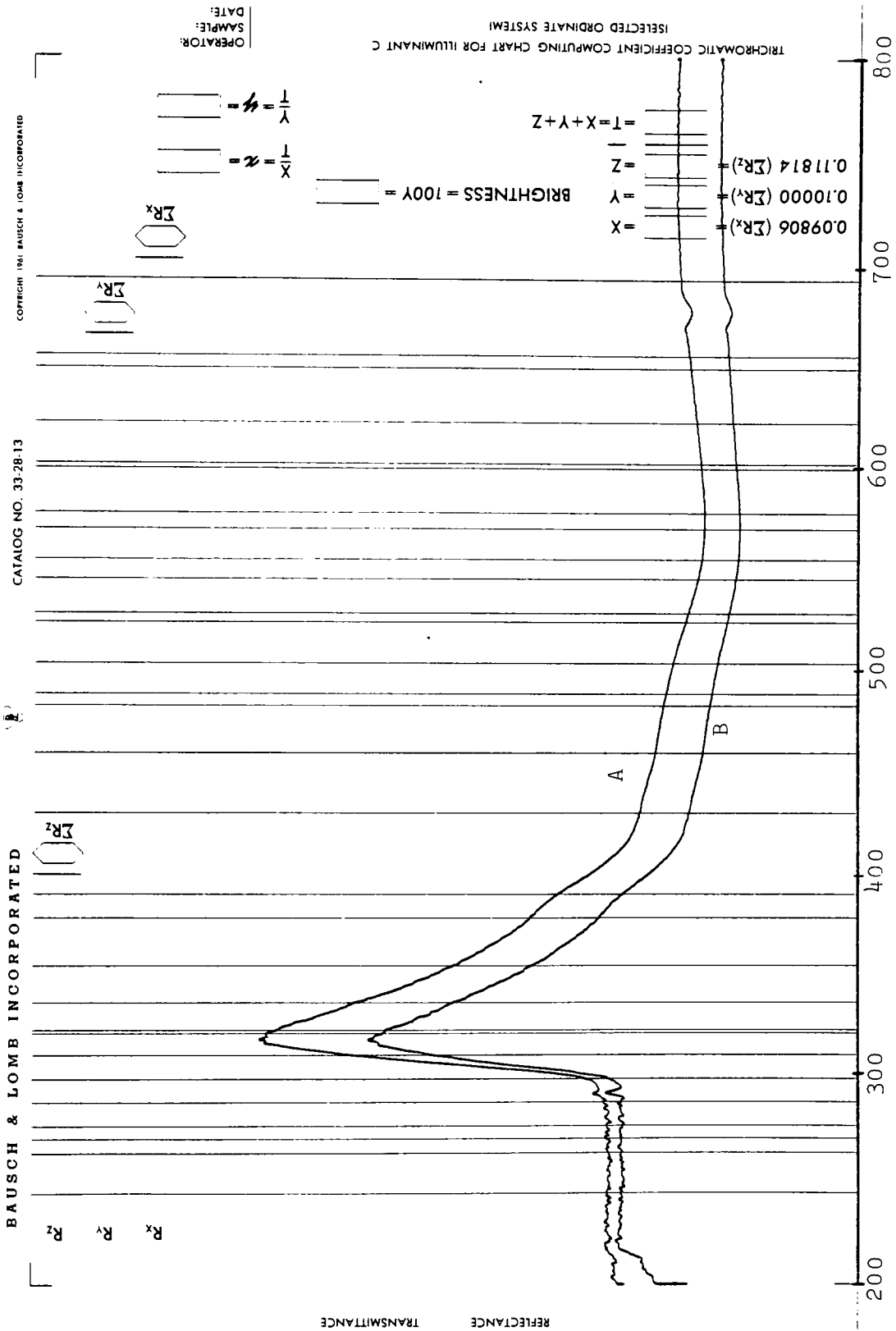


Figure 9: Spectrophotometric curve of both the affected(A) and unaffected(B) areas

readings were taken per sample, because when the machine is at a fixed setting (400 nm) it will fluctuate slightly

It should be mentioned that the author is well aware that the spectrophotometer has been used in a slightly unorthodox fashion. It has been used only as a tool to find some measurable difference between samples. The visual appearance of the affected area versus the unaffected area is quite perceptible. The author tried optical, physical and had contemplated chemical methods of quantitatively measuring the differences. The means were unimportant, only that they correlated with the actual phenomenon.

In addition to the measurement done by the spectrophotometer, it was felt that subjective tests needed to be performed by observers. Observers were used to rank samples from lowest ghosting to highest. Details of the tests can be found in the forthcoming section entitled "Ghosting Experiment." This subjective optical evaluation proved to be the most useful way of determining ghosting differences. The objective of the thesis was to determine if there are changes in the coating, would it affect the ghosting. The eye of the observers proved to be a valuable tool with which to compare and rate the amount of ghosting.

The observers were asked to rate 5 sets of ghosted samples from least ghosting to most. Each individual viewed the samples under a standard light source which was a FZ0T1Z Sylvania, day light fluorescent bulb mounted in a portable viewing booth. Figure 10 illustrates the layout of the viewing booth. Each observer was first shown examples of high and low ghosting. This formed the criteria for their judgments.

The procedure was to lay before the observers a 16%, 12% and 8% ghosted sample. They would then rank them from lowest ghosting to highest.

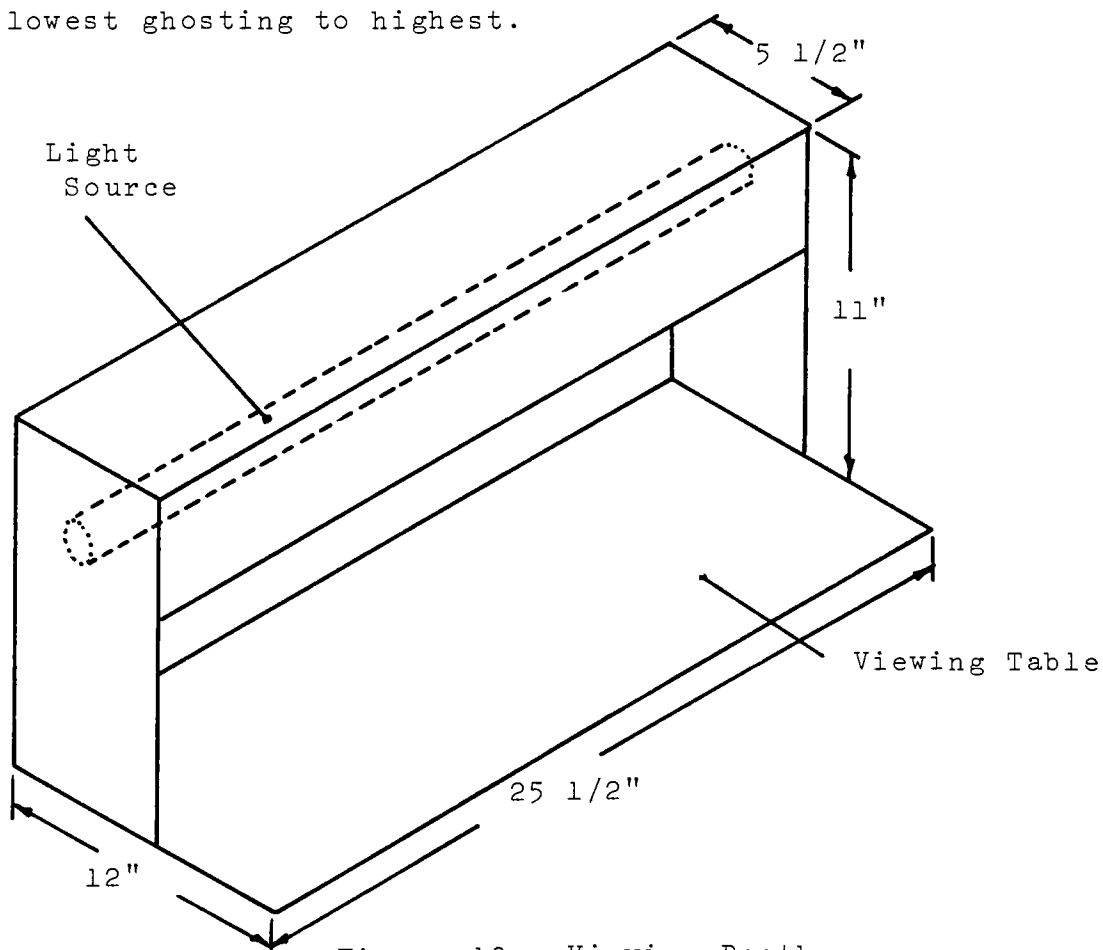


Figure 10: Viewing Booth

Method For Making Coating Samples

In order to keep the experimentation as free from variability as possible, the same base stock was used for all samples. Not only did the base stock remain the same, but all sheets were taken from one single ream. This eliminates the possibility of variable moisture content, stock pH, etc.

Coatings were mixed with the appropriate concentration of ingredients. Mixing and agitation were kept consistent. Coatings were applied with a wire wound coating rod (#20) which kept the thickness of coating at a constant. Samples were dried immediately with a hand dryer and then placed in a print drier for one minute. Table III indicates the full range of coatings that were made and tested. From previous tests it was known that both starch and latex cause the same general reaction to take place when added to the coating formulation; that is, both will decrease absorption and porosity. For this reason, only the latex ingredient will be manipulated.

The base stock was a 47.25 lb. book paper. After coating, the average basis weight was 62.4 lbs. The range was 58.67 lbs. to 64.9 lbs. with no trend as to the latex level. The paper was coated on one side with its coating making up 24.2% of the weight. Half the sheets were calendered by passing the sheets through the Noble and Wood sheet machine four times each.

Table II: Coating Formulations

Latex Level	2%	4%	8%	12%	16%
Clay Slurry @50% Solids	39.2g	38.4g	36.8g	35.2g	33.6g
Latex @50% Solids	.8g	1.6g	3.2g	4.8g	6.4g
Total Weight of Coating Mixture	40.0g	40.0g	40.0g	40.0g	40.0g

Ghosting Experiment

The method of obtaining ghosting samples was to print a film of ink on a slip of coated paper and overlay it with various samples to evaluate the effect they have on the drying ink. Figure II illustrates the sample orientation.

This orientation will yield three different areas each dried under different conditions.

Area A: The wet film overlaid by the coated sample plus ink.

Area B: The wet ink film covered only by the coated sample.

Area C: The wet ink film exposed to air. This area represents maximum permeability.

This provides three treatments, each of which have been dried under different conditions ranging from maximum

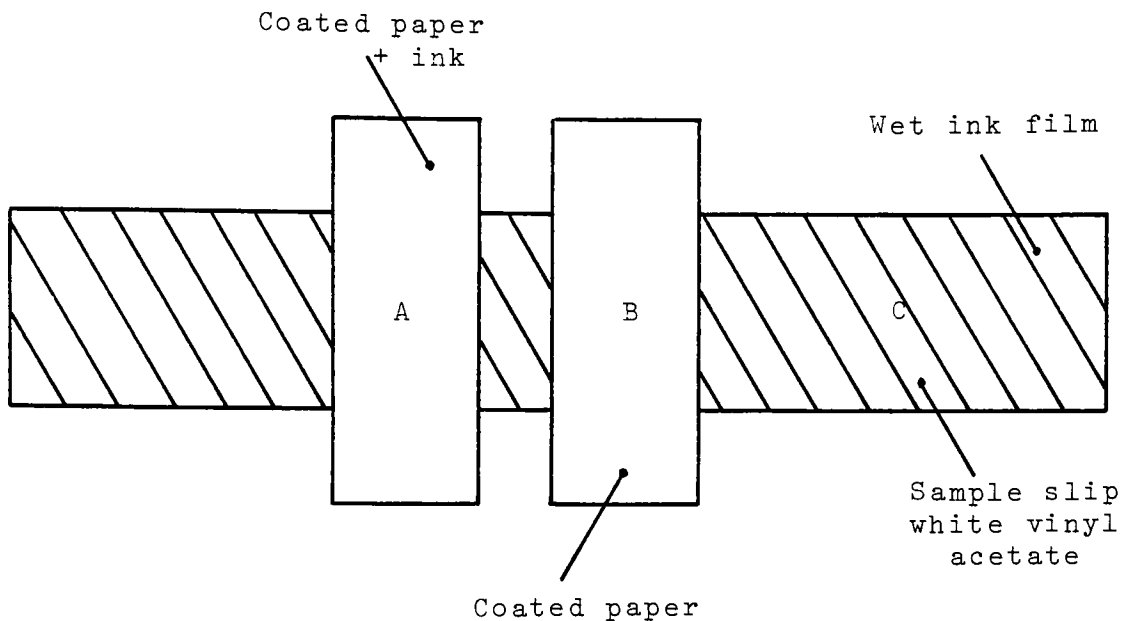


Figure 11. Overlay orientation

impermeability to maximum permeability. It must be kept in mind that in actuality only areas A and B would appear on a printed job because drying ink would only be in contact with paper plus ink or just paper. Area C will be included on all samples for control purposes. Measurement of the degree of ghosting which has taken place will be determined by the method used in the previous section.

It was found that ghosting was not produced by laying one film of ink down on the sample slip, however, if printed on acetate or the paper slip was printed twice, then ghosting occurred. This is explained by the fact that when only printed once, the volatile by-products and

solvents will escape through the bottom of the ink film. When one film is printed and allowed to dry, and then a wet film of ink is printed over it, the dry film acts as a impermeable barrier which will not allow the volatiles to gas off through the sheet. Consequently, the volatiles migrate to the surface of the wet ink. Depending on which treatment the volatiles encounter (A, B or C), they will be selectively retained at the surface in proportion to the permeability of the barrier.

The IGT Printability Tester was used in conjunction with the Wesvaco disk to make all sample slips. The Wesvaco disk is a device which meters out exactly 15 microns of ink. This then is split to the sample slip leaving approximately 7.5 microns of ink. The same substrate was always used for the sample slip which insured the consistency of the ink film thickness. Although the actual ink film thickness produced by offset lithography fall between .5 and 2 microns, it is believed that the experimental data (although exaggerated) and the conclusions, correlate with actual printing conditions.

Experimental procedure:

1. Print a number of slips which have a coating containing 8% latex.
2. Let slips dry exactly 24 hours.
3. Print a statistically acceptable number of samples.

Ink was printed on - 4 mil white vinyl, permanent adhesive, made by the Central Decal Company.

4. Place the following substrates on the wet ink film of each sample slip.

A. 1" x 1" square piece of paper plus ink obtained from step #1

B. 1" x 1" square piece of plain coated paper (8% latex).

The remainder of the slip will be exposed to air drying.

5. Allow sample slips to dry for 48 hours.

6. Disregard overlays and measure immediately.

This test was then repeated for all of the coating combinations in Table III.

The ink used for this experiment was a black quick-set drying oil ink. The following is a list of its components:

Vehicle

3% Linseed varnish

28% synthetic alkyd varnish

Dryer

6% cobalt

Solvent

Unknown % Magi solvent

Pigment

Carbon black

Blue toner pigment

CHAPTER V

RESULTS

The forthcoming pages contain the data which was obtained for the various tests.

Three experiments were performed to measure ghosting. One of the tests is concerned with calendered samples while the remaining two used uncalendered samples. .

Ghosting Experiment I - Calendered

This experiment was conducted using both subjective and objective tests. The first test which was subjective employed the assistance of seven observers. Table III contains the data collected for the subjective observer evaluation.

Early in the research, it was found that 2 and 4 percent latex samples, when printed, picked excessively. For this reason, only 8, 12, and 16 percent latex levels were used in all ghosting experiments.

Results:

8.57% of the observers chose 16% as the highest level of ghosting.

34.28% of the observers chose 12% as the medium ghosting level.

17.14% of the observers chose 8% as the lowest level

of ghosting.

The results indicate that the observers were unable to distinguish any difference between the samples.

Table III: Ghosting I - Subjective Data

	<u>Degree of Ghosting</u>	<u>Latex Level</u>
Observer 1	High ghosting	8,8,12,8,16
	Medium ghosting	16,12,16,12,12
	Low ghosting	12,16,8,16,8
Observer 2	High ghosting	8,8,8,16,12
	Medium ghosting	12,12,12,12,8
	Low ghosting	16,16,16,8,16
Observer 3	High ghosting	12,12,12,12,12
	Medium ghosting	16,8,16,16,8
	Low ghosting	8,16,8,8,16
Observer 4	High ghosting	12,8,12,12,8
	Medium ghosting	8,16,8,16,12
	Low ghosting	16,12,16,8,16
Observer 5	High ghosting	8,12,8,8,12
	Medium ghosting	12,8,16,12,16
	Low ghosting	16,16,12,16,8
Observer 6	High ghosting	12,12,12,16,8
	Medium ghosting	8,16,8,12,12
	Low ghosting	16,8,16,8,16
Observer 7	High ghosting	12,8,12,12,8
	Medium ghosting	8,12,16,16,16
	Low ghosting	16,16,8,8,12

The samples were then evaluated using the spectrophotometer. Table IV lists the data collected from this experiment.

Table IV: Ghosting I - Objective Data
Spectrophotometric Analysis

Overlay 8%-Calendered		Overlay 12%-Calendered		Overlay 16%-Calendered	
Air Dried Ink+Paper		Air Dried Ink+Paper		Air Dried Ink+Paper	
*					
2.97	3.18	3.07	3.11	2.9	2.92
3.11	3.05	2.68	3.24	2.84	3.29
2.81	3.10	3.12	3.18	2.89	3.35
3.09	2.99	2.95	3.06	2.90	3.24
3.10	3.15	2.88	3.15	3.14	3.54
3.05	2.98	3.14	3.11	3.07	3.20
3.07	2.79	3.09	3.02	3.04	3.27
3.07	2.76	3.08	3.07	2.88	3.19
3.0	2.95	3.11	3.34	2.9	3.48
2.97	2.96	3.34	3.04	3.11	3.14
3.06	3.20	2.81	2.95	3.04	3.20
3.25	3.12	3.06	3.16	3.08	2.78
3.10	3.27		3.22	2.96	2.96
3.04	3.23		3.09	3.11	2.93
	2.73		3.17	3.18	2.93
	2.76		3.10	3.01	2.78
	3.10		3.04		3.76
	2.87		3.54		3.45
	2.92		3.24		2.88
	2.93		3.01		3.89
	3.0		3.11		3.31
	3.16		3.13		3.89
	3.12		3.06		3.17
	3.28		3.19		3.74
	3.02				3.96
	2.72				3.55
	3.0				3.46
	3.35				3.13
	2.90				3.18
					3.0
					3.45

* All readings are in percent reflectance

Results:

Table V: Spectrophotometric Results

	Air Dried				Ghost			
	\bar{X} % Reflect- ance	σ	σ^2	N	\bar{X} % Reflect- ance	σ	σ^2	N
8% Latex	3.049	.0977	.0095	14	3.020	.1730	.0300	29
12% Latex	3.049	.1836	.033	13	3.138	.1222	.0149	24
16% Latex	3.003	.1078	.01162	16	3.29	.327	.107	31

σ = Standard deviation

σ^2 = Variance

N = Population size

Ghosting, which is represented by reflectance, does appear to increase as the latex level increases. The standard deviation and range at each level of latex appears to be excessive.

The spectrophotometric analysis, although offered some interesting data, did not entirely agree with the visual examination. The visual observation examinations were deemed to be entirely sufficient to determine different levels of ghosting, when differences existed. For this reason, no further tests were performed on the spectrophotometer.

Ghosting Experiment II: Uncalendered

For this experiment 5 observers were employed to evaluate samples. The method of evaluation has previously been mentioned in the Chapter entitled Methodology. Table VI lists the data collected.

Table VI: Ghosting II - Subjective Data

	<u>Degree of Ghosting</u>	<u>Latex Level</u>
Observer 1	High ghosting	16,16,12,16,16
	Medium ghosting	8,12,16,8,12
	Low ghosting	12,8,8,12,8
Observer 2	High ghosting	16,16,16,16,12
	Medium ghosting	12,12,12,12,16
	Low ghosting	8,8,8,8,8
Observer 3	High ghosting	16,8,8,12,12
	Medium ghosting	12,16,12,16,8
	Low ghosting	8,12,16,8,16
Observer 4	High ghosting	16,16,16,16,12
	Medium ghosting	12,12,8,8,16
	Low ghosting	8,8,12,12,8
Observer 5	High ghosting	16,12,16,16,16
		12,16,16,16,16
	Medium ghosting	12,12,8,16,12
		16,12,12,12,12
	Low ghosting	8,8,12,8,8
		8,8,8,8,8

Results:

68% of the observers chose 16% latex as the highest level of ghosting.

54% of the observers chose 12% as the medium ghosting level.

70% of the observers chose 8% latex as the lowest ghosting level.

If the results are divided into two groups and the medium 12% is counted for either the high or low group when it appears there, the results look like this:

92% of the observers chose 12%-16% as the highest ghosting level.

92% of the observers chose 8%-12% as the lowest ghosting level.

Ghosting Experiment III: Uncalendered

It was felt that in order to firmly establish conclusions it was necessary to perform another test identical to "Ghosting Experiment II." This was done to assure proper replication of the experiment. Therefore, all procedures for this experiment are identical to those of Ghosting Experiment II. Table VII contains the results of the experiment.

Table VII: Ghosting III - Subjective Data

	<u>Degree of Ghosting</u>	<u>Latex Level</u>
Observer 1	High ghosting	16,8,16,16,8
	Medium ghosting	8,16,8,12,12
	Low ghosting	12,12,12,8,16
Observer 2	High ghosting	12,16,16,16,16
	Medium ghosting	16,12,12,12,8
	Low ghosting	8,8,8,8,12
Observer 3	High ghosting	16,16,16,12,16
	Medium ghosting	12,12,12,8,12
	Low ghosting	8,8,8,16,8

Observer 4	High ghosting	16,16,16,12,16
	Medium ghosting	12,12,12,16,12
	Low ghosting	8,8,8,8,8
Observer 5	High ghosting	16,8,16,16,16
	Medium ghosting	8,12,12,8,8
	Low ghosting	12,16,8,12,12
Observer 6	High ghosting	12,16,16,16,12
	Medium ghosting	16,12,8,12,16
	Low ghosting	8,8,12,8,8

Results:

78.3% of the observers chose 16% latex level as yielding the highest amount of ghosting.

65% of the observers chose 8% latex levels as yielding the lowest amount of ghosting.

91.6% of the observers chose from 8-12% latex levels as ghosting the least.

90% of the observers chose from 12-16% latex levels as ghosting the most.

Ink Holdout Test:

Ink holdout is defined in this research as the amount of vehicle held out on the surface of the paper. The lower the ink holdout the greater will be the drainage of vehicle into the stock, which will in turn affect gloss. For this reason, gloss measurements were collected. Table VIII indicates the data collected for the ink holdout experiment. The information in Table VIII pertains to uncalendered sheets. No difference in gloss was found on the calendered sheets.

Table VIII: Ink Holdout Data

% Latex	Gloss*	Average
8	75.5, 62.5, 64.0, 65.0 63.5, 65.0, 66.0, 66.0	65.56
12	72.5, 71.0, 72.0, 73.0 65.0, 70.0, 77.5, 71.0	71.44
16	74.5, 79.0, 77.0, 75.0 71.0, 70.0, 73.5, 72.5	74.06

* The information was collected using the Photovolt Corporation Gloss Meter Model #610. The meter was standardized using a Hunter Lab D16-1785 white plaque. The meter has a 20° light source.

Absorption Test

The K+N testing ink was used to determine the relative absorbencies of the coated samples. The ink was applied for two minutes and then wiped clean. The samples were then measured for density using a Mcbeth Optical Densitometer Model #TR927. The higher the density the greater is the absorbence of the sample. The following is the data collected for this experiment.

Table IX: Absorption Test-Data

Calendered

Sample	Density at 8% Latex	Density at 12% Latex	Density at 16% Latex
1	.35	.25	.20
2	.35	.23	.22
3	.36	.25	.22
Average	.35	.24	.21

Uncalendered

Sample	Density at 8% Latex	Density at 12% Latex	Density at 16% Latex
1	.44	.35	.32
2	.43	.36	.33
3	.45	.36	.32
Average	.44	.36	.32

Ink Film Thickness Test

Papers exhibiting different surface characteristics can accept ink differently. For this reason it was believed that a test needed to be performed to determine the ink transfer qualities of the coated samples at the various latex levels. By determining that all the samples were receiving the same amount of ink, it was possible to eliminate the notion that the difference in ghosting was caused by the difference in ink film thickness. Table X contains the test results.

The test was performed using the IGT inking unit, the IGT printability tester, and the Mettler Analytical Balance. The balance is capable of measuring to the nearest 10 thousands of a gram. An IGT disk was supplied with a specific amount of ink and then weighed. The ink was then transferred to the sample. The disk was then reweighed to determine the amount of ink the sample received.

Table X: Ink Film Thickness Test Data

% Latex	Disc Weight/Gr.	Disc+Ink Weight/Gr.	Disc After Transfer/Gr.	Average Transfer	Grand Avg.
8%	84.5575	84.6118	84.5869	46%	45%
8%	84.5569	84.6197	84.5899	47%	
8%	84.5547	84.6057	84.5843	42%	
12%	84.5447	84.6108	84.5863	37%	43%
12%	84.5555	84.6103	84.5856	45%	
12%	84.5554	84.6063	84.5820	47%	
16%	84.5556	84.6109	84.5850	47%	47%
16%	84.5558	84.6116	84.5850	47%	
16%	84.5540	84.6073	84.5820	47%	

Results:

As indicated by the data, no trend appears to be apparent. All figures are relatively confined to a small area. Based on this data the assumption has been made that all samples are receiving the same amount of ink and would not contribute to any differences which took place in the ghosting experiment.

Porosity Test:

Porosity tests were conducted on the sample coated sheets to determine the relative porosity the sheet possessed at the various latex levels.

The tests were conducted using the Sheffield Porosity Test Model D60080005. This instrument measures the amount of air forced through the sheet at a constant pressure. The units are measured in Sheffield units. The tests were conducted using a 3/4 inch orifice. The higher the number, the greater the porosity. The following is the test data.

Table XI: Porosity Data

	Latex Content of Coating	Porosity	Average Porosity
Uncalendered	8	25,22,25,27,26	25
	12	19,21,18,22,20	20
	16	35,33,38,33,34	34.6
Calendered	8	6,6,7,6,5	6
	12	8,7,7,7,8	7.4
	16	26,27,27,26,25	26.2

CHAPTER VI

CONCLUSIONS

The tests that were conducted can be broken down into three basic groups. The first group of tests were those which were concerned with the actual phenomenon of ghosting. The second group of tests could be classified as those which verified the actual physical state of the sample (ie. porosity, absorbency, etc.). The third and last group, were tests which confirmed the validity of the ghosting experiments.

The major portion of this thesis was devoted to the ghosting experimentation. These tests were performed to determine whether to accept or reject the null hypothesis. The following is a list of conclusions pertaining specifically to the ghosting experimentation.

Note: These conclusions are based on the specific paper-coating-ink system used for this research.

1. When a film of fresh ink was overlayed by printed coated uncalendered paper, ranging from 8% latex to 16% latex, the greatest ghosting level was found to correspond to the highest latex level. Likewise, the lowest level of ghosting corresponded to the lowest level of latex. Restated:

Increased latex concentration in uncalendered coatings, will increase ghosting of the samples.

2. No significant difference in ghosting was found at the different latex levels, with calendered samples. Restated:

Increased latex content in calendered coatings will not increase the ghosting of the samples.

3. Ghosting will increase as absorption decreases.
4. Ghosting will increase, until reaching a transition absorption point, and will not increase any further, but remain constant.
5. Porosity appears to play no significant role in the ghosting phenomenon.
6. Ghosting occurs in proportion with the degree of ink holdout.
7. Ink films covered by plain coated paper show no difference in appearance at increasing latex levels, whether calendered or uncalendered.

As stated, the second type of testing was conducted to determine the physical properties of the samples. These tests include the absorption test, the porosity test, and the gloss test, and the following conclusions pertain to these specific tests.

1. Increasing the coating latex content will decrease absorption.
2. Increasing the coating latex content will decrease porosity to above 12% latex. Above 12% will increase porosity.
3. Gloss of printed samples will increase as the latex content in the coating on which they were printed, increases.

The third group of tests were needed to establish the validity of the ghosting experiments. These tests include coating weight determination, and the test for determining

consistent ink film thickness.

1. No significant difference was found in coating weight for the various levels of latex.
2. No significant difference was found in ink film thickness on the 8%, 12% and 16% coated samples.

At the onset of this research the question existed as to whether ghosting is constant or variable. What is meant by this is, does the level of ghosting in an area overlaid by paper plus ink stay in proportion with the amount of ghosting in an area overlaid by plain coated paper. Or, on the other hand, are both areas affected independently. Figure 12A illustrates graphically a situation where the areas are both affected in unison by the change in absorbency (constant ghosting). Figure 12B represents an independent reaction.

Through the various experimentation it was found that the area overlaid by coated paper was consistent in the amount it had been affected. This held true despite the latex level or whether or not it had been calendered. This would then indicate that ghosting is variable in nature as illustrated in figure 12B.

As previously stated, ghosting will increase as absorption decreases but will reach a level of constancy. More accurately, ghosting could be represented as in Figure 13. This illustrates the fact that once a certain

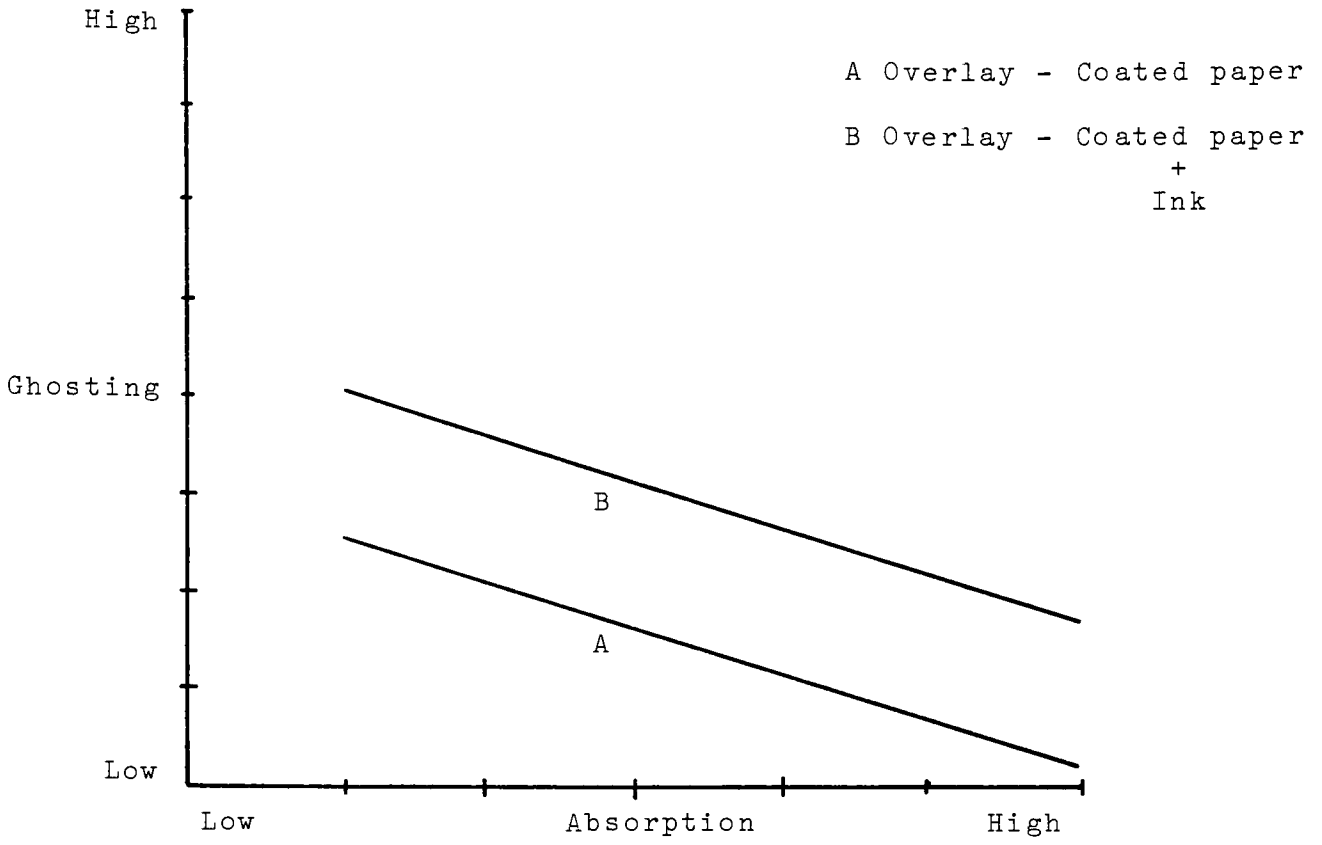


Figure 12A: Constant ghosting

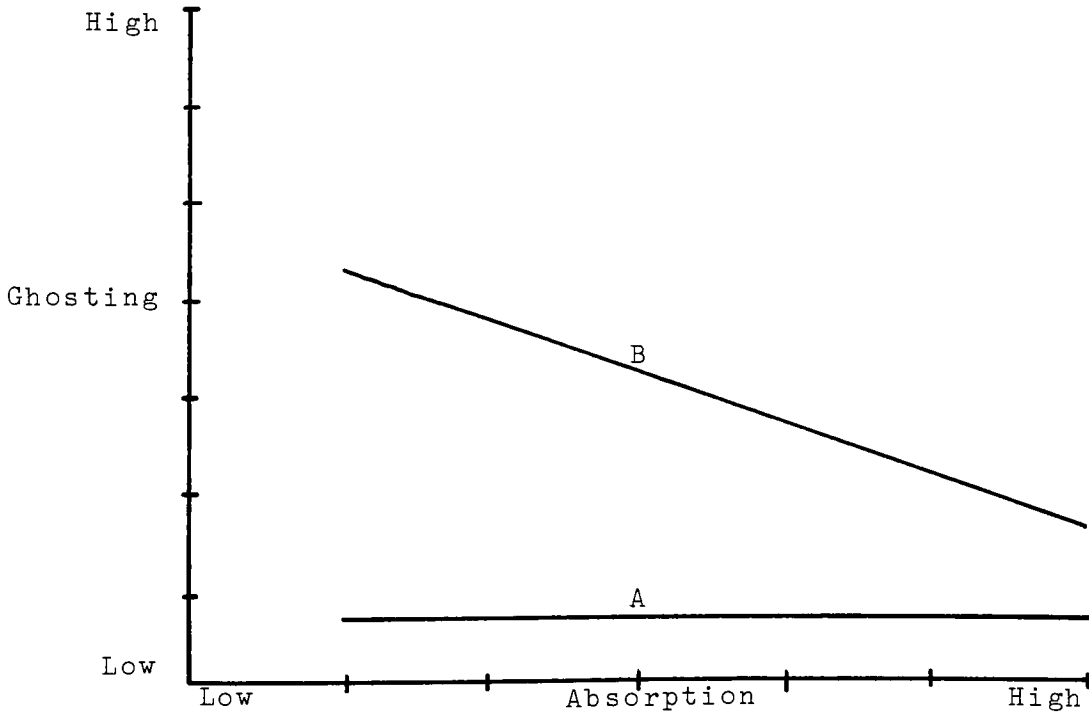


Figure 12B: Variable ghosting

low absorption level is reached (point X), it is non-absorbent enough to result in the maximum of ghosting. Despite the decreasing absorption the sample will not be affected any more than at point X.

Figure 13 simulates the situation encountered during this research. The uncalendered samples showed different ghosting at different latex levels. The calendered samples however, showed very little if any differences. The objective of this thesis was not to define at what level point X exists, but rather to merely substantiate its existence.

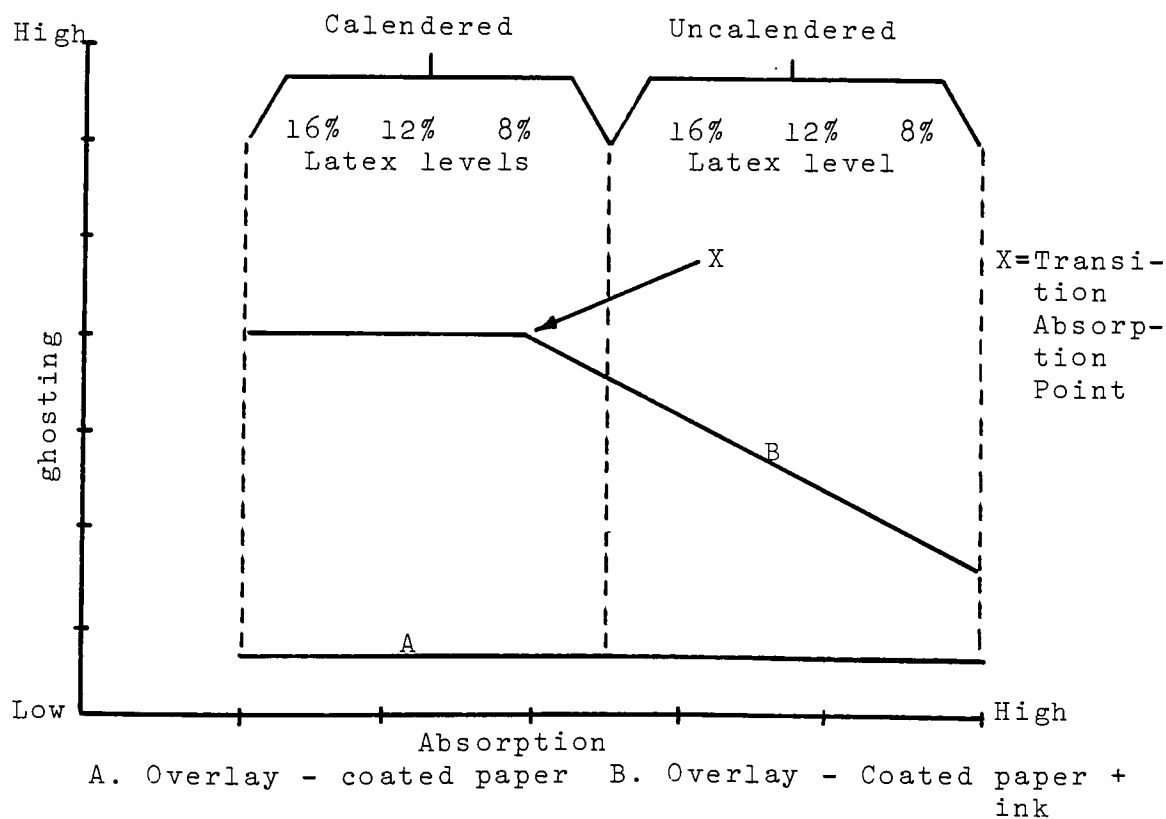


Figure 13: Ghosting model

CHAPTER VII

RECOMMENDATIONS FOR FUTURE RESEARCH

The objective of this thesis was to determine what affect that changing the coating constituent levels would have on the ghosting phenomenon. It is believed that conclusive evidence was found to prove that the coating formulation does indeed play a role in the degree of ghosting occurrence. There are however, some questions which remain unanswered and could possibly warrant further investigation.

One area which requires further research is the area of so called "transition absorption point." This thesis did not attempt to define at exactly what value this point would appear. However, the knowledge of its exact location could prove useful to determine which paper samples fall above this point and would be subject to maximum ghosting for a given ink.

In addition, it is felt that a better means should be developed for measuring colored ghosting. The spectrophotometric procedure used in this research was found not to be entirely sufficient for the needs of the research. Ideally a better method could be developed which can more successfully quantify the phenomenon.

CHAPTER VIII

LITERATURE REVIEW

Great effort has been expended to obtain all pertinent information on the subject of chemical ghosting. It was found that most information of any real value was found in reports and research projects by printing industry organizations. Hence, very little information was obtained from literature such as periodicals. Most of the literature in the periodicals dealt with the subject in a purely introductory fashion.

It was found that up until the 1960's no experimentation had been performed to gain any understanding of the ghosting mechanism. Initially work was done which was not associated with ghosting, but rather with ink drying. Paul Hartsuch of the Interchemical Corporation and who was also associated with the Graphic Arts Technical Foundation presented a paper at the 1960 Conference for the Technical Association for the Graphic Arts.⁵⁵ His research revealed that dried inks give off "volatile drying accelerators" which could influence the drying rate of an adjacent wet ink film. Work in this area was later continued by Chen in 1970 and Bock in 1972.^{56,57}

It was this work by Hartsuch which motivated GATF to undertake a series of ghosting research projects throughout the 60's and 70's. The greatest amount of research was done by Robert Bender who from 1965-69 did a three-part study on chemical ghosting.^{58,59,60} The major goals of his studies were to obtain information on how to prevent chemical ghosting, obtain information to improve ink gloss and utilize the information to synthesize new drying systems. His major strategy was to identify the chemical components in the volatiles emitted from the ink. He was successful in identifying 15 separate chemicals (See Appendix I).

In 1974 Anthony Gimbrone (GATF) completed a voluminous project which tested various inks, dryers, papers and time intervals between impressions, etc..⁶¹ Throughout all the literature Gimbrone's was the only work which actually mentions ghost measurement, and his was based on subjective evaluation. As late as 1980 GATF was still working on chemical ghosting with a paper written by David Gerson.⁶² His was not an experimental study but rather a literary paper based on the theory of ghosting.

Markuze did a lengthy study on the wetability of drying ink and the relationship it has on ghosting.⁶³ Dr. Markuze headed a staff which investigated ghosting.

They contributed their findings to the Ghosting Symposium held in November 1967 by IARIGAI.

In 1973 work was done by Schlapfer and Kung.⁶⁴ This work was completed after most of the major work had been done at GATF and cast a new light on the ghosting phenomenon. They revealed new findings regarding "phase separation" and set forth the proposal that ghosting is not necessarily caused by an adjacent ink film but rather is influenced by the permeability of the adjacent substrate. Their work, however, was taken no further than this basic proposal.

The list of reports mentioned in the previous paragraphs is not by any means the entire collection of literature obtained. The reports mentioned are however, those which yielded the greatest amount of information pertinent to our topic.

Two reports have been obtained from the SD Warren Company and the Mead Corporation.^{65,66} Both reports are introductory in nature, however they both contain an interesting section. Both companies state their position and policy regarding chemical ghosting. The following is Mead's policy.⁶⁷

It is the stated policy of the Customer Service Department of Mead Papers that under no circumstances nor with any evidence collected to date will we accept any responsibility for this

problem. Naturally we will consider any new evidence as it occurs.

No literature has been found which deals with paper coatings relationship to ghosting with the exception of a report written by Vidal⁶⁸ which considers the relationship between casein binder and the aldehydes formed during ink drying. Since the report is dealing with a coating constituent that we have not used, little emphasis has been placed on it.

A literature search regarding paper coatings has been conducted to better acquaint the author with the subject. Most information was derived from the book by Libby.⁶⁹ The book is in textbook form and deals with the fundamentals of paper coatings. Other sources of information have been publications by the Mead Corporation and the Westvaco Corporation.^{70,71}

FOOTNOTES

1. Robert Bender, "Gloss Ghosting - Chemical Study," T.A.G.A. 1967 Proceeding (1967), p. 191.
2. K. Schlapfer and P. Kung, "Investigation of Mechanism of Gloss Ghosting," IARIGAI Twelfth International Conference, Versailles (1973), p. 73.
3. Bender, Gloss Ghosting - Chemical Study, p. 196.
4. Ibid., p. 199.
5. David Gerson, "Gloss Ghosting," GATF Research Department - Reports of Progress (1980), p. 45.
6. Anthony V. Gimbrone, "Gloss Ghosting Study," GATF Research Department - Reports of Progress (1974), p. 189.
7. Schlapfer and Kung, Mechanism of Ghosting, p. 73.
8. Paul J. Hartsuch, "Drying of Overprint Ink Films," TAGA 1960 Proceedings (1960), p. 47.
9. Ibid., p. 47.
10. Ibid., p. 48.
11. Ralph F. Bock, "Accelerated and Retarded Drying of Lithographic Inks," GATF Research Department - Reports of Progress (1972), p. 204.
12. Bender, Gloss Ghosting - Chemical Study, p. 198.
13. Bock, Acceleration and Retardation of Drying Inks, p. 212.
14. Anon., "Ghosting Presents Serious Problems: 'Spooks in Print' Haunt Sheet Fed Printers," GATF Technical Service Report 3 (1970): p. 3.
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17. Ibid., p. 4.
18. Ibid., p. 4.
19. Schlapfer and Kung, Mechanism of Ghosting, p. 75.
20. Bender, Gloss Ghosting - Chemical Study, p. 198.
21. Gimbrone, Gloss Ghosting Study, p. 186.
22. Ibid., p. 186.
23. Bender, Gloss Ghosting - Chemical Study, p. 197.
24. Ibid., p. 198.
25. Schlapfer and Kung, Mechanism of Ghosting, p. 75.
26. Anon., "Chemical Ghosting of Printing Inks," Graphic Arts Bulletin 1 (1970), Mead Corp., Chillicothe, Ohio, p. 2.
27. Jane Vidal, "The Affect of Ghosting," Invest. Tec. Papel 5 16 (April, 1968), pp. 449-465.
28. Robert Bender, "Gloss Ghosting - Chemical Studies II," GATF Research Department - Reports of Progress (1967), p. 23.
29. Bender, Gloss Ghosting - Chemical Study, p. 192.
30. Bender, Gloss Ghosting - Chemical Studies II, p. 24.
31. Ibid., p. 27.
32. Ibid., p. 30.
33. Gimbrone, Gloss Ghosting Study, p. 189.
34. Schlapfer and Kung, Mechanism of Ghosting, p. 76.
35. Gimbrone, Gloss Ghosting Study, p. 189.
36. Schlapfer and Kung, Mechanism of Ghosting, p. 76.
37. Ibid., p. 76
38. Anon., Papermaking (Mead Corp., 1975), p. 41.

39. Earl Libby, Pulp and Paper Science and Technology, (New York: McGraw-Hill, 1962), p. 307.
40. Ibid., p. 308.
41. Mead, Papermaking, p. 44.
42. Ibid., p. 44.
43. Ibid., p. 46.
44. Libby, Pulp and Paper Science, p. 297.
45. Mead, Papermaking, p. 45.
46. Ibid., p. 45.
47. Libby, Pulp and Paper Science, p. 298.
48. Mead, Papermaking, p. 45.
49. Libby, Pulp and Paper Science, p. 304.
50. Ibid., p. 304.
51. Mead, Papermaking, p. 46.
52. Ibid., p. 46.
53. Ibid., p. 47.
54. GATF, Ghosting Presents Serious Problems, pp. 1-6.
55. Hartsuch, Drying of Overprint Ink Films, pp. 47-54
56. Bock, Acceleration and Retardation of Drying Inks, pp. 199-215.
57. J.H. Chen, "Accelerated and Retarded Drying of Lithographic Inks II," GATF Research Department - Reports of Progress 1970 (1971) pp. 247-267.
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59. Bender, Gloss Ghosting - Chemical Studies II, pp. 23-58.
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British Ink Maker, Vol. II, No. 2 (1969), pp. 101-106.
64. Schlapfer and Kung, Mechanism of Ghosting, pp. 73-78.
65. SD Warren, Spooks in Print, pp. 1-15.
66. Mead, Chemical Ghosting of Printing Inks, pp. 1-4.
67. Ibid., p. 1-4.
68. Vidal, The Affect of Ghosting, pp. 449-465.
69. Libby, Pulp and Paper Science, pp. 273-319.
70. Mead, Papermaking, pp. 41-53.
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APPENDICES

APPENDIX I

THE ORGANIC VOLATILE BY-PRODUCTS IDENTIFIED
(LISTED BY ORGANIC CLASS AND PERTINENT PHYSICAL DATA)

<u>Common Name</u>	<u>Formal Name</u>	<u>Number of Carbons</u>	<u>Physical State</u>	<u>Molecular Weight</u>
^O aldehydes (-C-H)	ethanal	2	colorless liquid	44.05
propionaldehyde	propanal	3	colorless liquid	58.08
butyraldehyde	butanal	4	colorless liquid	72.10
valeraldehyde	pentanal	5	liquid	86.13
caproaldehyde	hexanal	6	colorless liquid	100.16
^O <u>Ketones (-C-)</u>				
acetone (DMK)	2-propanone	3	colorless liquid	58.08
methyl ethyl ketone (MEK)	2-butanone	4	colorless liquid	72.11
diethyl ketone (DEK)	3-pentanone	5	colorless liquid	86.13
^{OH} <u>Alcohols (-C-H)</u>				
normal butanol	1-butanol	4	colorless liquid	74.12
normal pentanol	1-pentanol	5	colorless liquid	88.15

Aliphatic hydrocarbons

propane	propane	3	colorless gas 44.09
butane	butane	4	colorless gas 58.12
pentane	pentane	5	colorless liquid 72.15

Aromatic hydrocarbons

benzene	benzene	6	colorless rhombohedral crystals or liquid 78.11
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Epoxides

ethylene oxide	2-epoxyethane	2	colorless gas or liquid 44.04
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R. Bender (1967)

APPENDIX II

SIMULATED GHOSTING SAMPLE

Ghosted Area -



Unghosted Area -

A simulated ghost is used here due to the fact that the actual colored ghosting effect diminishes over a period of time.