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## To determine the drying rate and the rewettability characteristics of water based flexographic news inks

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TO DETERMINE THE DRYING RATE AND THE REWETTABILITY  
CHARACTERISTICS OF WATER BASED FLEXOGRAPHIC NEWS INKS

by

Parthasarathy Varadarajan

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

April, 1990

Thesis Advisor : Chester Daniels

Certificate of Approval -- Master's Thesis  
School of Printing Management and Sciences  
Rochester Institute of Technology  
Rochester, New York

CERTIFICATE OF APPROVAL

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MASTER'S THESIS

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This is to certify that the Master's Thesis of

Parthasarathy Varadarajan

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has been approved by the Thesis Committee as satisfactory  
for the thesis requirement for the Master of Science  
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## ABSTRACT

A major problem in the printing of newsprint by flexography with water-based inks is the filling-in of halftones. Drying of the ink and rewettability, the ability of the fresh ink to wet the dried ink, appear to be primary in the understanding of the filling-in problems. Quantification and qualification of critical factors are essential in resolving this problem. In this study black water based flexographic news inks from different manufacturers were compared in terms of their drying and rewettability characteristics. The change in weight with time and contact angle measurements are the response parameters considered.

Proper care has been exercised to maintain constancy of parameters while conducting the experiments. Four samples of black ink were analyzed in this study.

The critical balance-weight differential-gravimetric method was adopted to determine the drying rates and the sessile drop method was used for finding the contact angle.

This study has yielded information which will enable a better understanding of the drying properties of the inks. More important, the contact angle will serve as the determinant of the fresh ink's ability to wet the dry ink.

## CHAPTER I

### INTRODUCTION

In August of 1977 the United States Congress amended the Clean Air Act and in doing so created panic in all industries that evaporate organic solvent into the atmosphere. The industry was faced with oppressive installation and operational costs for equipment to either burn or capture solvent. The alternative was to replace solvent with water.

Apart from being the most economically feasible answer to the air pollution problem, flexography using water-based inks makes it possible to produce prints with such performance advantages as: outstanding rub resistance, no strike-through, a reduction in fire hazard and the use of light-weight stocks without the loss of quality.<sup>1</sup>

With all these advantages flexographic water based inks is yet to be fully accepted. The major criticism by newspaper personnel is "plate plugging". Plugging occurs when dried ink or bits of loose paper fiber build up in areas between the dots on the plate. This dictates proper understanding of the drying characteristics of the ink.

Another important property of ink which demands equal attention is rewettability. Good rewettability means that when

fresh ink is re-introduced, the new ink will rewet the existing ink on the plate. If the ink on the plate is not rewet properly with fresh ink, the ink will build-up on the plate, rather than self clean and will plug the crevices between the dots printing in the non-image area much like scumming in lithography.

An exhaustive literature search reveals that at this time there are no means of characterizing the response variables suggested as being critical for plugging or filling-in of water-based flexographic inks. Techniques such as drying rate and contact-angle determination were adapted from areas of chemistry and ink technology.

Using a critical balance and an external heat source, drying studies were conducted in the laboratory. The sessile-drop method was used to understand the rewettability property of the ink by studying the contact angle measurements of ink on a film of the dried ink.

## FOOTNOTES FOR CHAPTER I

<sup>1</sup>

Cser, Frank "Water-Based News Inks Are Becoming A Commercial Reality," Flexo, September 1984, p. 38.

## CHAPTER II

### THEORETICAL BASIS

#### Background

In a recent survey, of users of the flexographic process, conducted by Feeney<sup>1</sup> it was observed that 62% of the participants were using Water Based inks and printing on newsprint. This clearly shows flexography's impact on the newspaper industry.

It is expected that by the middle of 1990 there will be at least 30 installations printing newspaper, Sunday comics, comic books, telephone directories and ad inserts via publication flexo. The inks used in the process described above are 100 percent water based. In most cases the printed product is bright, clean and does not rub-off on the reader's hand. Inks are supplied at 20-25 seconds, #2 Zahn cup, viscosity and cut with 25-30 percent water to 18-20 percent #2 shell cup.

Although the industry has achieved great strides in successfully implementing the technique, some problem areas are still being encountered. This explains why 52 percent of the participants in the Feeney<sup>2</sup> study were not satisfied with the available technology.

Halftone fill-in or plate plugging has been flexographic water based inks's most serious ink problem. With press speeds approaching 4000 feet per minute having to stop in between runs can prove to be extremely expensive. For water based flexographic inks to be fully accepted by printers, especially publication flexography, it is imperative that this problem be reduced or minimized-if not eliminated. The ink of the future should be formulated so as to tolerate reasonable amount of waste ink, paper dust and even cleaning solutions. Improvements in the print quality demands a lot of attention, study and research.

Another problem, second impression set-off, though minimized currently with the aid of enhanced drying and additional rollers, still persists. Second impression set-off occurs when ink from the first side printing of the web begins to build up on the second impression cylinder. However, if the ink's drying rate is drastically increased, it may lead to premature drying on the plate, or worse, the drying in the anilox cells. This calls for formulating inks with improved rewettability - i.e., an ink which will completely rewet itself. The difficult task for the ink maker is to balance drying and rewettability without sacrificing rub-off properties.

An important aspect which goes in hand with rewettability is press clean-up. What good is an ink which cannot be cleaned off the press at the end of the run? Ceramic anilox rolls, due to their uneven surface, have proven to be a problem to completely clean. Again, the drying characteristics of the ink must be known to ensure proper formulation.

Thus, it is important to understand those variables which aggravate the problem and every effort must be made to bring them under control.

## DRYING

The drying property of water-based liquid inks is of practical importance when measuring the performance of those inks. Due to the unique properties of water, the drying process of water-based systems is more complex and causes more problems, as compared with the behavior of conventional solvent based inks.

The development of water-based liquid inks is a challenging task. The unique properties of water has an impact on all the key properties of the medium for which it serves as solvent. These vital properties are: dispersion properties, solubility behavior, surface energetics and rheology.

There are two main problems associated with the drying process of water-based liquid inks:

1. The evaporation of water is more difficult than for most other solvents.

2. The character of the water-based ink is more complex than it is for conventional inks. One important feature is the two-phase character of the water-based systems. The binder is not truly dissolved in the water, but separates into its own phase. This creates a two-phase system - one phase predominantly containing water and the second phase predominantly composed of binder.

The evaporative drying of inks can be described as a simultaneous heat and mass transfer operation in which the heat required to evaporate the solvent is provided by drying air. The driving force for heat transfer is the temperature difference between the drying air and the ink surface.

The driving force for mass transfer is the difference between the saturated vapor pressure of the solvent and the partial vapor pressure of the solvent in the drying air. This drying process is influenced by 'external' factors such as air-circulation, air temperature, humidity, etc., as well as by 'internal' factors such as solvent composition, nature of the binder and interactions between the constituents. In the physical drying of inks, drying can be illustrated by



characteristic drying graphs, in which the drying speed can be divided into two parts: the constant rate period and the falling rate period. The constant rate period is controlled externally and the drying speed for a given solvent depends on the air velocity and the thermodynamic state of the drying air, ink film thickness and the percentage of the solvent of the ink. During early stages of drying, solvent can reach the free surface within a sufficient time period to maintain it in a saturated condition.

The falling rate period is an internally controlled process where solvent molecules must pass through the solidifying layer of non-volatiles. It is the resistance to this movement, i.e. diffusion which controls the drying rate. Diffusion is a spontaneous movement of particles which reduces the concentration gradient and produces equilibrium. Diffusion controlled drying processes are characterized by the fact that the drying rate diminishes exponentially with time. In such conditions the last traces of solvent are usually extremely difficult to remove from the 'dry' ink film<sup>3</sup>. The solvent diffusion coefficients depend on molecular geometry<sup>4</sup>; small planar, solvents molecules diffuse more easily than large, branched solvent molecules, which are thus retained more. Whereas diffusion constants depend upon solvent concentration.

Although in practice the 'internal' and the 'external' parameters are treated differently, however in reality they are interconnected. The solvent balance is, for example, influenced by the external conditions, and the optimization of the external conditions depends on the solvent mixture in use, i.e. the nature of solvent mixture determines the right combination of air and temperature.

Similar to the above mentioned theory, Stratta, et.al.,<sup>5</sup> suggest that drying of a water-based formulation falls into two limiting stages. First, there is a 'wet' stage where the major fraction of volatiles is lost under conditions analogous to the evaporation of a polymer-free liquid solution. In this stage the drying rate is maximum and is limited by how fast liquid molecules evaporate from the moist surface. After 'skinning,' the entrained liquid is lost much more slowly during a 'dry' stage that is controlled by the rate of liquid diffusion through the polymer matrix towards the interface. A transition phase is usually observed as condensed phase diffusion gradually becomes the controlling mechanism<sup>6</sup>. It has been suggested that the relative evaporation rates of the various solvents depends on the molecular weight and effective cross-sectional area of the solvent.<sup>7</sup> However, to better understand the role of organic co-solvents and the drying of water-based formulations its composition must be defined.

The constant-rate period and the falling rate period in the drying graph are separated by the critical point. The critical point in the characteristic drying curve is reached, when the diffuse flux equals the evaporative flux. When no more solvent can reach the free surface sufficiently to keep it saturated, the drying speeds begin to fall.

#### THE MAIN FEATURES

The ink can be described as a two-phase colloidal dispersion, where the binder and the water, respectively, are the main components in the two phases. The organic solvents and the coalescing agents (usually high boiling solvents) are distributed between these two phases.

The evaporation of volatiles from the described system involves the following steps:

1. The volatiles must diffuse to the ink surface. This process takes place instantaneously over the main part of the drying process. In the last stages of drying, when a solid film has formed, a diffusional resistance can build up in the ink film.
2. At the ink surface the volatiles must be evaporated. They must be brought from a liquid state to a vapor state. This process requires energy, leading to an evaporative cooling of

the ink surface, if the energy loss is not compensated by an energy supply from the surroundings.

3. The vaporized volatiles must be transported from the ink surface to the surroundings.

4. Depending on the relative evaporation rates of the different solvents, the solvent balance is changed during the drying process. The solvent-solvent and solvent-binder interactions change, thereby changing the thermodynamic properties of the ink. This in turn influences the evaporation rates of the solvents.

5. At a certain stage in the process, water ceases to be the dominant component. This indicates the beginning of the film formation. Two quite different situations may arise. The system may continue to be a two-phase system, now with water as the minor phase, or the system may evolve into a one-phase system with water and organic solvents dissolved in the binder.

#### THE INTERNAL DRYING MECHANISMS

In the main part of the drying process, the processes in the ink are so rapid, that equilibrium conditions can be

assumed.<sup>8</sup> In the final stages of the drying process, a diffusion resistance can build up in the film. When organic solvents almost insoluble in the water-phase are used, a diffusion resistance can play a role in the evaporation of these components.

Assuming equilibrium conditions implies that the properties of the ink can be evaluated with the aid of thermodynamics. In particular, the drying process can be evaluated on a thermodynamic basis. The evaporation rate ( $R_i$ ) of the volatile component ( $p_i^\circ$ ) is proportional to the vapor-pressure of the component above the solution:

$$R_i \propto p_i$$

The vapor pressure ( $p_i$ ) in turn is proportional to the activity ( $a_i$ ):

$$p_i = a_i p_{i0}$$

where ( $p_{i0}$ ) is the vapor pressure of the single component ( $i$ ).

The total evaporation rate ( $R$ ) can thus be calculated as the sum of the individual rates:

$$R = \sum R_i = \sum a_i R_i^\circ \propto \sum a_i p_i^\circ$$

Knowing the evaporation rates of the individual components and the activities in the mixture, it is possible to simulate the drying process.

Various models have been specified to calculate the drying rate. However, to achieve predictable results, accurate data regarding the composition of the inks in question is required. One of the available model is UNIFAC.<sup>9</sup>

#### THE EXTERNAL DRYING MECHANISMS

For the internal drying mechanisms, we can assume constant external conditions. The equation:

$$R = \sum a_i R_i$$

is used to calculate evaporative behavior. However, in this equation  $a_i$  and particularly  $R_i$  depend on the effective temperature in the ink film and  $R_i$  furthermore depends on air-circulation, humidity and other external drying conditions.

The effective temperature of the ink film is a result of the combined effect of heat loss during the evaporation process and the heat supply from the surroundings. Using a shell thermometer, where the drying conditions are moderate compared with those appearing on a press drying equipment, some experimental film temperatures were calculated.<sup>10</sup>

Table 1.

Evaporative Cooling of neat solvents (Shell, Temperature 25°C)

---

Water	15.6°C
Acetone	0.0°C
Ethanol	12.2°C
Toluene	18.4°C
n-butlyacetate	22.0°C

---

It can be seen that the film is substantially cooled due to the enthalpy [heat] loss during the evaporation process. The vapor pressure of the solvents and thus their evaporation rates are very sensitive to the effective film temperature. Furthermore the driving force of evaporation is the difference between the equilibrium vapor-pressure above the film ( $p_{i0}$ ) and the partial pressure of the component in the drying air,  $P_{i\infty}$  :

$$R_i \propto \Delta p_i = p_{i0} - p_{i\infty}$$

If  $p_{i0}$  is lowered due to evaporative cooling, the difference  $\Delta p_i$  will decrease even more.

These effects are very critical when water is involved. The evaporative cooling is high because of the high enthalpy

of evaporation. The resulting vapor-pressure decrease is high for the same reason and finally, the partial pressure of water in the drying air, corresponding to the humidity, increases the total effect on the drying rate.

As a consequences of the difference in the temperature-response of the individual volatiles, the drying process will depend not only quantitatively but also qualitatively on the drying conditions. When simulating drying on the press, the combined effect of the internal and external parameters must be evaluated simultaneously. H. Hardisty<sup>11</sup> suggests:

Heat Transfer:

$$\Sigma N_i \Delta H_i = h(T_\infty - T_o) + Q_s$$

This equation states that the heat consumption due to evaporation equals the heat supply due to convection,  $h(T_\infty - T_o)$ , and due to supplementary heat supply ( $Q_s$ ).

Mass Transfer:

$$N_i = k_x (x_{i0} - x_{i\infty})$$



Equilibrium conditions in the ink.

$$x_{i0} = a_i p_i^{\circ}(T_o)/p$$

- $N_i$  : mass-flux of component (i)
- $h$  : heat-transfer constant
- $\Delta H^{\text{vap}}$ : heat of evaporation of component (i)
- $T_{\infty}$  : temperature of drying air
- $T_o$  : film temperature
- $Q_s$  : supplementary heat supply
- $k_x$  : mass-transfer constant
- $x_{i0}$  : concentration of component (i) just above the film
- $x_{i\infty}$  : concentration of component (i) in the drying air
- $a_i$  : activity of (i) in the liquid
- $p$  : ambient pressure
- $p_i$  : vapor-pressure of (i) at film temperature  $T_o$

In the above equations, the heat and mass transfer constants ( $h, k_x$ ), which depend on air velocity and geometry of the drying equipment, can be evaluated according to the established theory of heat and mass transfer. The values of heat of vaporization is available in standard references and the vapor pressures of the pure component as a function of the temperature can be calculated.

Researchers have noted that under defined drying conditions, the water does not evaporate at all in the initial stages of drying<sup>12</sup>. Whereas, a sample of isopropanol flashes off, cooling the ink film down to 14°C. This temperature corresponds to the dew point of the water in the drying air and consequently water will not evaporate. This condition will lead to a total change of the solvent balance of the system and can render the remaining ink thermodynamically unstable.

Thus it is important to understand the exact composition of the system and how each individual component would behave, not only on their own but also when they are combined with other components of the defined system.

Drying rates can be calculated using simulation packages combined with actual experiments. Once such computer program developed at SPPIRI calculates rough estimates of total drying rates and solvent balance during the drying process, as a function of ink formulation as well as external drying conditions.<sup>13</sup>

#### CONTACT ANGLE

Assuming that the surface of a solid is perfectly uniform (a condition which never actually holds), then if a drop of pure liquid is placed on a horizontal surface it may

spread out indefinitely, or it may spread only to a limited area and come to rest so that the film at the edge of the drop meets the surface at a definite angle called the angle of contact (or more commonly referred to as the contact angle). This angle will increase as the adhesion between the liquid and the solid decreases. It is fairly obvious that the more nearly this angle approaches zero the more nearly will the liquid spread completely over the surface. An angle of  $180^\circ$  would be indicative of zero adhesion to the surface.<sup>14</sup>

If the drop of liquid A covers an extra sq. cm. of B, the free energy lost in the process is

$$\gamma_B - \gamma_A - \gamma_{AB}$$

When the drop is in equilibrium, making an angle of contact  $\theta$ ,

$$\gamma_B = \gamma_A \cos \theta + \gamma_{AB}$$

but  $\gamma$  and  $\cos \theta$  are the only measurable quantities. However, spreading occurs only when the adhesion of liquid for solid, exceeds the cohesion of the liquid,  $2\gamma_A$ .

Using the above relation to substitute for the  $\gamma_A - \gamma_{AB}$  quantity we have for the work of adhesion of A to B the expression  $\gamma(1+\cos\theta)$ , which contains only directly

measurable quantities.

Obviously,  $2\gamma_A > \gamma_A(1+\cos\theta)$  so long as  $\theta$  is finite. Consequently spreading entails the condition that  $\theta=0$  or that the adhesion is as great as the cohesion.

#### MECHANICAL CONDITIONS FOR SPREADING ON SOLIDS

a. Effect of immobility of surface of a solid. For the process of spreading over a liquid, the fluidity of the lower liquid was of prime importance, since it was diffusion in this that caused the adhering molecules of the upper liquid to be carried outward. This factor cannot operate in the case of a solid, and its absence changes the mechanism of spreading in such a way that, generally speaking, "active" substances do not spread readily on a solid and may in fact be used to retard the spreading of the less active components of a liquid. For example, the COOH groups in the molecules of fatty acids become fixed at a metal surface, thus yielding an immobilized layer of molecules having their saturated ends outward. Over this layer spreading does not readily occur. Also, it was observed by Woog<sup>15</sup> that over either water or mercury the unsaturated (active) oils spread most rapidly whereas on the solid metals the saturated oils showed more spreading.

b. The vapor pressure theory of spreading. Based on Hardy's<sup>16</sup> experiments with vapor-pressure reduction, the distillation theory of spreading was developed: namely a primary film is formed over the solid by condensation from the vapor phase and that the thicker film subsequently spreads over this primary film. Nietz<sup>17</sup> followed this approach and found that the spreading of water on an active solid was stopped by covering the vessel so that the space became saturated with vapor of the water. A drop of distilled water spreading over mercury is stopped by saturating the air with water vapor. In this case the vapor condensing on the surface reduces the surface tension sufficiently to make the spreading coefficient zero or negative.

c. Surface migration. Since the work of Volmer, there has been a growing recognition that the surface of a solid and the molecules adsorbed thereto constitute a much less static system than had previously been pictured. Observing Hg crystallizing from its vapor, it was found that the growth of crystals could be explained only if all the molecules which struck the crystal condensed and then travelled along the face of the crystal to settle down on the growing edge. It is now well known that at higher temperatures molecules may diffuse over the surface of solids.

One result of the immobility of the molecules in the surface of the solid is that just those factors which promote spreading over the surface of a liquid may retard the process on the surface of a solid. Active molecules on the surface of water are spread by the diffusion of the water molecules. When placed on the surface of a solid the active molecules simply become anchored by attachment to the surface and so are incapable of further spreading.

In the industrial processes which involve the behavior of liquids with respect to the surface of solids it is frequently a matter of indifference whether the liquid will spread spontaneously over the surface or not; the fundamental requirement in some cases is that the liquid, once spread shall maintain a stable layer; in other cases it is fundamental that the solid surface shall not retain a stable layer of liquid over it, but that a bubble of air shall be able to make contact with the surface of the solid and displace the liquid from part of the surface.

Active substances added to a liquid in order to secure the stability of a layer and prevent it retreating from the surface over which it has been spread are called wetting agents.

## Contact Angle:

### 1. It's reality and importance.

The angle of contact between a liquid and solid is the only directly measurable quantity which conveys any information about the free energy of the liquid-solid interface.

The non-uniformity of solid surfaces, and particularly the fact that the angle measured was frequently that between liquid and a film of contamination rather than between liquid and the solid under observation, led to much uncertainty and inconsistency in early observations on contact angles. Subsequent research and improved techniques enhanced the accuracy of the results.

### 2. Hysteresis of the contact angle.

If a drop of water is placed on a plane surface of wax, or if a drop of mercury is placed on a glass or steel and the surfaces are tilted till the drop moves, then the contact angle on the advancing edge is always greater than that on the receding edge. Sulman called this effect the hysteresis of the contact angle. The advancing angle is that between the liquid and the unwetted surface of the solid, the receding angle that between the liquid and a surface that has been in contact with the liquid. These represent the limiting values which the contact angle can assume.

The experiments of Wark<sup>18</sup> and his colleagues on specially clean and smooth mineral surfaces suggest that this hysteresis is a result of frictional resistance to movement of the liquid over the surface of the solid. If so it is to be expected that a drop at rest should eventually settle down with the same angle of contact on all sides, since the friction in a fluid cannot supply a static force.

The conditioning of the surface, particularly by a previous heating, will reduce the hysteresis in many cases, but in some instances there seems to be no doubt that the difference in contact angle persists. Hysteresis indicates that the passage of the drop has changed the nature of the surface over which it has passed, i.e. the dry surface of the solid from which the drop has receded differs from the surface that has not yet come into contact with the liquid. The contact of the liquid and solid has increased the adhesion between them.

$$\gamma_B = \gamma_A \cos\theta + \gamma_{AB}$$

If  $\theta$  is decreased  $\gamma_B$  must have increased, or the surface energy of the solid from which the liquid has retreated is greater than it was before wetting. This increase cannot be brought about by adsorption, which would occur only if it



reduced the free energy of the surface. It may be that the drop effects some sort of clean-up of the surface, permitting better control between liquid and solid. It is still just possible that hysteresis of contact angle may be phenomenon akin to that of the lowering of the surface tension of mercury in vacuum, i.e. that it must be attributed to some contamination that has defied detection.

In technical applications one is usually concerned, not with conditions of static equilibrium, but with more or less rapid movement of liquid over solids. In such cases there are generally appreciable differences between advancing and receding angles of contact, and it depends on the particular problems whether it is one of the limiting angles of contact or their average values that matters.

The non-mobility of the surface particles of a solid results in the surface being often extremely uneven, unless special means such as polishing have been employed to smooth out the irregularities. The atoms in a solid surface stay where they are placed when the surface is formed, and this may result in no two adjacent atoms or molecules having the same properties.

Most solid surfaces which have been exposed to air for any appreciable time will be covered more or less completely with a film of contamination. This may well change the free

energy of the surface and consequently alter its behavior in regard to the spreading of liquids over it. The work required to produce a fresh surface of a solid varies from atom to atom, and the surface tension is therefore not uniform.<sup>19</sup>

Also, another factor which contributes to the variation of contact angle measurements is the fact that vapor pressure over a convex surface is greater than that over a plane; and over a concave surface it is less. The difference depends on the fact that condensation of vapor on a small convex drop of a liquid increases its surface area, so that the surface tension tends to oppose the condensation and to increase the vapor pressure. On a plane surface condensation does not alter the surface area, and on a concave surface the area is diminished by condensation of more vapor.

Extreme caution has to be exercised in the measurement and interpretation of contact angle values. Variation in their values is not uncommon for the surface of a solid will differ from point to point both in its structure and in the resultant fields of force and free energy. Even the most highly-polished surface will not be comparable in uniformity of level and structure with the surface of a liquid.<sup>20</sup>

## MEASUREMENT OF CONTACT ANGLES

There are numerous methods that could be used to measure contact angle. Each one of them are not without drawbacks. Among the methods available, the Sessile Drop method is the most common one usually adopted in the laboratory.

1. Plate Method: In this method a plate of the solid is immersed in the liquid and rotated until optical tests show that the liquid and solid meet on one side in a sharp line without curvature. The angle  $\theta$  is then the angle of contact and this can be measured by a protractor giving the angle which the plate makes with the horizontal.

2. The Capillary Height Method: The well-known rise of a liquid in a capillary tube is simply an automatic recording of the pressure difference across the meniscus of the liquid in the tube, the curvature of the meniscus being determined by the radius of the tube and the angle of contact between the solid and the liquid. If  $r$  is the radius of a cylindrical tube, and  $\theta$  the contact angle between the liquid and the glass. The radius of curvature of the meniscus is  $r/\cos\theta$ , and the pressure under the meniscus becomes less than that at the same height, in a liquid with a plane surface, by  $2 \cos\theta/r$ . This produces a driving pressure, tending to force the liquid up the tube, and the meniscus will rise to a height  $h$ , such that the weight of the column of liquid elevated above the

plane surface outside the tube just balances the pressure deficiency under the curved meniscus. The energy relations determine the stable contact angle; the fluidity of the liquid permits the molecules to move about until they rest at this stable contact angle; the contact angle and the curvature of the tube curve the liquid surface.

When the contact angle is greater than  $90^\circ$ ,  $\cos\theta$  is negative, and the contact angle can be determined by the following expression:

$$2 \cos\theta/r = ghD$$

3. The sessile drop method: This method directly measures the contact angle from a sessile drop resting on a solid surface. Tangents are constructed at the three-phase line of contact using a projected image or photograph of a drop profile or measuring directly the angle using a telescope with a goniometer eyepiece.

This technique does not require knowledge of the liquid's surface tension or density. It can be easily carried out with the use of simple instruments and requires only small amounts of liquid samples. The technique does claim an accuracy of  $\pm 3^\circ$ , however this may not be true for angles less than  $10^\circ$  or more than  $160^\circ$ .

Contact angle measurements give a good indication of the rewettability of the ink. The lower the angle of contact the more easily will the fresh ink rewet itself to the dried ink. Thus improving the contact angle by the addition of surfactants would only enhance the rewettability characteristics, however would also affect the drying rates of the ink.

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### CHAPTER III

#### LITERATURE REVIEW

The transfer of ink from a container to a page is the purpose of the entire printing industry. Though simple in description, that process is affected by many variables, the identification and control of which consumes and often confounds us all.

Flexography seems a viable alternative to non-heatset web offset, promises improvement in quality, production speeds, decreased waste, as well as cost reduction. It meets the specifications and requirements for an acceptable newspaper printing system - one that must be able to come down, change over and come back up quickly, with a minimum of lost time and paper waste.<sup>1</sup>

In flexography, printing ink is first applied onto an anilox roller. The patterned crevices on its surface, as well as ink properties, control how much ink is taken up. Ink is then transferred onto the flexographic printing plate and from there, directly onto the paper substrate. Printing press conditions, ink properties, plate and paper characteristics all contribute to the overall quality of the ink transfer and laydown on the paper surface.<sup>2</sup>



Initially, the water based flexographic inks developed over the years for corrugated stock, were tried on newspapers. However, these inks proved inadequate, mainly because of high-speed production requirements and two-sided printing on newspapers.<sup>3</sup>

Problems were abundant in those early trials. They included ink foaming, poor viscosity control, one color moire, ink set off onto both idlers and second impression cylinders, plate tack, solid and shadow area mottling, low anilox bearing life, poor registration, loss of impression in the middle of press run, uneven printability, non-optimized gradations, excessive anilox wear, low black solid print density, inability to vignette, marking, divergent ink hues and PLATE FILL-IN. On this list all have been solved but one, - the (halftone) plate fill-in. Fill-in or plugging still occurs during long runs and the press has to be stopped every 30-40 thousand impressions. Having to stop the press between such short intervals is not running trouble free.<sup>3</sup>

There are many causes for this particular problem including anilox rollers, ink, plates and paper. Poorly formulated inks can aggravate the problem. Paper is always a potential problem especially when it is linty. The release of material from the paper surface accumulates in the non-image area of the plate, which builds up and causes undesirable

transfer of ink.<sup>4</sup>

Using 15 different test samples, Aspler et.al.<sup>5</sup> studied the various stages in the development of halftone fill-in. They identified three separate steps of the halftone fill-in process.

Step 1: Build-up of Dried Ink and Paper Fines Around the Halftone Dots.

It was observed that the spikes at the bottom of each dot are all on the leading edge, pointing in the direction of printing. It is suspected that these spikes may be the means by which dots start to merge into each other. Also, a common feature on most dots in the early stages of fill-in was the bald center of the dot, surrounded by a ring of material. The bald spots were actually covered with a thin layer of carbon black containing paper fines. The ring around the dot consisted of carbon black and fines and were held together by the ink binder. The progressive build up of the material around the circumference of a dot clearly suggests that with each compression of the dot in the printing nip, the material picked up in the nip can be forced further and further below the plate surface. As fill-in becomes more severe the cap of dried ink may break off and be trapped in the relief of the plate.

Step 2: Joining of Two or More Dots. This was caused by the collection of long fibers in the relief area, particularly between two or more dots. Arlow<sup>6</sup> claimed that in later stages of fill-in, the ink/fiber deposits are very tacky, thereby increasing the removal of fiber from the paper surface.

Step 3: General Fill-In of the Plate. In this stage the entire background of the plate gets covered with dried ink.

Also, in extreme cases the fill-in was as high as 150 gm/m<sup>2</sup>.

One theory states that because it dries so rapidly, the ink may begin to dry right on the plate at the perimeter of the half-tone dots. Gradually this ink breaks away, falling between the dots where it becomes trapped with paper lint. After a period of time, the buildup itself begins to print, virtually destroying the dot pattern.

It has been observed that the problem of fill-in is greater with black inks than with colors.<sup>7</sup>

Ink viscosity is also an important factor: The more viscous the ink, the worse the fill-in. Similarly, an inappropriate anilox roller - one which carries too much ink to the plate-contributes to the problem. So do excessive anilox-to-plate and plate-to-paper pressure settings. Finally, improperly processed plates having residual tack may be a factor.

Another problem, second impression set-off could aggravate the halftone fill-in. The buildup on the second impression cylinder affects the diameter of that cylinder, increasing pressure between the impression and plate cylinders. This results in dot growth and contributes to halftone fill-in. Research has indicated that as rapidly as flexography ink seems to dry, there exists a minuscule dwell-time in which the droplet of ink remains on the surface of the paper. That dwell-time, combined with the speed of the web and the short distance between impression cylinders, prevents the ink's drying adequately between nips.

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#### CHAPTER IV

##### THE HYPOTHESES AND RESEARCH QUESTION

The main question of this research can be stated as follows: "Can the difference between water based flexographic inks be characterized in terms of their rewettability and drying characteristics?"

From the question above, we can formulate the following null hypothesis. "There is no significant difference between the flexographic water based inks tested in terms of both their volatile content and their drying rate."

To expand the analysis to include contact angle another null hypothesis can be stated. "There is no difference between the flexographic water based inks based on their contact angle."

## CHAPTER V

### METHODOLOGY

Water based flexographic black news ink samples were obtained from four different manufacturers, however their composition is proprietary and was not revealed.

To ensure proper results the viscosity of the inks was standardized. It is important to bring the inks to a common frame of reference, which would reduce the variations due to differing formulations. A Zahn Cup viscometer is used to measure the viscosity of the inks. This type of viscometer determines viscosity by the amount of time that is required for a predetermined amount of liquid to drain from a cup.

Since the viscosity of the inks could not be increased in our laboratory the ink with the lowest viscosity was chosen as the standard. The initial viscosity of this ink was determined using a Zahn #2 cup viscometer with 125ml of ink. All other samples were diluted with 6-10% of Demineralized water. The "samples" were stored in an air tight container for experimentation.

The inks were labelled A, B, C and D. However, if the experiment was repeated more than once a suffix was added. For example, if Ink A's drying experiment was repeated once, the

results of the first would be labelled A1, the second A2.

Ink A had the lowest viscosity - 21 seconds in a Zahn #2 cup. Using this as a standard of reference, all other ink samples were diluted to achieve this same viscosity. This procedure simulates actual press conditions where the pressman would dilute the inks to achieve a desired viscosity. Water was chosen as the viscosity reducing agent since it does not alter the chemical properties of the ink. The viscosities were determined by averaging three replications of the drainage times for each sample.

TABLE 2

VISCOSITY TABLE

<u>Ink</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
Initial Viscosity (secs)	21.5	28.5	105	110
Final Viscosity (secs)	21.5	21	20	22
Volume of Water Added (ml)	0	12	40	42
to 25 ml of ink				



## DRYING RATE MEASUREMENTS

A differential weight technique was adopted to calculate the drying rate of the ink samples.

A constant volume of the prepared ink sample was syringed into an aluminum pan. A different pan was used for each sample. The pan was placed on a sensitive balance, Figure 1, which could be read to 0.01 grams and exposed to a heat source. The temperature of the heat source was maintained throughout the experiment by the use of a wattmeter.

The weight of the pan was zeroed out and the weight of the ink sample was read at equal intervals of one minute till there was no considerable weight loss. This procedure was applied to all the ink samples. For two out of the four samples the above procedure was repeated once. Due to unavailability of a larger ink volume, the repetitions could not be carried out for Ink B and Ink C. It is important to understand that the replications are not duplications-new sample had to be prepared for each new replication.

Humidity plays a major role in the evaporation drying of water based inks. Higher relative humidity would lead to slower evaporation of water, conversely lower values would increase the rate of evaporation. So every effort was made to conduct the experiment under similar conditions. The relative humidity of the room fluctuated between 65 and 75 percent

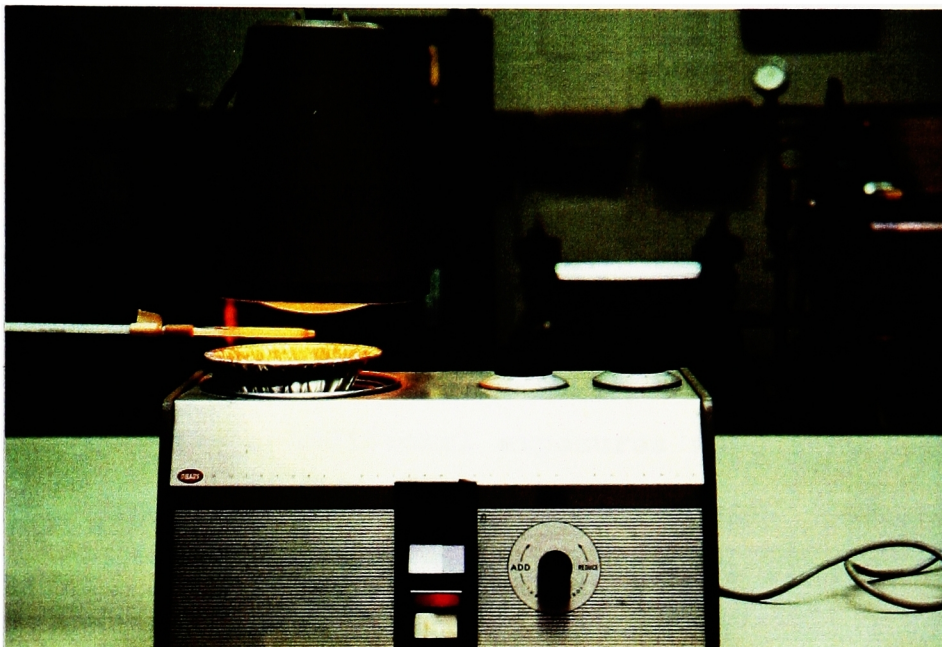


Figure 1. Apparatus Set-Up for Drying Rate Measurements

during the experimental period.

The results of the experiment are shown in Table 3.

#### CONTACT ANGLE MEASUREMENTS

Measurement of the contact angle was performed by using a Bausch and Lomb microscope and attaching a Polaroid camera, Model 3907-10. Total magnification was 20 times (20 x). Color prints were produced and used to measure the contact angle of the ink droplet on the inked glass surface.

A droplet of the ink sample was applied to a plate evenly coated with a dried film of the same ink. Exposure of the print film was made as soon as the droplet came in contact with the plate surface. Additional exposures were also made after a time delay of three minutes. Each droplet contained approximately three microliters. Figure 2, shows the apparatus setup for making the photographic prints used to measure the contact angle.

Measurement of the contact angle was calculated by determining the tangent of the angle  $\theta$  (theta). Since the droplet was convex in shape and symmetrical this calculation can readily be determined. By using one half the length of the droplet covering the plate surface and measuring the height of the droplet at this point, the angle can be calculated. The contact angle of each ink sample for two different time periods are presented in Table 6.

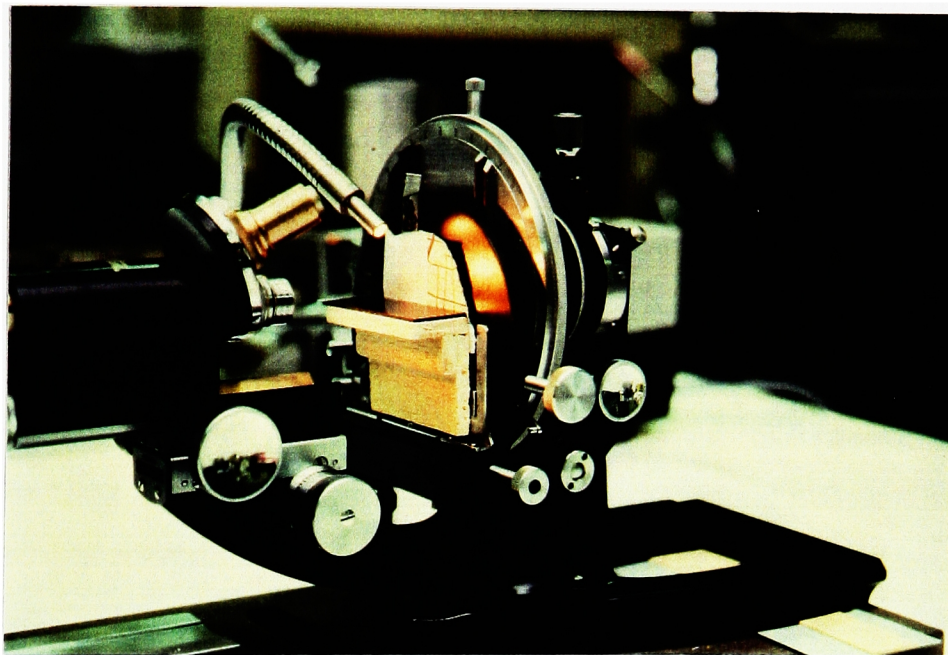
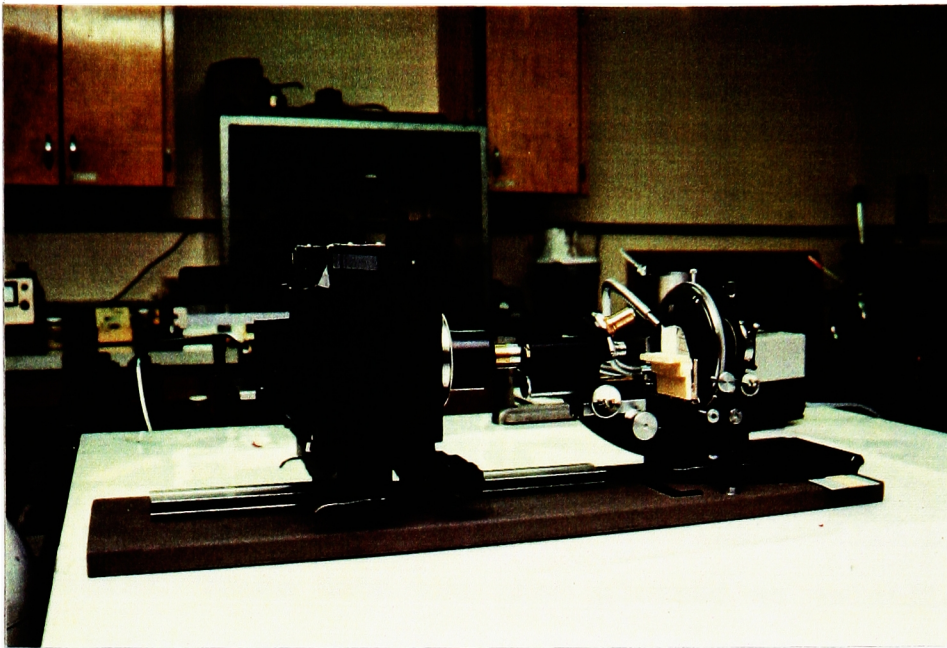


Figure 2. Apparatus Set-Up for Rewettability Measurements

## CHAPTER VI

### THE RESULTS

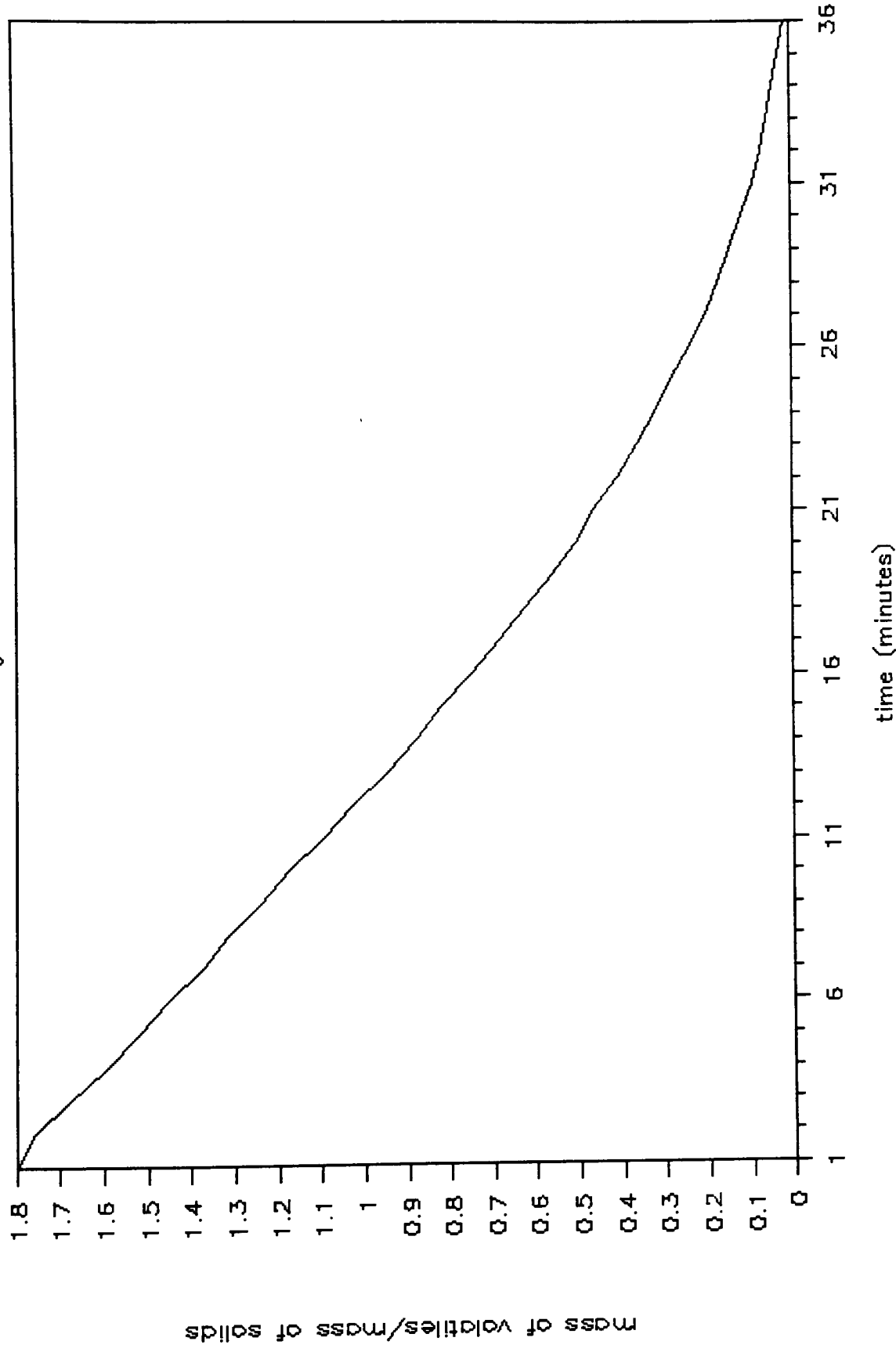
#### DRYING RATE

When an ink is dried experimentally, data are usually obtained relating volatile content to time. Volatile content is defined as the ratio of the mass of volatiles divided by the mass of solid. These data are then plotted as volatile content, (dry basis)  $x$  vs. time  $t$ , as shown in figure 3. This curve represents the loss of volatiles first by evaporation from a saturated surface on the ink film followed in turn by a period of evaporation from a saturated surface of gradually decreasing area and finally when the volatiles evaporate from the interior of the ink's solid.

The mass of volatiles is computed by subtracting the mass of solid from the mass of the sample for any given time  $t$ . Dividing this value by the mass of the solid normalizes and factors out the effect of the initial mass of the sample, which is the dry basis. To further illustrate this point let us take two ink samples. One has an initial mass of 3.00 gms and the other 5.00 gms. If the composition of the two inks are such that their components are 80 percent solids and 20 percent volatiles, then:

# DRYING RATE CURVE

Figure 3



INKS	A	B
Volatiles	2.4	4.0
Solids	0.6	1.0
x	3.0	3.0

Thus this method enables the comparison of two inks with differing initial mass.

From the drying rate graph, the difference between the inks may be observed by studying the y axis intercept as well as the slope.

The intercept with the y axis defines the amount of volatile (volatile content) in the ink and the slope represents the drying rate.

Although the drying rate is subject to variation with time or volatile content, this variation can be better illustrated graphically or numerically differentiating the curve and plotting  $dx/dt$  vs.  $x$  or  $dx/dt$  vs.  $t$ . These rate curves would show that the drying process is not smooth, continuous one in which a single mechanism controls throughout.<sup>1</sup> However, this method of studying drying rates requires higher precision and accuracy which can be achieved only with the aid of sophisticated computers and expensive instruments.

Due to constraints on the equipment availability, the first method of analysis of data was chosen in the laboratory.

In this technique the constant-rate period is shown by a straight line on the rate curve. The falling-rate period is typified by a continuously changing rate throughout the remainder of the drying cycle. The point where the constant rate ends and the drying rate begins to fall is termed as the critical moisture content. Again, determination of the critical moisture content dictates the use of sophisticated techniques in strictly controlled environments.

The inks may be differentiated based on two response parameters, volatile content and their drying rates.

Results of the drying experiment are shown in Table 3. From this table we can compute the volatile content of each ink, by subtracting the mass of solids from the mass for any given time  $t$  and dividing this value by the mass of solid, see Table 4. Based on these results, we can plot mass of volatile/mass of solids ( $x$ ) vs. time, figures 4, 5, 6 & 7.

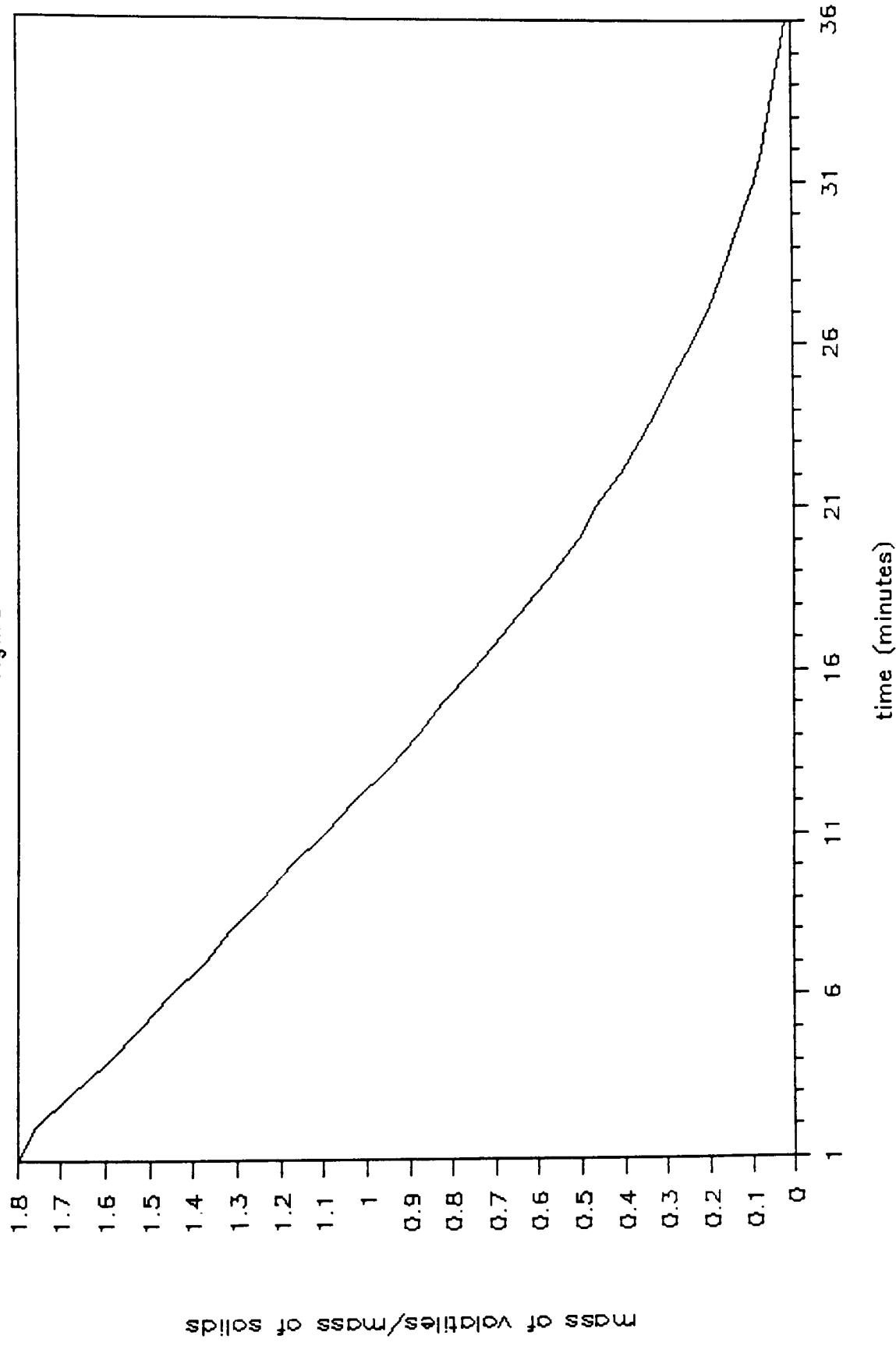
The division by mass of solids factors out the effect of the initial mass of the ink sample used in the experimentation. A dimensionless (ratio) quantity, helps to better understand the difference between the inks irrespective of their individual initial mass.

Slopes of the graphs (mass of volatile/mass of solids vs. time) for those regions where they are a straight line were calculated and reported in table 5.



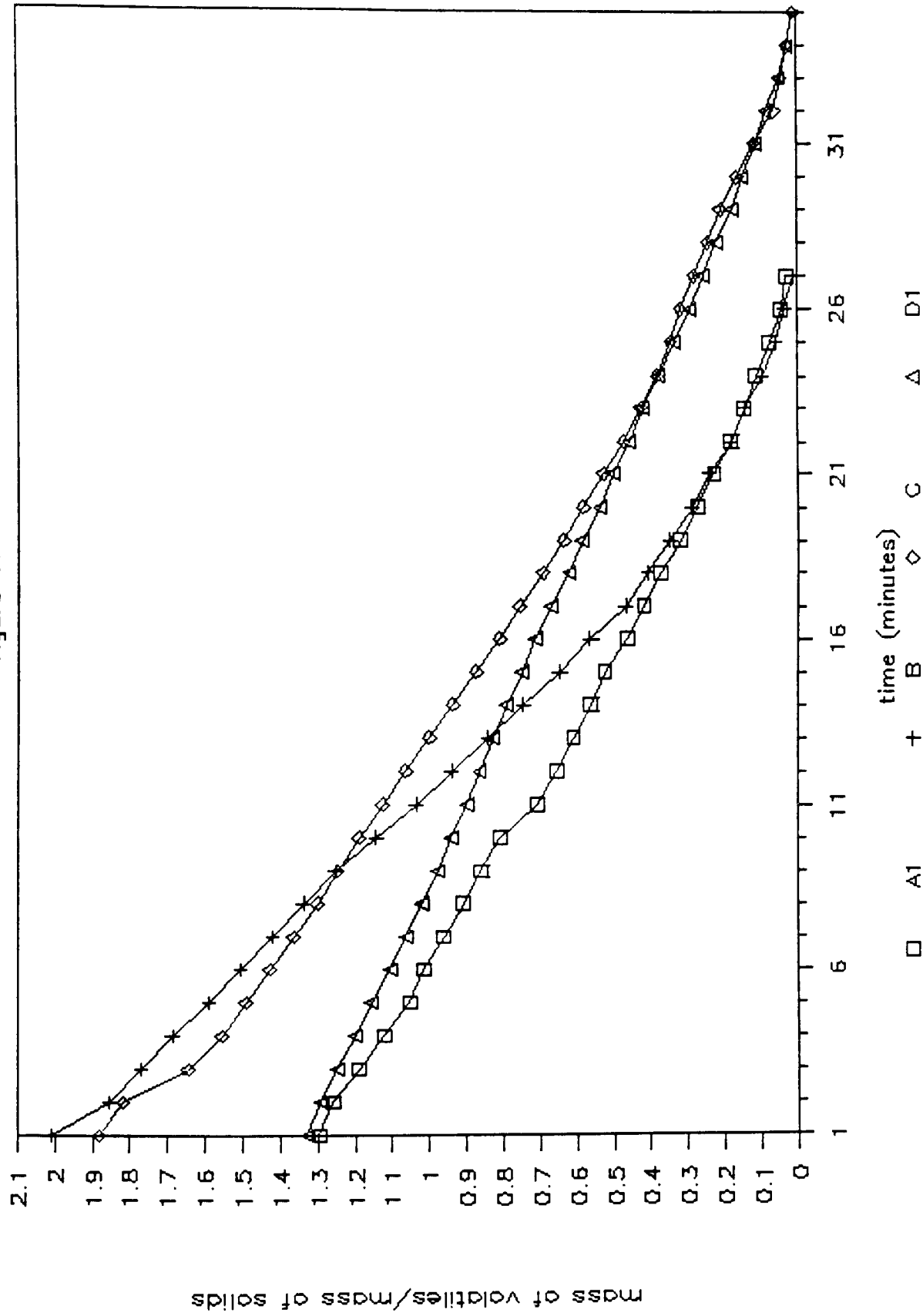
# DRYING RATE CURVE

Figure 3



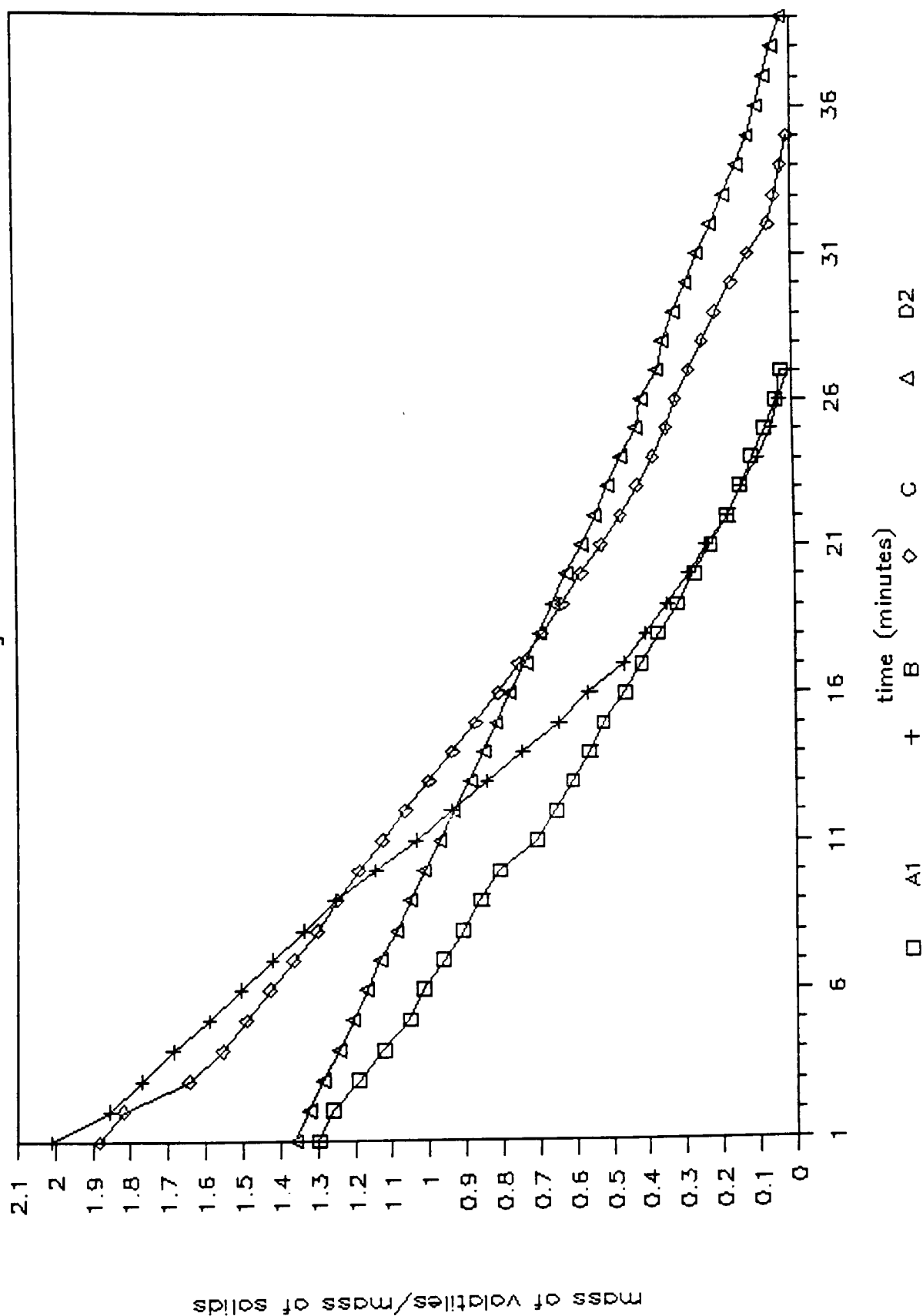
# DRYING RATE CURVES

Figure 4



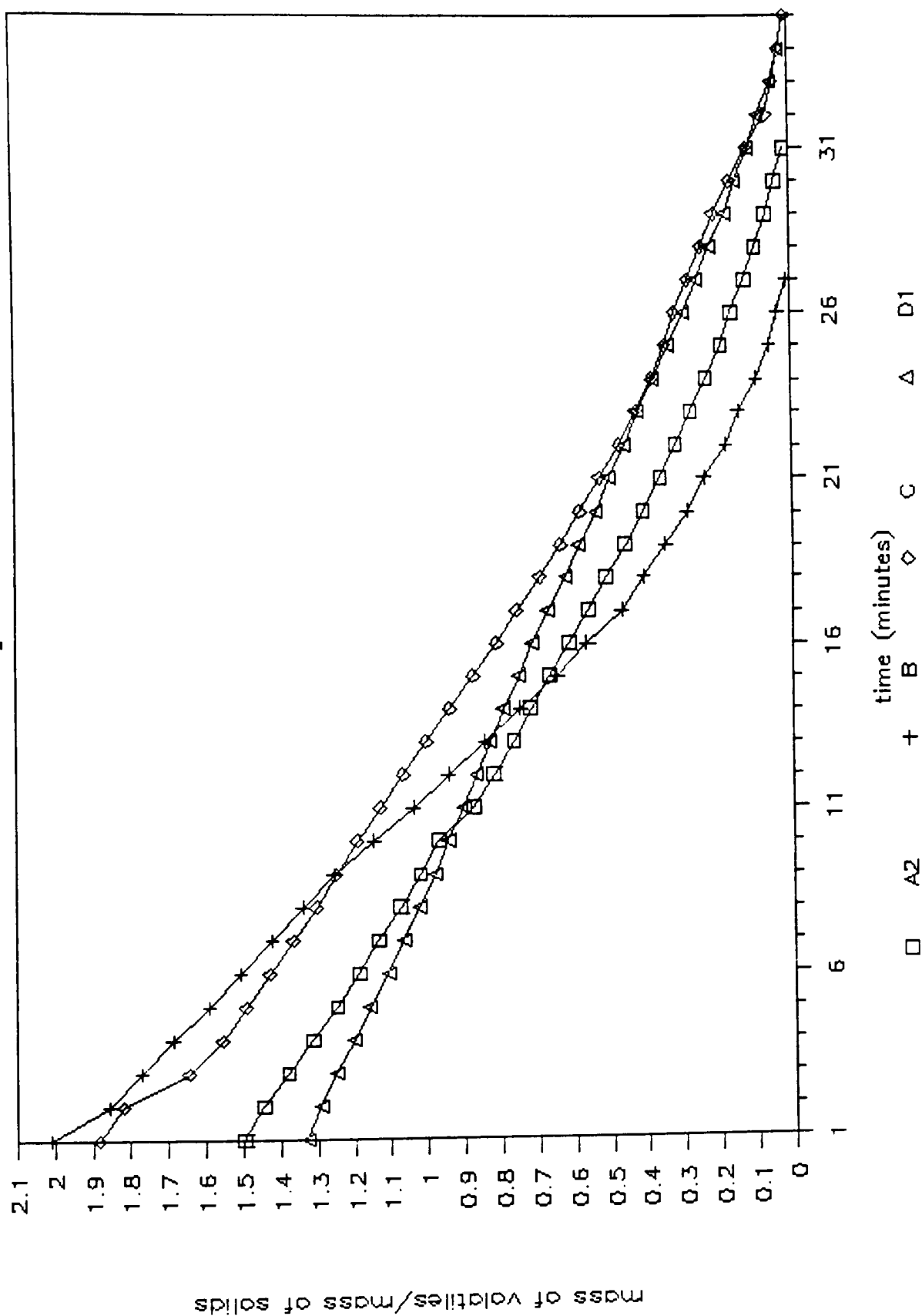
# DRYING RATE CURVES

Figure 5



# DRYING RATE CURVES

Figure 6



# DRYING RATE CURVES

Figure 7

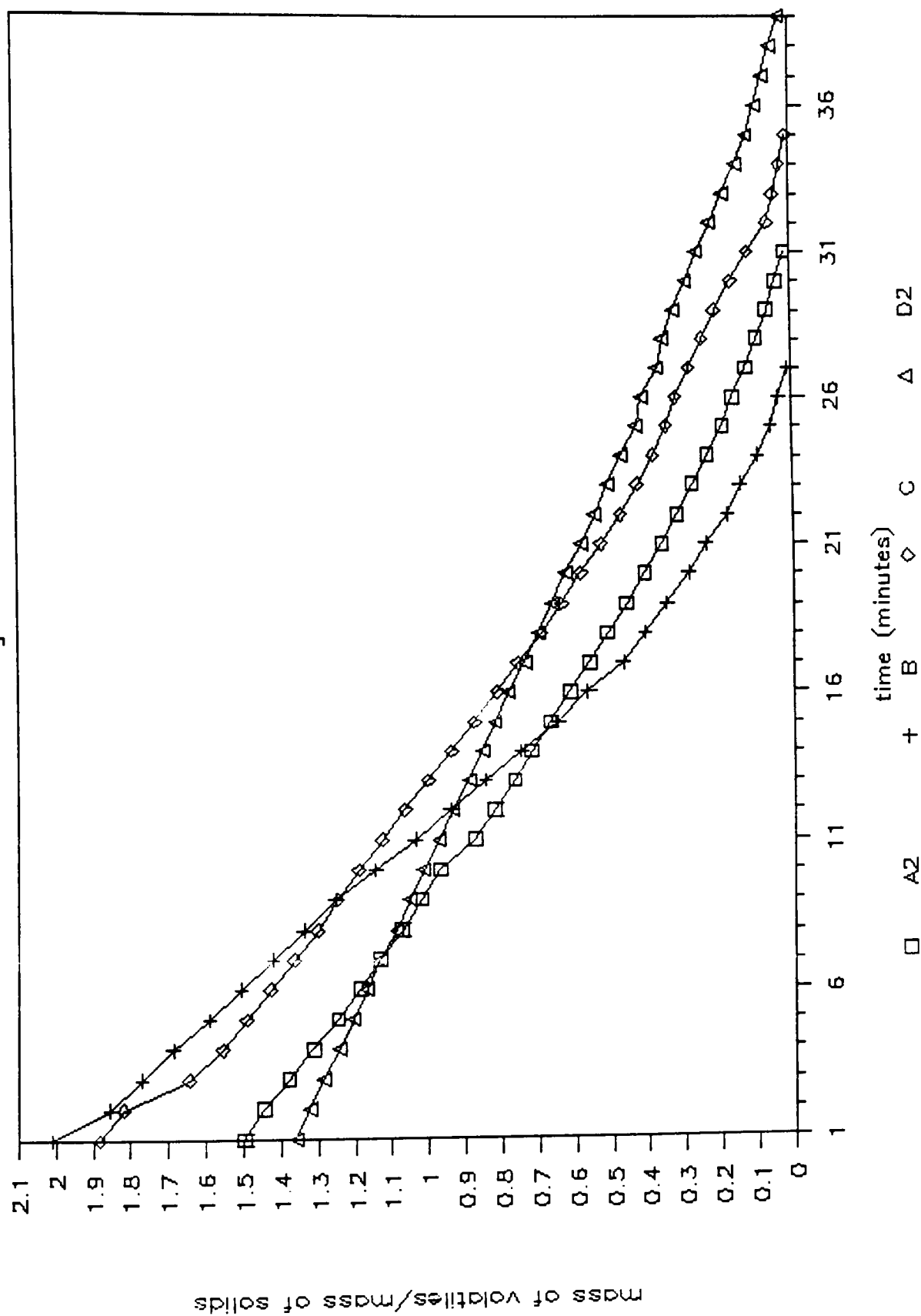


TABLE 3

MASS (gms) OF INKS WITH TIME (minutes)

TIME	A1	A2	B	C	D1	D2
1	3.01	4.15	2.50	3.17	3.26	3.21
2	2.96	4.06	2.37	3.10	3.21	3.16
3	2.87	3.95	2.30	2.91	3.15	3.11
4	2.78	3.84	2.23	2.81	3.08	3.05
5	2.69	3.73	2.15	2.74	3.02	3.00
6	2.64	3.63	2.08	2.67	2.95	2.95
7	2.57	3.54	2.01	2.60	2.89	2.90
8	2.50	3.44	1.94	2.53	2.83	2.84
9	2.44	3.35	1.87	2.47	2.77	2.79
10	2.37	3.27	1.78	2.41	2.72	2.74
11	2.24	3.11	1.69	2.34	2.66	2.68
12	2.17	3.02	1.61	2.27	2.61	2.63
13	2.11	2.93	1.53	2.20	2.56	2.57
14	2.05	2.85	1.45	2.13	2.51	2.52
15	2.00	2.77	1.37	2.06	2.45	2.47
16	1.92	2.68	1.30	1.99	2.40	2.42
17	1.86	2.59	1.22	1.93	2.34	2.36
18	1.80	2.51	1.17	1.86	2.27	2.31
19	1.73	2.42	1.12	1.80	2.22	2.26
20	1.67	2.34	1.07	1.74	2.15	2.21
21	1.61	2.26	1.03	1.68	2.10	2.15
22	1.55	2.19	0.98	1.62	2.04	2.10
23	1.50	2.12	0.95	1.57	1.99	2.05
24	1.46	2.05	0.91	1.52	1.93	2.00
25	1.41	1.98	0.88	1.48	1.87	1.94
26	1.37	1.93	0.86	1.45	1.81	1.92
27	1.35	1.87	0.84	1.41	1.76	1.86
28	1.31	1.82	0.83	1.37	1.71	1.84
29		1.77		1.33	1.65	1.80
30		1.73		1.28	1.61	1.75
31		1.69		1.23	1.56	1.71
32		1.66		1.17	1.52	1.66
33				1.15	1.47	1.61
34				1.13	1.44	1.56
35				1.11	1.40	1.52
36				1.10		1.49
37						1.46
38						1.43
39						1.40
40						1.36

TABLE 4

## VOLATILE CONTENT (x)

[mass of volatiles/mass of solids with time]

TIME	A1	A2	B	C	D1	D2
1	1.30	1.50	2.01	1.88	1.33	1.36
2	1.26	1.45	1.86	1.82	1.29	1.32
3	1.19	1.38	1.77	1.65	1.25	1.29
4	1.12	1.31	1.69	1.55	1.20	1.24
5	1.05	1.25	1.59	1.49	1.16	1.21
6	1.02	1.19	1.51	1.43	1.11	1.17
7	0.96	1.13	1.42	1.36	1.06	1.13
8	0.91	1.07	1.34	1.30	1.02	1.09
9	0.86	1.02	1.25	1.25	0.98	1.05
10	0.81	0.97	1.14	1.19	0.94	1.01
11	0.71	0.87	1.04	1.13	0.90	0.97
12	0.66	0.82	0.94	1.06	0.86	0.93
13	0.61	0.77	0.84	1.00	0.83	0.89
14	0.56	0.72	0.75	0.94	0.79	0.85
15	0.53	0.67	0.65	0.87	0.75	0.82
16	0.47	0.61	0.57	0.81	0.71	0.78
17	0.42	0.56	0.47	0.75	0.67	0.74
18	0.37	0.51	0.41	0.69	0.62	0.70
19	0.32	0.46	0.35	0.64	0.59	0.66
20	0.27	0.41	0.29	0.58	0.54	0.62
21	0.23	0.36	0.24	0.53	0.50	0.58
22	0.18	0.32	0.18	0.47	0.46	0.54
23	0.15	0.28	0.14	0.43	0.42	0.51
24	0.11	0.23	0.10	0.38	0.38	0.47
25	0.08	0.19	0.06	0.35	0.34	0.43
26	0.05	0.16	0.04	0.32	0.29	0.41
27	0.03	0.13	0.01	0.28	0.26	0.37
28		0.10		0.25	0.22	0.35
29		0.07		0.21	0.18	0.32
30		0.04		0.16	0.15	0.29
31		0.02		0.12	0.11	0.26
32				0.06	0.09	0.22
33				0.05	0.05	0.18
34				0.03	0.03	0.15
35				0.01		0.12
36						0.10
37						0.07
38						0.05
39						0.03

TABLE 5  
VOLATILE CONTENT AND THE DRYING RATE

<u>Ink</u>	<u>x</u>	<u>Slope</u>
A1	1.3	0.54
A2	1.5	0.59
B	2.01	0.97
C	1.88	0.61
D1	1.33	0.41
D2	1.36	0.42

where  $x = \text{mass volatile/mass of solid at } t=1$ , the  
initial volatile content (gms/gms)

Behavior of an ink may be better understood by studying their volatile content and drying rate. Although these parameters are interdependent to some extent they are not perfect substitutes. This fact can be illustrated by comparing Ink B and Ink D. Even though Ink B has the highest amount of volatiles it also has the maximum drying rate. However, Ink D has a lower volatile content, compared to Ink B, and the slowest drying rate. The quality of the choice of volatiles in the ink formulation may explain this behavior.

Interestingly, Ink A also has the lowest volatile content but certainly does not rank very high in it's drying rate.



Coupled with the fact that no water was added to this ink, we may infer that it has the highest amount of water in its formulation since water is probably the least expensive volatile component that could be used.

Ink C maintains a balance in its drying characteristics by occupying a middle position both for the amount of volatiles and rate of drying.

To summarize, it is not sufficient to differentiate the two inks based on their volatile content or their drying rates alone, but rather be judged on the basis of a combination of the two.

$$\text{INKS : } H_o : I_A = I_B = I_C = I_D$$

There is difference in the inks in terms of their slope which is indicative of their drying rate. For a 95 percent confidence interval the null hypothesis may be rejected.

On this basis we can infer that drying rate differences between inks can be detected using the rather straight forward methodology suggested here.

## CONTACT ANGLE

Contact angle measurements were analyzed using statistical methods. A two-way Analysis of Variance (ANOVA) test was applied. The contact angle technique is a two factor experiment that is twice replicated. Throughout the analysis of test data, an alpha risk of 0.05 was used.

Making use of the contact angle measurements for each of the four inks at two different times, a two-way ANOVA was conducted. The null hypotheses (which indicated no difference between levels) for this ANOVA are:

$$\text{INKS : } H_0 : I_A = I_B = I_C = I_D$$

$$\text{TIME : } H_0 : T_1 = T_2$$

$$\text{INTERACTION : } H_0 : T_{ij} = I_{ij}$$

The requirement for a two-factor case is that we must replicate or have some previous estimate of random error. Replication, repetition of test procedures, allows us to obtain an estimate of error from the differences in the results of the repetitions. To replicate requires the preparation of two or more independent samples treated as nearly alike as possible. Any differences observed among

samples can be attributed to chance factors.

The mathematical model for a replicated two-factor experiment is:

$$X_{ijk} = \mu + R_i + C_j + (R \times C)_{ij} + e_{(ijk)}$$

The term  $(R \times C)_{ij}$  represents the joint influence of the row and column factors, and thus the interaction.

The mathematical model thus indicates that each single observation (for any column, row, and replication) depends on the mean of the population from which the observation is drawn, an influence due to the row factor, an influence due to the column factor, an interaction, and error. The total sum of ANOVA will be made up of four parts, thus;

$$SST = SSR + SSC + SSI + SSE$$

where the new term SSI represents sum of squares for interaction.

Based on the above discussion and established procedures<sup>2</sup> an ANOVA table could be conducted for the four ink types and two time intervals; immediate and three minutes. Immediate signifies that the picture was taken immediately after placing the drop on the dried ink film and the latter the time lag of three minutes before the next picture was taken.

TABLE 6

## Contact Angle Measurements

TIME INK TYPE	IMMEDIATE	3 MINUTES
A	28° 61 26° 57	24° 44 21° 57
B	26° 56 30°	16° 7 20°
C	12° 76 13°	8° 75 8° 75
D	24° 23 28° 4	17° 53 18°

Based on the data from Table 6, the following ANOVA summary table was derived.

TABLE 7  
ANOVA Summary

<u>SOURCE</u>	<u>SS</u>	<u>DF</u>	<u>MSS</u>	<u>F - value</u>	<u>CRIT F</u>
INKS	508.1606	3	169.3868	51.3395	4.0662
TIME	184.8920	1	184.8920	56.0390	5.3177
INTERACTION	24.8945	3	8.2981	2.5150	4.0662
ERROR	26.3947	8	3.2993		
TOTAL	744.3419	15			

The calculated F ratios are in each case the quotient of the mean square for time, temperature, and interaction. The critical F values are obtained from tables for a confidence interval of 95 percent.

The conclusions based on the analysis of variance are: For a 95 percent confidence interval the null hypothesis for time and inks can be rejected and the null hypothesis for interaction can be accepted.

Having rejected the null hypothesis the next step is to identify those inks which are significantly different. A Duncan Multiple Range test was used which compares the means

of the replicates of different inks with the Least Significant Difference values. The Least Significant Difference values are obtained as follows:

$$LSD_{0.05} = 2t_{0.025} S_e/n$$

where,  $2t_{0.025}$  is called the significant studentized range

$S_e$  is the Sum of Squares for the Error term (SSE)

Comparing the differences in the means between various inks to this LSD, it was observed that the difference between Inks A and B, and Inks B and D were not significant. However all other differences were significantly different.

Also, an ANOVA table was constructed for the differences between the two time intervals of an ink. These differences are shown in Table 8. It can be seen from the ANOVA summary, Table 9, that the null hypothesis

$$INKS : H_o : I_A = I_B = I_C = I_D$$

may be rejected at a 95 percent confidence interval since the computed F ratio exceeds the critical value.

A Duncan Multiple Range test was conducted and it was observed for a 95 percent confidence interval the differences in the change in contact angle for the Inks B and D, and Inks

TABLE 8

Differences in Contact Angle  
between the two time intervals

<u>INKS</u>	<u>Differences in Contact Angle</u>	
	<u>Replicates</u>	
	1	2
A	4°17	5°
B	9°86	10°
C	4°01	4°25
D	6°70	10°40

A and C were not significantly different. The differences in contact angle between immediate and 3 minutes for all the other inks were significant.

TABLE 9

ANOVA summary for the differences between the time interval

<u>SOURCE</u>	<u>SS</u>	<u>DF</u>	<u>MSS</u>	<u>F-Value</u>	<u>CRIT F</u>
TIME	49.79	3	16.66	9.2556	6.9474
ERROR	7.23	4	1.80		

---

Lower contact angle signifies better wetting. Thus a significant decrease in the contact angle may improve the rewettability characteristic of the ink.



## FOOTNOTES FOR CHAPTER VI

1

Perry and Chilton, "Drying Fundamentals," Chemical Engineers Handbook, Fifth Edition, McGraw-Hill, p. 20-10.

2

Rickmeyers A. D. and Todd N. H., Statistics - An Introduction, McGraw-Hill, 1967, p.174.

## CHAPTER VII

### SUMMARY AND CONCLUSIONS

The first null hypothesis was that there is no difference among the flexographic water based inks, in terms of their drying rate and volatile content. A careful study of these two factors for the four inks, Table 5, reveals that the inks do differ. No two inks have identical volatile content and drying rate. Thus this seems to be a good method of characterizing the differences between the inks.

From Table 5, it can be seen that Ink B has the highest volatile content and the highest slope. This may indicate the presence of increased cosolvents and reduced amounts of water in the formulation compared to other inks.

Conversely, Ink D has a lower volatile content and a slower drying rate which may be indicative of lower cosolvents and higher amounts of water. The results of Ink D may be due to the high volume of water added in the laboratory to decrease the viscosity. However, this procedure only depicts the pressroom condition where the pressman will be required to add water to achieve the desired viscosity. This may also indicate the presence of high solids when the ink is supplied to the pressroom by the manufacturer.

In this procedure no water was added to Ink A but it's comparable volatile content to Ink D and low drying rate may suggest a high fraction of water in the ink's formulation.

Thus it can be seen that this method is a good technique to differentiate the water based flexographic inks based on their drying characteristics.

However, it is difficult to determine the ink with the 'best' drying characteristics. Since the drying requirements are a strong function of the environment and the usage conditions, it is the inkmaker's responsibility to establish standards. The standards once established will enable the researcher to understand the behavior of new formulations, with the standard curve as reference guide.

The second null hypothesis states that the flexographic water based inks are the same with reference to their contact angle. According to the results of the ANOVA presented in Table 7, the inks and the two time periods for which they were tested indicate a significant effect, and the interaction was an insignificant factor. This suggests that the inks were different on the basis of their contact angle. The ink with the lowest contact angle indicates that it spreads well on the surface of the dried ink. Better spreading on the dried ink film indicates better rewettability characteristic. Thus in terms of rewettability, Ink C may be considered the best since

it has the lowest contact angle for both the immediate and three minute time delay. Thus this may be a good technique to compare inks and study how well the fresh ink will rewet dried ink on the flexographic printing plate using water based ink.

For future research, it may be interesting to compare the laboratory results to field trials with the knowledge of how well the inks performed on the press. The technique mentioned in this study may be utilized to study the characteristics of both a "good" and a "bad" ink.

## GLOSSARY

## Solubility

Solubility of one liquid or solid in another is the mass of a substance contained in a solution which is in equilibrium with an excess of the substance.

## Free Energy

Due to the mutual attractions between molecules in a liquid, a molecule in the interior is attracted in all directions, but one at the surface is only attracted inwards from the surface. The work done in creating unit area of surface against these forces at constant temperature is called free energy.

## Rheology

The study of the deformation and flow of matter.

## APPENDIX A

Based on the experimental data a mathematical model was jointly developed with J. A. Stephen Viggiano of the Rochester Institute of Technology Research Corporation.

The model was derived based on the one dimensional flow of heat.

$$m(t) = \beta_0 + \frac{\beta_1}{(1 + e^{-t/\beta_3})}$$

where,

$m(t)$  : mass at any given time  $t$

$\beta_0, \beta_1, \beta_3$  : regression coefficients

Also, mass of non-volatile component is  $\beta_0$ ,

mass of volatile component is  $-\beta_1/2$

and the Initial rate of change of mass is  $\beta_1/4\beta_3$ .

Quintessentially, this model predicts the mass of a given ink sample for a time  $t$ , within limits specified and known to the ink chemist.

The regression coefficients vary depending on the ink's quality and quantity of volatile content.

This model has an excellent predictive ability, with very low residuals, and a plot of the predicted versus actual mass is shown in figures 8,9,10,11,12 and 13. The actual and the predicted values, along with the statistical summary, are also shown in Tables 10 through 21.

## Centered Sigmoid (3 Parameter)

OBS	TIME	XMASS	P
1	0	3.01	2.99857
2	1	2.96	2.92604
3	2	2.87	2.85360
4	3	2.78	2.78135
5	4	2.69	2.70940
6	5	2.64	2.63783
7	6	2.57	2.56673
8	7	2.50	2.49619
9	8	2.44	2.42631
10	9	2.37	1.72126
11	10	2.24	2.28882
12	11	2.17	2.22136
13	12	2.11	2.15487
14	13	2.05	2.08940
15	14	2.00	2.02502
16	15	1.92	1.96179
17	16	1.86	1.89975
18	17	1.80	1.83896
19	18	1.73	1.77945
20	19	1.67	1.72126
21	20	1.61	1.66442
22	21	1.55	1.60897
23	22	1.50	1.55492
24	23	1.46	1.50228
25	24	1.41	1.45108
26	25	1.37	1.40132
27	26	1.35	1.35300
28	27	1.31	1.30612

Table 10. Predicted Values for Ink AI



Centered Sigmoid (3 Parameter)

NON-LINEAR LEAST SQUARES SUMMARY STATISTICS

SOURCE	OF SUM OF SQUARES	MEAN SQUARE
REGRESSION	3 127.29071953	42.43023984
RESIDUAL	25 0.45608047	0.01824322
UNCORRECTED TOTAL	28 127.74680000	
(CORRECTED TOTAL)	27 7.85238571	

PARAMETER	ESTIMATE	ASYMPTOTIC STD. ERROR	ASYMPTOTIC 95 % CONFIDENCE INTERVAL	
B0	5.80450755	0.9418451530	LOWER	UPPER
B1	-5.61187634	1.9485943572	3.8647566671	7.744258424
B3	19.33795892	8.7778015154	-9.6250494254	-1.598703261
			1.2598829801	37.416034858

ASYMPTOTIC CORRELATION MATRIX OF THE PARAMETERS

CORR	B0	B1	B3
B0	1.0000	-0.9981	0.9800
B1	-0.9981	1.0000	-0.9897
B3	0.9800	-0.9897	1.0000

NOTE: ALL ASYMPTOTIC STATISTICS ARE APPROXIMATE. REFERENCE: RALSTON AND JENNRICH, TECHNOMETRICS, FEBRUARY 1978, P 7-14.

Table 11. Summary of Regression Coefficients for Ink A1

INK A1  
 PLOT OF XMASS+TIME      SYMBOL USED IS A  
 PLOT OF P+TIME          SYMBOL USED IS P

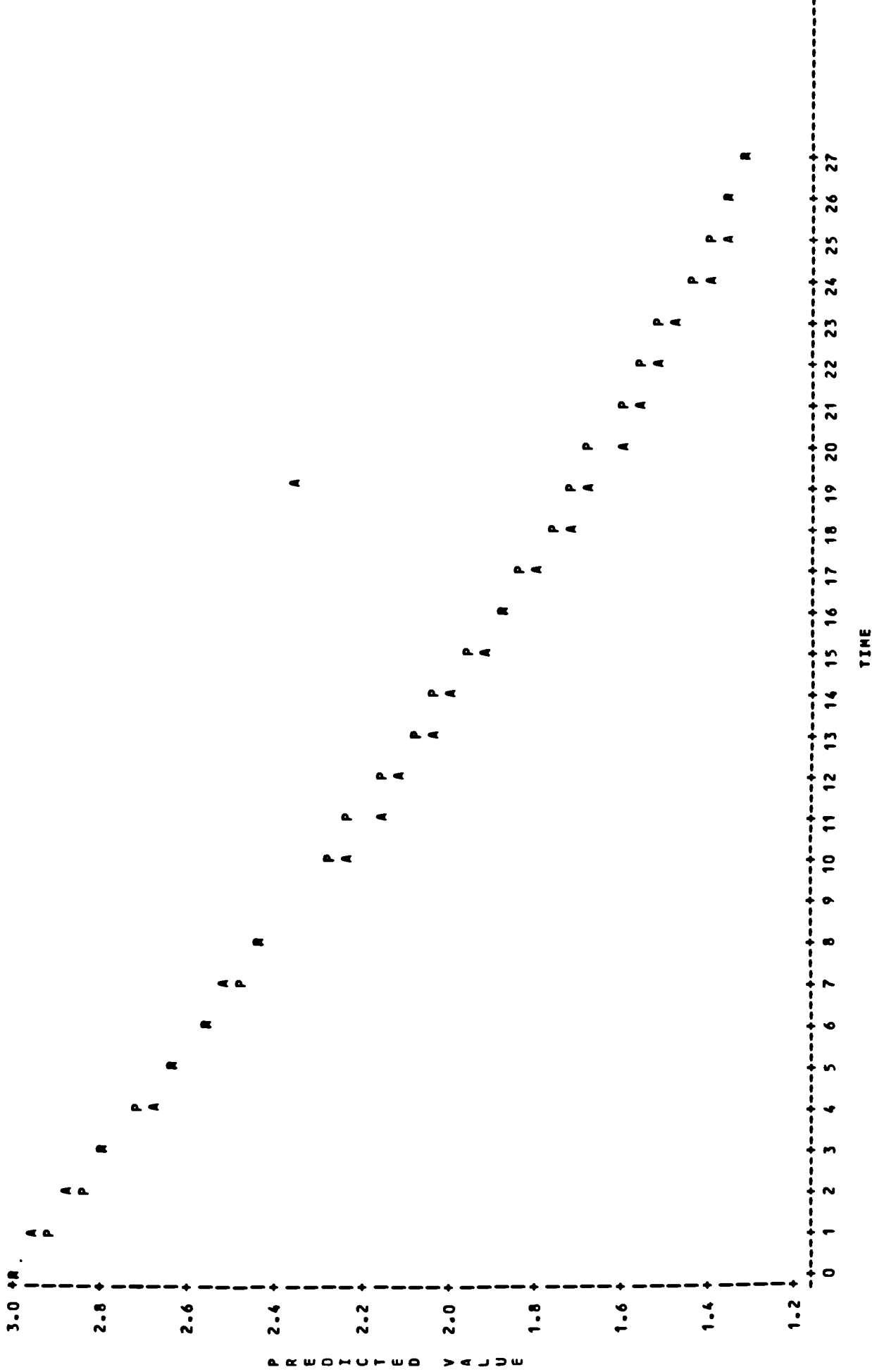


Figure 8. Predicted vs. Actual Values for Ink A1

NOTE: 1 OBS HIDDEN

Centered Sigmoid (3 Parameter)

OBS	TIME	XMASS	P
1	0	4.15	4.14314
2	1	4.06	4.04420
3	2	3.95	3.94542
4	3	3.84	3.84694
5	4	3.73	3.74893
6	5	3.63	3.65154
7	6	3.54	3.55490
8	7	3.44	3.45916
9	8	3.35	3.36446
10	9	3.27	3.27093
11	11	3.11	3.08784
12	12	3.02	2.99852
13	13	2.93	2.91081
14	14	2.85	2.82480
15	15	2.77	2.74057
16	16	2.68	2.65821
17	17	2.59	2.57777
18	18	2.51	2.49931
19	19	2.42	2.42287
20	20	2.34	2.34850
21	21	2.26	2.27623
22	22	2.19	2.20607
23	23	2.12	2.13804
24	24	2.05	2.07215
25	25	1.98	2.00840
26	26	1.93	1.94677
27	27	1.87	1.88726
28	28	1.82	1.82986
29	29	1.77	1.77452
30	30	1.73	1.72124
31	31	1.69	1.66997
32	32	1.66	1.62068

Table 12. Predicted Values for Ink A2

Centered Sigmoid (3 Parameter)

## NON-LINEAR LEAST SQUARES SUMMARY STATISTICS

SOURCE	OF SUM OF SQUARES	MEAN SQUARE	DEPENDENT VARIABLE XMASS
REGRESSION	3	256.90220574	85.63406858
RESIDUAL	29	0.01049426	0.00036187
UNCORRECTED TOTAL	32	256.91270000	
(CORRECTED TOTAL)	31	19.02012188	

PARAMETER	ESTIMATE	ASYMPTOTIC STD. ERROR	ASYMPTOTIC 95 % CONFIDENCE INTERVAL	
			LOWER	UPPER
B0	7.66905083	0.05826053425	7.549895537	7.788206115
B1	-7.05182436	0.12317286491	-7.303739289	-6.799909433
B3	17.81394271	0.47450954520	16.843468916	18.784416509

## ASYMPTOTIC CORRELATION MATRIX OF THE PARAMETERS

CORR	B0	B1	B3
B0	1.0000	-0.9902	0.9272
B1	-0.9902	1.0000	-0.9683
B3	0.9272	-0.9683	1.0000

NOTE: ALL ASYMPTOTIC STATISTICS ARE APPROXIMATE. REFERENCE: RALSTON AND JENNRICH, TECHNOMETRICS, FEBRUARY 1978, P 7-14.

Table 13. Summary of Regression Coefficients for Ink A2

PLOT OF XMASS\*TIME      SYMBOL USED IS A  
 PLOT OF P\*TIME        SYMBOL USED IS P

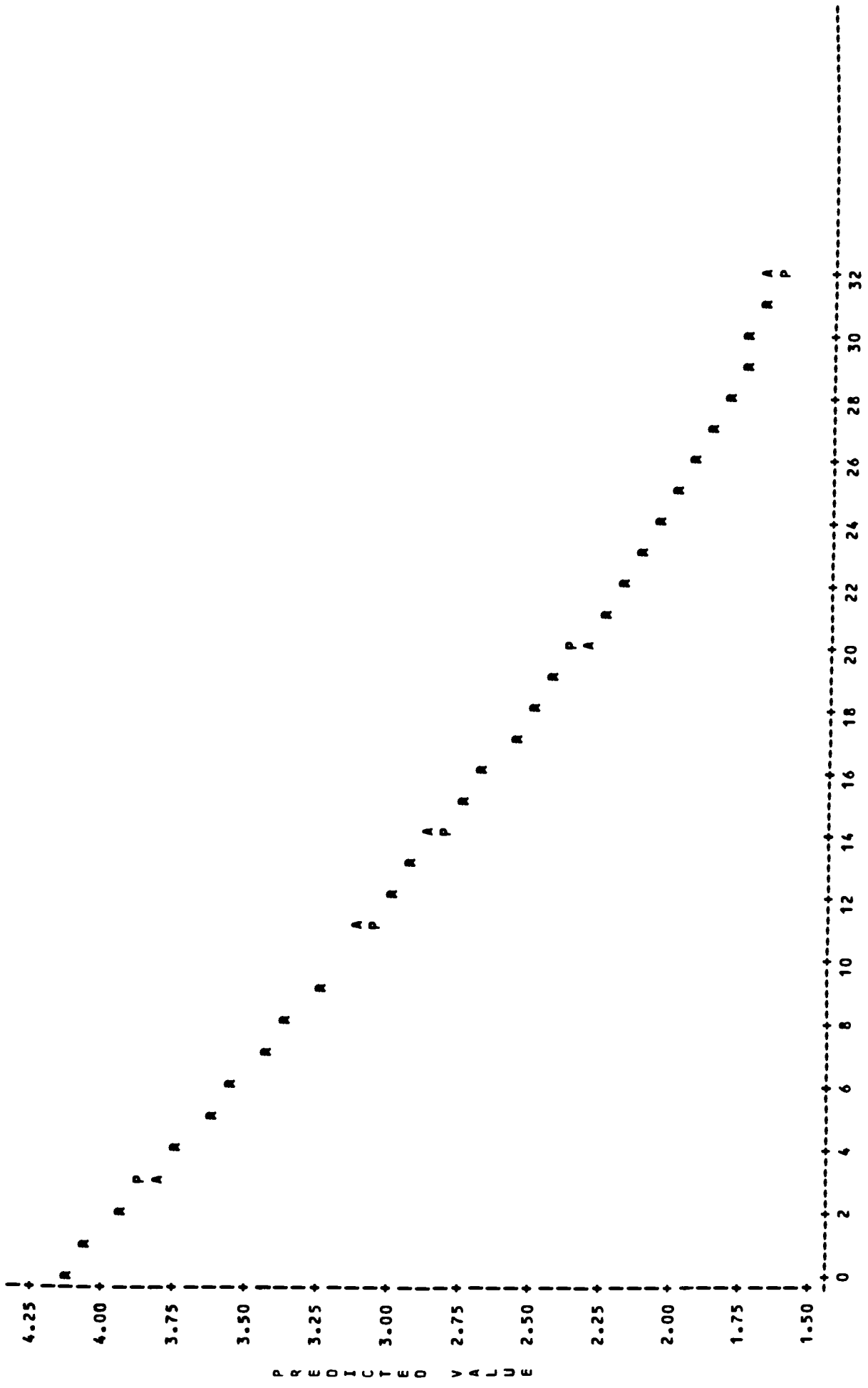


Figure 9. Predicted vs. Actual Values for Ink A2

Centered Sigmoid (3 Parameter)

OBS	TIME	XMASS	P
1	0	2.50	2.50670
2	1	2.37	2.41750
3	2	2.30	2.32861
4	3	2.23	2.24034
5	4	2.15	2.15300
6	5	2.08	2.06687
7	6	2.01	1.98223
8	7	1.94	1.89932
9	8	1.87	1.81838
10	9	1.78	1.73960
11	10	1.69	1.66319
12	11	1.61	1.58927
13	12	1.53	1.51799
14	13	1.45	1.44944
15	14	1.37	1.38370
16	15	1.30	1.32081
17	16	1.22	1.26080
18	17	1.17	1.20367
19	18	1.12	1.14941
20	19	1.07	1.09798
21	20	1.03	1.04934
22	21	0.98	1.00343
23	22	0.95	0.96016
24	23	0.91	0.91945
25	24	0.88	0.88123
26	25	0.86	0.84538
27	26	0.84	0.81181
28	27	0.83	0.78041

Table 14. Predicted Values for Ink B

Centered Sigmoid (3 Parameter) 1

NON-LINEAR LEAST SQUARES SUMMARY STATISTICS      DEPENDENT VARIABLE XMASS

SOURCE	OF SUM OF SQUARES	MEAN SQUARE
REGRESSION	3 70.902125071	23.634041690
RESIDUAL	25 0.021074929	0.000842997
UNCORRECTED TOTAL	28 70.923200000	
(CORRECTED TOTAL)	27 7.803142857	

PARAMETER	ESTIMATE	ASYMPTOTIC STD. ERROR	ASYMPTOTIC 95 % CONFIDENCE INTERVAL LOWER      UPPER
B0	4.63151979	0.05027059018	4.527986400      4.735053180
B1	-4.24963877	0.10472113312	-4.465314256      -4.033963287
B3	11.90303498	0.54123685685	10.788345724      13.017724226

ASYMPTOTIC CORRELATION MATRIX OF THE PARAMETERS

CORR	B0	B1	B3
B0	1.0000	-0.9569	0.7537
B1	-0.9569	1.0000	-0.9064
B3	0.7537	-0.9064	1.0000

NOTE: ALL ASYMPTOTIC STATISTICS ARE APPROXIMATE. REFERENCE: RALSTON AND JENNRICH, TECHNOMETRICS, FEBRUARY 1978, P 7-14.

Table 15. Summary of Regression Coefficients for Ink B

Centered Sigmoid (3 Parameter)

PLOT OF XHASS\*TIME      SYMBOL USED IS A  
 PLOT OF P\*TIME        SYMBOLD USED IS P

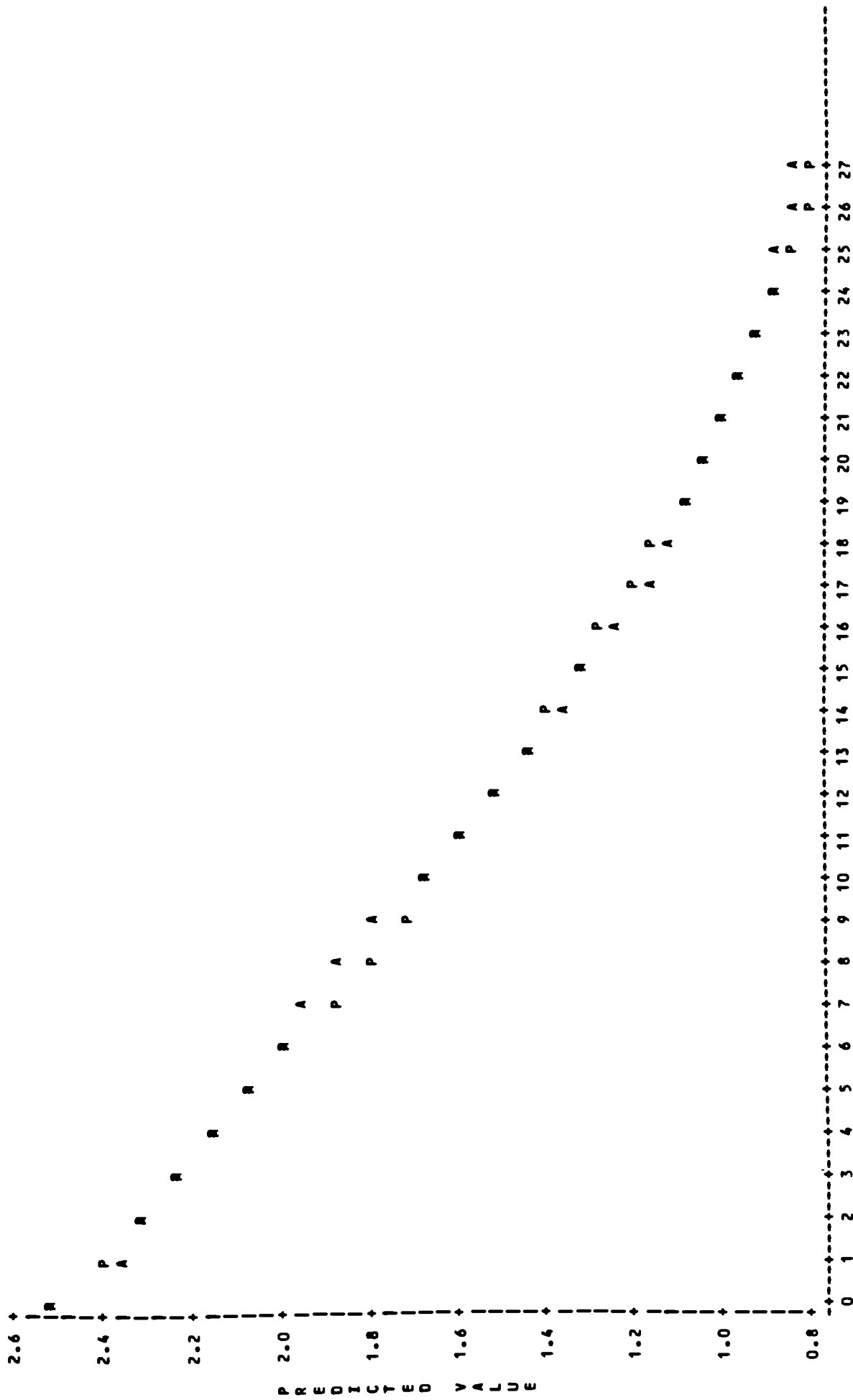


Figure 10. Predicted vs. Actual Values for Ink B



Centered Sigmoid (3 Parameter)

OBS	TIME	XMASS	P
1	0	3.17	3.10569
2	1	3.10	3.02510
3	2	2.91	2.94468
4	3	2.81	2.86460
5	4	2.74	2.78501
6	5	2.67	2.70608
7	6	2.60	2.62796
8	7	2.53	2.55079
9	8	2.47	2.47473
10	9	2.41	2.39989
11	10	2.34	2.32641
12	11	2.27	2.25439
13	12	2.20	2.18394
14	13	2.13	2.11515
15	14	2.06	2.04809
16	15	1.99	1.98284
17	16	1.93	1.91946
18	17	1.86	1.85799
19	18	1.80	1.79847
20	19	1.74	1.74092
21	20	1.68	1.68537
22	21	1.62	1.63182
23	22	1.57	1.58027
24	23	1.52	1.53071
25	24	1.48	1.48313
26	25	1.45	1.43751
27	26	1.41	1.39380
28	27	1.37	1.35199
29	28	1.33	1.31203
30	29	1.28	1.27388
31	30	1.23	1.23749
32	31	1.17	1.20282
33	32	1.15	1.16981
34	33	1.13	1.13841
35	34	1.11	1.10857
36	35	1.10	1.08022

Table 16. Predicted Values for Ink C

Centered Sigmoid (3 Parameter)

NON-LINEAR LEAST SQUARES SUMMARY STATISTICS

SOURCE	OF SUM OF SQUARES	MEAN SQUARE	DEPENDENT VARIABLE XMASS
REGRESSION	3	147.07799497	49.02599832
RESIDUAL	33	0.02330503	0.00070621
UNCORRECTED TOTAL	36	147.10130000	
(CORRECTED TOTAL)	35	13.58327500	

PARAMETER	ESTIMATE	ASYMPTOTIC STO. ERROR	ASYMPTOTIC 95 % CONFIDENCE INTERVAL	
B0	5.60358855	0.04127636335	5.519611696	5.687565404
B1	-4.99580672	0.08632241167	-5.171429848	-4.820183585
B3	15.49293336	0.49321411649	14.489488183	16.496378537

ASYMPTOTIC CORRELATION MATRIX OF THE PARAMETERS

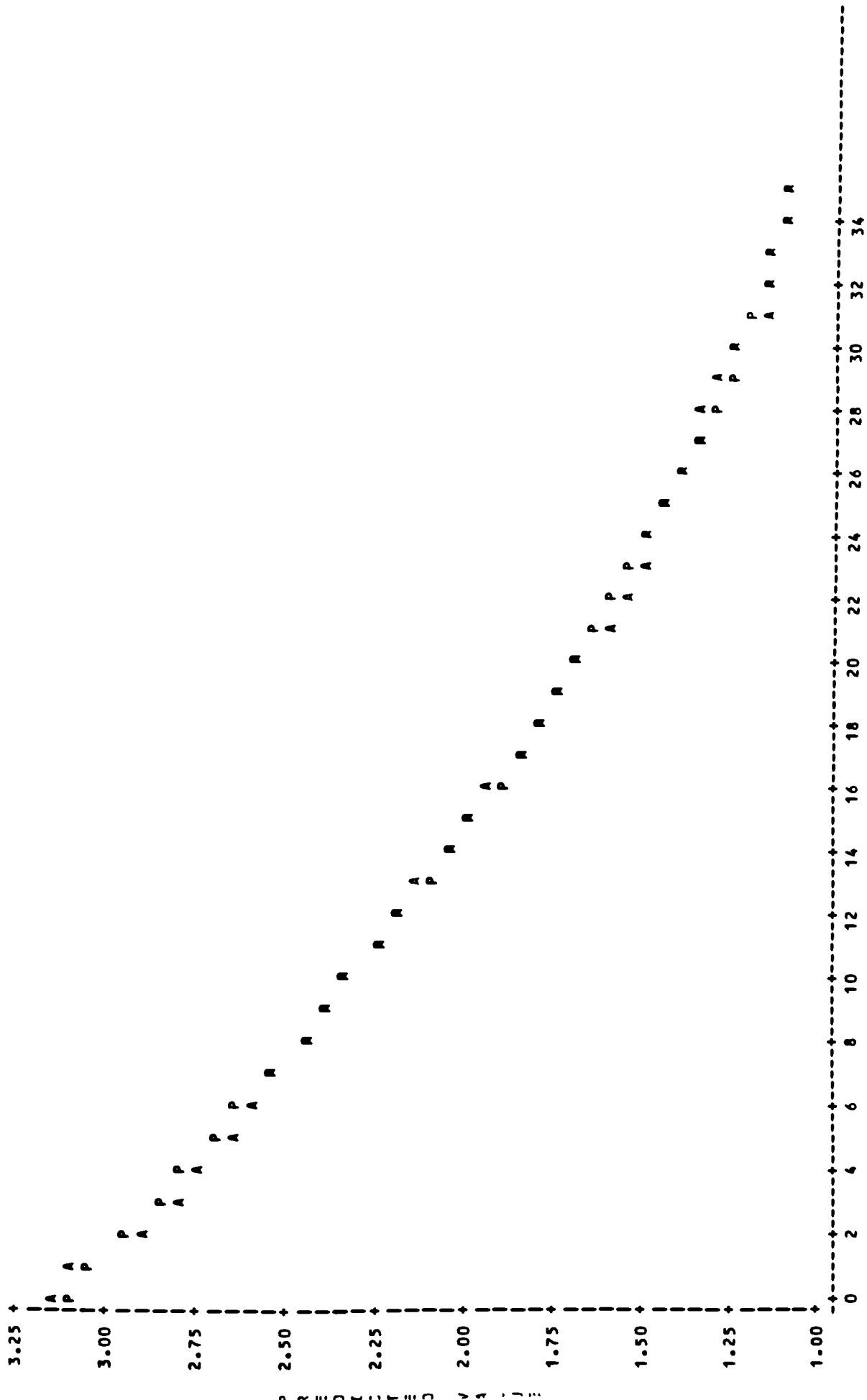
CORR	B0	B1	B3
B0	1.0000	-0.9576	0.7583
B1	-0.9576	1.0000	-0.9086
B3	0.7583	-0.9086	1.0000

NOTE: ALL ASYMPTOTIC STATISTICS ARE APPROXIMATE. REFERENCE: RALSTON AND JENNRICH, TECHNOMETRICS, FEBRUARY 1978, P 7-14.

Table 17. Summary of Regression Coefficients for Ink C

Centered Sigmoid (3 Parameter)  
 INK C

PLOT OF X\*MASS\*TIME      SYMBOL USED IS A  
 PLOT OF P\*TIME          SYMBOL USED IS P



Centered Sigmoid (3 Parameter)

OBS	TIME	XMASS	P
1	0	3.26	3.26128
2	1	3.21	3.20144
3	2	3.15	3.14162
4	3	3.08	3.08185
5	4	3.02	3.02215
6	5	2.95	2.96255
7	6	2.89	2.90308
8	7	2.83	2.84375
9	8	2.77	2.78459
10	9	2.72	2.72563
11	10	2.66	2.66689
12	11	2.61	2.60839
13	12	2.56	2.55016
14	13	2.51	2.49221
15	14	2.45	2.43456
16	15	2.40	2.37725
17	16	2.34	2.32029
18	17	2.27	2.26370
19	18	2.22	2.20750
20	19	2.15	2.15170
21	20	2.10	2.09634
22	21	2.04	2.04142
23	22	1.99	1.98696
24	23	1.93	1.93299
25	24	1.87	1.87950
26	25	1.81	1.82653
27	26	1.76	1.77408
28	27	1.71	1.72217
29	28	1.65	1.67081
30	29	1.61	1.62001
31	30	1.56	1.56979
32	31	1.52	1.52015
33	32	1.47	1.47111
34	33	1.44	1.42268
35	34	1.40	1.37485

Table 18. Predicted Values for Ink D1

Centered Sigmoid (3 Parameter)

NON-LINEAR LEAST SQUARES SUMMARY STATISTICS

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE
REGRESSION	3	193.57847147	64.52615716
RESIDUAL	32	0.00502853	0.00015714
UNCORRECTED TOTAL	35	193.58350000	
(CORRECTED TOTAL)	34	11.13755429	

PARAMETER	ESTIMATE	ASYMPTOTIC STD. ERROR	ASYMPTOTIC 95 % CONFIDENCE INTERVAL		
			LOWER	UPPER	
B0	7.41630704	0.2271168256	6.953688309	7.878925762	
B1	-8.31004549	0.4607217339	-9.248498647	-7.371592336	
B3	34.71212962	2.2129041044	30.204621757	39.219637491	

ASYMPTOTIC CORRELATION MATRIX OF THE PARAMETERS

CORR	B0	B1	B3
B0	1.0000	-0.9998	0.9963
B1	-0.9998	1.0000	-0.9977
B3	0.9963	-0.9977	1.0000

NOTE: ALL ASYMPTOTIC STATISTICS ARE APPROXIMATE.- REFERENCE: RALSTON AND JENNRICH, TECHNOMETRICS, FEBRUARY 1978, P 7-14.

Table 19. Summary of Regression Coefficients for Ink D1

Centered Sigmoid (3 Parameter)

PLOT OF X\*MASS\*TIME      SYMBOL USED IS A  
PLOT OF P\*TIME            SYMBOL USED IS P

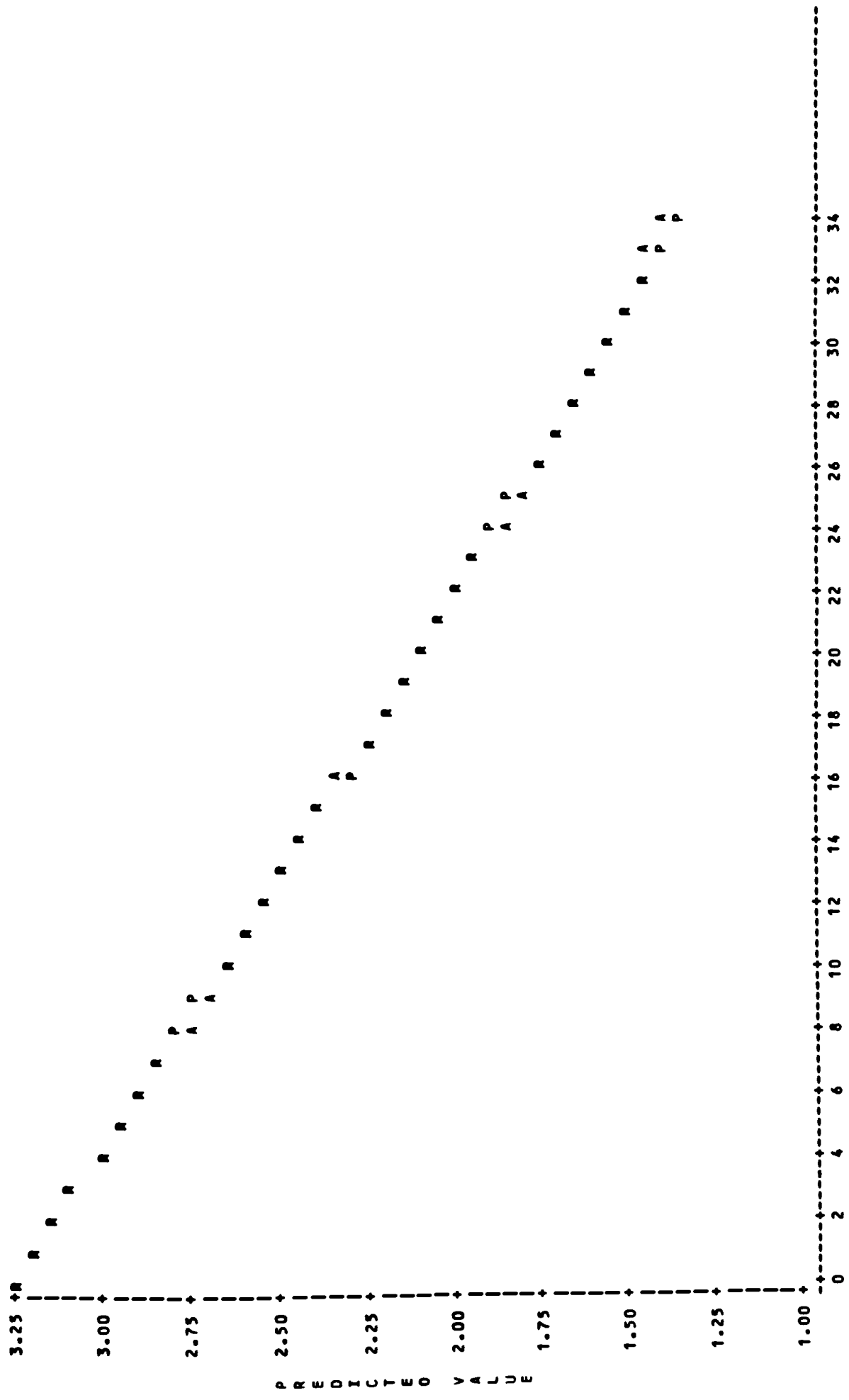


Figure 12. Predicted vs. Actual Values for Ink D1

Centered Sigmoid (3 Parameter)

OBS	TIME	XMASS	P
1	0	3.21	3.22474
2	1	3.16	3.16910
3	2	3.11	3.11349
4	3	3.05	3.05795
5	4	3.00	3.00233
6	5	2.95	2.94724
7	6	2.90	2.89213
8	7	2.84	2.83724
9	8	2.79	2.78258
10	9	2.74	2.72821
11	10	2.68	2.67415
12	11	2.63	2.62043
13	12	2.57	2.56708
14	13	2.52	2.51414
15	14	2.47	2.46163
16	15	2.42	2.40958
17	16	2.36	2.35802
18	17	2.31	2.30697
19	18	2.26	2.25646
20	19	2.21	2.20651
21	20	2.15	2.15715
22	21	2.10	2.10839
23	22	2.05	2.06025
24	23	2.00	2.01276
25	24	1.94	1.96593
26	25	1.92	1.91977
27	26	1.86	1.87431
28	27	1.84	1.82955
29	28	1.80	1.78550
30	29	1.75	1.74218
31	30	1.71	1.69960
32	31	1.66	1.65776
33	32	1.61	1.61667
34	33	1.56	1.57633
35	34	1.52	1.53676
36	35	1.49	1.49795
37	36	1.46	1.45991
38	37	1.43	1.42263
39	38	1.40	1.38612
40	39	1.36	1.35038

Table 20. Predicted Values for Ink D2

Centered Sigmoid (3 Parameter)

NON-LINEAR LEAST SQUARES SUMMARY STATISTICS

SOURCE	OF SUM OF SQUARES	MEAN SQUARE	DEPENDENT VARIABLE X MASS
REGRESSION	3	209.69430683	69.89810228
RESIDUAL	37	0.00379317	0.00010252
UNCORRECTED TOTAL	40	209.69810000	
(CORRECTED TOTAL)	39	12.60649750	

PARAMETER	ESTIMATE	ASYMPTOTIC STO. ERROR	ASYMPTOTIC 95 % CONFIDENCE INTERVAL LOWER	UPPER
B0	6.32881458	0.05902139232	6.209226522	6.448402634
B1	-6.20813550	0.12244743449	-6.456256229	-5.960054766
B3	27.89048191	0.72272259716	26.426114724	29.354849096

ASYMPTOTIC CORRELATION MATRIX OF THE PARAMETERS

CORR	B0	B1	B3
B0	1.0000	-0.9981	0.9797
B1	-0.9981	1.0000	-0.9895
B3	0.9797	-0.9895	1.0000

NOTE: ALL ASYMPTOTIC STATISTICS ARE APPROXIMATE. REFERENCE: RALSTON AND JENNRICH, TECHNOMETRICS, FEBRUARY 1978, P 7-14.

Table 21. Summary of Regression Coefficients for Ink D2



Centered Sigmoid (3 Parameter)  
-INK D2

PLOT OF XMASS\*TIME      SYMBOL USED IS A  
PLOT OF P\*TIME        SYMBOL USED IS P

