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PHYSICO-CHEMICAL ASPECTS  
OF FLEXOGRAPHIC PRINTING

by  
William G. Jenkins

A Thesis  
Presented to the Graduate Committee  
of Lehigh University  
in Candidacy for the Degree of  
Master of Science  
in  
Chemistry

Lehigh University

June 1984

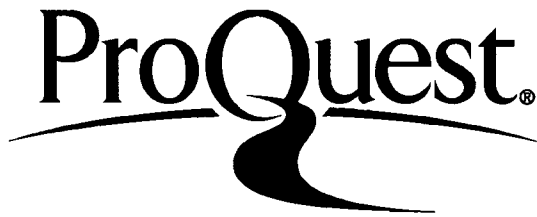
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This thesis is accepted and approved in partial fulfillment of the requirements for the degree of Master of Science.

5/4/84  
Date

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Chairman of Chemistry  
Department

## Acknowledgement

It is a pleasure to express my gratitude to Dr. A. C. Zettlemoyer for his guidance, suggestions and criticisms. I would also like to thank Dr. P. Pendleton for his assistance and valuable advice concerning the experimental aspects and theoretical concepts involved in this study.

The author wishes to thank Lehigh University for the award of a Buch Fellowship which provided support for 2 years and the E. I. DuPont de Nemours Co. for financial grants which supported the experimental work.

Finally, the author wishes to express his deep gratitude to his wife for her encouragement, love and understanding during his period of graduate studies.

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## ABSTRACT

Reflectance spectroscopy, scanning electron microscopy and macro-photography were used to evaluate the printability and ink transfer of DuPont photopolymer flexographic printing plates and its competitors, BASF Nyloprint, and Uniroyal Flex-Light K.

Photographs of the photopolymer plate surfaces, both DuPont and competitors, before and after printing, have been placed in order of decreasing surface roughness. Before printing, the rating was Cyrel FR capped > Cyrel FR > BASF Nyloprint > Uniroyal Flex-Light K. However, after printing, the order became: Cyrel FR capped > Cyrel FR > Uniroyal Flex-Light K > BASF Nyloprint. An overall smoothing of the plates occurred with printing time. D-values of a printed solid region plateaued after approximately 20 minutes of printing. No correlation was found between plateau D-values and plate surface roughness.

Good reproducibility of D-values was obtained as a function of press speed provided the press was not stopped. Using D-value measurements, it was found that upon increasing or decreasing the roller nip pressure, the pressman demonstrated an inability to reproduce the original printing conditions.

From a series of repeated printing tests of Cyrel FR exposed to similar conditions, the reproducibility of the Gallus-Stanford press and/or its operator, on a day-to-day basis, has been found to be poor. However, reproducibility during any given day for both press and/or its operator was found to be good.



The D-value (ink thickness) of a solid region are always initially low and increase to a plateau after about 20 minutes of printing for all plates tested. The D-value remains constant (within experimental error) for the remainder of the run. Differences of as little as 3% change in D-value can be detected by the eye. A change in viscosity of less than 5% was found to result in a negligible variation in the resulting D-value.

An extensive SEM analysis of plates subjected to printing, stored in a partially dried condition then reprinted, shows that the effect of storing the plates before complete drying has occurred can lead to premature image wear or fracture.

Halo effects, a common occurrence in half-tone printing, were observed as a result of plate swelling with time on the press. The cause of the halo has also been discussed in terms of character deformation on passage of a character through the plate roller/substrate nip. The BASF plate was found to give the greatest deformation, or halo lengthening, beyond its original print dimensions because of its tendency to swell to a greater extent in the ink solvent than any of the other plates tested.

## I. INTRODUCTION

### A. The Flexo Process

Flexography is a form of rotary letterpress printing which uses a flexible plate, such as rubber or photopolymer, and fluid inks.

Originally the process was used for paper bag printing but flexography subsequently proved ideally suited for the printing of almost any kind of flexible packaging materials.

The growth of flexography has been extremely rapid in the past two decades with the introduction of many plastic films for packaging. These include the various polyolefins, polystyrene, polyesters, and others where the rapid-drying flexo inks are well suited to their non-porous surfaces. Of course, flexo inks print equally well on tissue, kraft, and other paper stocks, as well as aluminum foils, paperboard, and corrugated liners. It prints well on box coverings, folding cartons, gift and trademark wrappings, paper cups and containers.

Since the early 1970's the flexible packaging market has also seen a phenomenal growth in the lamination of films and foils in a myriad of combinations. Flexographic inks have played an important role in this growth because of their adaptability to different substrates, low residual odor, and compatibility with laminating adhesives.

The flexographic process offers versatility and quality at an economic cost. The process permits multi-color printing at speeds approaching 1000 f.p.m. and is often run in line with slitting, forming, and laminating machines.

## B. Flexographic Presses

Flexographic presses are rotary machines with color stations either stacked, in-line, or around a common impression cylinder. The press which was used for this work was of the common impression cylinder type.

A flexographic press can contain one to six or more printing stations. Each printing station has three basic parts (Fig. 1-1):

1. an inking unit
2. a plate cylinder
3. an impression cylinder

In the inking unit a fountain roller, usually rubber covered, carries ink from the ink fountain to the nip or junction between the two inking rollers. At the nip, ink is metered to the form or transfer roller and carried by it to the plate or plates mounted on the plate cylinder. The surface of the form roller is usually either rubber, chrome-plated smooth steel or chrome-plated engraved steel, the latter being known as an anilox roller. The proper choice is governed by such factors as the stock to be printed and the nature of the operation.

The function of the plate cylinder is to carry the printing plate, originally rubber, but now more often a photopolymer, containing the copy to be printed from the inking section where ink is deposited on the printing surface of the plates to the web on which the ink in the form of printed copy is laid down.

The function of the impression cylinder is to support the web so that the lightest possible contact, "just-kiss", can be made between the plate and the web in order to transfer the ink properly from the surface of the plate to the web.

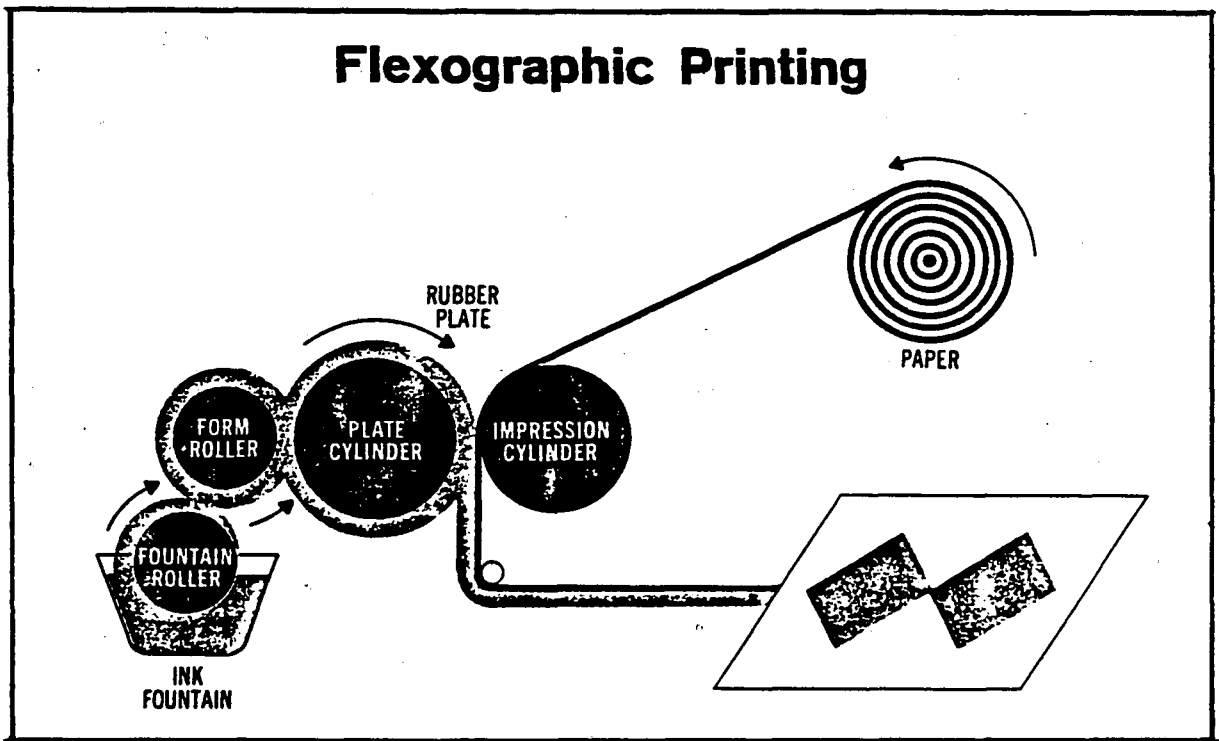


Figure 1-1: The Flexographic process

The central impression press supports all of the color stations around a single steel impression cylinder mounted in the main press frame. The web is supported by the impression cylinder and is thereby "locked" to the cylinder as it passes by all color stations. This prevents register shift from color to color.

Since the primary advantage of the central impression cylinder press is its ability to hold excellent register, this press has become the mainstay of converters primarily interested in the printing of extensible materials. Also, with graphic designs becoming more complicated and the steady demand for process printing, its positive register ability lends itself to all types of substrates.

### C. Flexographic Inks

Flexographic inks generally consist of pigment dispersed in a vehicle made by dissolving one or more resins in solvent. The inks dry mainly by evaporation of volatile solvents which include the lower alcohols together with esters, glycol ethers, and the lower aliphatic hydrocarbons. These solvents are used to dissolve a wide variety of binders such as nitrocellulose, cellulose ethers and esters, polyamides, acrylics, and modifying resins such as modified rosins and ketone resins.

The aforementioned resins can be modified with a variety of plasticizers and waxes to impart flexibility, scratch resistance, slip, and adhesion.

Water-based flexographic inks are widely used on paper and paperboard including bleached or brown kraft and corrugated. Vehicles for these water-based inks are usually made from ammonia or amine-solubilized protein, casein, shellac, esterified fumarated rosins, acrylic copolymers or their mixtures. Advantages of the water-based inks include:

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good press stability and printability; absence of fire hazard (although water-based ink containing sufficient alcohol may have flash points in the flammable range); convenience and economy of water as a diluent and for wash-up. Disadvantages include low gloss and slow drying which limits their use to absorbent stocks. Due to pressure from the EPA the use of solvent-based inks will be reduced in favor of water-based inks where possible.

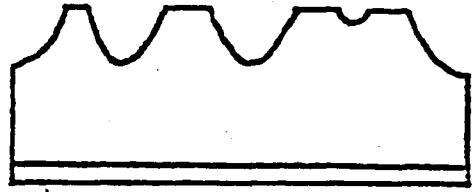
#### D. Flexographic Printing Plates

Up until 1973 with the introduction of elastomeric photopolymer plates, the printing plates for flexo were made of rubber which was either engraved or molded. Since the 1973 introduction of the elastomeric photopolymer plate for flexographic printing, its growth and acceptance has been phenomenal. Among the basic advantages which photopolymer plates have over rubber plates for half-tone printing are excellent ink transfer, improved thickness tolerance, and longer press life. It can be virtually guaranteed that each plate made from the same negative will be the same, so that there will be little or no printing difference from plate to plate, improving plate registration for multi-color printing.

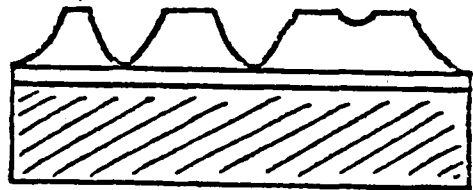
Photopolymer plates have a relatively simple structure (Fig. 1-2). The majority consist of a photopolymer material bonded to a polyester or steel support. The photopolymer determines the ink compatibility of the printing plate, and the support provides the plate with dimensional stability for tight register and accurate mounting.

There are many photopolymer plates available today. Most of them are produced by four major plate manufacturers in the U.S.: DuPont, BASF, Uniroyal, and Hercules.

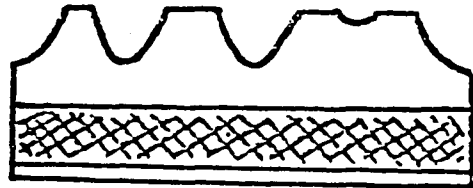
One Photopolymer  
Layer structure



Multilayer Structure



Compressible Back



Capped Plate



Figure 1-2: Photopolymer plate construction



## 1. DuPont Cyrel

Cyrel plates manufactured by DuPont consist of a photopolymer bonded to a polyester film support covered by a protecting strippable Mylar sheet. Exposure to ultraviolet light through a photographic negative hardens the image area. The unexposed area is washed away in a processing step. After the plate is dried, finished and post exposed, it is ready for press. Features of the Cyrel plate include:

1. Uniform thickness
2. Dimensional stability
3. Clean and sharp image
4. Excellent printing uniformity
5. Good durability

Cyrel plates are compatible with water, hydrocarbon (Cyrel LP) and alcohol/acetate based inks (Cyrel FR).

## 2. BASF Nyloprint

Another photopolymer plate is the Nyloprint (Heavy Hitter) from BASF. This plate consists of three layers comprising a photopolymer laminated to a thin polyester support mounted to a soft polymer. The surface photopolymer is harder than the softer backing layer which acts as a cushion to absorb press imperfections. The hard printing image produces a sharp impression with low distortions, the polyester support in the center provides the necessary dimensional stability. Thus, BASF "suggests" that printing quality is improved. Compromises involving, for example, over-impression to remove variation in plate thickness resulting in poor half-tone quality are avoided. Nyloprint has a wider exposure range than any other plate; thereby it can be pushed more in the exposure unit to hold finest detail, without reverses filling in. These photopolymer plates are not recommended for use with hydrocarbon

based inks. The plates have been designed to be used with water/alcohol and alcohol/acetate based inks with up to 20% acetate.

### 3. Uniroyal Flex-Light

A third photopolymer plate is Flex-Light manufactured by Uniroyal, which consists of a standard photopolymer plate mounted onto a cushion mount of a closed-cell polyurethane foam material. It does not employ a conventional dissolution process for development of the relief image and so avoids many of the limitations and added costs normally associated with that process. The photopolymer material is supplied with either dimensionally stable polyester or metal backing. The durometer of these plates may be varied by the amount of ultraviolet exposure given to the plates, either in the normal exposure sequence or as a post exposure step; differential hardnesses within the same plate can also be produced. The relief depth may be varied, and solvent resistance is compatible with all commonly used ink systems, including oil-based inks. Special features include: solvent re-use through many platemaking cycles before the need for solvent replacement or reclamation, wide variety of material thicknesses and large sheet sizes, no safelights required, choice of backing i.e. polyester or metal for use on magnetic cylinders, and solvent resistance, even in oil-based inks and aliphatic hydrocarbons.

### 4. Hercules Merigraph

The fourth photopolymer plate is Merigraph by Hercules, which consists of a hard photopolymer bonded to a softer compressible material which in turn, is laminated to a polyester support. The Merigraph plate making system utilizes a liquid photopolymer resin, a two-sided exposure technique and a washout cycle based on water not solvents. The system

can produce plates to accommodate dry offset, rotary and flat bed letter press, and flexo printing applications. Versatility is the key feature of the Merigraph system! Liquid photopolymers provide distinct advantages in plate productivity, unexposed photopolymer recovery and environmental considerations. The Merigraph plates are alcohol/acetate resistant.

Extensive work by Hsiung (1) on the characterization of the various photopolymer plates showed the total surface energies are quite similar. The Young's modulus of each plate was measured and found to be nearly constant; there appeared no correlation between Young's modulus of a plate and the corresponding ink transfer. Shore A2 hardness of the plates was measured as a function of total immersion in solvent. After immersion, then drying for 3 days, only Cyrel FR and LP were the same as the original Shore A; all the other plates were softer under the same controlled conditions, implying that either the printing section or the cushion backing had been physically affected by total immersion in the common solvent.

Earlier work again by Hsiung (1) using a K101 proof press and conventional press assessed the ink transfer by weighing and measuring the reflectance of white light by the printed page. D-values were discussed as a tool for the determination of print quality and plate/print relationships with time on the press. The use of D-values for these purposes was carried further in this work.

The work reported in this thesis makes extensive use of scanning electron microscopy to determine the effects of printing on the plate surface and the interrelationship between plate printability and plate

surface micro-roughness. Ink transfer by the various plates was studied using a reflectance technique as a function of time on the press, over- and under- impression at the roller nips and speed.

## II. REFLECTANCE SPECTROSCOPY

### A. Reflectance Spectrophotometers

Optical arrangements for reflectance measurements are one of three types;

1. integrating sphere
2. annular ellipsoidal mirror, and
3. reflection.

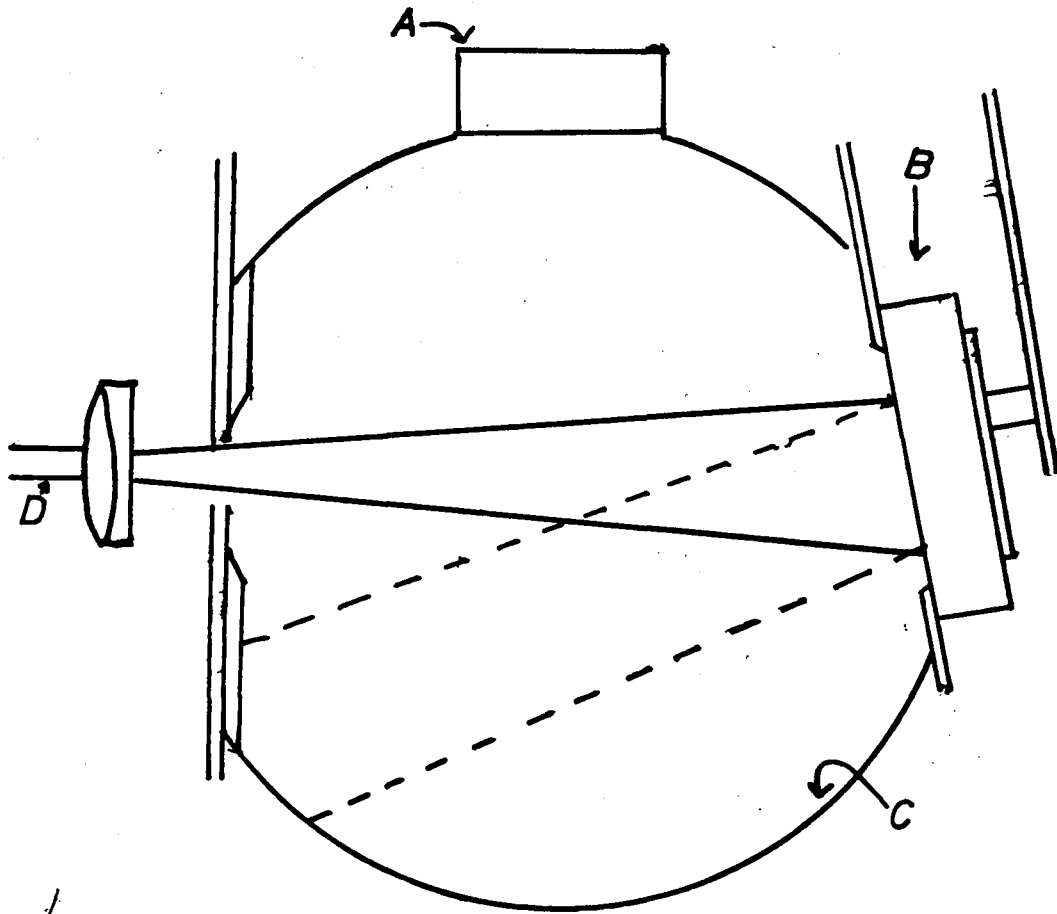
The integrating sphere type (Fig. 2-1) was used for this work. White light enters the sphere through a side aperture and illuminates the sample; the reflected radiation is collected by the sphere (which is coated on the interior with barium sulphate) where the intensity at each wavelength is measured by a photodetector. Sample and reference material are pressed against the measuring (and reference) aperture by means of a spring loaded disk.

### B. Transfer Measured by Reflectance

When monochromatic radiation passes through a sample containing an absorbing species, the radiant power of the beam is progressively decreased as more of the energy is absorbed by the particles of that species. The decrease in intensity depends upon the concentration of the absorber and the length of the path traversed by the beam.

Let  $I_0$  be the intensity of the beam upon a section of printed material that has a concentration of ink  $c$ . Further, let  $I$  be the intensity of the beam after it has traversed 1 distance of ink. As a consequence of reflectance,  $R$  will be,

$$R = I/I_0 \quad (2-1)$$



- A- Multiplier phototube
- B- White reflectance standard and/or sample
- C- BaSO<sub>4</sub> reflecting surface
- D- Beam from monochromator

Figure 2-1: Reflectance spectrophotometer

The logarithm (base 10) of the reciprocal of the reflectance is the absorbance D:

$$D = -\log R \quad (2-2)$$

$$D = \log (1/R). \quad (2-3)$$

By Beer's Law:

$$\log I_0/I = \epsilon lc = D. \quad (2-4)$$

Where  $\epsilon$  is the extinction coefficient of the material being tested and is dependent upon the wavelength of light,  $l$  is the thickness of the sample and  $c$  is the solids concentration of coloring material (either pigment or dye). Clearly D-values are directly proportional to the solids concentration and thickness of the printed layer. Obviously, for a single color and constant viscosity (i.e. solids concentration) ink, any variation in ink reflectance will be directly attributable to a proportional variation in ink thickness.

Reflection occurs whenever a ray of light encounters a boundary between two media. Color may be represented in terms of tristimulus values for red, blue, and green spectral colors (CIE System of X, Y, Z, coordinates); or green, amber, and blue reflectance (GAB System); or R, a and b or its closely related system; L, a and b. With these scales it is possible to represent color by position in a three coordinate system (Fig. 2-2). The diffuse reflectance term, R, is the percentage of light reflected by a magnesium oxide standard, it is equal to the value Y (CIE System) or G (GAB System).

Reflectance curves of colored materials look somewhat like a transmittance curve. A perfectly white sample would reflect all of the light and its curve would be a horizontal line at 100%. A theoretically

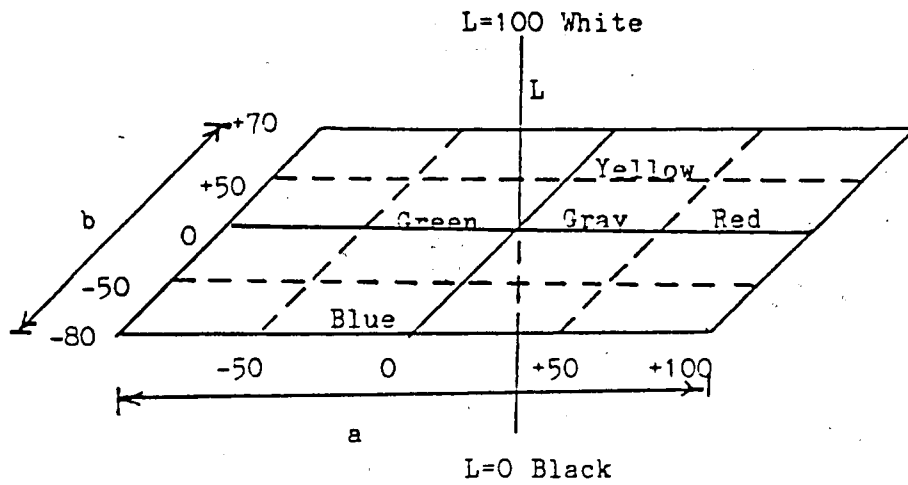


Figure 2-2: Dimensions of the rectangular L, a, b surface color solid used with the color difference meter



perfect black sample would absorb all of the light and its curve would be a horizontal line at 0% (2, 3).

### III. EXPERIMENTAL

This work evaluated the printability and ink transfer of photopolymer plates used in flexographic printing. Four types of plates were used:

1. Cyrel FR from DuPont,
2. Cyrel FR with a 0.05 mm cap from DuPont,
3. Nyloprint from BASF, and
4. Flex-Light K from Uniroyal.

The photopolymer plates were exposed through the same photographic negative and thereby contained the same image. This allowed for a consistent comparison between the various plates. The plates measured 0.23 m by 0.15 m and had thicknesses of 2.3 mm (Cyrel FR and Nyloprint), 2.8 mm (Cyrel FR capped), and 2.9 mm (Flex-Light K). Fig. 3-1 is a representative print made by the test plate.

The ink used was a polyamide resin alcohol/acetate reducible phthalocyanine blue ink supplied by Immont Chemicals. The ink was diluted to a viscosity in the range of 13 to 14 seconds drain time, using a #3 Shell cup.

The substrate used was .06 mm corona discharge treated clear polyethylene.

In all cases the prints were generated by a Gallus-Stanford press capable of multiple, precalculated, reproducible speeds (at the DuPont Graphics Center, Boothwyn, PA). The plates were secured to the plate cylinder using 0.51 mm thick double-sided sticky tape (3M Company). Throughout all press runs the ink was constantly circulated, by means of an ink pump, between a periodically monitored correct viscosity reservoir and the inking station on the press.

#### A. Ink Transfer Studies

Ink transfer studies were made as a function of time on the press,



<sup>®</sup>  
**CYREL**  
TRADE MARK



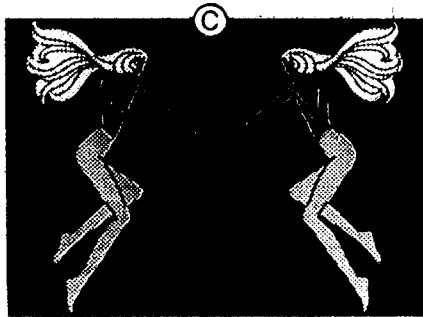
# Photopolymer Flexographic Printing Plate

(B)

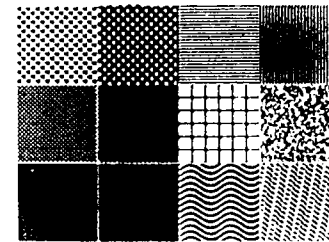
EACH DU PONT CYREL FLEXOGRAPHIC PLATE IS AN ORIGINAL PREPARED DIRECTLY FROM A FILM NEGATIVE. NO ENGRAVING OR MATRIX IS USED. EXCELLENT DIMENSIONAL STABILITY ASSURES REGISTER AND FIT EACH AREA OF YOUR PRINTING PLATE.

Each Du Pont CYREL flexographic plate is an original prepared directly from a film negative. No engraving or matrix is used. Excellent dimensional stability. ABCDEFGHIJKLMNOPQRSTUVWXYZ 1234567890%&.

Each Du Pont CYREL flexographic plate is an original prepared directly from a film negative. No engraving or matrix is used. Excellent dimensional stability. ABCDEFGHIJKLMNOPQRSTUVWXYZ 1234567890%&.



(D)



(E)



(F)

## Du Pont CYREL Flexographic Plate

- Each plate is an original—  
No engraving or matrix needed.
- Dimensionally stable—  
Close register is assured.
- Uniform in thickness—  
0.067" (1.70mm) or 0.112" (2.85mm)
- Sheet size: 18" x 30" (46 x 76 cm)

(G)



Figure 3-1: Test print

over and under impression at the anilox/plate and plate/substrate nips and press speed. In all cases, the press operator would obtain an optimum print by adjustment of roller contact in the various roll nips of the ink train. These adjustments would take typically 4 to 5 minutes.

#### 1. Ink transfer as a function of press time

After obtaining an optimum print, a sample was obtained. This sample was always regarded as the initial sample of a press run analysis. Samples were also taken at specific intervals of time during the press run. A minimum of ten samples were usually taken to determine a statistical average of the D-value.

#### 2. Ink transfer as a function of roll nip pressure

A study of the effect of over/under impression on the D-values (ink thickness) was made using the Gallus-Stanford press. Strain gauges were implanted in the photohardened image of the plate to allow measurement of the nip pressures. The procedure for the impression tests was as follows: obtain an optimum print; increase the pressure between plate/substrate (or anilox/plate) nip; return to the original conditions; reduce the nip pressure; return to an optimum print. Prints were sampled at each of these conditions. Also, each print had to be a complete image, particularly in the "under-impressed" condition.

#### 3. Ink transfer as a function of press speed

The speed tests were conducted by having the pressman obtain an optimum print at a press speed of 1.02 m/s. The speed of the press was then increased to 2.03 m/s, then decreased to 0.25 m/s. Samples were taken at 0.25 m/s intervals. Reproducibility was checked by sampling at 0.51 m/s intervals from a starting speed of 0.25 m/s up to 2.03 m/s

## B. Print Analysis

The effect of plate swelling on ink transfer was determined as a proportionality to reflected ink density. The reflectance measurements were made using a KCS 18 Kollmorgan Color Systems Analyzer. The light source was a Tungsten Halogen lamp. The wavelength of measurement was 620 nm which is the wavelength of minimum reflectance (or maximum absorbance) of the printed blue ink.

The samples were analyzed for ink reflectance in the solid and several different half-tone regions. The solid sample area was a 5.0 mm diameter circle located approximately 50 mm from the left-hand side of the print and approximately 5 mm from the top printed edge. Each half-tone region was also examined using a 5 mm diameter circle.

The effect of plate swelling on the ink transfer of half-tones was determined by reflectance spectroscopy and macrophotography. 70%, 30%, and 20% half-tones were examined using reflectance spectroscopy; these same half-tones and the characters in the word "Photo" were examined by macrophotography.

## C. Scanning Electron Microscopy of Plates

Several alcohol/acetate resistant plates were compared with each other to determine if a relationship exists between plate surface roughness and print quality. The plates examined were: DuPont Cyrel FR and a capped Cyrel FR; BASF Nyloprint; Uniroyal Flex-Light K.

The plates were examined as received and after being printed for 1 hour on a Gallus-Stanford press. Sample preparation for microscopic analysis consisted of coating the samples with a 1nm gold film and viewing with an ETEC scanning electron microscope.

#### D. Printing Ink Characterization

These studies were made at Haake, Inc. (Service and Facilities Lab Saddlebrook, N.J.) using a Haake RV 100/CV 100 and a Haake RV 12. The Haake RV 100/CV 100 was used to determine the shear rate/shear stress relationship from 0-300 s<sup>-1</sup>; the RV 12 was used from 0-20,000 s<sup>-1</sup>. The RV 100/CV 100 was used with a guard-ring arrangement to reduce evaporation effects and to enable subsequent measurements without changing the ink sample. Both sets of measurements were made at 23°C. The inks examined were supplied by Immont Chemicals and Sakata Shokai Chemicals of Japan.

A study of the viscosity of the Immont ink and how it relates to the dry solids concentration was carried out. 5 ml samples of inks of known viscosities, as measured with a #3 Shell cup were pipetted and transferred to tared cups. The samples were allowed to dry and the dry solids concentration (g/cc) was determined.

Calculation of the viscosity of the ink uses Equation (3-1) is used to convert the ink drain for the #3 Shell cup to kinematic viscosity (centistokes),

$$\nu = 1.51 (t-2) \quad (3-1)$$

A division of the kinematic viscosity by the density of the ink yields the viscosity in centipoise.

#### IV. RESULTS AND DISCUSSION

##### A. Ink Transfer as a Function of Press-Time

###### 1. Reflectance spectroscopy analysis

The method used to monitor ink transfer is to measure the amount of light reflected from a printed ink film, as compared to a white standard. A D-value is calculated as follows:

$$D = -\log (\text{Reflectance}) \quad (4-1)$$

and the following relation:

$$D = \epsilon lc, \quad (4-2)$$

where  $\epsilon$  is the extinction coefficient of the printed ink,  $c$  is the concentration of the dry solids in the ink and  $l$  is the thickness of the ink film. The D-value is thus proportional to ink thickness. Fig. 4-1 shows a typical plot of D-value as a function of time on the press for Cyrel FR; the results indicate that the D-values plateau after approximately 20 minutes of printing.

The results of reflectance measurements in Fig. 4-2 and 4-3 are an attempt to determine the reproducibility of the Cyrel FR print thickness and as a test of the method of examination. As the percentage of half-tone increases to a solid print the difference in plateau value increases. However, the D-value for the initial sample (time = 0 minutes) in each test appears to be the same for each individual area examined. The apparent increase is from approximately 0 to 3%. The viscosity of the ink during the test increased by 2%. The increase in the D-value of the solid area is considered to have been caused only by the increase in the viscosity of the ink during the test. Assuming the two plates have swollen to the same extent then the print area of each half-tone

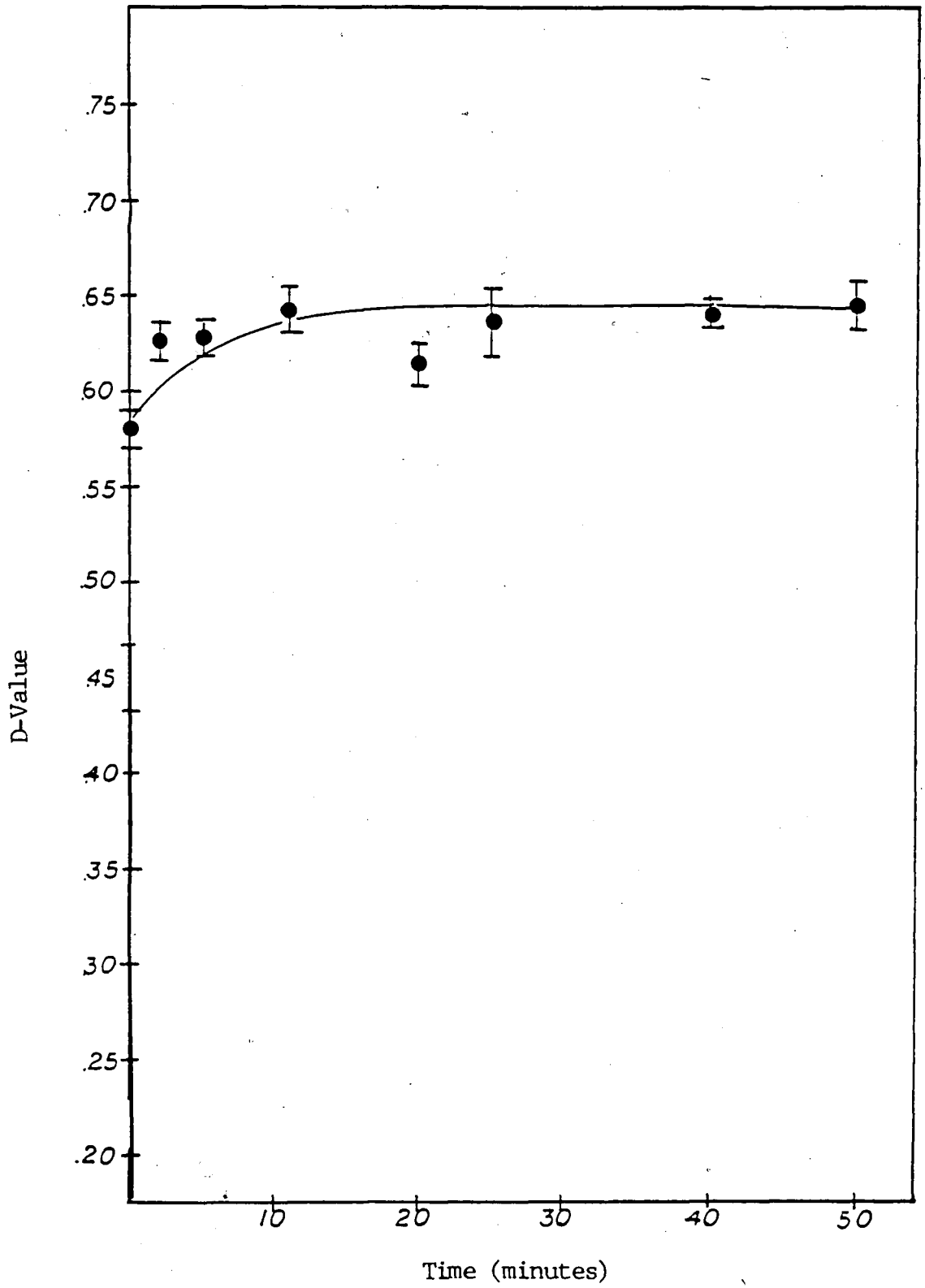


Figure 4-1: Typical plot of D-value vs. time on press  
24



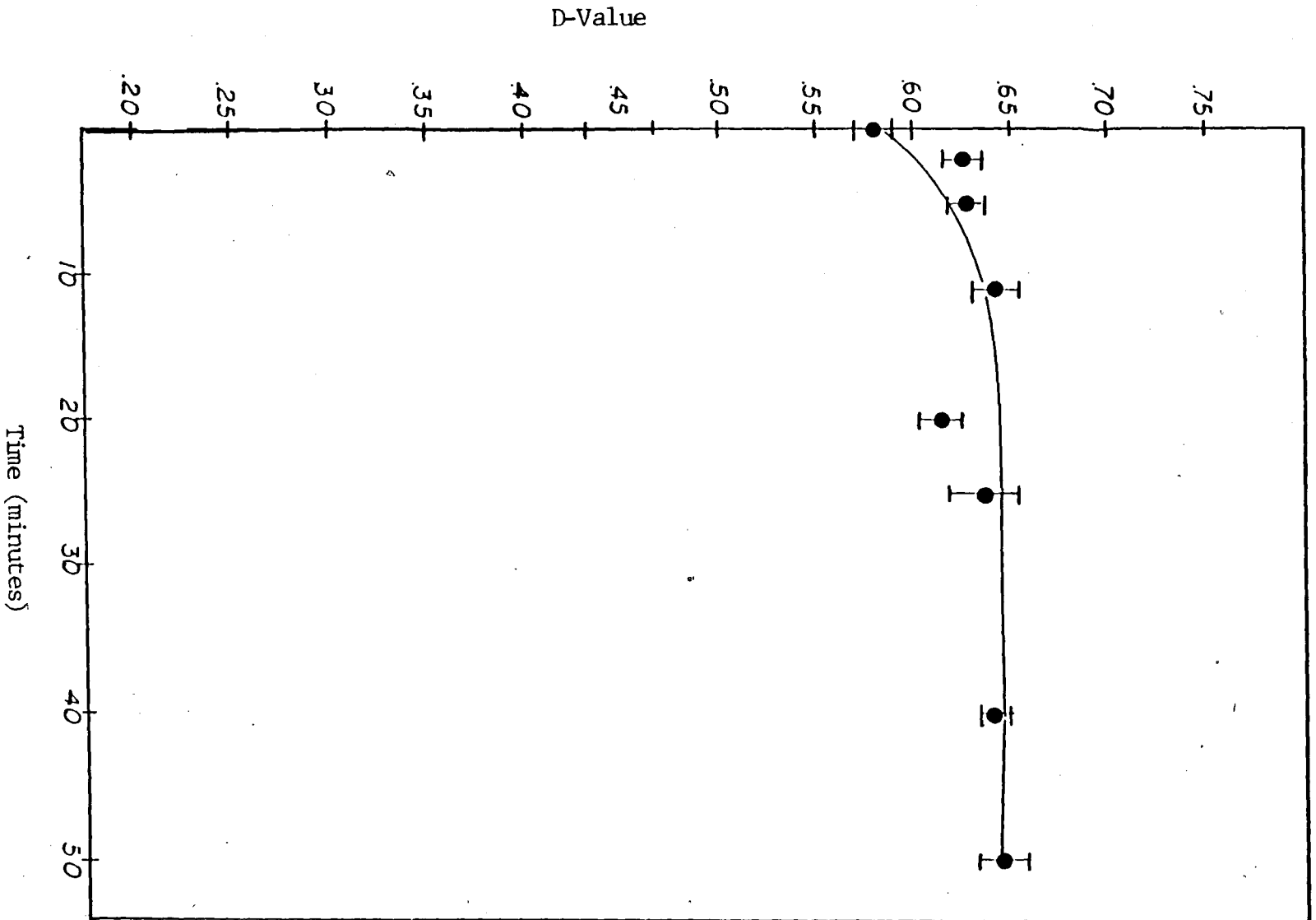


Figure 4-1: Typical plot of D-value vs. time on press  
24

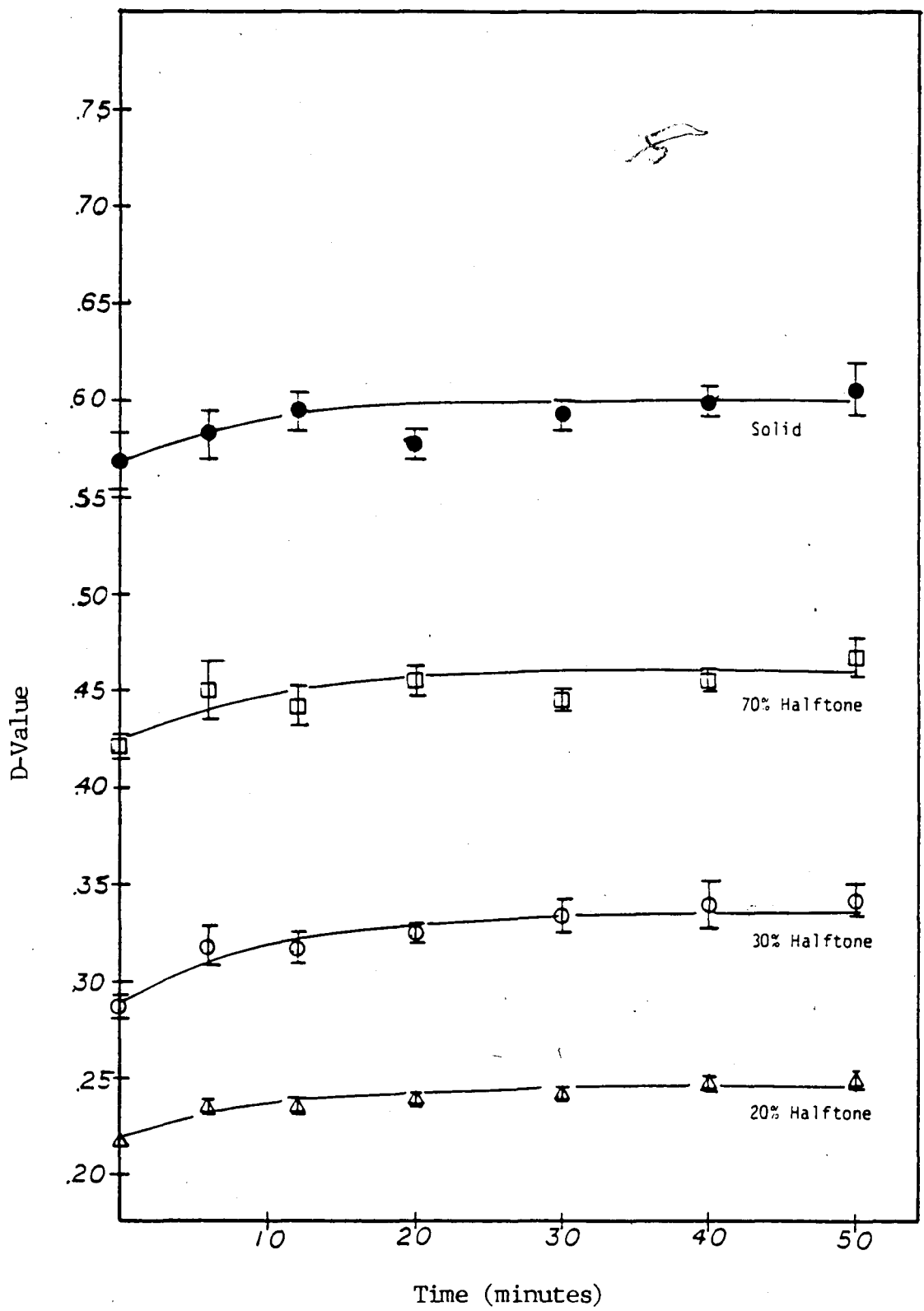


Figure 4-2: D-value vs. time for Cyrel FR

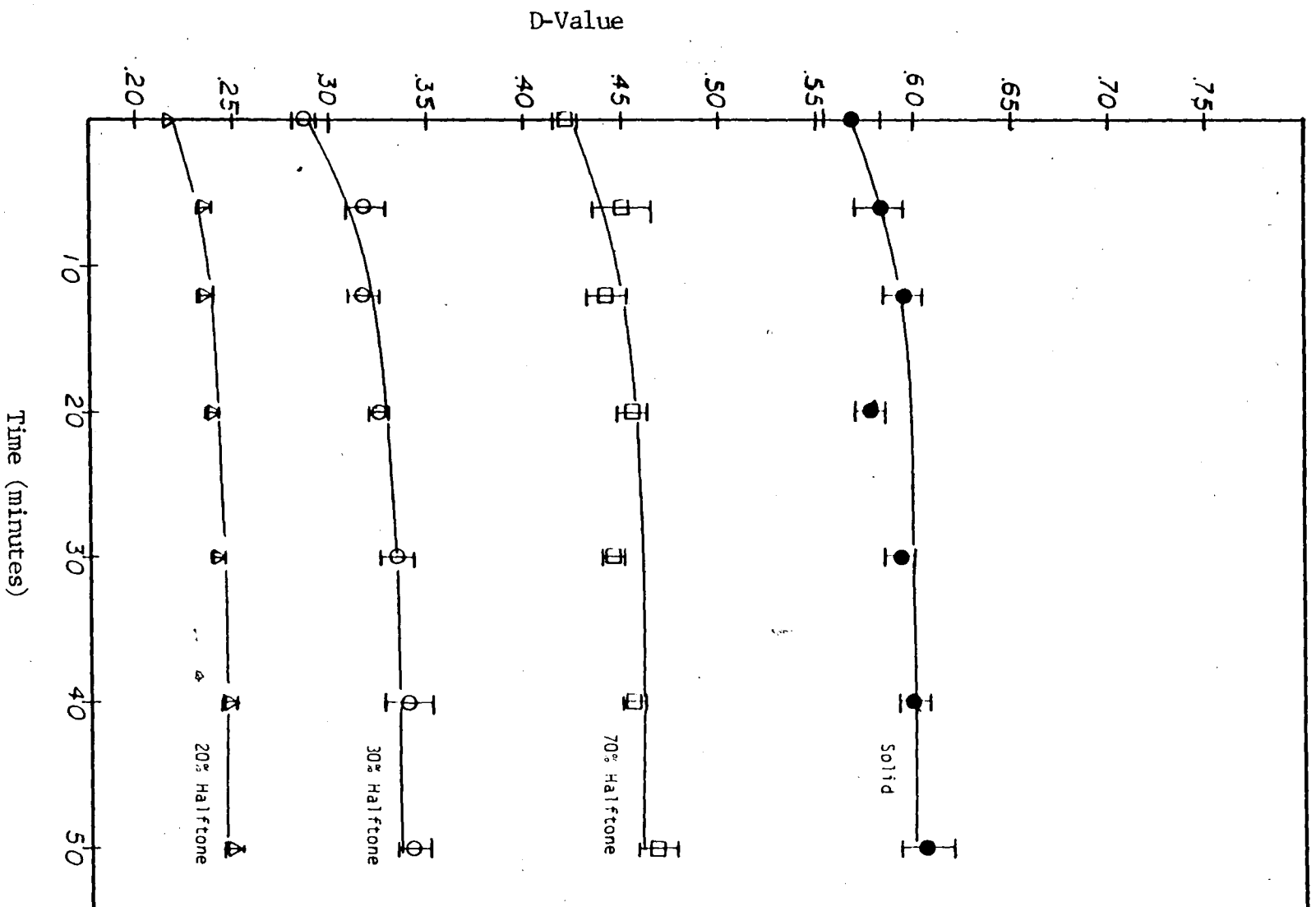


Figure 4-2: D-value vs. time for Cyrel FR

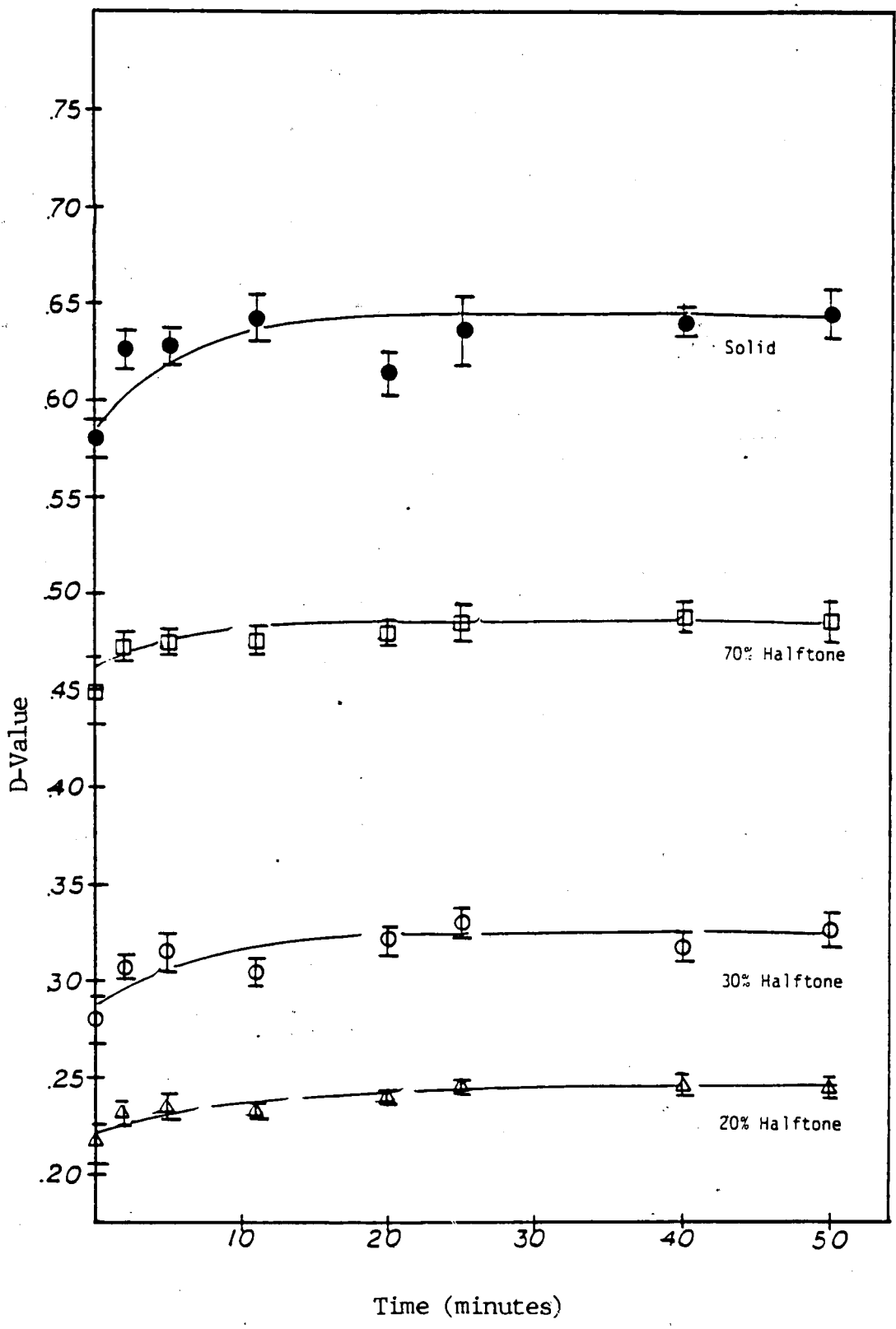


Figure 4-3: D-Value vs. time for Cyrel FR

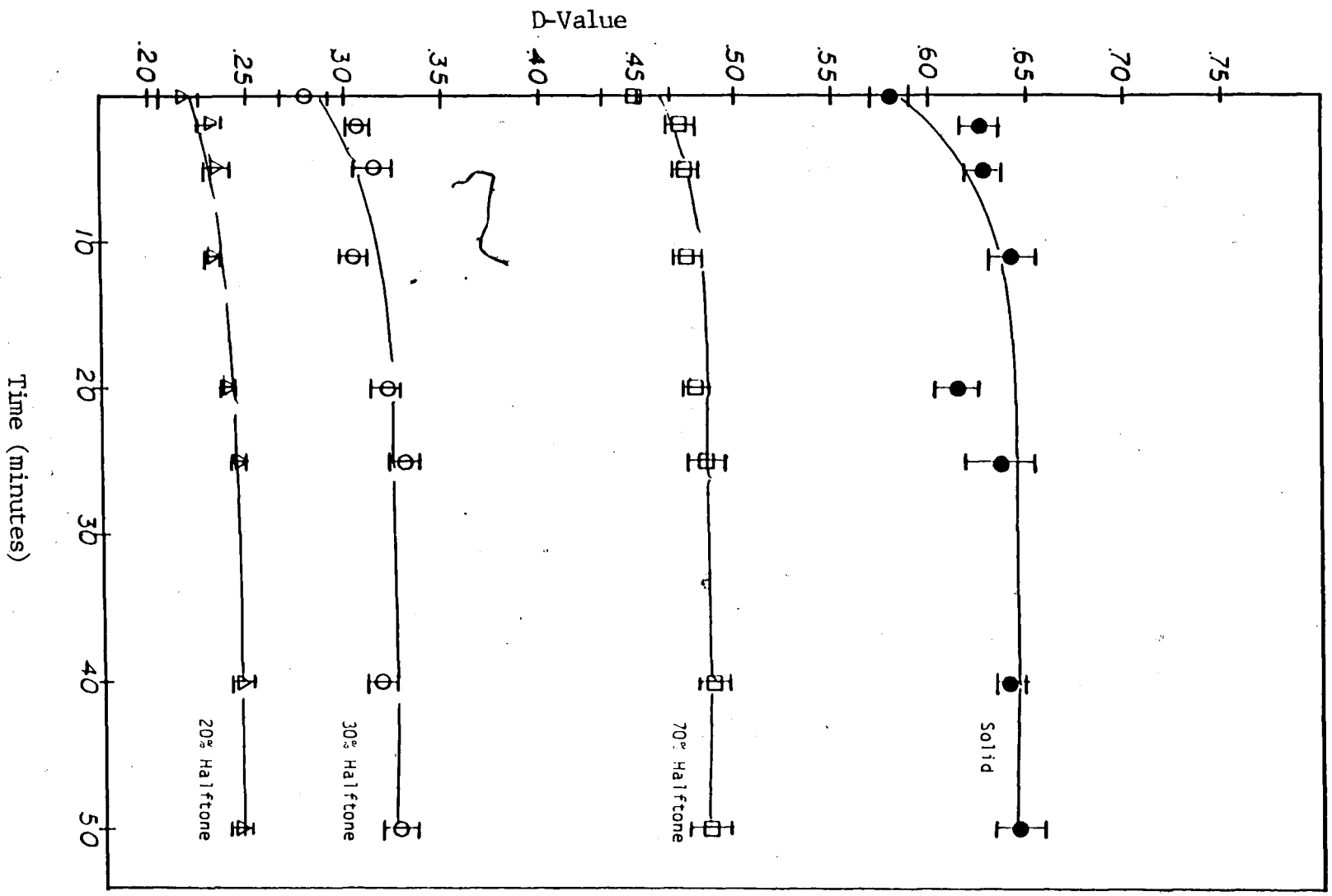


Figure 4-3: D-Value vs. time for Cyrel FR

should be the same for each half-tone comparison. Therefore a 20% half-tone is presumably the lower limit of the reflectance analysis to determine a small change in thickness printed.

Figs. 4-4 and 4-5 show the effect of aging on a plate, by printing for 1 hour then storing for approximately 1 month, then printing. The results in Fig. 4-4 are from prints made by a different plate from that used to generate the results in Fig. 4-5, however, both plates were Cyrel FR. Although the D-values in Fig. 4-4 after printing for 20 minutes are approximately the same as those in Fig. 4-5, the starting D-values are considerably different. These starting D-values are the result of sampling as soon as the press operator is satisfied with a complete image of the plate on the substrate. The time taken to obtain an optimum print was usually 4-5 minutes, but on some occasions, took as long as 10 minutes.

In Fig. 4-5 the D-value for the first printing are approximately 12% greater than those for the second printing of the same plate. Variations in D-value demonstrate clearly the lack of control that the press operator has over the impression pressure exerted between the various nips.

One factor which could have a profound influence on the D-value is the solids concentration of the ink. The solids concentration is controlled by monitoring the viscosity of the ink very closely and not allowing the viscosity to vary more than 5%. Fig. 4-6 is a plot of drain time of a #3 Shell cup as a function of the dry solids content of the ink used. Press ready ink has a drain time from a #3 Shell cup of 13.5 - 14.0 seconds. The rate of change of drain time with solids concentration is greatest in this range implying that a large variation in

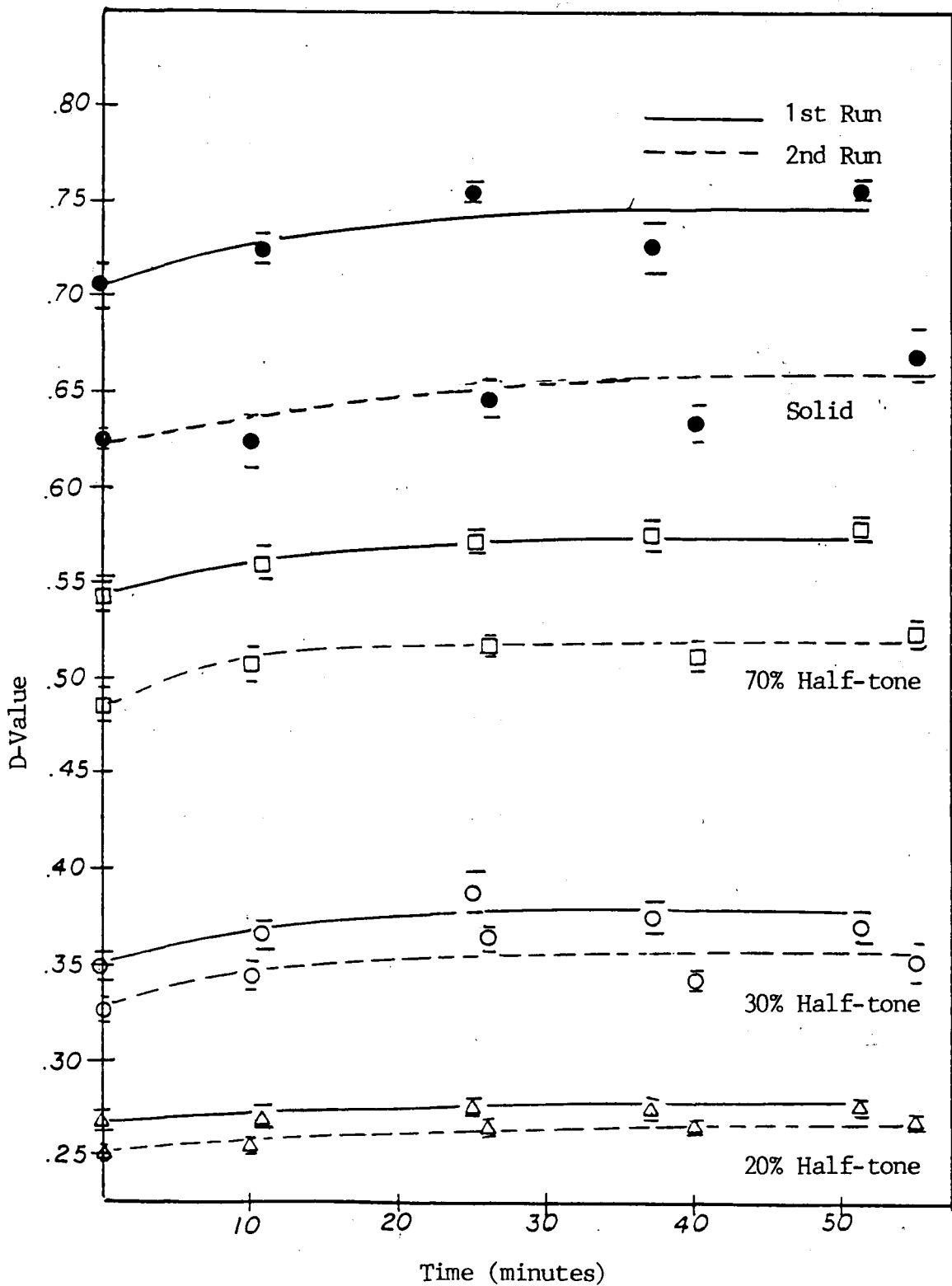


Figure 4-4: D-Value vs. time for Cyrel FR

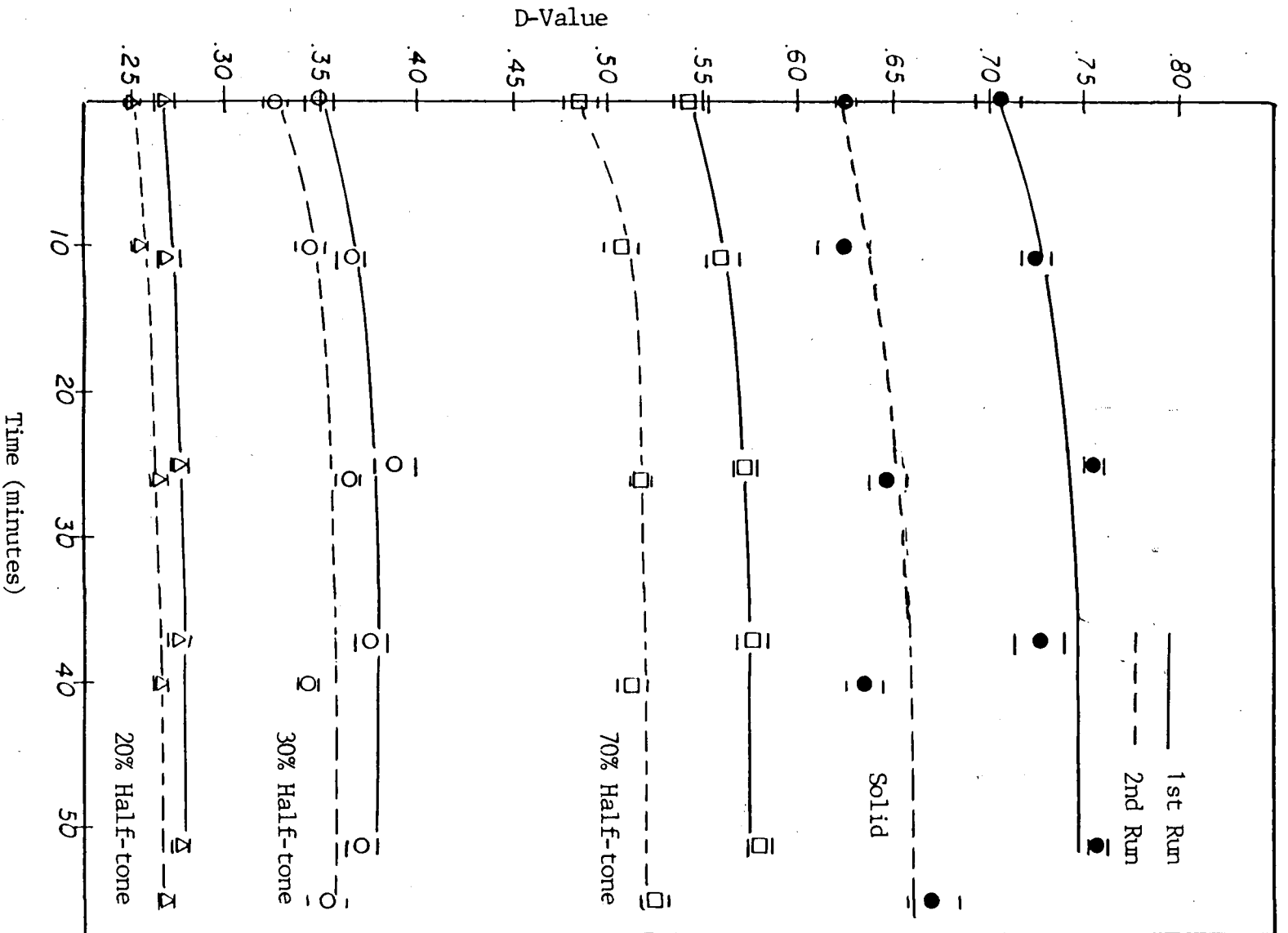


Figure 4-4: D-Value vs. time for Cyrel FR



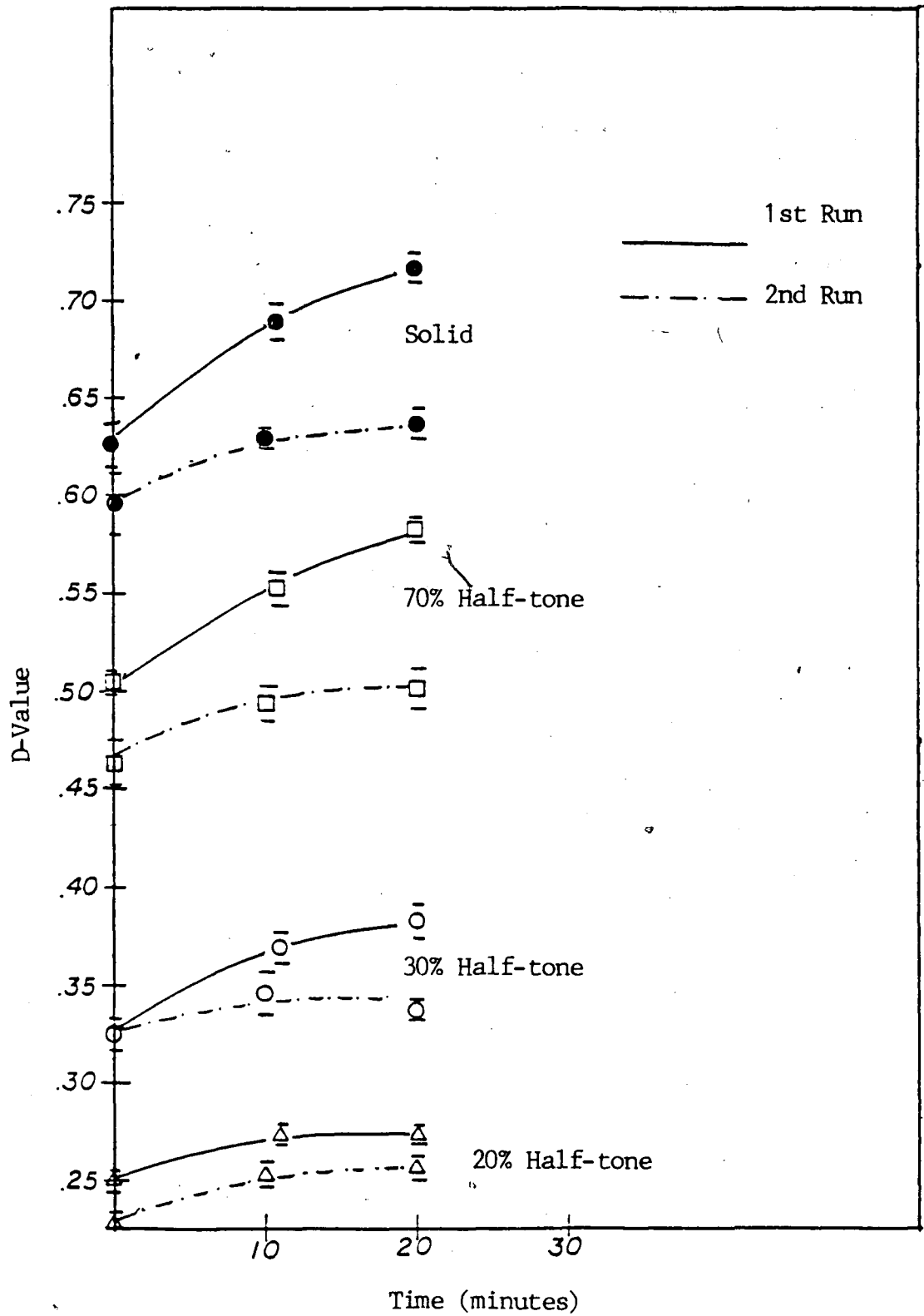


Figure 4-5: D-Value vs. time for Cyrel FR

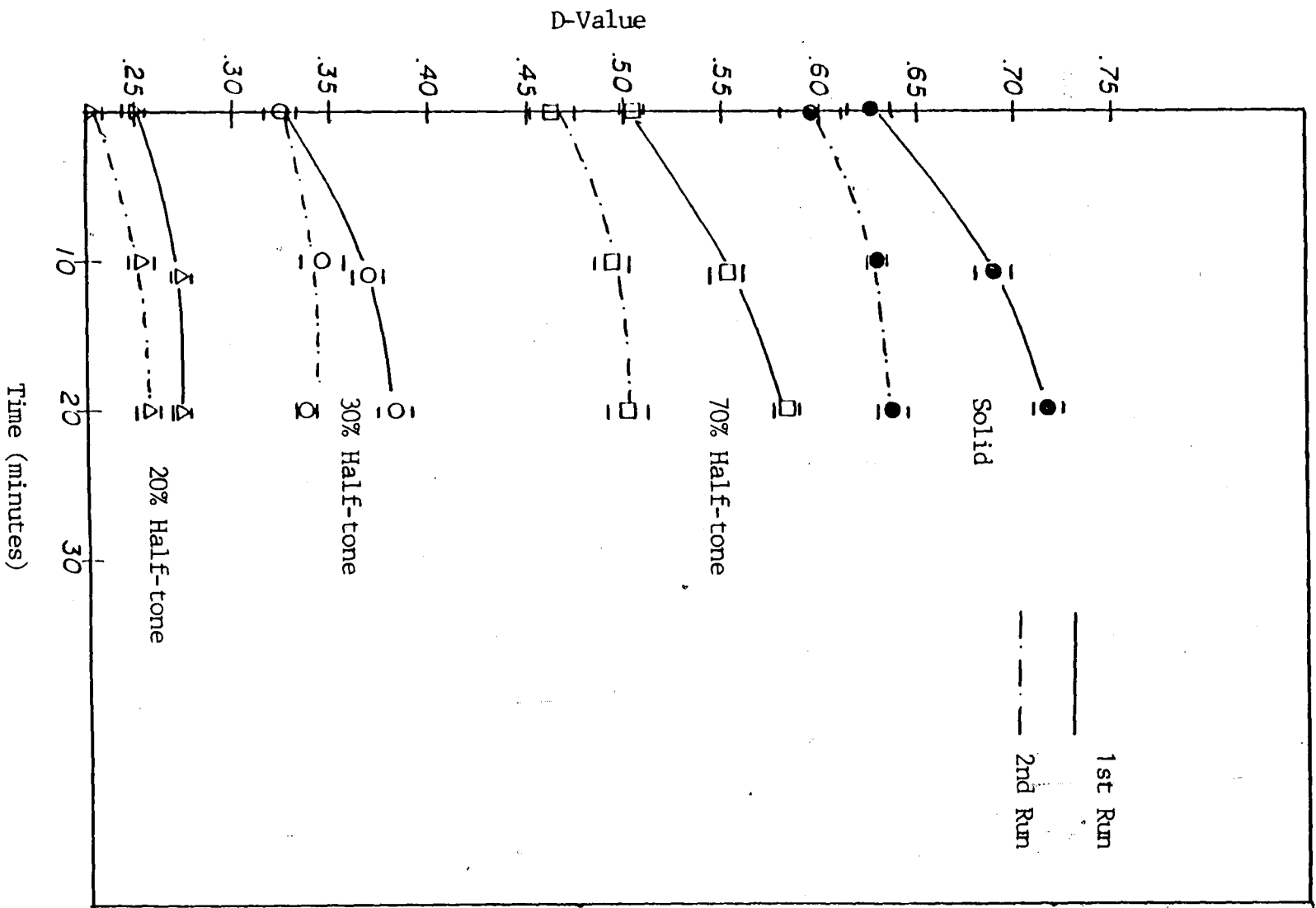


Figure 4-5: D-Value vs. time for Cyrel FR

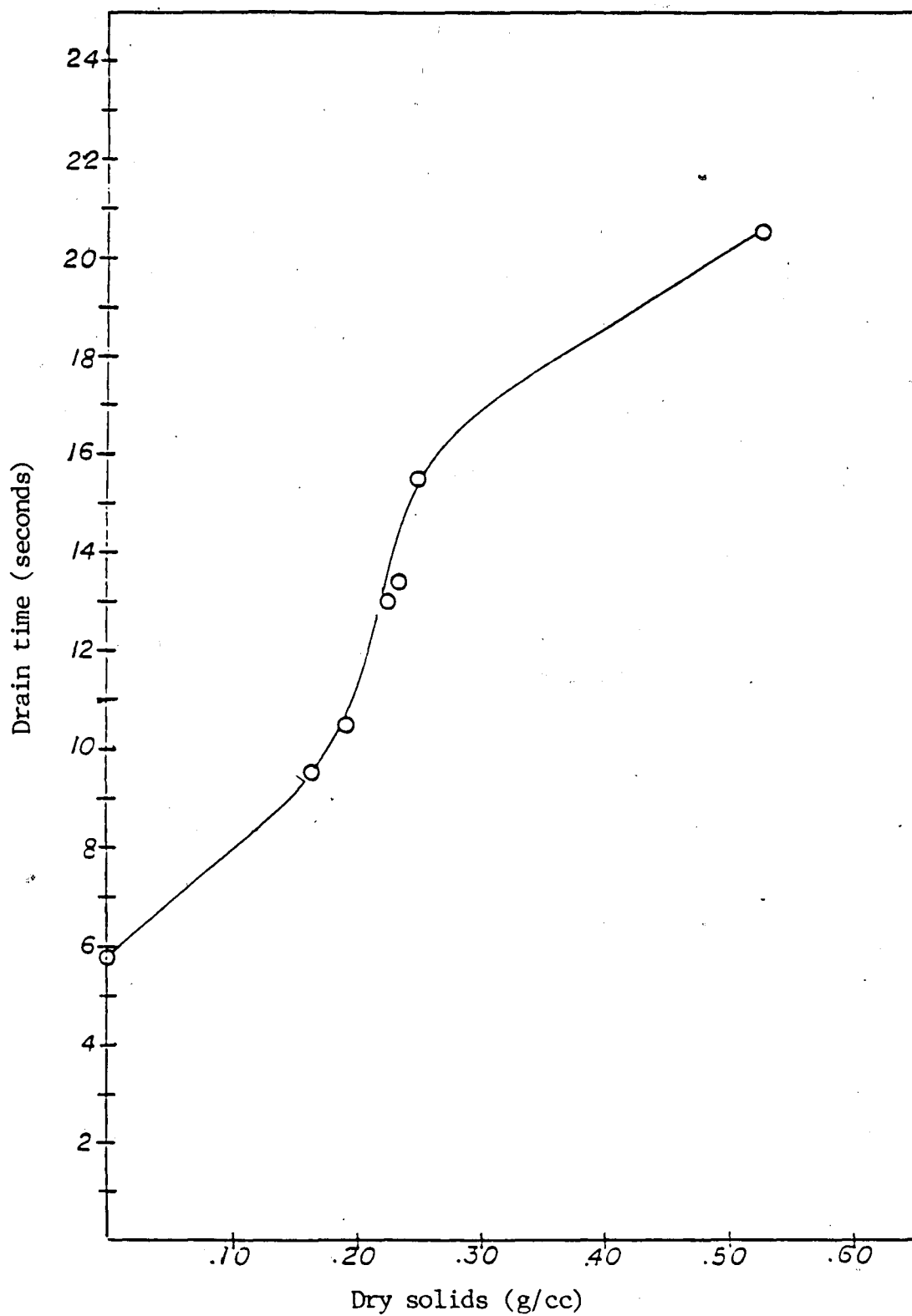


Figure 4-6: Drain time for #3 Shell cup vs. dry solids concentration for Irromont blue ink

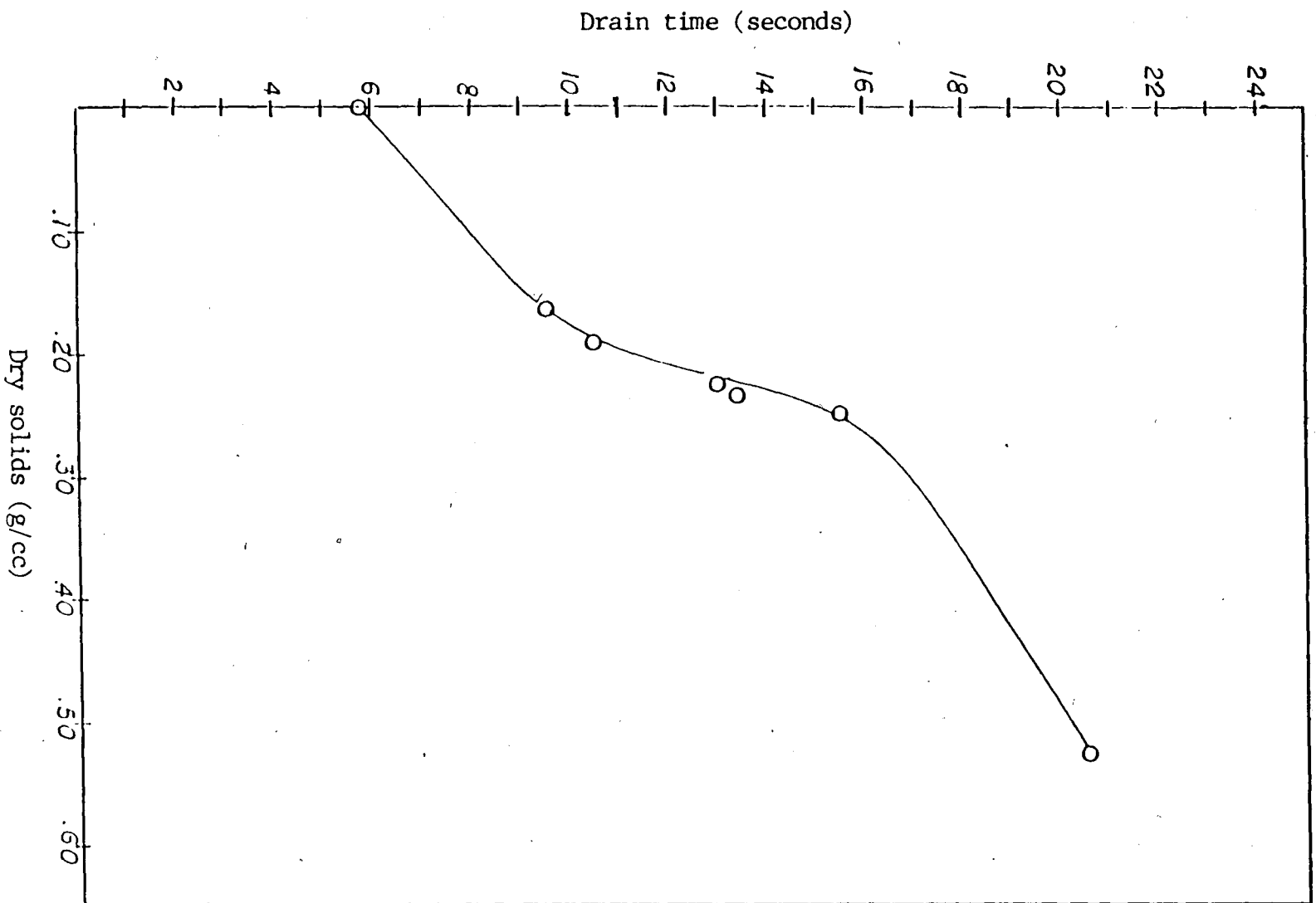


Figure 4-6: Drain time for #3 Shell cup vs. dry solids concentration for Immont blue ink

calculated viscosity would not result in a large variation of dry solids. Thus, the reflectance of the printed image should not be greatly affected by slight variations in ink viscosity. Previously it was suggested that a small change in ink viscosity produced a small change in D-value, however since the viscosity change was small but the D-value change was large, the press and/or operator are probably the major variables in the printing process.

Fig. 4-7 is a comparison of D-values of prints made using Cyrel FR plates on the same day and on different days. Plates 5-1 and 10 were run on one day and plates 5-2, 26 and 27 were run on a different day. The ink viscosity was held constant for all runs, implying a constant solids concentration in the ink for each run. Different plates examined during the course of the day resulted in reasonably reproducible D-values. However, a poor comparison was found between D-values for the plates run on different days, plates 5-1 and 5-2.

These results seriously question the reproducibility of the press and press operator. One can conclude that the press operator can adjust the roller nip pressures to obtain a consistent print during the same day, but on a day-to-day basis he cannot reproduce exactly the original press settings to obtain the same ink transfer as on previous days.

It was originally postulated that the change in D-value from first printing to second printing within a given day was due to the rubber fountain roller in the inking train becoming saturated with ink and becoming less efficient as a metering device, i.e. more ink may be transferred along the ink train to the substrate. To test this theory, two plates of BASF Nyloprint, and Cyrel FR with a 0.05 mm cap and Cyrel FR

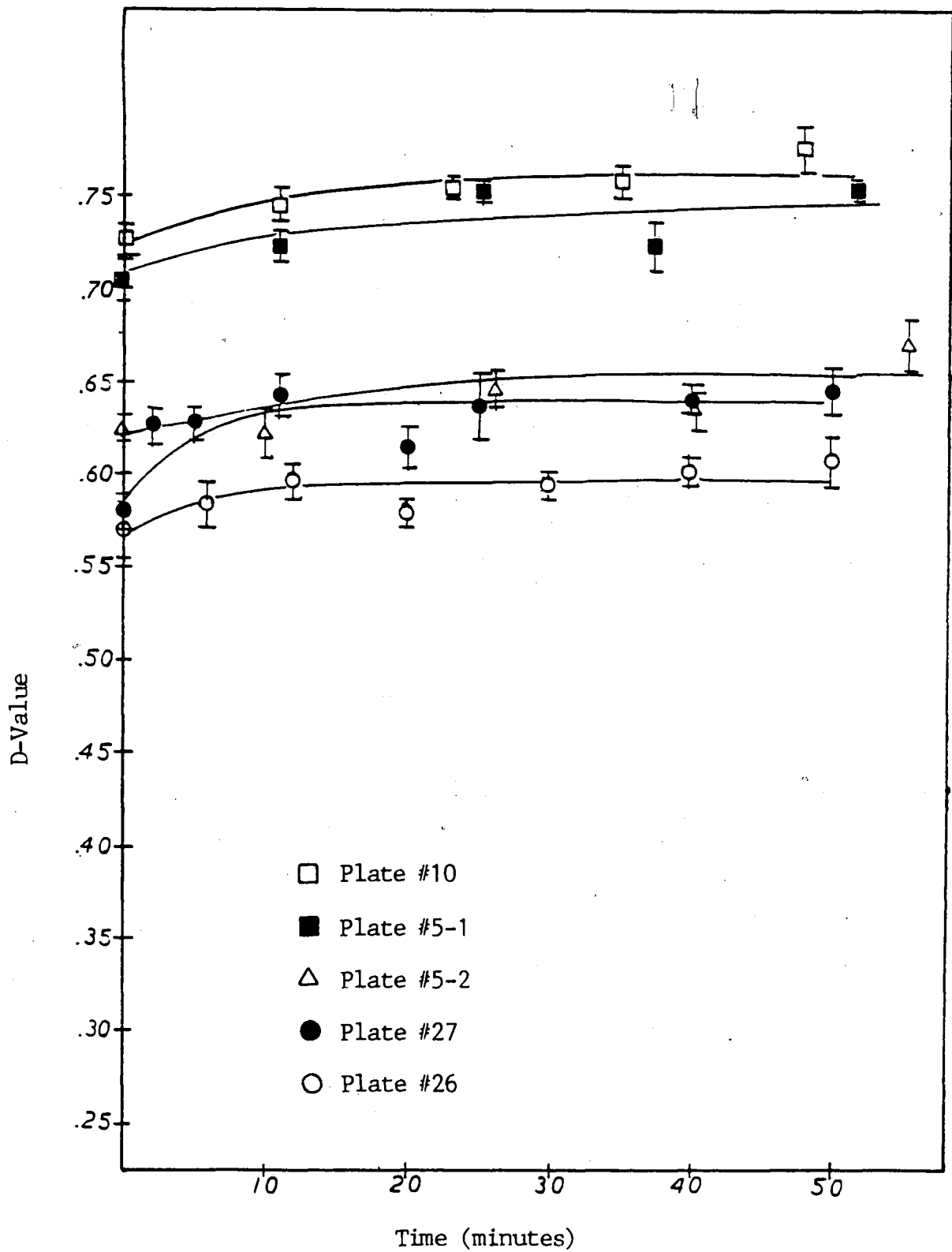


Figure 4-7: D-value vs. time for multiple runs of Cyrel FR plates

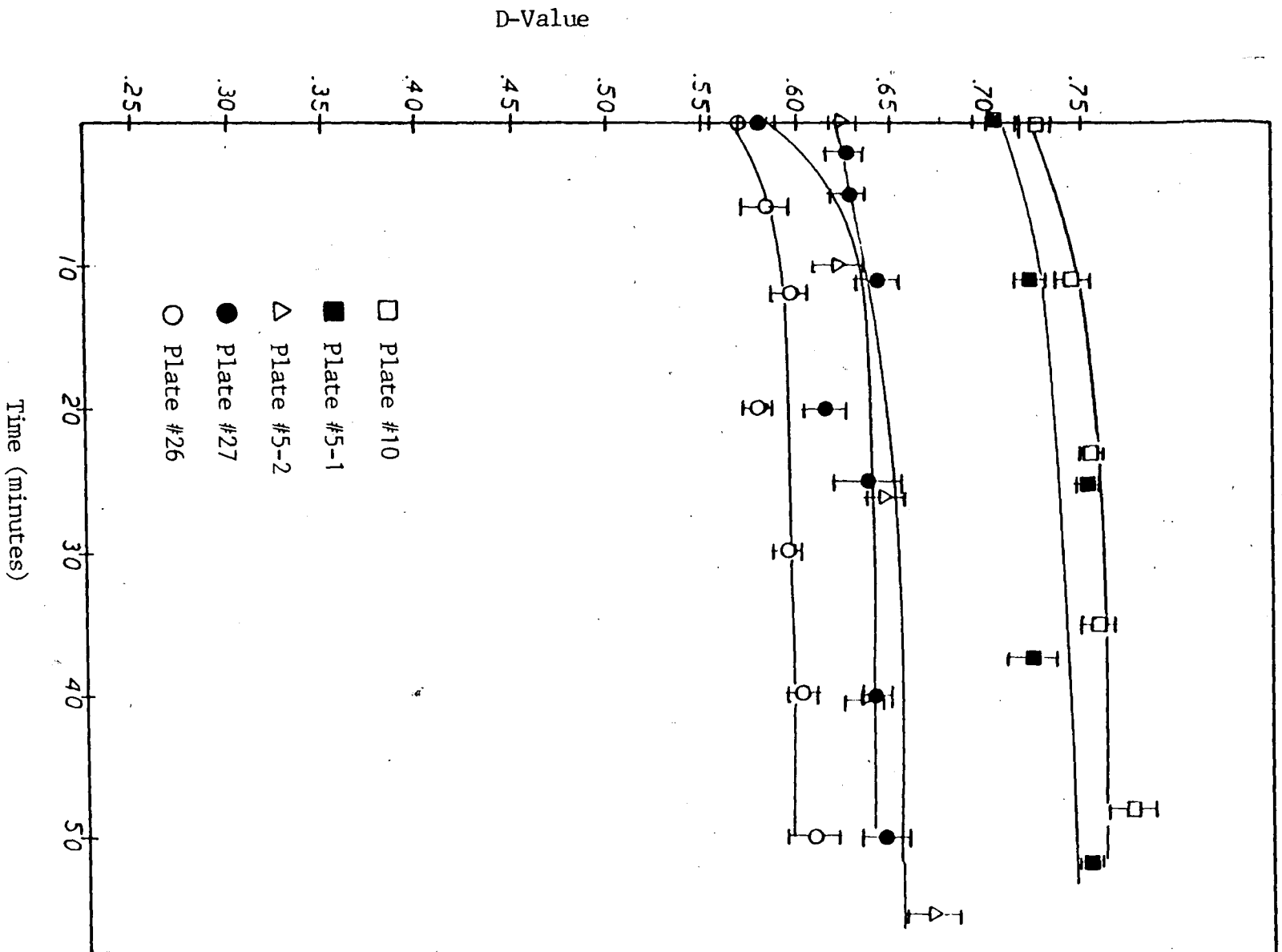


Figure 4-7: D-value vs. time for multiple runs of  
 Cyrel FR plates  
 32

were printed with a two to three day interval between press runs thus allowing the fountain roller sufficient time to dry out. Figs. 4-8 through 4-10 show the results of these experiments respectively. The BASF (Fig. 4-8) and the Cyrel FR capped (Fig. 4-9) show a large increase in D-value (i.e. increase in ink thickness or ink transferred) from the first to the second run: 8% and 5% respectively. Both differences are discernable with the naked eye. The second run of Cyrel FR (Fig. 4-10) resulted in a much smaller (2%) increase in D-value which could not be easily detected with the naked eye. By a reverse interpolation one can assume that the press and/or operator is responsible for these changes in D-value, particularly for the Cyrel FR, since a large (10%) deviation is also evident for plates 25 and 26 in Fig. 4-7, comparable with those for BASF and Cyrel FR capped. However, it is interesting to note that in these experiments the second run always had a higher D-value than the first run. Therefore, it is reasonable to assume that, for constant roller nip pressures, the fountain roller does contribute to the amount of ink transferred.

## 2. Plate swelling analysis

The effect of time on the press on print quality (and hence on plate behavior) is examined in Fig. 4-11 and 4-12. Fig. 4-11 concerns the word "Photo" located at the top left hand side of the test plate. Fig. 4-12 is a comparison of the 0.58 mm diameter half-tone patterns printed by the four test plates (Cyrel FR, Cyrel FR capped, Flex-Light, and BASF) prepared from the same photographic negative image.

Fig. 4-11 shows prints made by Cyrel FR (a and b), Cyrel FR capped (c and d), Flex-Light K (e and f), and BASF Nyloprint (g and h) at time



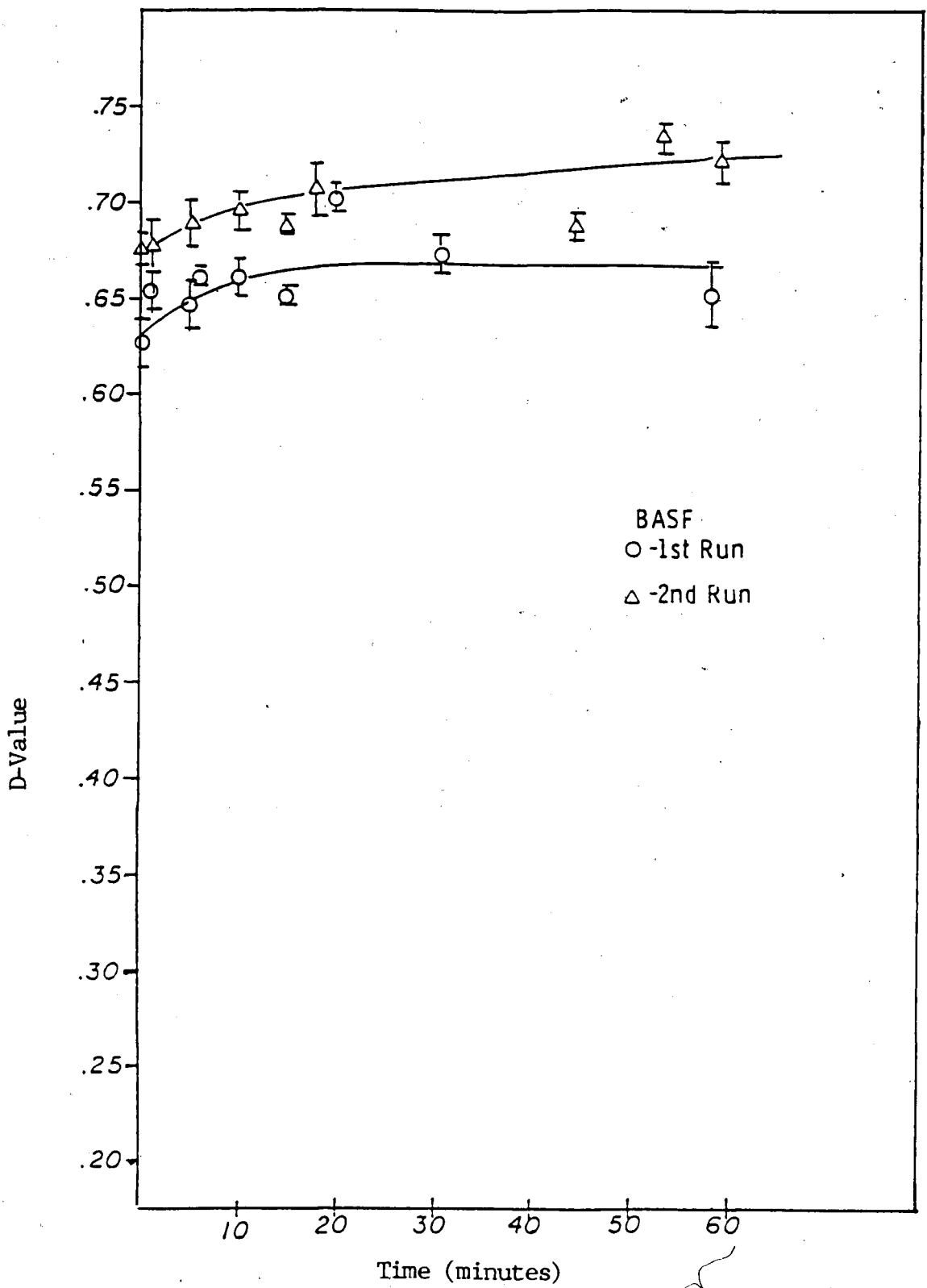


Figure 4-8: D-value vs. time for BASF Nyloprint

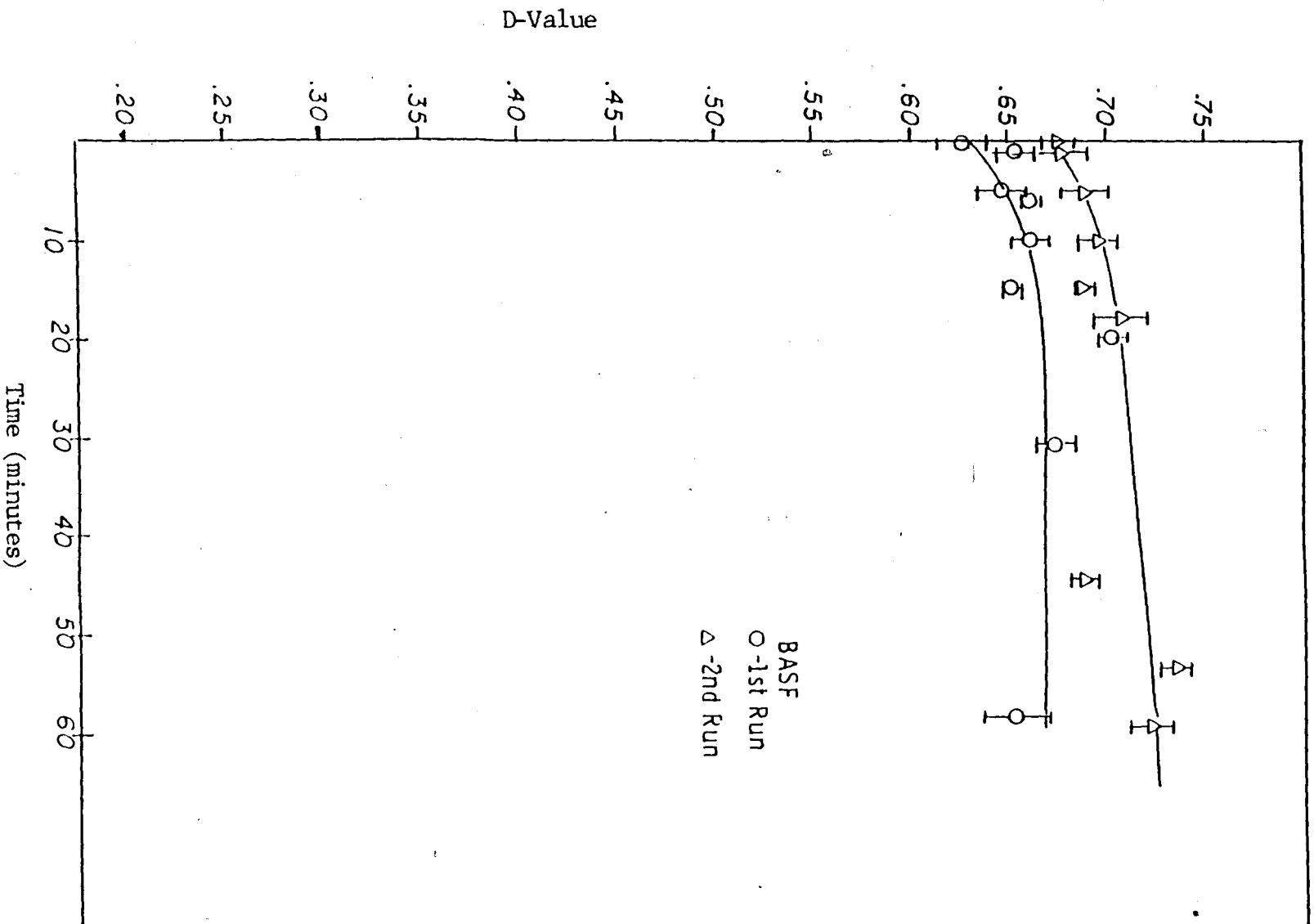


Figure 4-8: D-value vs. time for BASF Nyloprint

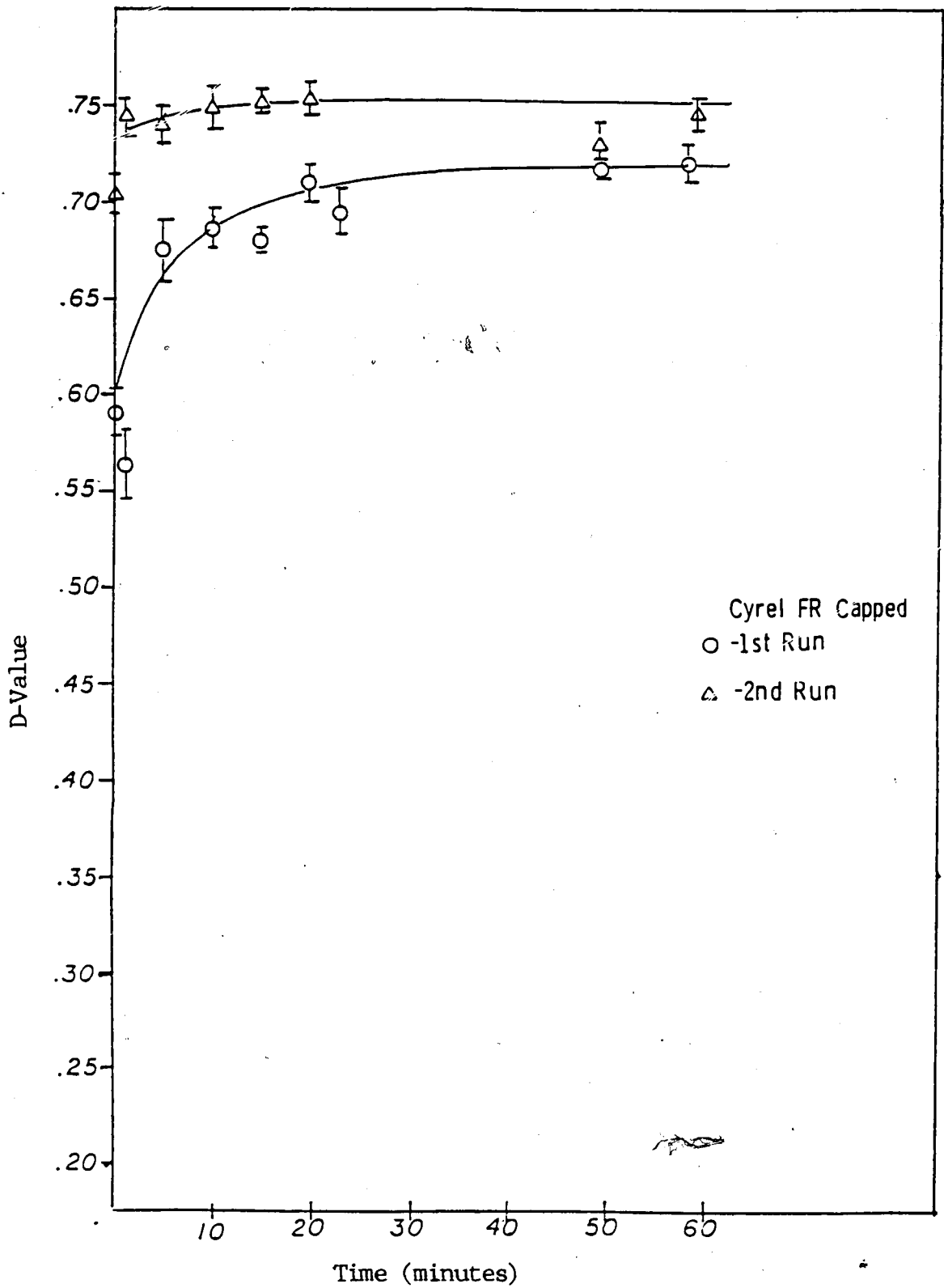


Figure 4-9: D-value vs. time for a capped Cyrel FR

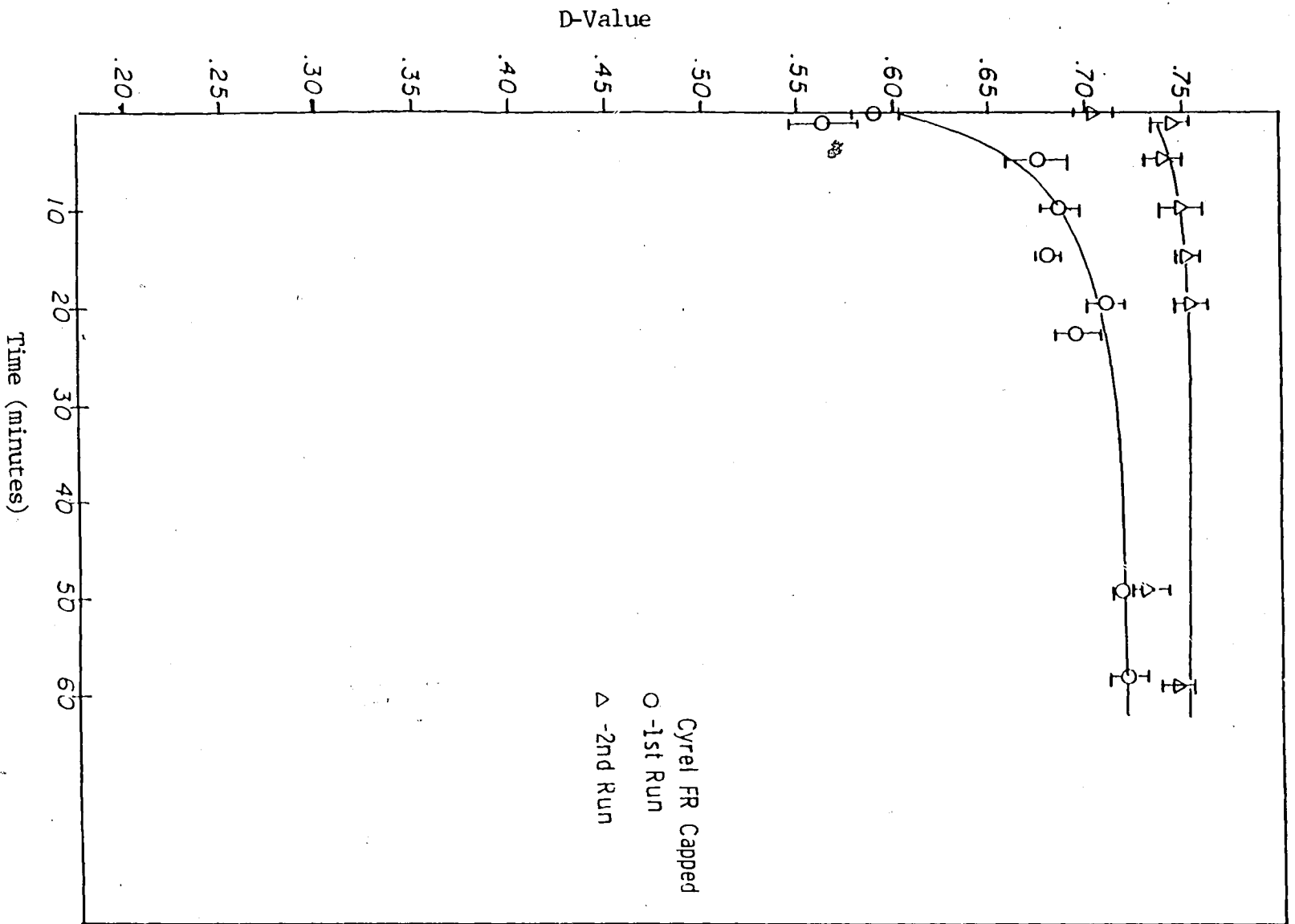


Figure 4-9: D-value vs. time for a capped Cyprel FR

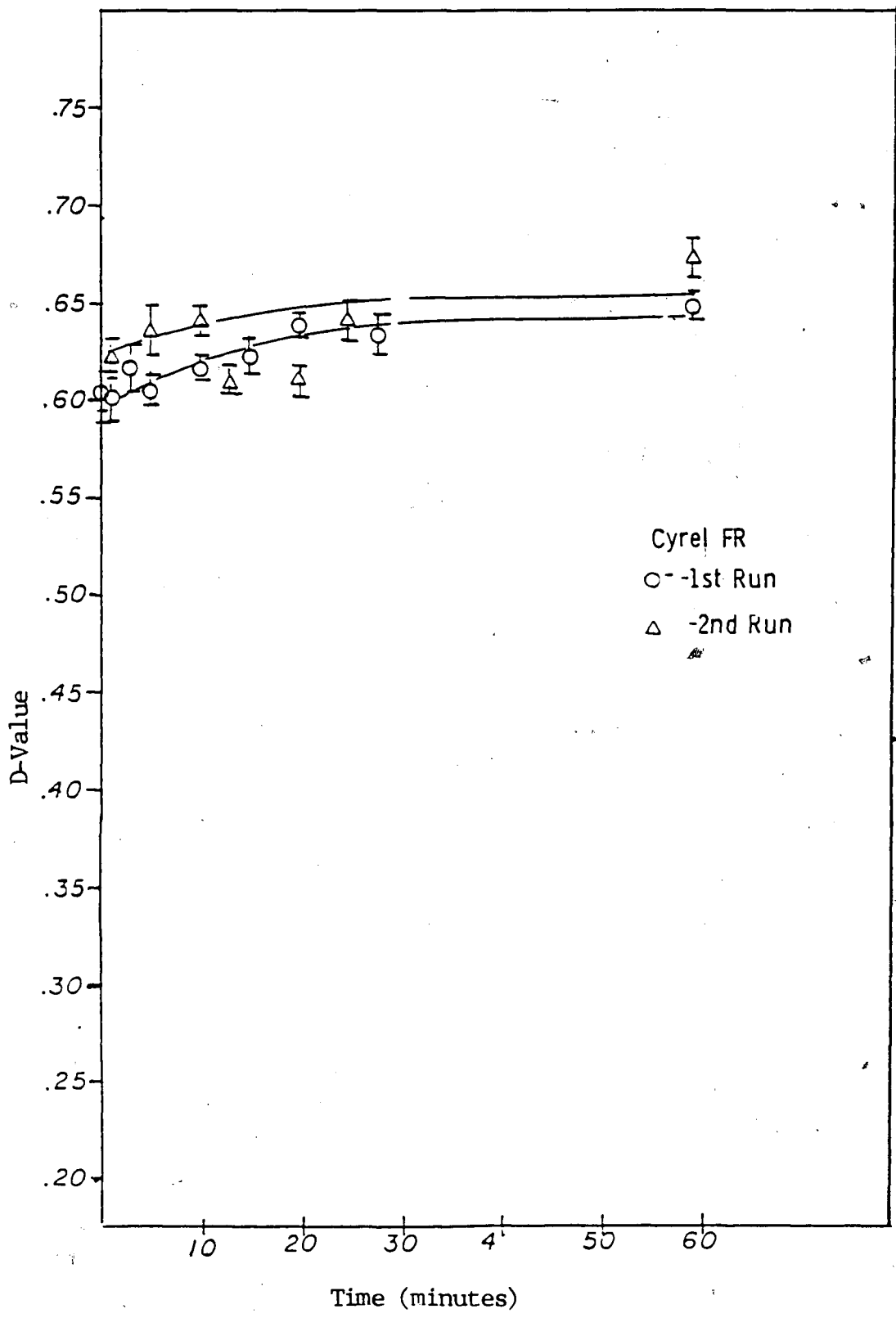


Figure 4-10: D-value vs. time for Cyrel FR

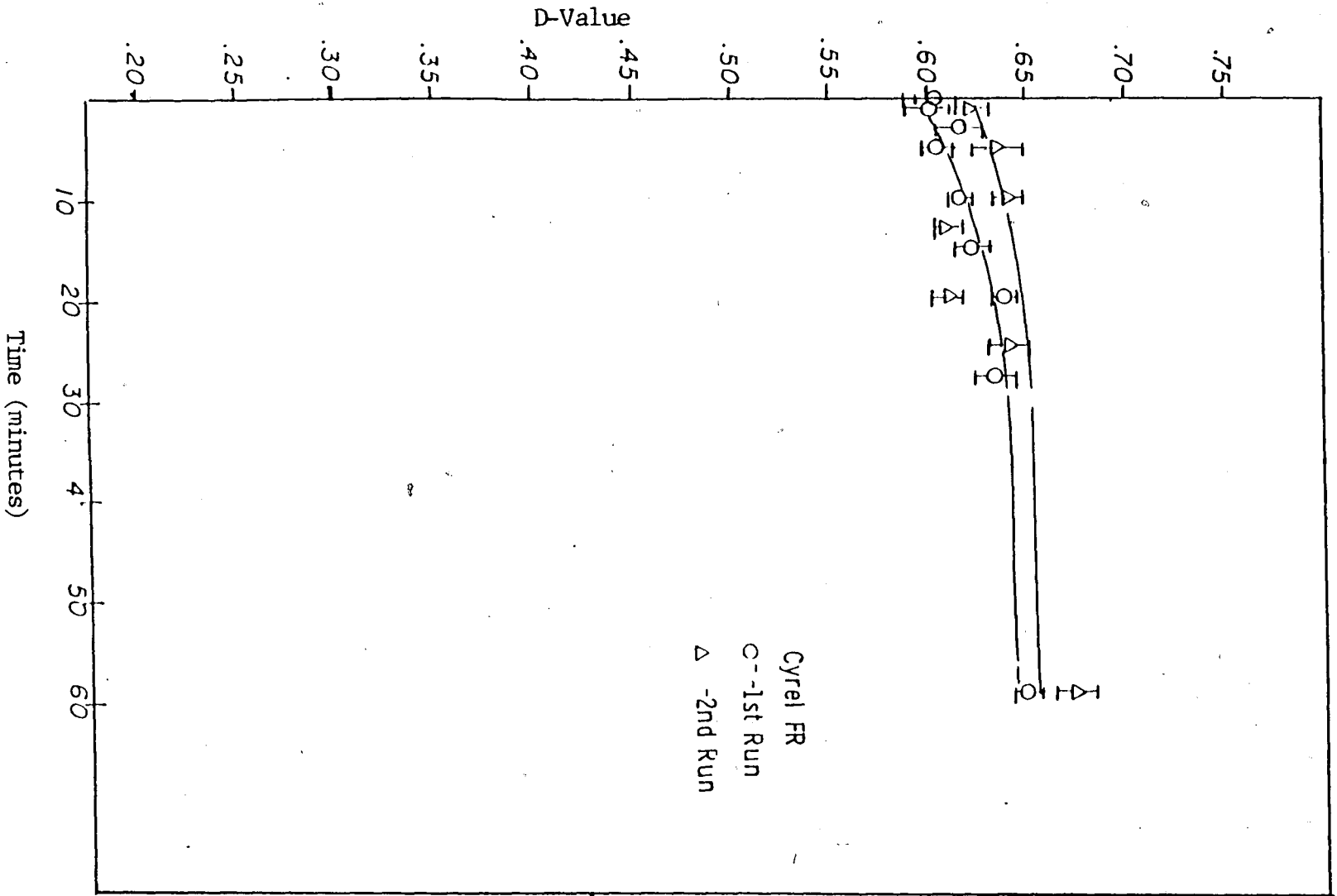
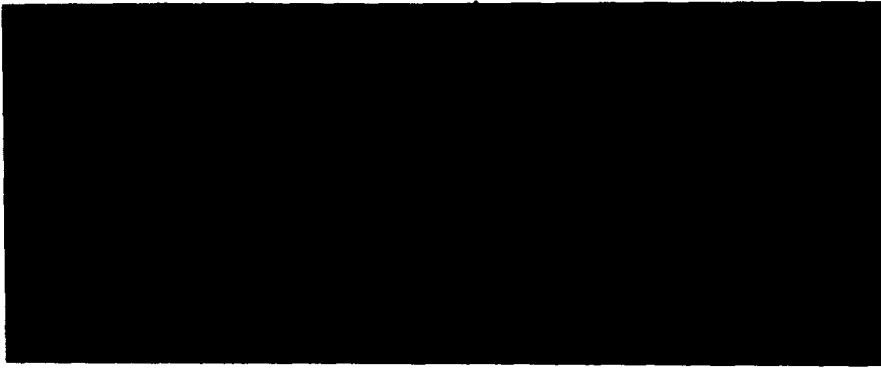
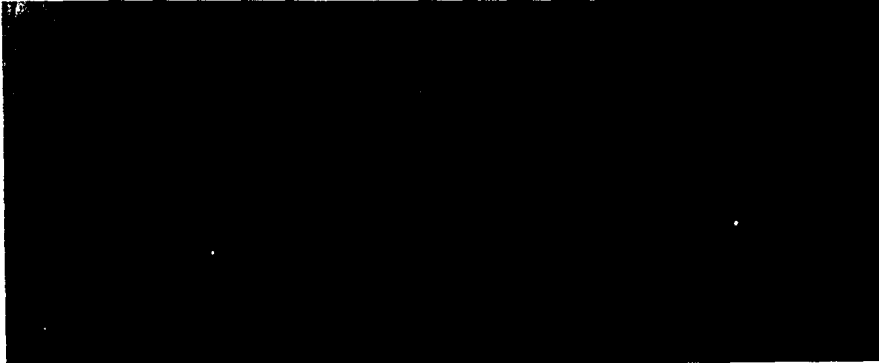


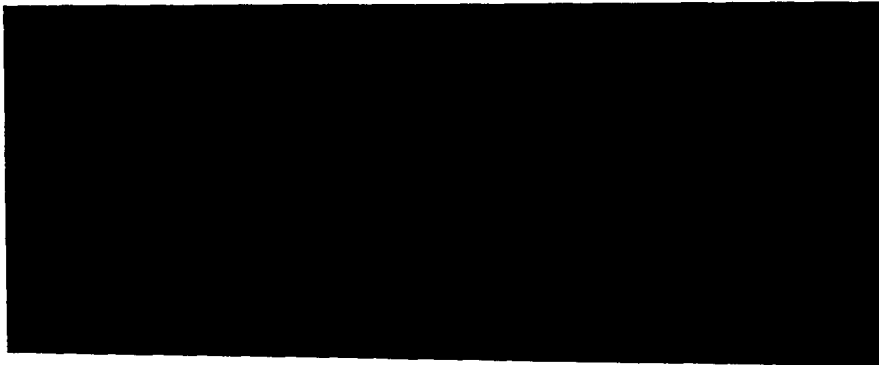
Figure 4-10: D-value vs. time for Cyrel FR



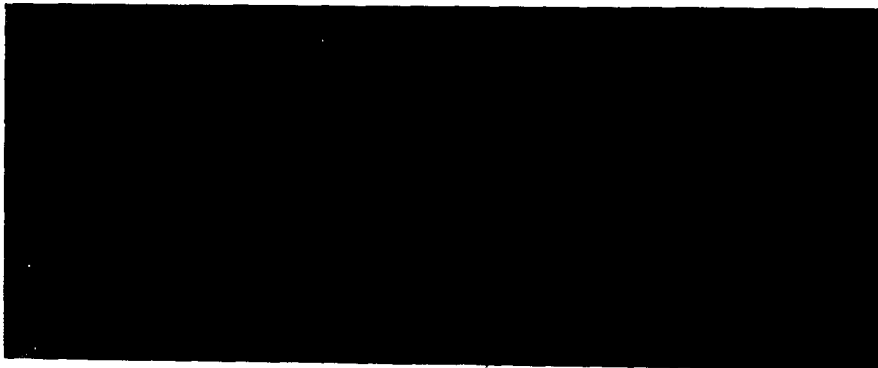
A-Cyrel FR  
Start



B-Cyrel FR  
45 minutes

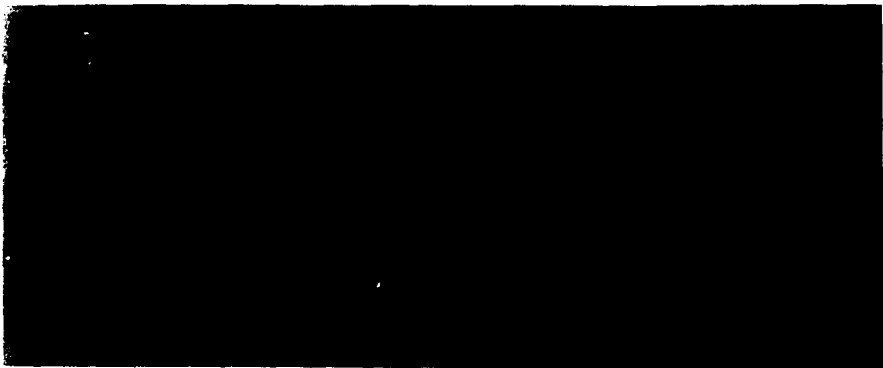


C-Cyrel FR  
Capped  
Start

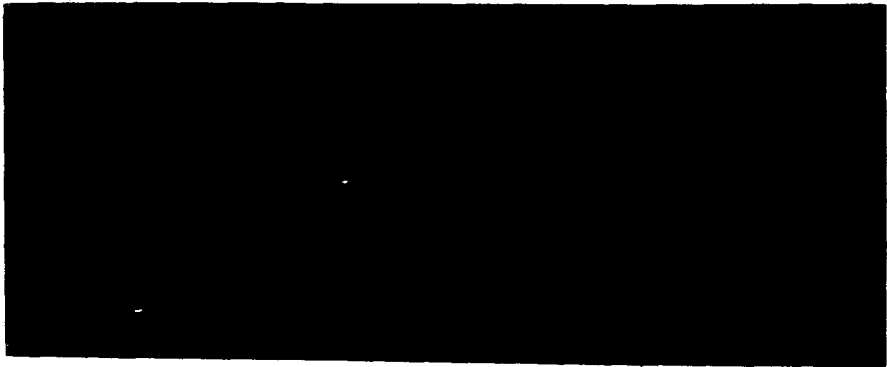


D-Cyrel FR  
Capped  
45 minutes

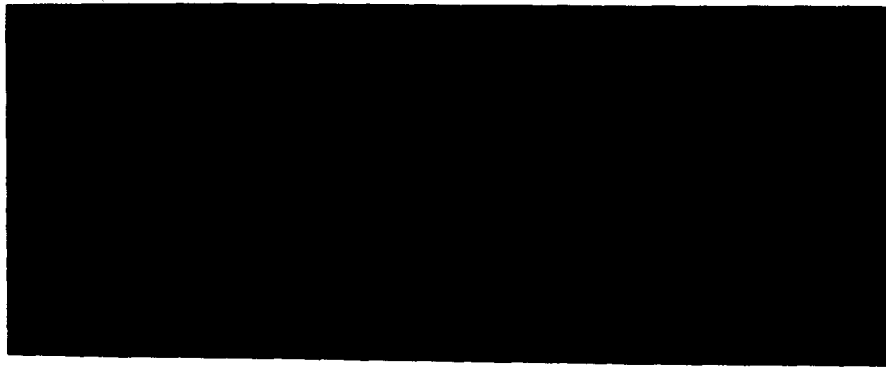
Figure 4-11: Prints made from the various plates



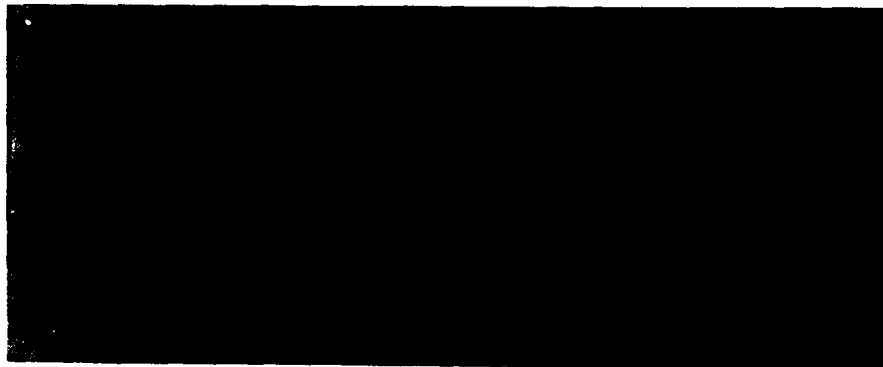
E-Flex-Light K  
Start



F-Flex-Light K  
30 minutes



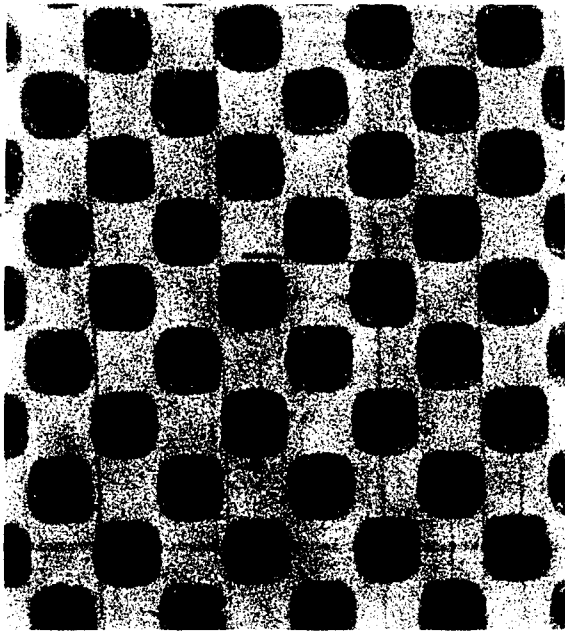
G-BASF Start



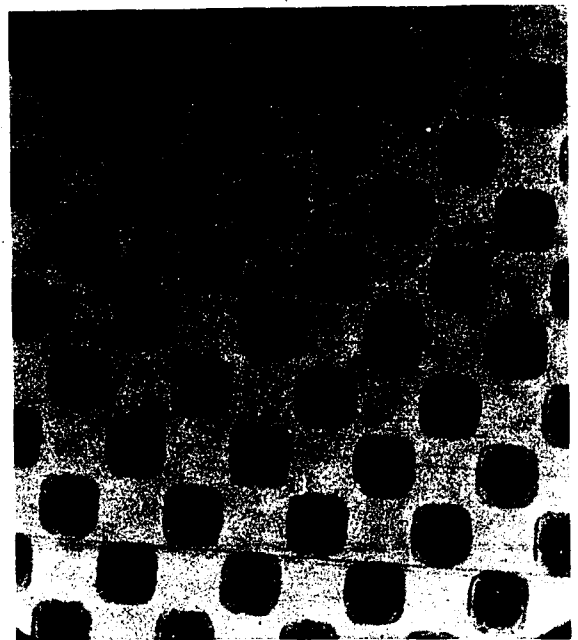
H-BASF  
45 minutes

Figure 4-11: Continued

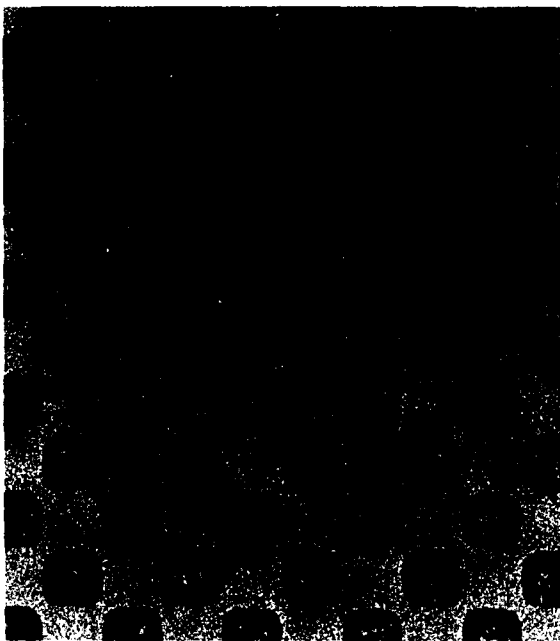




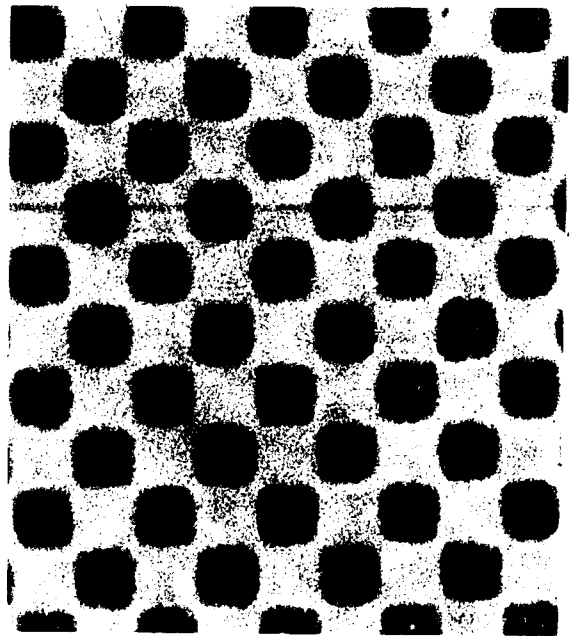
A-Cyrel FR Start



B-Cyrel FR 45 minutes

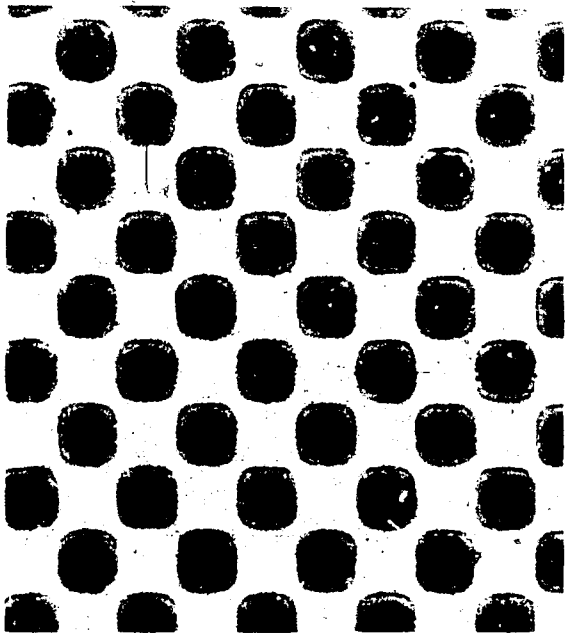


C-Cyrel FR Capped Start

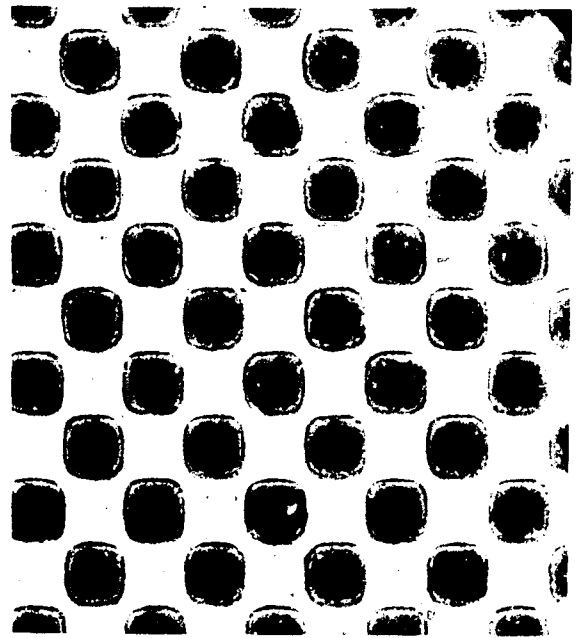


D-Cyrel FR Capped 45 minutes

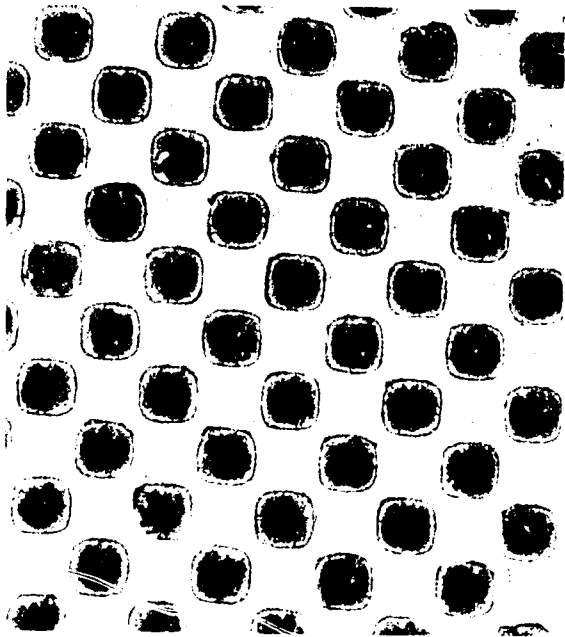
Figure 4-12: Half-tones printed by the various plates



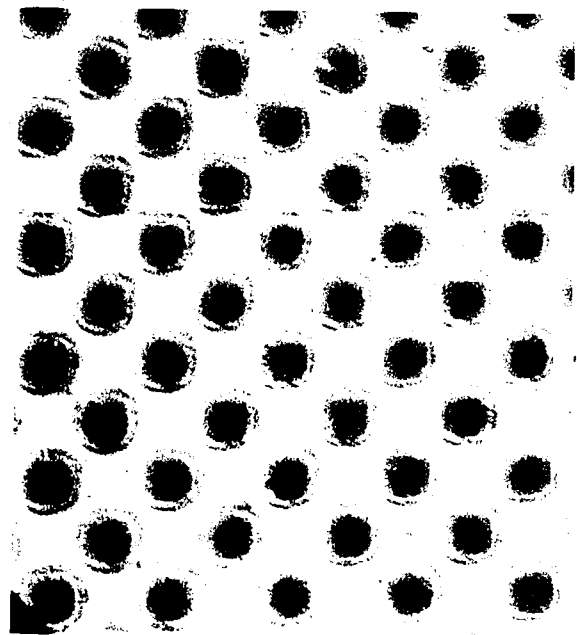
E-Flex-Light K Start



F-Flex-Light K 30 minutes



G-BASF Start



H-BASF 45 minutes

Figure 4-12 Continued

t = 0 and 45 minutes (30 minutes for Flex-Light K), respectively. The direction of printing was from the right to the left for each of the figures. A sharp, leading edge is seen on the prints from the start of each run and also at the end of the run, except in the case of BASF (Fig. 4-11). The BASF print has a halo at both the leading and trailing edges.

An explanation for the halo effect is shown in Fig. 4-11. As a deformable body passes between two rollers, the leading edge is compressed but yields a sharp front contact line. Due to the nature of the plates, deformation in the opposite direction to motion occurs extending the upper trailing edge of the character beyond its static position, resulting in the halo beyond the raised portion of the plate. As the plate swells, the thickness of the plate increases, the nip clearance remains constant, and thus more pressure is exerted on the swollen plate as it passes through the nip, resulting in a larger trailing edge and hence a larger halo.

The solvent effects on the halo can be seen in each of the prints from the end of the runs, the effect of solvent being most pronounced in the case of the BASF plate. Fig. 4-13 shows swelling data for the alcohol/acetate resistant plates, which shows that the BASF plate swells the most, thus accounting for the large halos that are clearly visible on the prints from the end of the run (Fig. 4-11h and 4-12h).

Fig. 4-12 shows half-tone areas of dots that are 0.58 mm in diameter, printed by Cyrel FR (a and b), Cyrel FR capped (c and d), Flex-Light K (e and f), and BASF (g and h) at time t = 0 and 45 minutes (30 minutes for Flex-Light K), respectively.

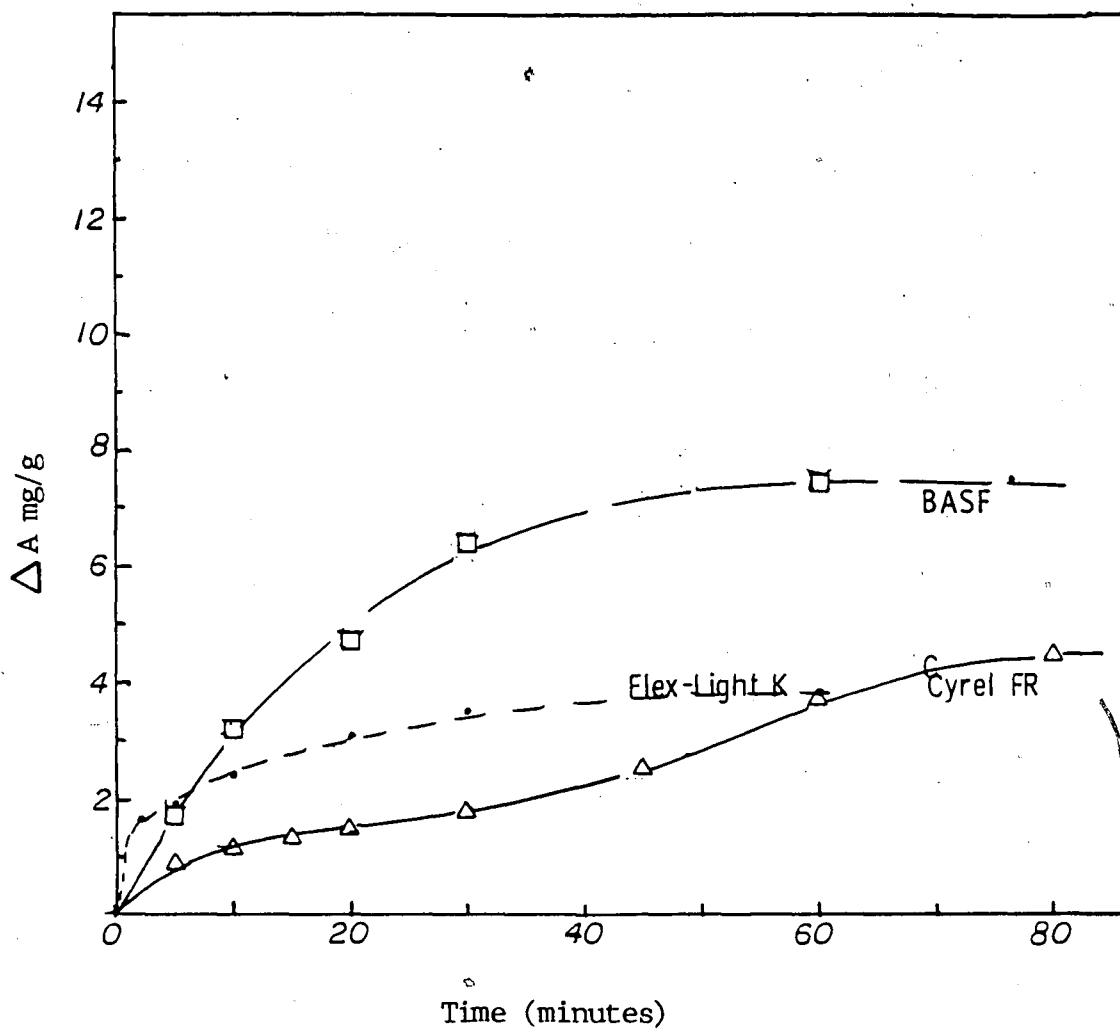


Figure 4-13: Plate swelling by weight uptake of solvent (1-Propanol/1-Propylacetate, 90:10)

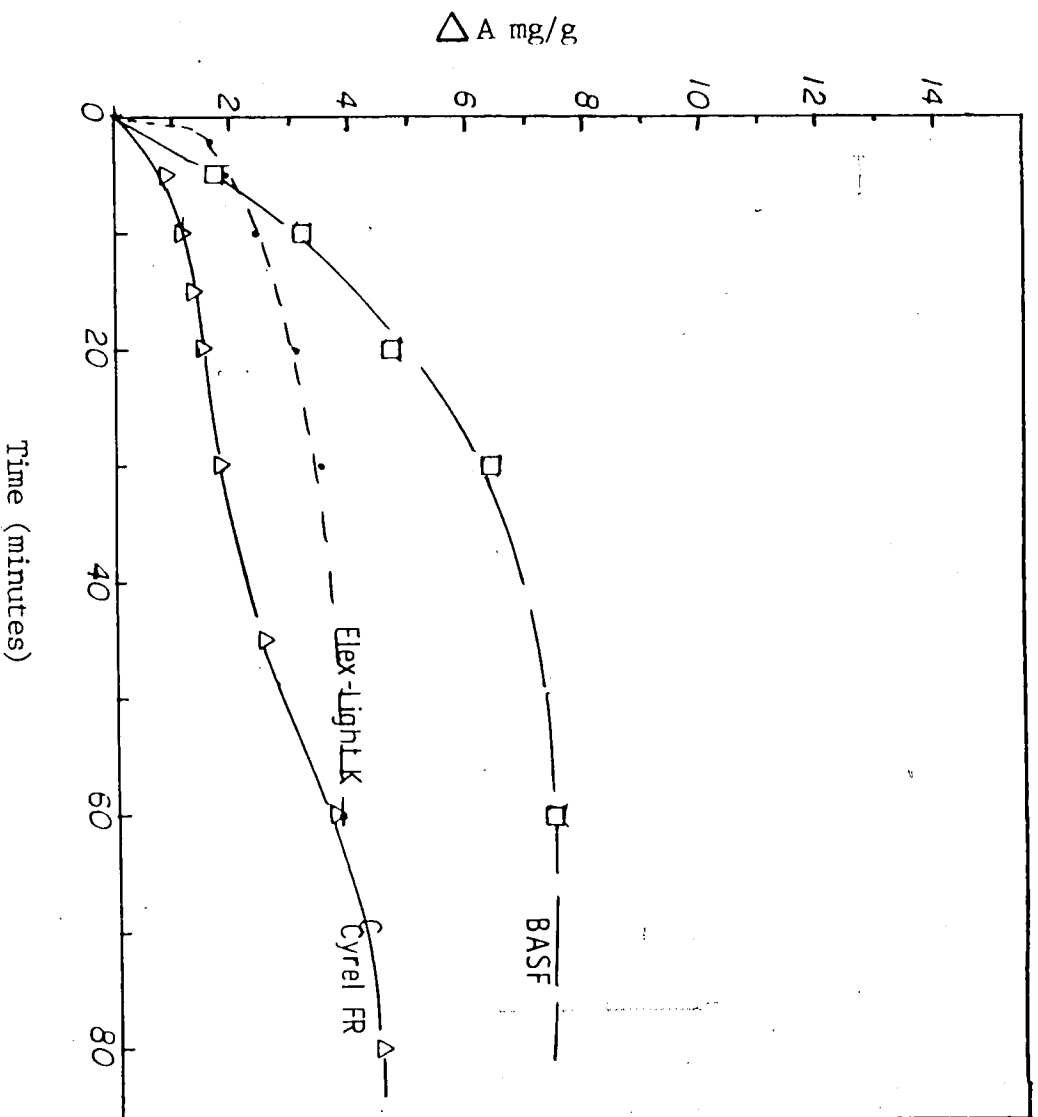


Figure 4-13: Plate swelling by weight uptake of solvent  
(1-Propanol/1-Propylacetate, 90:10)

A halo appears around the half-tone dots in all cases: start ( $t = 0$ ) and for later times on the press. In the case of BASF (Fig. 4-12h), the halo has become very pronounced. The halo arises from the fact that to obtain a complete image of a print, more than a "just-kiss" touching of plate and substrate is necessary. In fact, a "just-kiss" roller setting is not possible because of the unevenness across a plate; the result is that there is always a small amount of overimpression on any print. As the half-tone dots pass through the nip they are compressed (Fig. 4-14); i.e. the surface is pushed down and the sides bulge outwards. The halo results when the bulges on the sides of the dots print. As the plate remains on the press, swelling of the plate by the ink solvent occurs; the dots increase in size but the nip clearance remains unchanged. Thus, the dots are further compressed and the bulge on the sides become larger and a more pronounced halo appears. Again, this effect is most apparent on the print from the BASF plate (Fig. 4-12 h). The prints from the Cyrel FR capped (Fig. 4-12 c - d) do not show a halo, which could be due to the fact that it has a hard 0.05 mm cap which does not allow for the bulges to reach the substrate.

#### B. Ink Transfer as a Function of Roll-Nip Pressure

Fig. 4-15 shows the effect of over and under impression on the D-value. In the solid region the D-value is decreased by 3.9% when over impression occurs. The ink is squeezed out of the plate/substrate nip with increased pressure, which causes less ink to be transferred to the polyethylene. Under-impression also causes a decrease in the D-value but to a lesser extent. In half-tone dots the D-value measures an over-impression because as the ink is squeezed out a larger half-tone dot is printed.

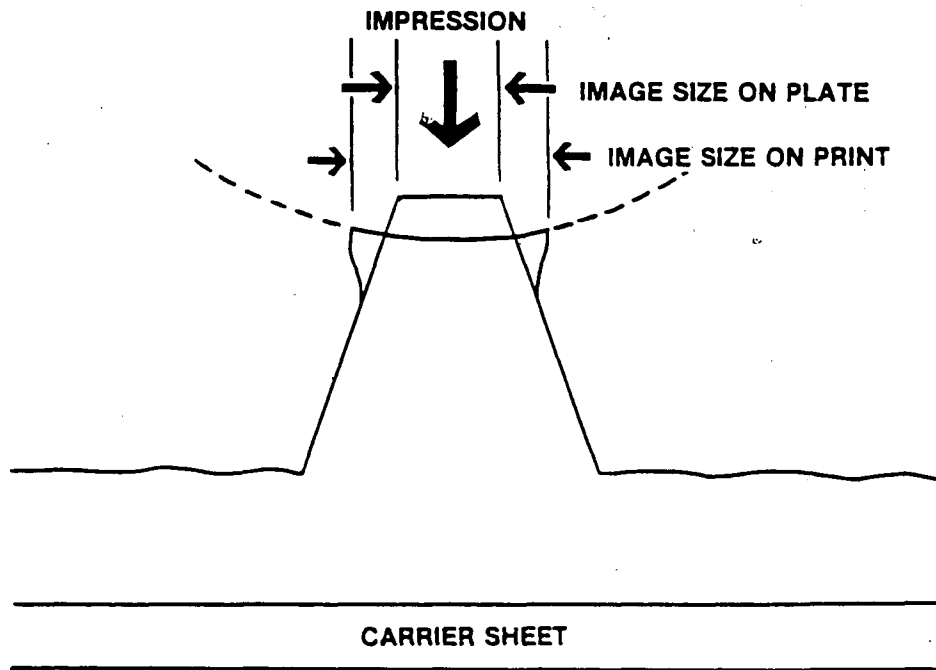


Figure 4-14: Half-tone dot as it passes through the nip

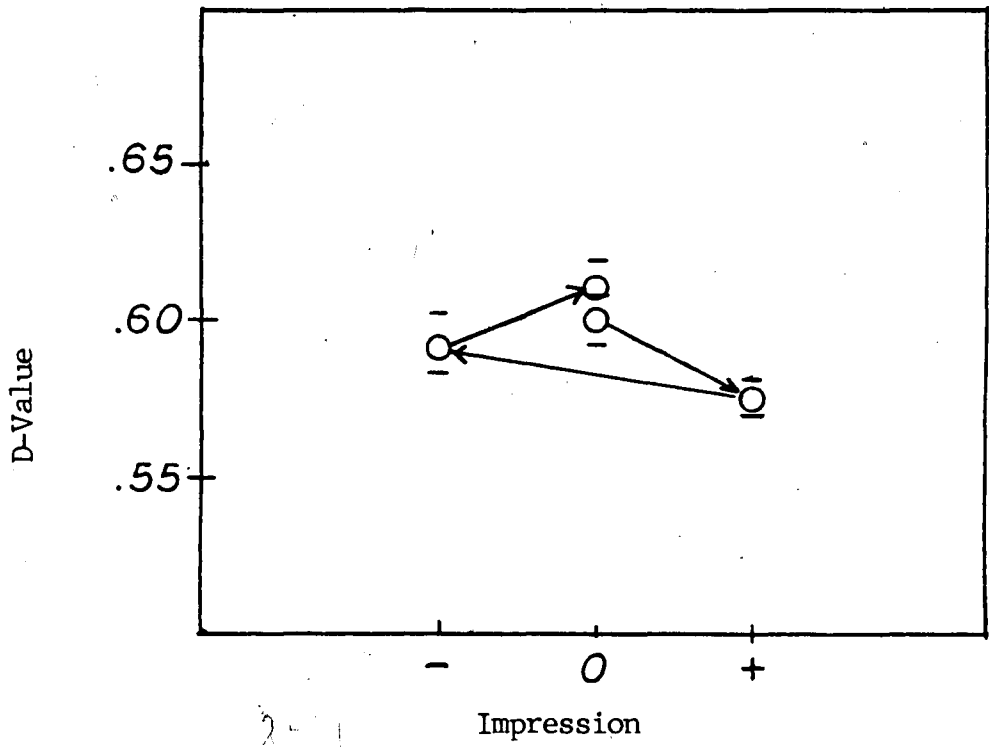


Figure 4-15: D-value vs. impression, 0-optimum print, (+) over impression, (-) under impression



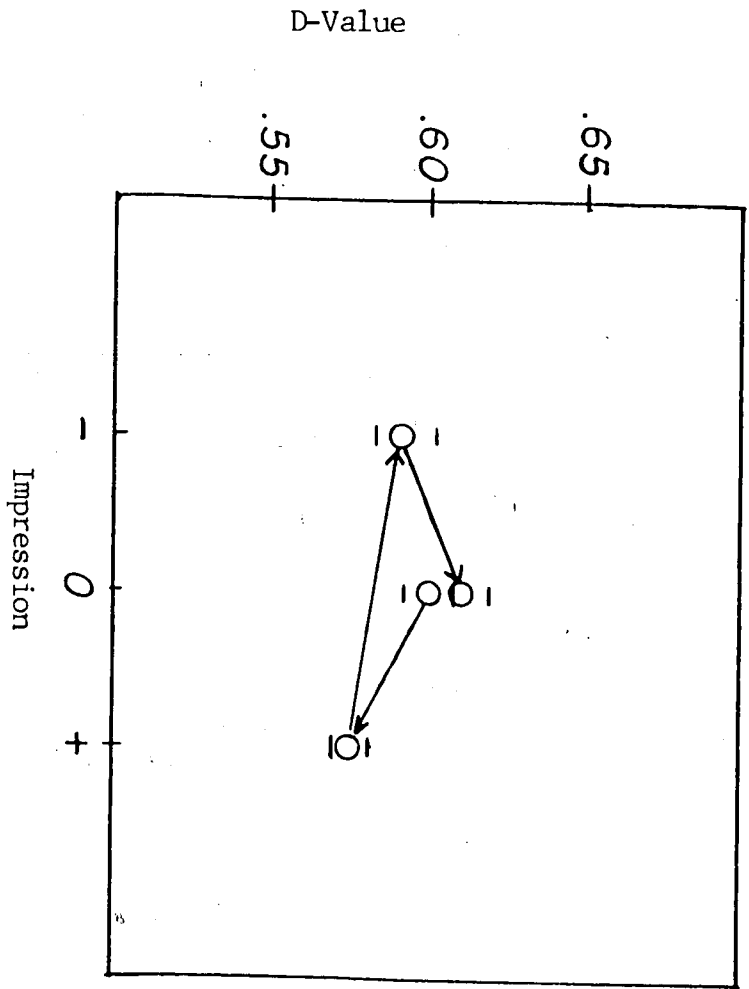


Figure 4-15: D-value vs. impression, 0-optimum print, (+) over impression, (-) under impression

### C. Ink Transfer as a Function of Press Speed

Figs. 4-16 and 4-17 show D-value and roller nip pressures as a function of press speed, respectively. In this experiment an excellent reproducibility of D-value was found in the cycle 2.03-0.25-2.03 m/s (Fig. 4-16). The increase in D-value from 0.25 m/s to 2.03 m/s was 31%, a difference which is very easily detected with the naked eye. The pressure profiles shown in Fig. 4-17, imply that the pressure in the two nips, anilox/plate and plate/substrate, are independent of roller speed. Thus, the amount of ink transferred is a function of press speed.

The ink is metered from the ink fountain by means of a rubber fountain roller impinging on a 360 line screen anilox roller. The metering efficiency of the rubber fountain roller decreases with increasing speed (4). This effect causes more ink to be transferred to the plate roller. However, since the nip pressures are constant, the nip clearance will also be constant at the plate/substrate nip, yet the D-value is increasing with increasing speed. An explanation for this is that as the speed of the rollers increase the position of ink split changes, i.e. the position of split is moving closer to the plate roller (Fig. 4-18). As the position of split moves towards the plate roller a thicker ink layer is layed down on the substrate resulting in a higher D-value.

### D. Scanning Electron Microscopy Analysis of Plates

The microscopic analysis of the effect of printing on the plate surface was given some degree of consistency by analyzing groups of three Cyrel FR plates of similiar thickness, where each plate was exposed to the same conditions. Figs. 4-19 to 4-22 are representative

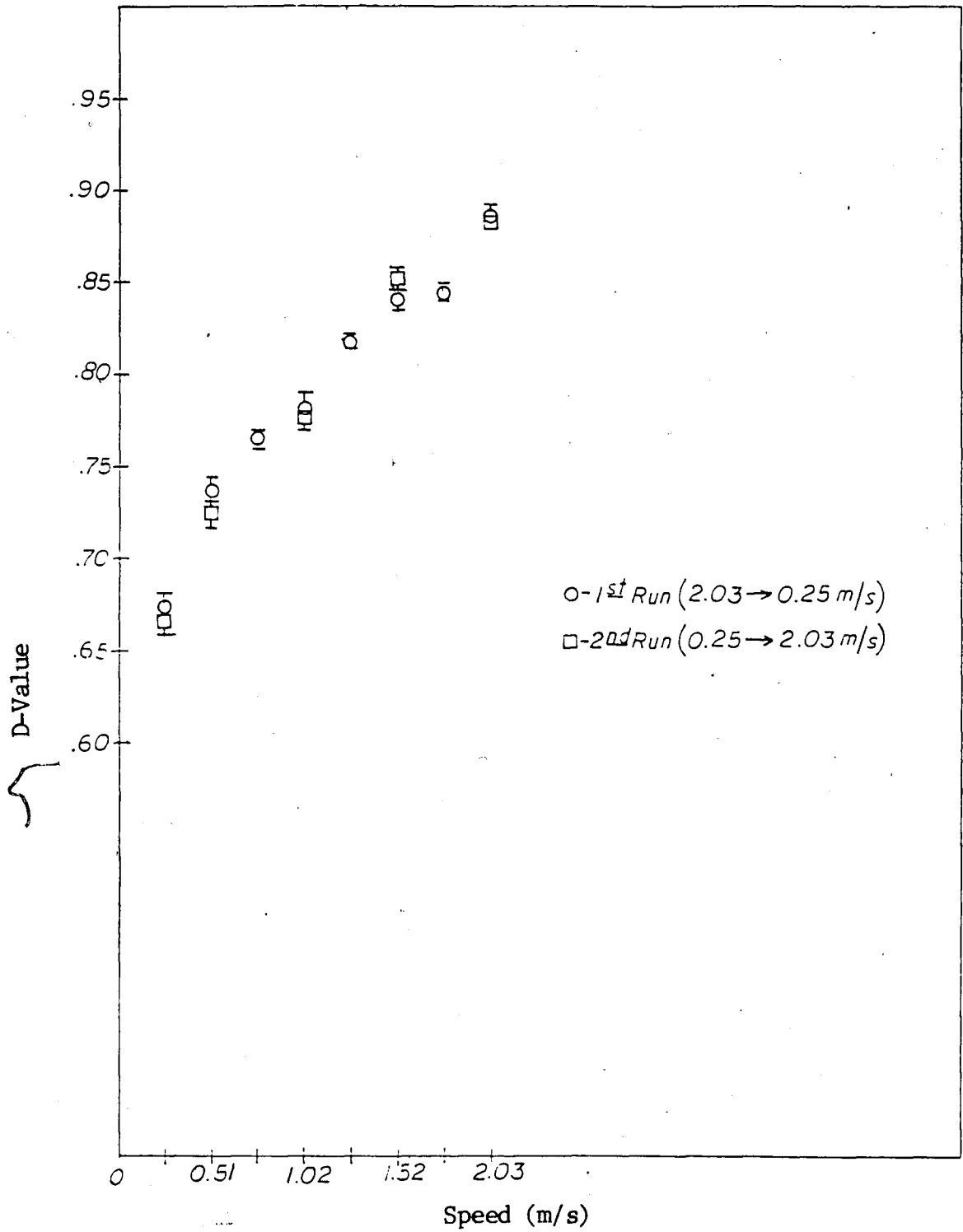


Figure 4-16: D-value vs. printing speed for Cyrel FR

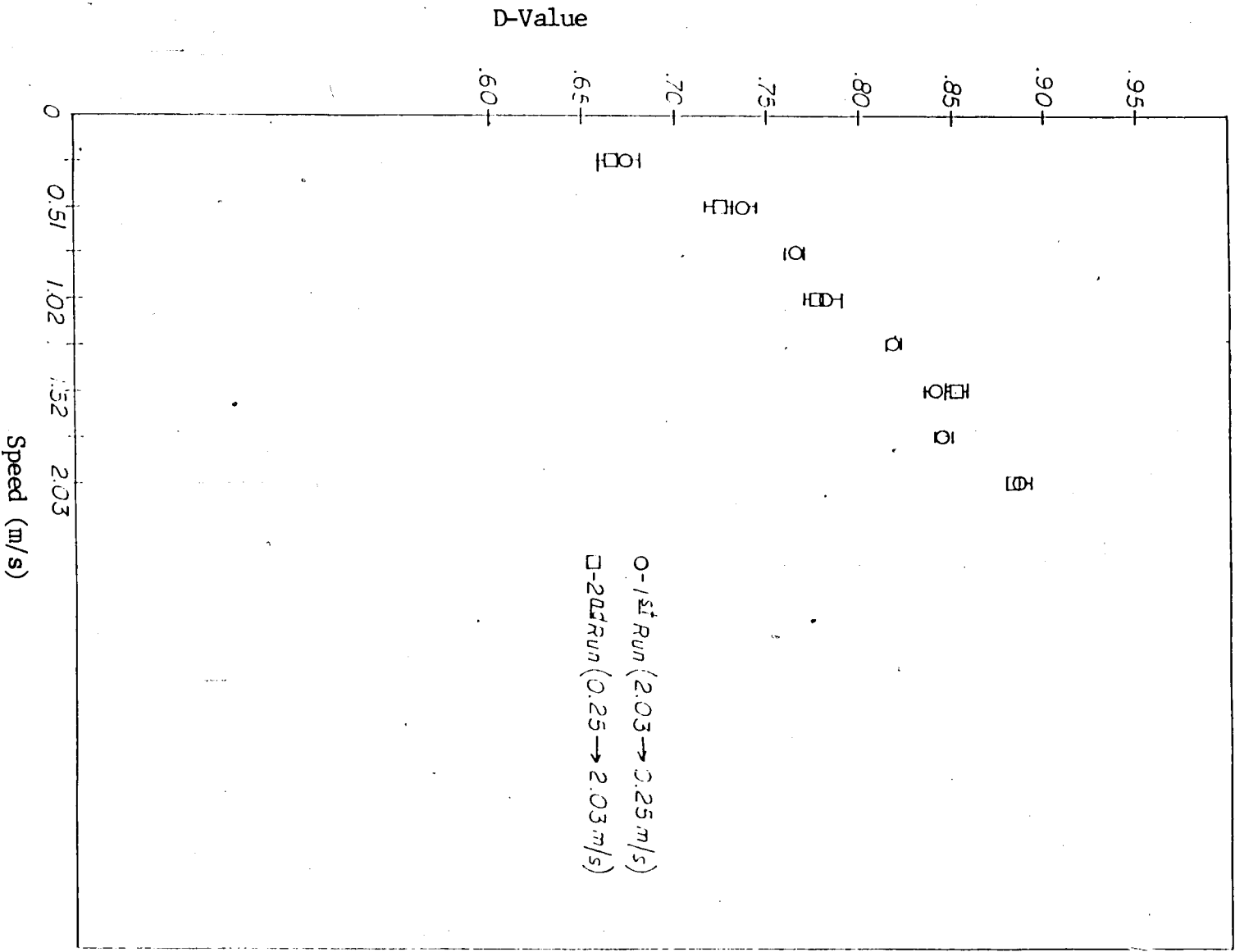


Figure 4-16: D-value vs. printing speed for Cyrel FR

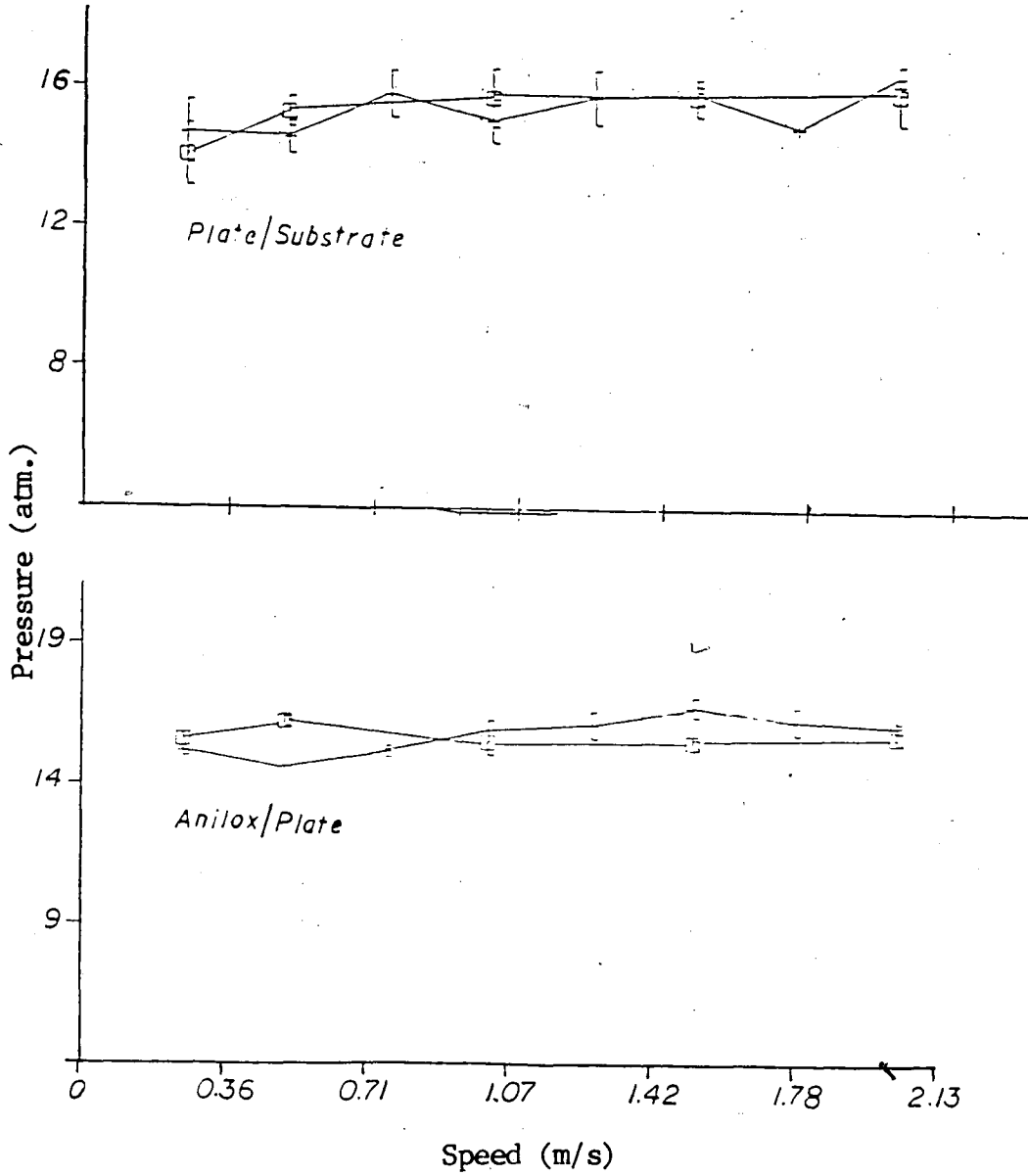


Figure 4-17: Nip pressure vs. printing speed  
 □ 2.03 to 0.25 m/s      □ 0.25 to 2.03 m/s

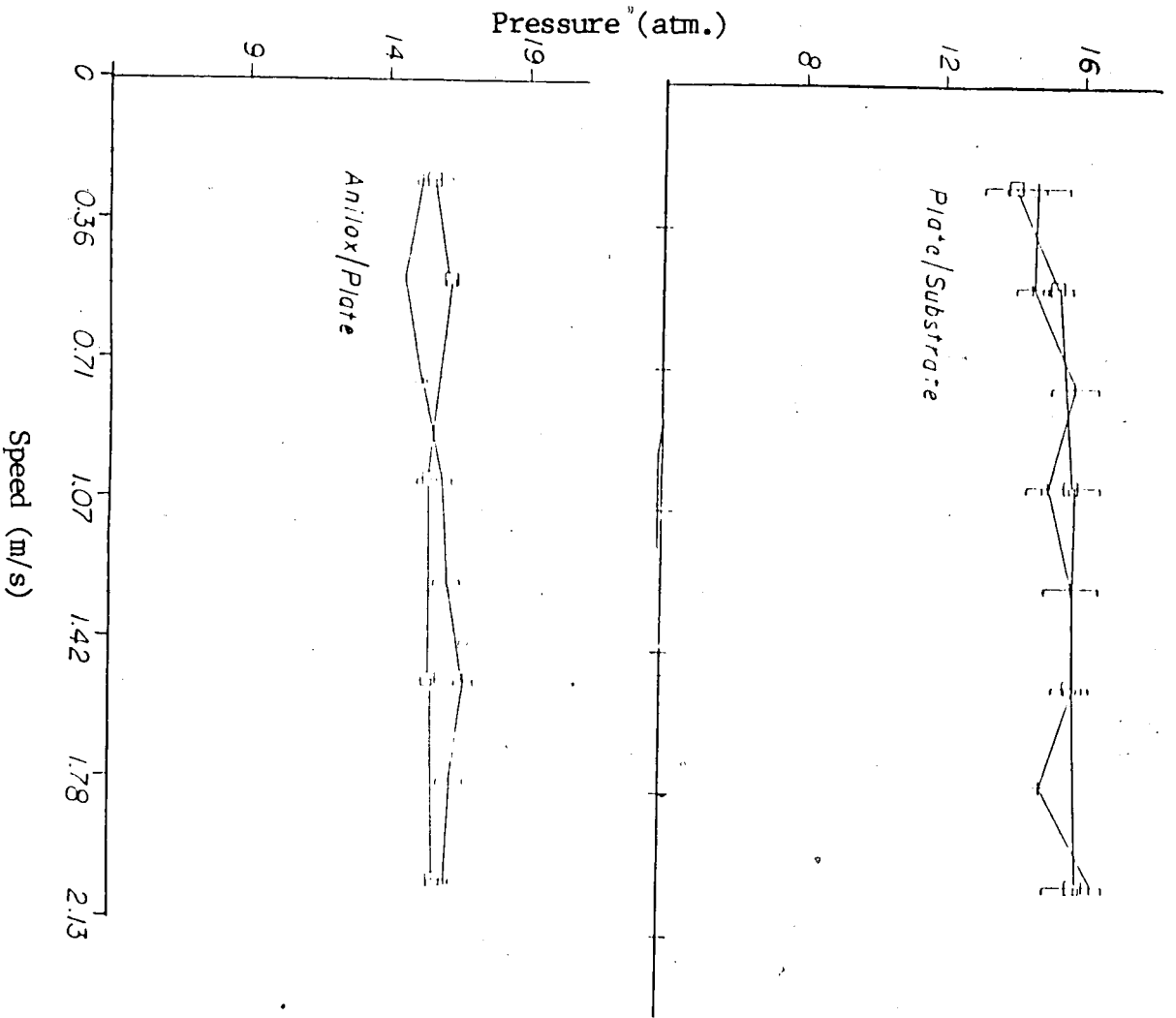


Figure 4-17: Nip pressure vs. printing speed  
 2.03 to 0.25 m/s     0.25 to 2.03 m/s

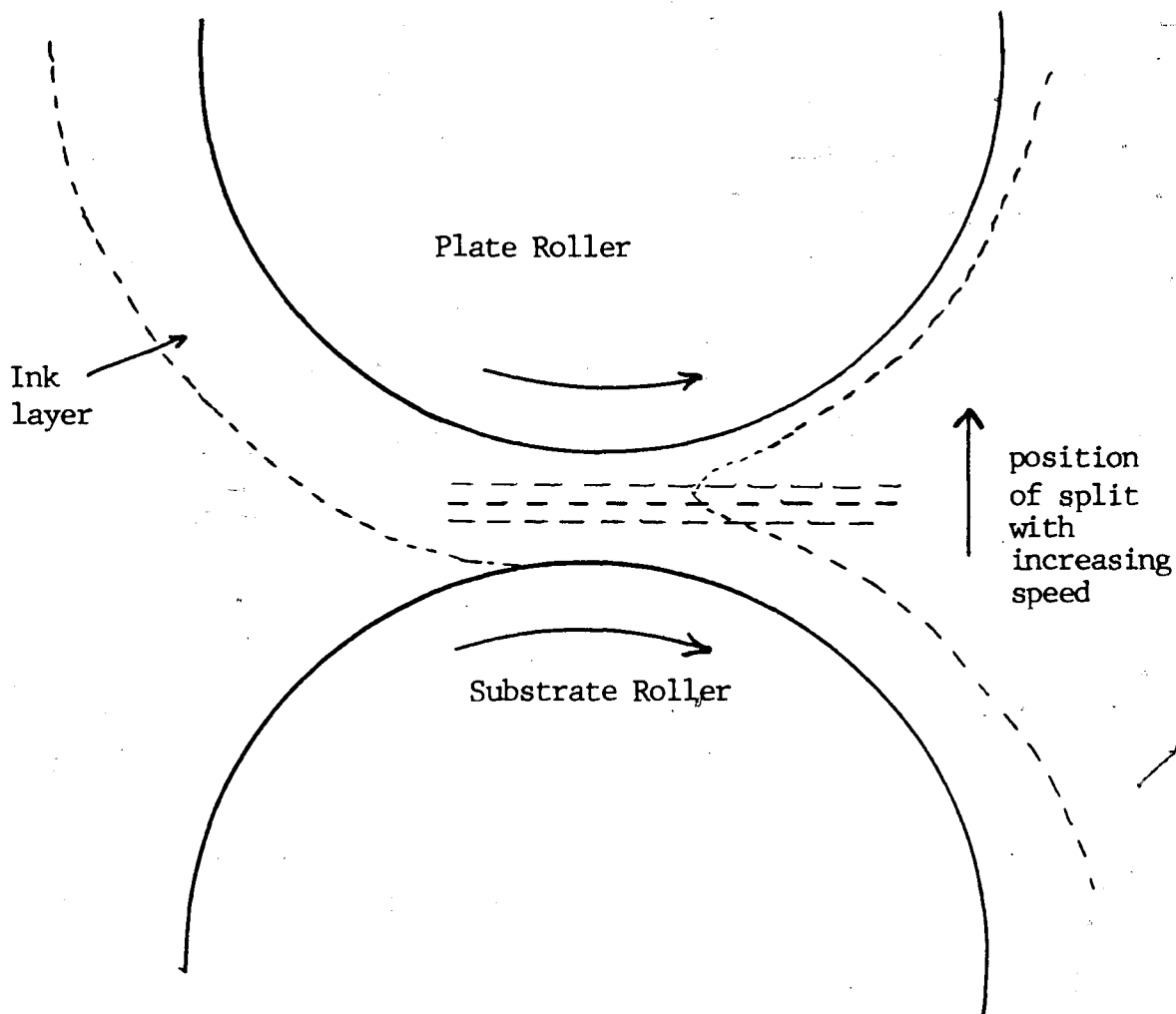


Figure 4-18: Position of ink split with increased speed

scanning electron micrographs of the plates after various printing conditions for the Cyrel FR plates.

Fig. 4-19 is representative of the plate surface as received. The continuous surface of the half-tone character appears smoother than the surface in the solid region. Also, the fissures evident in the solid region appear much shallower in the half-tone region. The increased smoothness, it is believed, occurs because the half-tone has a higher surface area exposed to the wash-out solvent (which partially swells the plate) during the plate preparation process.

Fig. 4-20 shows the effect on the cleaned surface caused by printing for approximately one hour. The solid area shows regions of increased pitting. The half-tone region appeared, at first, as though not all of the ink had been removed on cleaning. Micrographs of plates exposed to solvent only (Fig. 4-23) confirmed that the streaks were caused by the action of the ink solvent on the plate and were not an ink residue.

Plate exposure conditions resulting in Fig. 4-21 and 4-22 were taken one step further; exposed to ink for one hour of printing, washed then stored for approximately one month, then reprinted for one hour. The effects of the storage in an atmosphere of the ink solvent on the plate are quite devastating. The storage condition for plate A (Fig. 4-21) was more harsh than for plate B (Fig. 4-22). Plate A was washed free of ink, the top surface was wiped dry with a soft clean cloth, then placed in a sealable polyethylene bag; plate B was cleaned in the same manner as plate A, but was dried further using a warm air heat gun for 15 minutes, then stored in a sealable polyethylene bag. Both plates





a

Solid



b



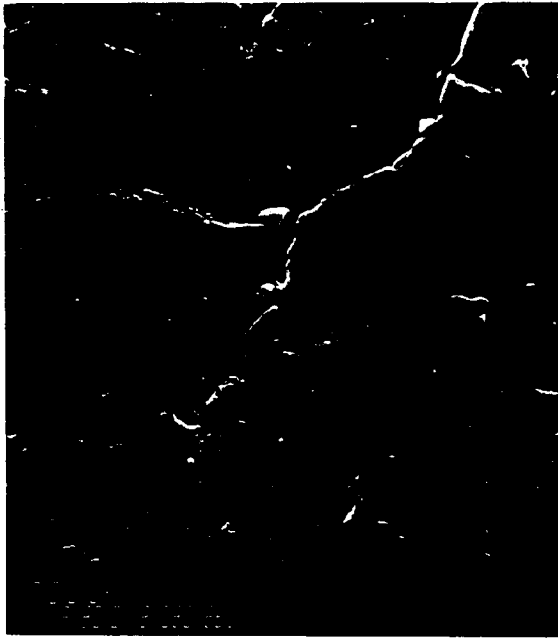
c

Half-tone



d

Figure 4-19: Cyrel FR, as received

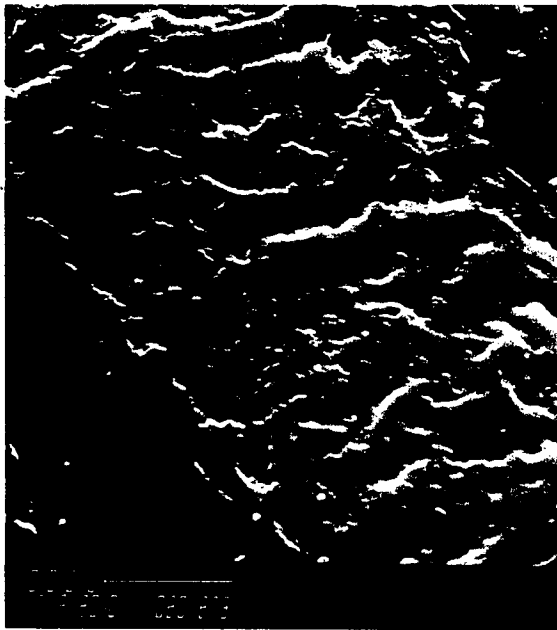


a



Solid

b



c



Half-tones

d

Figure 4-20: Cyrel FR, inked then washed



a

Solid



b



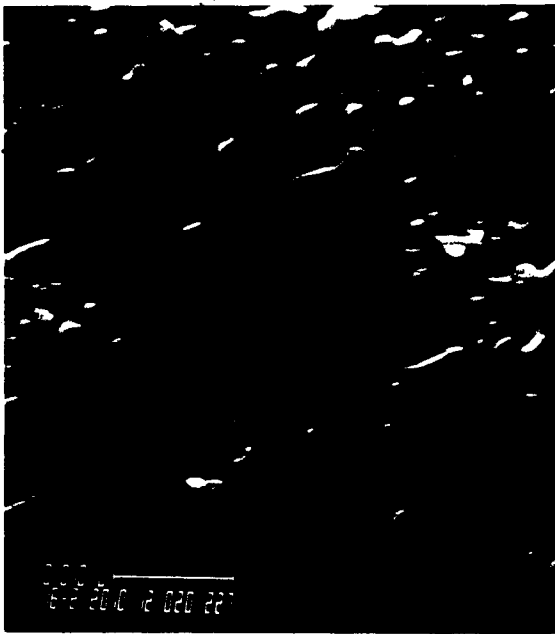
c

Half-tone



d

Figure 4-21: Plate A Inked/Washed/Stored/Inked/Washed

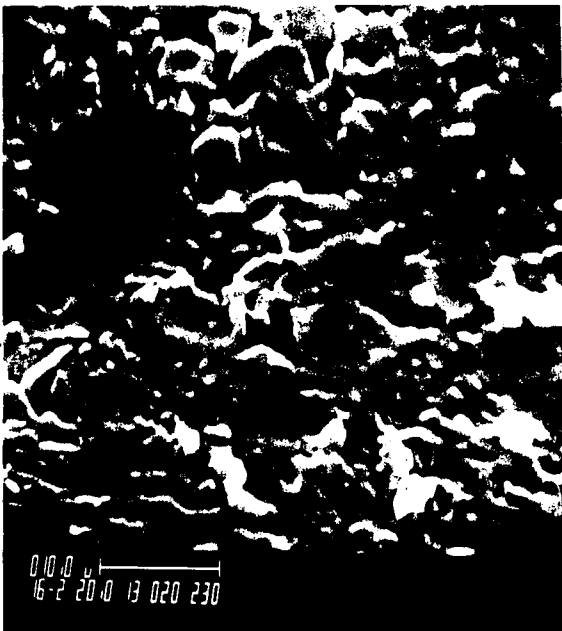


a

Solid

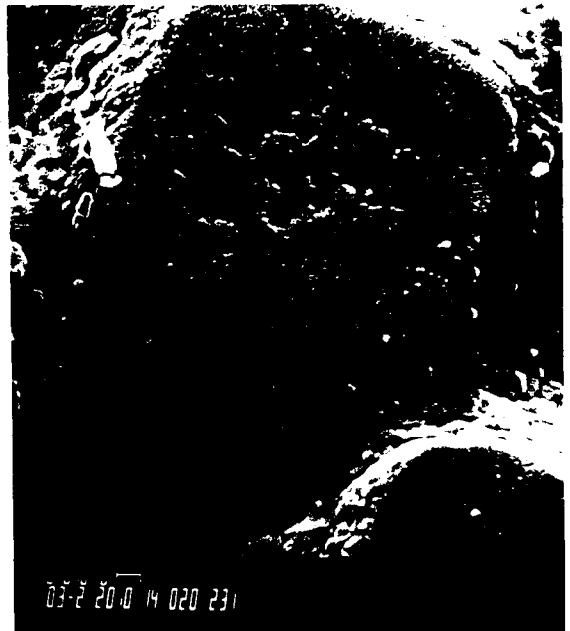


b



c

Half-tone



d

Figure 4-22: Plate B Inked/Washed/Stored/Inked/Washed

were stored in a controlled environment room for approximately one month. The results of earlier experiments by Zettlemyer et al (5) show that the plates take almost one week to dry completely free of solvent on exposure to solvent for one hour. Thus plate A was probably stored in an atmosphere of medium to high ( $> 0.5$ ) relative pressure of the ink solvent, whereas plate B was stored in a quite low (approximately 0.1) relative pressure of the solvent. The severe pitting of the solid region of plate A, Fig. 4-21 a, can be seen to a lesser extent in plate B, Fig. 4-22 c. These harsher storage conditions for plate A (Fig. 4-21 d) have resulted in an increased wear or fracture of the edges of the half-tone compared to that for on plate B (Fig. 4-22 d).

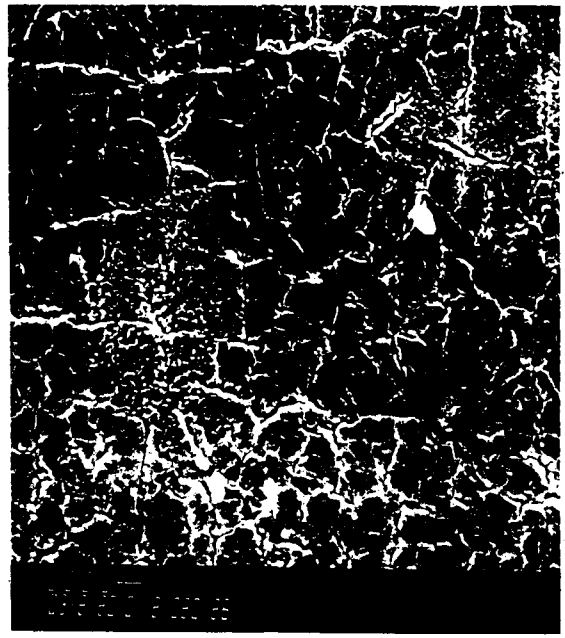
Scanning electron micrographs of plates which were exposed to solvent by printing with the ink solvent only are shown in Fig. 4-23. The surface of the solid region is seen to be very pitted (a and b) while the half-tones appear to have nodules on the side of the half-tones. These nodules are the same as those that are seen on the half-tones of plates A and B (Fig. 4-21 and 4-22). The presence of these nodules is a result of the effect of the ink solvent on the plate and will probably occur with any ink printed using the solvent system, 1-propanol/1-propylacetate. The origin of these modules is uncertain, but is probably a residue leached from the photopolymer plate.

#### E. Micro-Surface Roughness and Ink Transfer

A study was carried out to determine if a relationship exists between the surface roughness of a printing plate and the amount of ink transferred by a Cyrel FR plate and competitor plates. Again, the scanning electron microscope was used to examine the surface of plates as

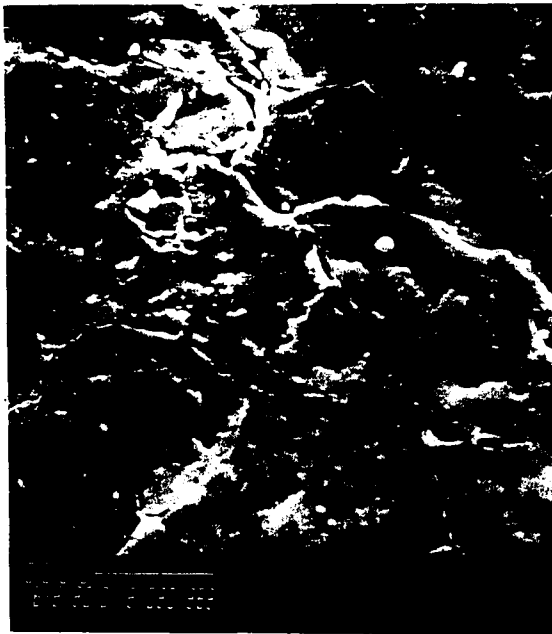


a



b

Solid



c



d

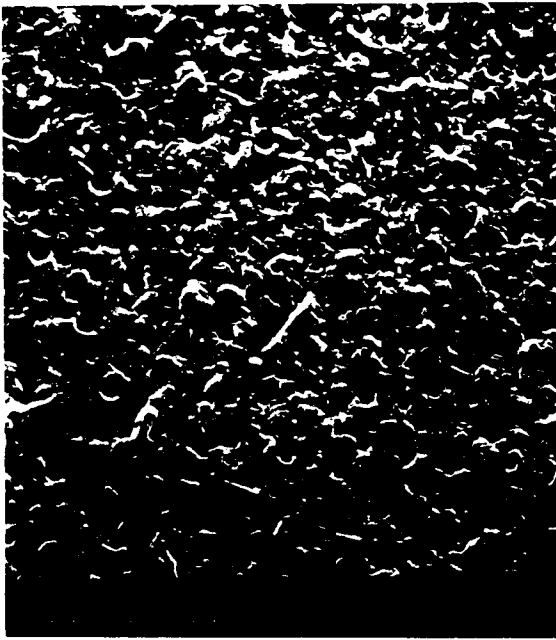
Half-tone

Figure 4-23: Cyrel FR, exposed to solvent

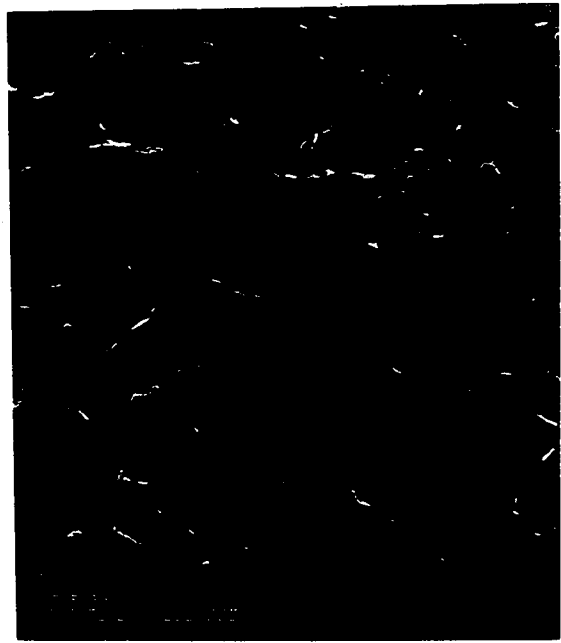
received, Fig. 4-24, and after the plates had been printed, then washed, (Fig. 4-25). The micrographs in Fig. 4-24 show that the plates can be arranged according to surface roughness as follows: Cyrel FR capped > Cyrel FR > BASF Nyloprint > Flex-Light K. The Cyrel FR capped plate having the roughest surface. Fig. 4-25 shows scanning electron micrographs of the test plates after they were printed for one hour, then washed: the order of decreasing surface roughness is now Cyrel FR capped > Cyrel FR > Flex-Light K > BASF Nyloprint.

The micrographs in Fig. 4-25 show a smoothing of the surface as compared to the surfaces in Fig. 4-24. This general smoothing of the plate surfaces is probably due to a combination of both plate wear and plate swelling (by the ink solvent, 1-propanol/1-propylacetate). Plate wear is most likely to be small compared to plate swelling. The solvent affects the BASF plate more than its competitors (Fig. 4-13). The effects of plate swelling on print definition have been clearly illustrated in Fig. 4-12, a photograph of a printed half-tone area of the plate.

The results of the reflectance measurements as a function of time on the press for the 4 test plates are summarized graphically in Fig. 4-26. The D-values ( $D = -\log \text{Reflectance}$ ) are directly proportional to the thickness of the printed ink layer. Sample prints at time = 0 minutes are those taken immediately after the press operator has determined visually an optimum print, the time required for the operator to obtain the optimum print is approximately 4 to 5 minutes. However, the operator does not set up the press at the anticipated press run speed but at a speed of approximately 0.25 m/s. The effect of press speed on D-value was discussed earlier, section IV C. In Fig. 4-26 the D-values of



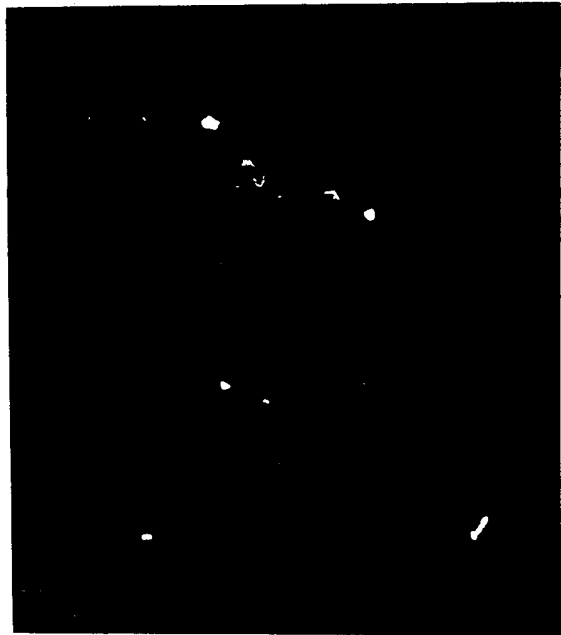
A-Cyrel FR Capped



B-Cyrel FR



C-BASF



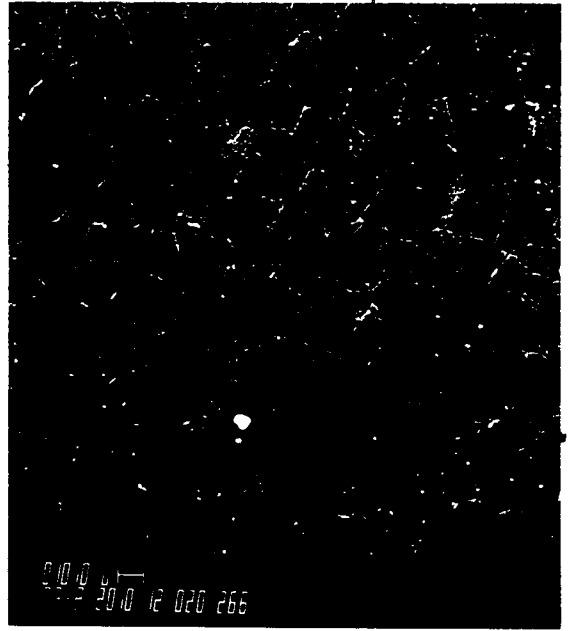
D-Flex-light K

Figure 4-24: Plates as received

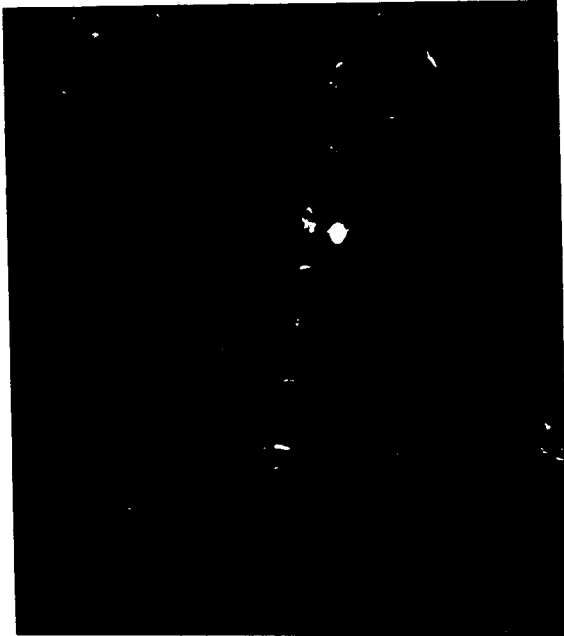




A-Cyrel FR Capped



B-Cyrel FR



C-Flex-Light F



D-BASF

Figure 4-25: Plates inked, then washed

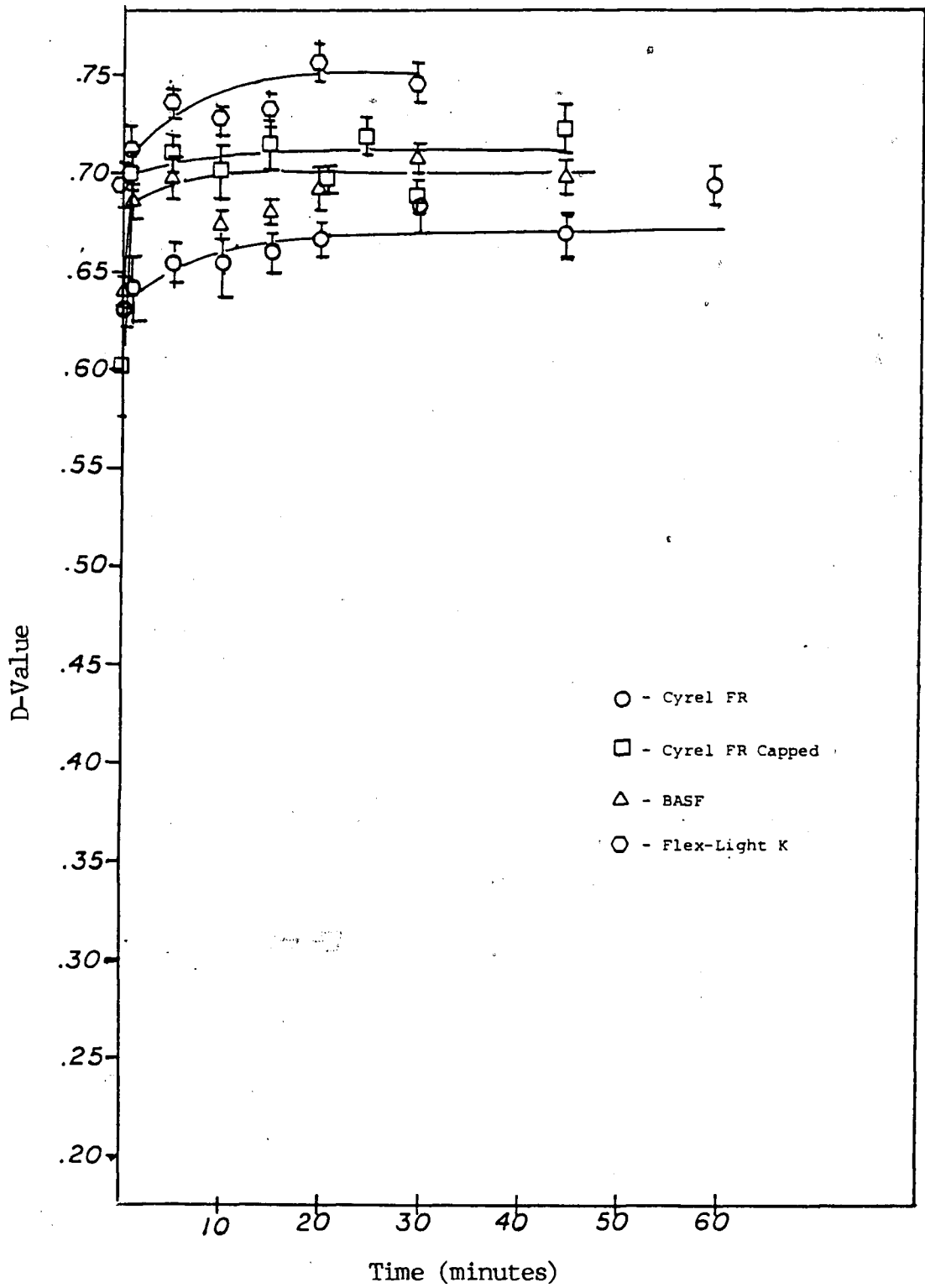


Figure 4-26: D-value vs. time for several plates

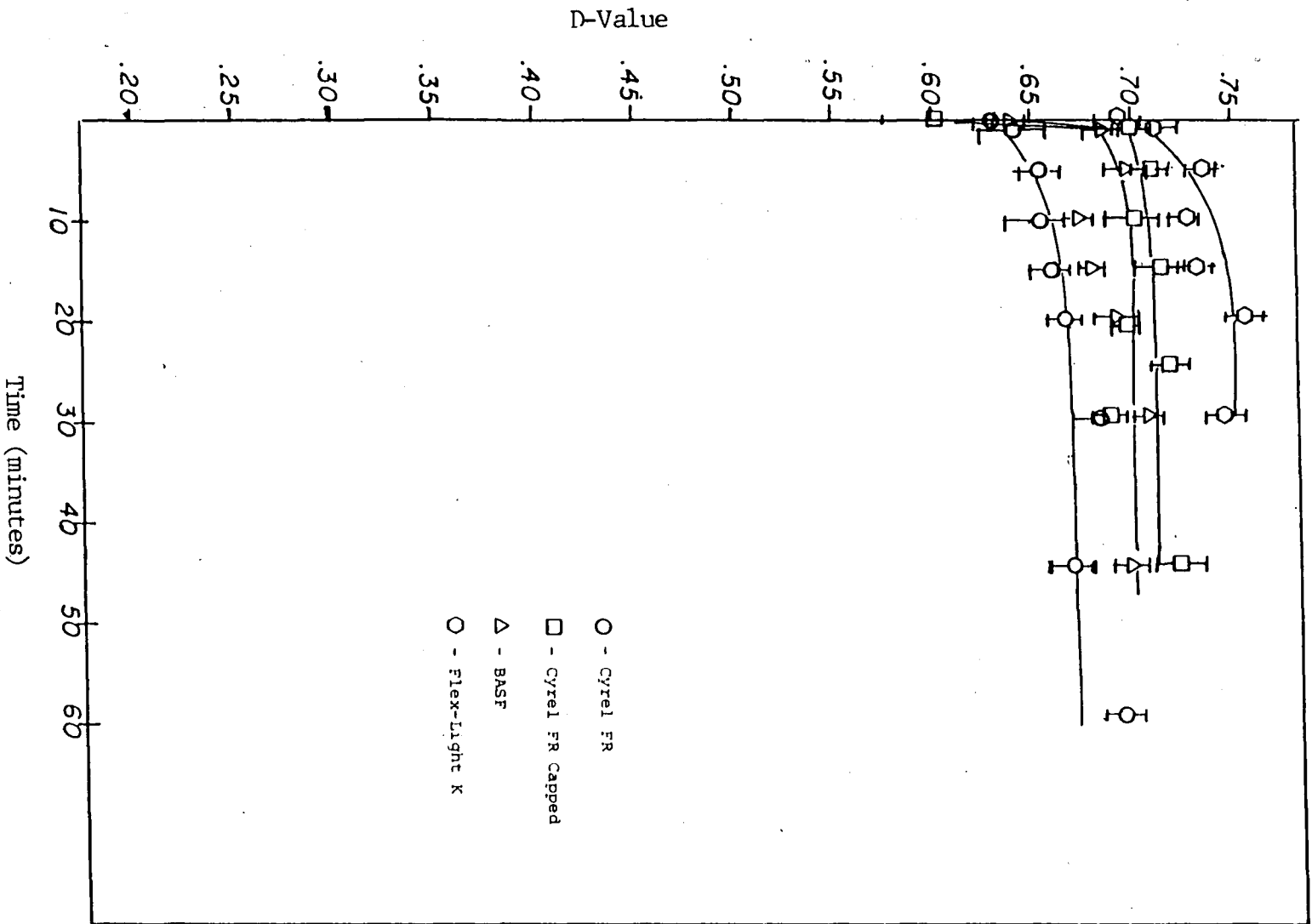


Figure 4-26: D-value vs. time for several plates

sampled prints follow the surface roughness order defined by the SEM analysis of the plates as received, the plate with the roughest surface giving the lowest D-value.

The results in Fig. 4-26 show that the D-values plateau after approximately 20 minutes of printing. The decreasing D-value or ink layer thickness is in the order of: Cyrel FR capped > Cyrel FR > BASF Nyloprint > Flex-Light K. The surface roughness of the plates after being printed for one hour (Fig. 4-25) are in the order of decreasing surface roughness: Cyrel FR capped > Cyrel FR > Flex-Light K > BASF Nyloprint. In contrast to the D-values at time = 0 minutes, there is no correlation between surface roughness and D-value after printing for more than 20 minutes. It is suggested that the surface roughness is not a part (or only a minor part) of the controlling factor in the amount of ink transferred from a plate to a substrate. Table 4-1 shows the percent change in D-value for each plate in Fig. 4-26. The percent change in D-value follows the roughness scale after printing for one hour, i.e. the roughest plate, Cyrel FR capped, gave the largest increase in D-value, 18% (time = 0 to plateau), and the smoothest plate, BASF Nyloprint, gave the smallest increase in D-value, 3% (time = 0 to plateau). One possible explanation is that as the plates are printing, the roughness of the surface is being filled in with ink, so that the surface which is printing is different from the surface which is shown on the scanning electron micrographs (Fig. 4-25): these are micrographs of the surface after the plate has been washed to remove residual ink.

Table 4-1: Change in D-value between start and plateau region for Cyrel FR

Plate	% Change D-Value
Cyrel FR Cap	18
Cyrel FR	8
Flex-Light K	9
BASF	3

## F. Printing Ink Characterizations

The results of a rheological analysis of the printing inks, Immont "Polyamide" and Sakata Blue, are shown in Fig. 4-27. These inks were analyzed because the Immont ink has been the ink used most often in the series of high speed printing tests and the Sakata sample has the highest solids concentration.

The Immont ink shows Newtonian behavior: no hysteresis on increasing then decreasing the rate of shear and passes through the origin linearly on decreasing from any applied rate of shear. Since this ink is Newtonian, the viscosity can be quoted without reference to an applied rate of shear. The viscosity is 16 cP.

The Sakata ink show some hysteresis on increasing and decreasing the rate of shear. The hysteresis is probably a result of the higher solids concentration compared with the Immont sample. The viscosity at  $20,480 \text{ s}^{-1}$  is 28 cP. A slight shear thinning is apparent on increasing the shear rate; i.e. the ink is becoming slightly less viscous as the shear rate increases. Since the decreasing shear rate passes through the origin linearly from  $20,480 \text{ s}^{-1}$ , the ink does not have a yield point. Further measurements, however, would have to be made to determine the extent of ink viscoelasticity.

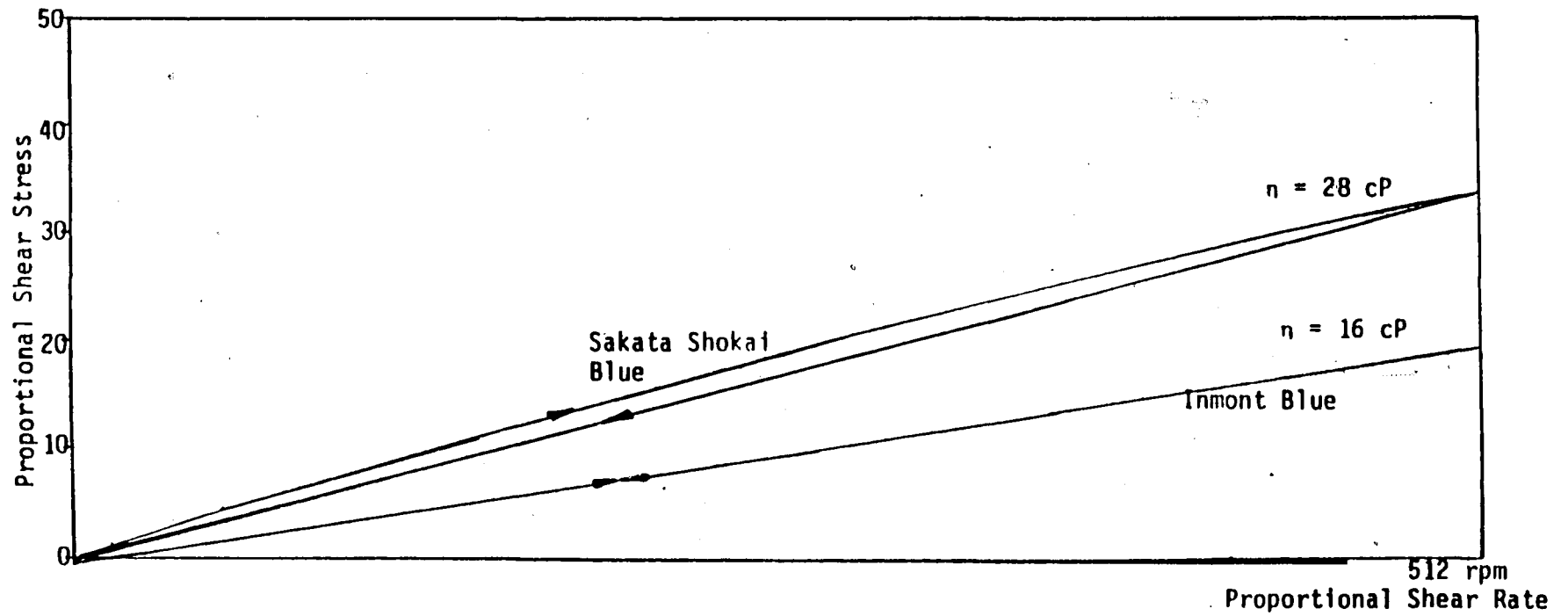


Figure 4-27: High speed rheogram of printing inks

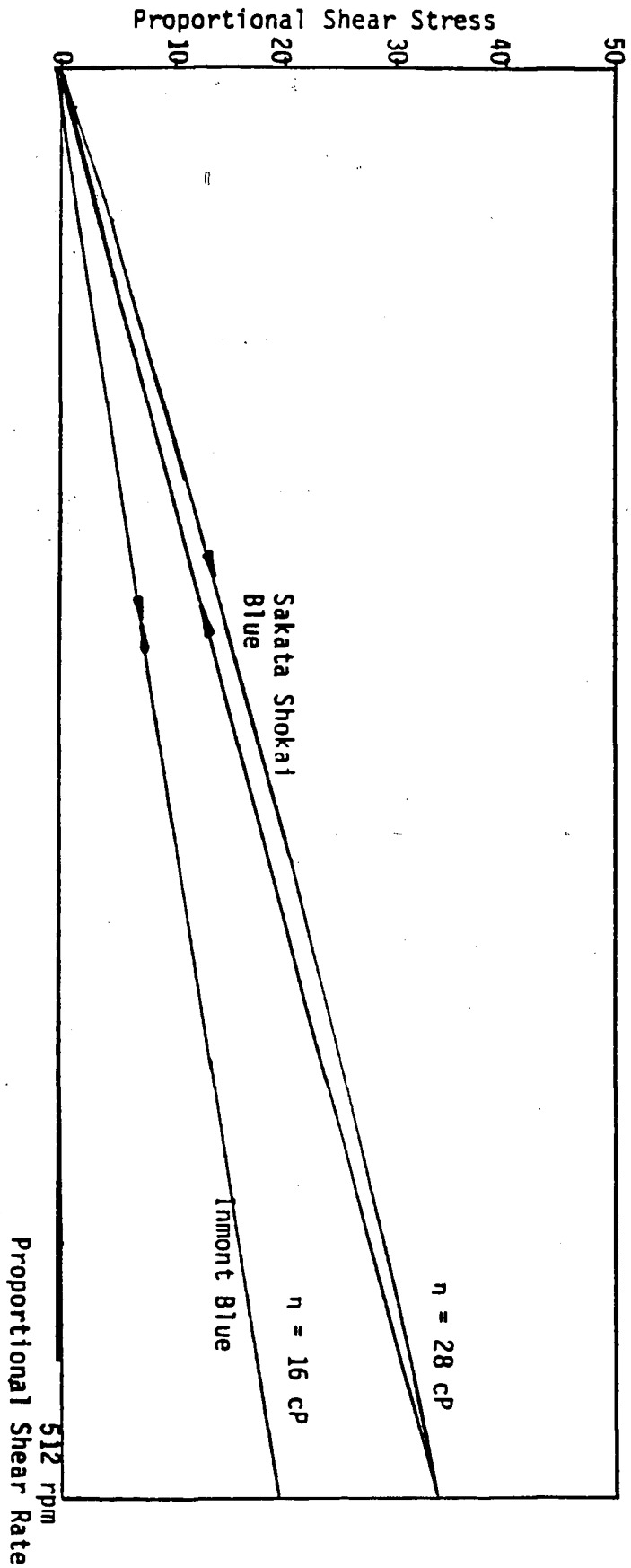


Figure 4-27: High speed rheogram of printing inks



## V. CONCLUSIONS

The conclusions that can be drawn from this work are as follows:

1. The D-values (ink thickness) of a solids region are always initially low and increase to a plateau after about 20 minutes of printing for all plates tested. The D-values remain constant (within experimental error) for the remainder of the run.
2. Small changes in viscosity ( $< 5\%$ ) for the ink used, result in a negligible variation in the resulting D-value.
3. The 20% half-tone was determined to be the lower limit of sensitivity for the reflectance analysis.
4. Storage of Cyrel FR plates in an atmosphere of the ink solvent (1-propanol/1-propylacetate) enhances the deterioration of the plate surface.
5. The press operator (for the reported experiments) was able to reproduce optimum printing conditions within a given day, but not on a day-to-day basis.
6. A difference in D-value of as little as 3 to 4% can be detected by the naked eye.
7. Plate swelling was found to be a major factor in the final print quality, in particular for half-tones and characters.
8. BASF Nyloprint swells to a much greater extent than any of the other alcohol/acetate resistant plates tested and hence produces a poorer print.
9. Ink solvent uptake during printing has a smoothing effect on the surface.

10. It is proposed that during printing, after the D-value plateau has been reached, ink transfer is unaffected by surface microroughness, due to the formation of an equilibrium ink layer thickness on the plate surface. Differences in D-values between the tested plates are due to variations in plate mechanical properties.
11. As the speed of the press increases (nip pressures being constant) the position of split moves closer to the plate, resulting in an increase in D-value or amount of ink transferred.

## VI. SUGGESTIONS FOR FURTHER WORK

Although the present work examined D-value and relative ink layer thickness, it is necessary to determine the absolute thickness of the transferred layer. Knowledge of the actual ink thickness will allow calculation of the extinction coefficient resulting in a direct calculation of the ink thickness from D-values. Some methods for evaluation of ink thickness are:

1. Interference microscopy;
2. Dissolution of ink layer - determining the amount of dye stuff by atomic absorption spectroscopy;
3. Isotopic labeling ( $^{14}\text{C}$ ) of the dye stuff in the ink.

Also, a knowledge of the final print thickness will permit a more informed speculation of the ink behavior within the plate/substrate nip. That is, it will be possible to analyze the pressure profile between the rollers and give a better understanding of half-tone behavior (and ink flow around the half-tone) within the nip during under- and over-impression studies.

Examination of the printability of the plates tested using inks of different color and viscosity transferred to substrates of different nature, i.e. paper of varying gloss, foil, card, and coated plastics. The results of such experiments will permit the development of a relationship between ink transfer and plate type, substrate and ink viscosity.

Determination of the mechanical properties of the plates in terms of their loss and storage modulus. These measurements should be determined as a function of ink solvent uptake. Such measurements will

will yield valuable information regarding plate relaxation time and properties and again will permit speculation regarding plate properties and ink transfer.



VII. REFERENCES

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