NBSIR 83-2691

Relationships Between Mechanical Properties and Performance of Inks As the Basis for Quality Control Techniques

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
Polymer Science and Standards Division
Washington, DC 20234

May 1983

Issued July 1983

Prepared for
U.S. Department of Treasury
u of Engraving and Printing
tment of Research and Technical Services
ngton, DC 20226

NBSIR 83-2691

RELATIONSHIPS BETWEEN MECHANICAL PROPERTIES AND PERFORMANCE OF INKS AS THE BASIS FOR QUALITY CONTROL TECHNIQUES

Donald L. Hunston

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
Polymer Science and Standards Division
Washington, DC 20234

May 1983

Issued July 1983

Prepared for
U.S. Department of Treasury
Bureau of Engraving and Printing
Department of Research and Technical Services
Washington, DC 20226

U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, *Secretary*
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, *Director*

Relationships between Mechanical Properties and Performance of Inks as the Basis for Quality Control Techniques

Background

For the last two years the National Bureau of Standards has been working with the Bureau of Engraving and Printing in a program designed to gain a better understanding of the factors that control ink performance in the manufacture of paper currency and through this knowledge to develop improved quality control (QC) tests for these inks. The purpose of this report is to summarize the results of this program to date and to recommend the most promising areas for continued research. Much of the detailed information developed during this study is contained in Appendix I and so the main test focuses more on recommendations and conclusions.

The approach taken in this program can be roughly divided into six steps. First, a small number of ink samples were to be rheologically characterized in a very complete way to develop the necessary test technology and equipment. Second, this technology was to be extended to develop the cabability for measuring the rheological changes that occur when the ink is cured under simulated press conditions. Third, a few ink samples were to be thoroughly characterized before and during cure so that those parameters most directly related to performance could be identified. This minimizes the number of tests that must be performed in subsequent part of the program and thus a larger number of ink samples can be examined. Fourth, the parameters identified in this way were to be determined for a larger number of selected ink samples with known performance so that property/performance relationships could be established.

Fifth, based on this information, specialized measurement techniques were to be designed and/or adapted for QC applications. Sixth, the validity of these tests was then to be established by again examining inks with known performance. This requires both the reexamination of inks previously tested and the characterization of new ink samples. It was felt that this approach provides not only insight into the fundamental properties that control ink performance on the press but also a basis for selecting the best QC techniques that can be developed.

During the past two years, the joint NBS/BEP program has completed steps 1, 2, and 3 and has made a significant start on step 4. (Details of this work are covered in Appendix I). Although future plans will be considered in more detail later in this report, it is worthwhile to point out here that the future work would involve the completion of step 4 and a major effort to address steps 5 and 6.

Experiments

In presenting the conclusions and recommendations of the work to date it is useful to discuss them in terms of the types of experiments performed. All of the techniques employed thus far looked at the shear properties of the inks. Three basic types of shear experiments were examined: Steady Shear, Oscillatory Shear, and a combination of the two. All of the experiments utilized the convensional cone and plate geometry similar to that used in the Haake viscometer at BEP but with a much more versatile instrument. As indicated in Appendix I the oscillatory behavior and thus the combined oscillatory and steady shear behavior were very complex. In general, however, the results lead to the same conclusions as the steady shear experiments. Consequently, only the latter tests will be discussed here but details of the other tests can be found in Appendix I and previous progress reports.

Steady Shear. In the steady shear tests the sample is initially at rest and then suddenly subjected to a constant rate of shear flow. The stress level associated with the initiation and maintenance of this shear is measured as a function of time. When the experiment first begins a high stress level is required to initiate the flow but then over a period of less than 10 seconds, the stress level falls and approaches a limiting value corresponding to steady-state flow (Figure 1 in Appendix I). A similar experiment can be performed in which a steady flow is suddenly stopped and the fall off of the stress is recorded as a function of time but the discussion here will be restricted to the former experiment. The other variable that can be examined in this test is the rate of shear. For the experiments performed here, the shear rate was varied from 5×10^{-2} sec^{-1} to 500 sec^{-1}. The experiments were conducted by allowing the ink to rest in the viscometer for ten minutes or more before each test with a new test for each shear rate.

The results for specific experiments are given in Appendix I but the general behavior can be illustrated by a 3-D plot showing the viscosity, η, as a function of time and shear rate. This is shown schematically in Figure 1. For a simple material information such as that in Figure 1 would provide a complete characterization of the shear properties, i.e., based on this data any flow behavior could be predicted. In this case however the material is not simple since the high values of η at short time are the result of a need to break-up a structure which forms when the ink is allowed to rest. If the experiment is stopped and then restarted without the rest time, the high values of η at short times are not obtained; i.e., the short time values are more similar to the steady state values. The magnitude of the short time viscosity therefore depends on the previous shear history of the ink. Only if the ink is allowed to rest for a significant period of time can the original behavior again be obtained.

In terms of quality control tests both the short time properties (yield behavior) and the steady state values may be of interest. In the test now performed by BEP the viscosity is measured for a specific time/shear rate history (i.e., both time and shear rate are changing simultaneously during the experiment). This means the properties are determined along a specific path such as that illustrated in Figure 1 by the dotted line. Consequently, this test provides some information about both the short time and steady state behavior but only to a very limited extent. In considering what aspects of the behavior shown in Figure 1 might be most appropriate for a QC technique, it must be noted that the short time (yield) behavior is not only complex but also dependent on how the experiments are performed (i.e. the shear history of the sample). Consequently, it is felt that a simple QC test is not well suited to examining such complex behavior in detail and thus we would conclude, for the moment at least, that the qualitative test of yield behavior now performed at BEP is as good as anything. Moreover, one can argue that since the ink in the fountain is in constant motion (no rest time), the yield behavior may not be as important in determining performance as the steady flow viscosity. (One exception to this general conclusion will be mentioned later.) As a result, the efforts in this program were channeled away from yield behavior into a detailed study of the steady-state flow viscosity for the inks.

The results of this aspect of the program are covered in Appendix I and previous Progress Reports. The general conclusions, however, can be illustrated with one particular example. Figure 2 shows a plot of the steady-state viscosity vs. shear rate for three ink formulations (BK-60, Bk-62, and Bk-62 Mod 3). At high and low shear rates all three inks have similar viscosities but at intermediate shear rates the viscosities are quite different. It is known that two of these inks give reasonable, although not ideal, press performance while the

other (BK-62) is unacceptable. Based on these data, if we ask how it is possible for two of the inks to work while the other does not, the only conclusion we can reach is that steady-state viscosity is not a very sensitive parameter for assessing performance. Obviously, there are limits on how much the viscosity can change before unacceptable performance is obtained and certainly some viscosity QC is needed to be sure that these limits are not exceeded. The results suggest, however, that the range of useable values is relatively broad. One explanation for this result is that the shear rates seen on the press are very high during ink transfer and very low in the fountain. For these ranges all the inks look quite similar. Our conclusion then is that steady-state viscosity is a useful but not sufficient QC parameter. It is worth noting, however, that the fabrication of the inks involves shear rate in the intermediate range where the viscosities of different ink formulations vary substantially. Viscosity information may therefore be quite important in ink fabrication.

Aging. One other aspect of the behavior of the uncured inks was measured, i.e. aging effects. A sample of BK-62 was stored at room temperature and during the first few days a hard crust formed on the ink surface that was in contact with air. After more than 6 months, the measured mechanical properties were examined for a sample extracted from a region that was about 1 cm below the crust. Dispite the aging time, the viscosity was quite similar to that obtained for the ink on the same day it was made (Figure 3). A similar test was performed using a sample of BK-62 Mod 3 that had been aged for 5 days in an oven at 60°C. In this case there was a measurable increase in the viscosity but this increase was quite small (less than 40%). The conclusion from these tests is that, at least after the first day, aging in the absence of oxygen does not change the mechanical properties of the ink very much. When oxygen is present, however, very large changes occur. These changes can be accelerated by heat but heat alone has only a small effect.

Curing. In addition to examining the behavior of the uncured ink it was felt that the curing behavior should be studied. To accomplish this, ink samples were placed on an apparatus with two rollers one of which could be heated to 80°C (roughly press temperature) and driven to produce rotation of the two rollers. In this way the ink could be cured under conditions that provide a crude simulation of what might be seen on the press: exposure to oxygen and heat in a thin film and a constant mixing and renewal of the surface to prevent the formation of an outer crust. At selected time intervals, samples were removed and cooled rapidly to room temperature. This cooling did not stop the cure reactions but did slow them sufficiently so that short time experiments could be conducted to characterize the mechanical properties at various stages of cure.

Details of the results for these tests are contained in Appendix I, but the conclusions can be briefly summarized as follows: (1) the cure behavior of the inks can be characterized, (2) different formulations have quite different curing behavior, and (3) the curing behavior of an ink can have an important influence on the performance on the press. These tentative conclusions have some important implications since it means that anything that advances the cure of the ink too soon can affect the press performance. There are a number of areas where this might happen but the two major situations involve over (or under) exposure to oxygen and temperature either during fabrication (particularly on the mill) or during printing while the ink is in the fountain. If these exposures could be better controlled and made more reproducible from batch to batch, we believe the variations in ink performance characteristics could be reduced.

Conclusions

Ink Problems. Before addressing the question of quality control techniques directly, it is useful to say a few words about ink problems. These problems can be divided into three categories: those unrelated to ink quality, those marginally or indirectly related to ink quality, and those directly related to ink quality. The first category can be illustrated by the results from split lots tested during the BEP effort last year to monitor inks. In some cases a single barrel of ink was used with several lots of paper. The spoilage figures for the lots printed with the same ink should be very similar but the results show the spoilage can be quite different. Regardless of why the results were different (press set up, paper, etc.), the important point is that there are major uncontrolled factors other than ink quality that influence performance. Consequently, some of the variations in spoilage have little to do with ink quality. This makes the establishment of QC relationships difficult although not impossible.

The second category of problems involve ink quality in only a marginal or indirect way. For example, the ink in the fountain is exposed to oxygen at the upper surface and as a result, some curing will take place. Since the ink in the fountain is rotating, however, on average the exposure time is short and thus curing is slow. In the corners of the fountain, however, it is possible for regions of ink to become stagnant and receive large exposures to oxygen. Curing may then produce a semi-solid chunk of ink which can get transferred to the rollers as a lump and lead to problems. There are also other places in the ink supply chain where similar things can happen. This problem is not attributable to the ink but rather to the design of the ink supply system of the press. Consequently, better quality inks will not solve this problem. Nevertheless, there are features of the ink which can aggravate the problem. For example, a high yield stress may make the ink more likely to develop stagnation regions in the

fountain. Thus ink quality may play an indirect role in the problem. The final category of problems are those that can be directly related to ink quality. Perhaps the most obvious example of this is a non-turning ink. Improved ink quality could greatly reduce spoilage associated with these problems.

Quality Control Tests. In terms of QC techniques, the methods presently used at BEP can be described as follows. The measurement of viscosity at 25 rpm provides information on steady-state viscosity at high shear rates. This is important for broad control of properties but is not very sensitive to the type of problems seen with the present inks. The yield viscosity may provide direct information with regard to the tendency for stagnation regions to develop in the fountain or elsewhere, but the yield measurement is in other respects more of an indirect measure of other properties which influence performance since on the press the ink is always in motion. Finally, the TIC and the tack-o-scope measurements provide a useful measure of cure which we have concluded is an important factor in determining press performance. The information obtained, however, is only a single point in each case. This provides a very limited picture of the cure behavior and in this sense may not be the information of most value in predicting performance. This suggests that the future work should seek to obtain methods for determining more comprehensive information on the cure behavior of the inks. Consequently, this area will receive a major effort next year.

Future Work. In future work on this program, 4 different cure monitoring techniques will be studied. First, viscometry will be investigated to determine what aspects of the behavior are most closely related to performance and the degree of sophistication in the measurement that must be used to obtain the desired information. Second, a close look at the tack-o-scope will be made to

determine how it might best be used as a QC technique. Third, a new measurement method that utilizes ultrasonic shear waves to examine the mechanical properties of thin films will be tested. Preliminary work during the past year has shown that this experiment can be used successfully to follow the cure of an ink sample (see Appendix II). Finally, an effort will be made to study the film splitting behavior of these inks. All of the work in this program to date has studied shear flow. For a simple material this is sufficient to completely characterize the flow behavior. With more complex materials, however, it is also useful to examine elongational flow particularly when the application involves film splitting since this has a substantial elongational component. During the last year, some initial studies have examined the elongational flow behavior of the inks in a qualitative way and found that batch-to-batch variations could be detected. Future studies will investigate this measurement approach in more detail.

In studying the relationship between QC measurements and ink performance, it is important to have ink samples whose press performance is known. A large number of samples from last years ink evaluation program are still available, however, a number of extraneous uncontrolled variables were present in that program. A new evaluation project at BEP is planned for this year and by utilizing what was learned during the previous effort, the new samples should provide a much clearer picture of the relationship between performance and properties. To the extent possible, these samples will be included in future work on this project.

Figure Caption

Figure 1: Schematic diagram of start-up viscosity plotted against time and shear rate. Figures 2 and 3 here and Figure 3 in Appendix I represent slices of this surface along planes of constant time while Figure 2 (and Figure 1 if converted to viscosity rather than shear stress) in Appendix I represent slices at constant shear rates.

Figure 2: Steady flow viscosities as a function of shear rate for X BK-60; △ BK-62; and □ BK-62 Mod 3.

Figure 3: The steady flow viscosity for samples of BK-62 unaged □ and aged X and of BK-62 Mod 3 unaged △ and aged ◇ .

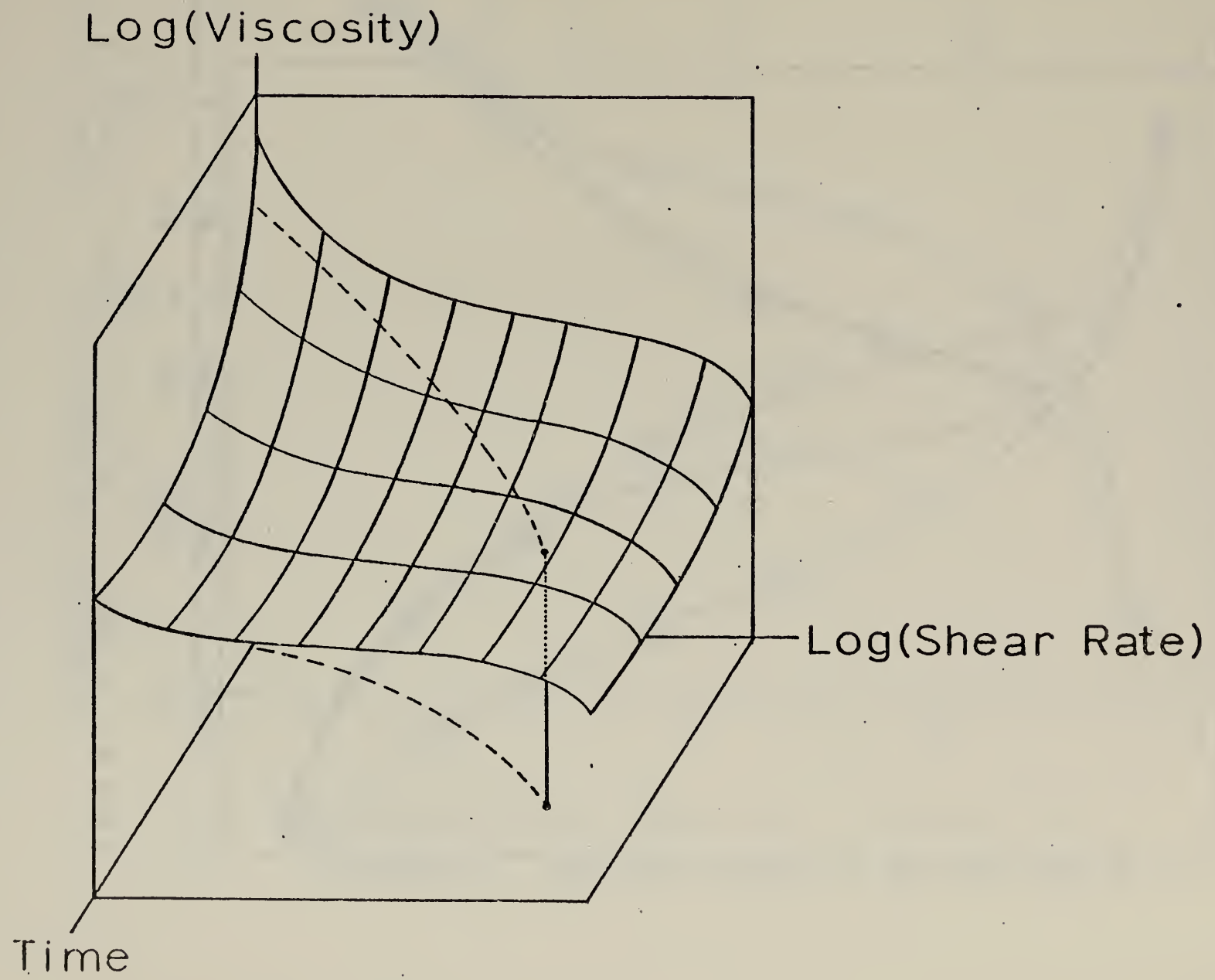


Figure 1

Figure 2

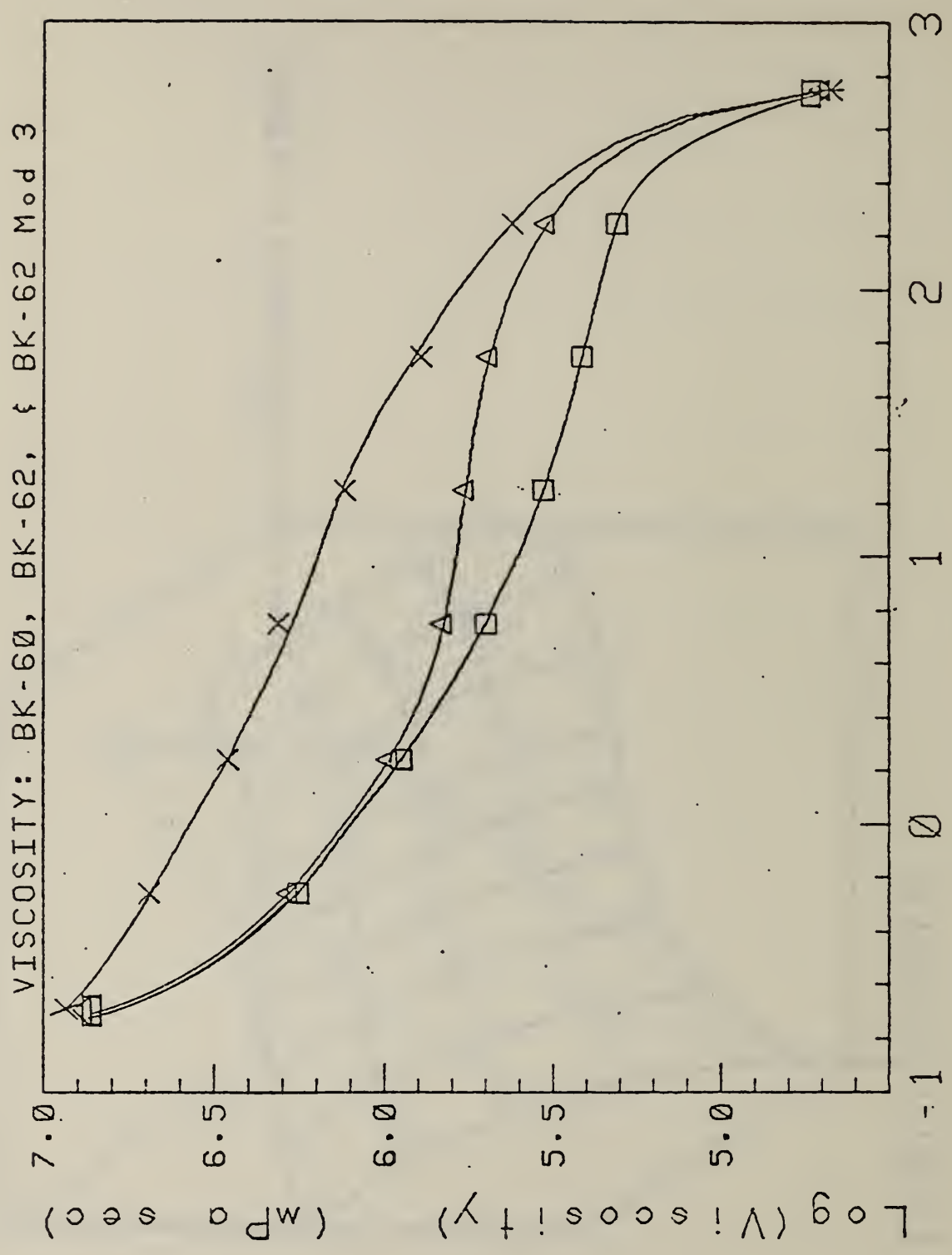
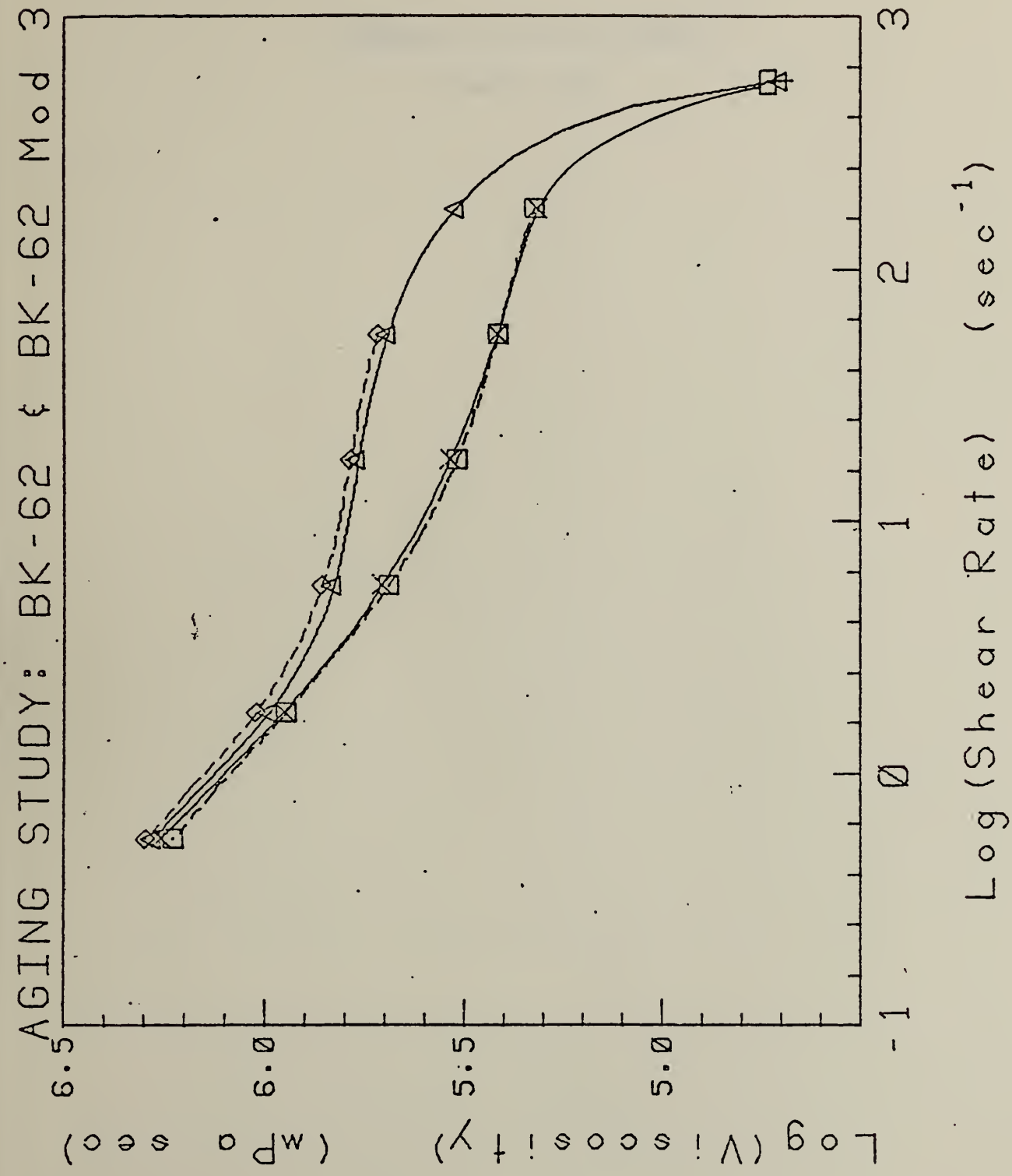

VISCOSITY: BK-60, BK-62, & BK-62 Mod 3
Log (Viscosity) (mPa sec)
7.0
6.5
6.0
5.5
5.0
-1
0
1
2
3
Log(Shear Rate) (sec^{-1})

Figure 3


AGING STUDY: BK-62 & BK-62 Mod 3
Log (Viscosity) (mPa sec)
6.5
6.0
5.5
5.0
-1
0
1
2
3
Log (Shear Rate) (sec-1)

Appendix I

Rheology of Cure for Intaglio Printing Inks

Rheology of Cure for Intaglio Printing Inks

D. L. Hunston and J. L. Rushford
National Bureau of Standards
Polymer Division
Washington, D.C. 20234

W. R. Newitt and B. A. Vaudreuil
Bureau of Engraving and Printing
Research Division
Washington, D.C. 20228

ABSTRACT

The intaglio inks used to print currency in the United States contain relatively little solvent and dry primarily by chain extension and cross-linking reactions in the vehicles. To obtain good performance, the initially fluid ink must change rheologically in the manner required to give proper transfer to the plate and then to the paper and to obtain sufficient hardness at the end of the process so that the printed sheets do not smear when stacked. To study these changes, the rheology of two ink formulations with very different press performances was examined, first in the uncured state and then during curing. The uncured inks exhibited complex rheological properties including time dependence, yield behavior, elasticity, and non-linearity. Curing of the inks produced an increase in both viscosity and elasticity. The viscosity change could be roughly fitted to a first order type equation. Comparisons between these results and the performances of the inks on the press show that if the rate at which properties change during cure falls outside a certain range, acceptable print quality cannot be achieved.

INTRODUCTION

The manufacture of paper currency in the United States is the responsibility of the Bureau of Engraving and Printing (BEP) which is the world's largest securities manufacturing establishment. BEP produces, on average, 16 million notes per day which represents an annual face value of 43 billion dollars. An

intaglio printing process is used because it is the most difficult process to perform and thus to counterfeit.[1] Other processes lack the fidelity of fine lines and the distinctive third-dimensional effect of raised line on paper inherent in intaglio printing.[1] The plates are hand-tooled by highly skilled engravers who engrave the designs using grooves of varying depths. The currency is then printed on high-speed sheet-fed rotary presses that employ two or four plates containing 32 notes each. The presses are capable of printing 9,000 sheets per hour. The ink is supplied to the roller containing the plates from the ink trough, or fountain, by a series of feed rollers. The ink in the fountain is heated and kept in slow but usually constant motion. After the hot ink is transferred by the feed rollers to the plate, ink is removed from the elevated portions of the plate by a series of three wiping cloths. A sheet of paper is then forced under heavy pressure against the plate so that it picks up most of the ink remaining in the fine engraved lines. The sheets are immediately stacked by the press and on the following day the reverse side of the sheets are printed in the same way.

To efficiently produce a high quality product requires the use of special formula, fast-drying inks, developed in BEP's laboratories. The rapid drying eliminates the time-consuming need for tissuing or interleaving between sheets to prevent smearing when stacked. Rapid drying on the sheets alone however is not sufficient to guarantee good results. The proper transfer of the initially liquid ink from the fountain to the plate via the feed rollers, the complete removal of the ink from the high portions of the plate by the wiping cloths, and the necessary transfer of the remaining ink to the paper require that the ink be in the proper rheological states at the appropriate times. As a result the rheological changes that occur during drying must proceed both rapidly and correctly if proper print quality is to be achieved.

To minimize the problems associated with poorly performing inks, a number of quality control (QC) tests are presently being used. Unfortunately, the complexity of the printing process is such that undetected variations in ink batches are still present and this leads to a higher than desirable percentage of ink batches with unacceptable performance. To help minimize the problem, a cooperative study was initiated between the National Bureau of Standards and BEP with the objective of obtaining a more complete picture of the basic rheological properties of the black ink and how these properties change as the ink cures. This information combined with the results of other studies[2-6] will provide both the basis for more reliable Q.C. techniques and the data required to help design improved ink formulations in the future.

BACKGROUND

The inks used in currency printing are complex formulations based on natural drying oils such as tung oil and linseed oil. These oils contain multiple double bonds which act as polymerization sites when exposed to oxygen. Although the details of the chemistry are not fully understood, some important observations can be made. If a bulk ink sample is exposed to air for several days a hard skin forms on the surface. Underneath this skin, however, the mechanical properties of the ink remain virtually unchanged for many months. Thus the polymerization requires direct exposure to oxygen and so the cure can be accurately studied only with experiments using films. The reactions are also greatly accelerated by increased temperature. Changes which require many hours at room temperature will occur in minutes or seconds at press temperatures.

It is the black currency ink which has been the most troublesome and is therefore the subject of this study. This ink contains very little solvent--drying experiments show a weight loss of less than 1% to full cure--and thus the hardening must proceed by polymerization and cross-linking reactions. In a recent study of this ink[2] it was demonstrated that cure reactions are a critical factor in the performance of the ink on the press. Consequently, an examination of curing behavior is necessary to the development of an understanding of ink performance.

In the present study two different ink formulations were examined. They are designated as BK-62 and BK-60 modification 17 (hereafter designated simply as BK-60). Formulations BK-60 was used for a number of years and gave acceptable performance although there was room for improvement. Formulation BK-62 was developed more recently as a trial material with a much simpler composition. Experiments with this ink on the press showed that it had unacceptable performance and this has led to a modification in the BK-62 formulation. This new version which shows marked improvement[2] is now being utilized in production and studied in this program. For the present discussion, however, it is useful to examine the original BK-62 and BK-60 as examples of an unacceptable ink and an acceptable, although not ideal, ink. It is also helpful to note that although a number of problems were observed with BK-62, a major difficulty[2] was "excessive drying on the plate".

EXPERIMENTAL SECTION

Various samples of the two different ink formulations were evaluated for mechanical properties prior to and during cure. Both formulations are based on

natural vehicles and are highly filled with pigments and additives. There are a number of differences between the two formulations but the most important is that the samples designated BK-60 contain a linseed oil vehicle system while those designated BK-62 contain a tung oil system. Details of the ink's composition are given in Table I.

The inks were examined by using transient, steady flow, and oscillatory tests performed at room temperature, 22±0.5°C. These experiments were performed on a specially modified and computerized cone and plate viscometer. The cone utilized was 2.5 cm in diameter and 0.5 degrees in angle. Details of the data acquisition system for this device have been described previously[7] and will only be summarized here. The plate can be driven in steady rotation or oscillatory rotation. The motion of the cone, which is attached to a torsion bar and held in line by an air bearing, is monitored to provide a measure of the stress. In the oscillatory experiments, the drive shaft is attached to a shaft angle encoder that generates 360 equally spaced pulses per cycle. Each pulse triggers the acquisition of position data from displacement transducers attached to the cone and the plate. This information is transferred to a minicomputer for storage and analysis. From this data the stress and strain in the sample can be calculated and thus the mechanical properties can be determined. In some cases it is useful to examine the stress curve itself and for this purpose the digitized data can be accessed. These data are in arbitrary units but for the test conditions used here they can be converted to stress in dynes/cm^2 by multiplying by 8.120. The experiments were performed at frequencies from 10 Hz to 6×10^{-4} Hz and amplitudes between 4×10^{-4} radians and 4×10^{-2} radians.

In the initiation of steady shear flow and the steady shear flow experiments, the shaft angle encorder was attached to a timing motor and data acquisition proceeds in the same way as in the oscillatory experiments. These tests were performed at shear rates between 5×10^{-2} sec^{-1} and 2000 sec^{-1}.

After characterizing the basic shear properties of the inks, their cure behavior was investigated by placing samples on a specially designed 2 roller apparatus where one of the rolls was heated to 80°C (roughly equivalent to the press temperature). This setup provides some of the important conditions seen on the press, i.e. the application of heat, the formation of a thin film for maximum exposure to oxygen, and the constant renewal of the free surface to prevent a hard crust from forming. After various cure times a small portion of the ink was removed from the mill and characterized for shear properties using the same techniques described previously. Once curing had begun on the mill, it continued even after the ink was removed and cooled to room temperature. Nevertheless, the cooling slowed the changes in mechanical properties due to curing sufficiently so that short term characterization tests could be performed. On the mill complete curing of the ink film required more than half an hour. This is much longer than required on the press. The difference can be attributed, at least in part, to the fact that the film thickness on the mill is much larger than that on the press. Dispite the difference in cure rate, however, this technique was throught to be a useful method for comparing the cure of different ink formulations and for determining the rheological changes associated with cure.

RESULTS AND DISCUSSION

Uncured Ink

The behavior of both ink formulations can be roughly divided into three regions: initiation behavior, short term steady flow, and long term steady flow. This can be illustrated by experiments on the start-up of steady shear. When the ink is allowed to rest in the instrument for 30 minutes or more and then steady shear is initiated, there is a significant stress overshoot (Figure 1). Subsequently, the stress level shows a significant time dependence for a period of time that depends on the experimental conditions but is generally less than 10 seconds. After this initial period the stress appears to level-off at what will be termed the short term steady flow value. If the steady shear is maintained for long periods of time, however, it is found that the stress is not constant but shows a small and very slow decrease. For the range of conditions tested here, the stress, and therefore the viscosity, drops by about 15% in one hour (Figure 2). The decrease is approximately linear in a log (η) vs log (time) plot.

If the shear flow is stopped and then reinitiated within a few minutes, the stress will return to the level achieved just prior to stopping the flow with little or no overshoot. Only if the ink is allowed to recover for a significant period of time, say 30 minutes, will the response be similar to that observed initially.

All three aspects of the ink behavior -- initiation, short term steady flow, and long term response -- may have importance in ink performance and are being studied in this program. This paper, however, focuses only on the short term steady flow regime and small amplitude oscillatory experiments.

Steady Shear:

The short term steady flow stress levels (average values achieved between 30 and 120 seconds) were determined as a function of shear rate and used to calculate viscosities. Values of these viscosities for samples of the two ink formulations are plotted against shear rate in Figure 3. Above shear rates of 500 sec^{-1} the data are unreliable because there is often a loss of adhesion between the sample and the cone or plate; however, the indications are that the viscosity may drop significantly at high shear rates. In the region between 80 and 500 sec^{-1} as well as the region between $6x10^{-2}$ and 0.6 sec^{-1}, the viscosities for the two ink formulations are similar. Only at the intermediate shear rates, 0.6 to 80 sec^{-1}, is the behavior substantially different. In this region the viscosity of BK-60 reaches values more than 3 times as large as those for BK-62.

This difference is important because a number of the mixing steps required to prepare these inks involve shear rates in this intermediate range. On the press, however, the ink sees only very low shear rates in the fountain and very high shear rates during printing. For these conditions the behavior of both inks is similar in Figure 3. Since the results in this Figure are for room temperature while the ink on the press is hot (50°C to 80°C), additional tests[2] were performed at high shear rates (475 sec^{-1}) and elevated temperatures (60°C). Here again the behavior of the two ink formulations was similar. Consequently, although the differences in short term steady flow viscosities may have an effect on ink preparation, they do not appear to be a likely cause of the poor press performance for BK-62.

Oscillatory Shear:

Because the viscosities of these inks are highly non-linear, the oscillatory behavior is quite complex. For example, Figure 4 shows the stress curves associated with a pure sine wave strain imposed on samples of BK-60 at 3 different frequencies. For the lowest frequency the stress curve is approximately sinusoidal although shifted in phase, but the curves become increasingly non-sinusoidal as the frequency is increased. Moreover, even at the lowest frequency, if the sample is subjected to steady shear for a few minutes before the oscillatory test, a non-linear response is obtained (Figure 5). A comparison between the behavior of the two ink formulations indicates a general similarity in the affects of changing the amplitude or frequency or shearing the sample before the test. In most cases, however, the stress levels are greater in BK-60 while the non-linearity is greater in BK-62 (Figure 6).

In light of this complexity only a simple analysis of the oscillatory results was performed. Nevertheless, this analysis provides several interesting general conclusions. First, the behavior of the inks is viscoelastic in that the stress leads the strain (Figure 4-6) by an angle between 0° (elastic) and 90° (viscous). Second, a simple Fourier analysis indicates that the stress curves can be fit quite well with a response involving the fundamental frequency and the first two odd harmonics. For example, Figure 7 shows the measured and calculated curves for the case that gave the poorest fit of all the experimental conditions analyzed. Even for this case the agreement is reasonably good. An examination of the results also indicates that in the calculated curves the total amplitude of the harmonics is in all cases less than 14% of that for the fundamental and in many cases less than 7%. Thus to a large extent the fundamental frequency dominates the response.

As a result it is of interest to examine some of the general characteristics of this component of the total response. If the real part of the dynamic shear viscosity is calculated for this component, η_1', it is found to be a strong function of the strain amplitude and frequency. Data were obtained for BK-60 at 6 different amplitudes and 9 different frequencies. In an effort to systematize this information, the dependence of η_1' on the shear rate was examined by plotting log (η_1') against the time average shear rate during the oscillatory cycle (Figure 8)

$$\text{time average shear rate} = \frac{2\,\omega\,A}{\pi \tan \theta} \qquad (1)$$

where ω is the angular velocity, A is the amplitude of oscillation (radians), and θ is the cone angle. Although this does not collapse the data to a single curve, it does compress the variations to a narrow band which is quite narrow at low shear rates and broadens somewhat as the shear rate is increased. If the short term steady flow data are added to the graph, they fall roughly within this same band. A much less extensive study using formulation BK-62 gave similar results. Consequently, although the oscillatory behavior is quite complex, there is an interesting correlation between the oscillatory data and the short term steady shear results.

Curing Study

Although the data on the mechanical properties of the uncured inks provide information that is useful in fabricating the inks, no explanation for the poor performance of BK-62 was found. As a result, experiments aimed at examining the cure behavior of the inks were conducted. Samples of the inks were cured on a heated 2 roller apparatus, and after various curing times small portions of ink were removed and characterized for oscillatory and

short term steady flow viscosity. In view of the complexity of the oscillatory behavior, most of the emphasis is on the steady flow tests; however, it is useful to examine the general trends exhibited in the oscillatory data.

Steady Shear:

Figures 9 and 10 illustrate the types of changes that are observed in the short term steady flow viscosity as the ink cures. Over the entire range of shear rates tested, the curing produces an increase in viscosity. For a given curing time the data for BK-60 show an approximately equal increase in log (η) at all but the highest shear rates. For BK-62 the longer cure times show the same trend but the 5 minute cure produces larger changes at the low shear rates than at the intermediate and high shear rates. One factor that could contribute to this difference in behavior at short cure times is the possibility of an induction period. Thermal experiments[2] have demonstrated that the cure reactions do not begin immediately but only after the sample has been held at the cure temperature for a few minutes. In the present experiment the cure temperature is reached very rapidly but as will be seen later, there is evidence for an induction period.

Before curing begins, BK-60 has a higher viscosity over most of the shear rate range than BK-62. Once curing starts however, the rate of increase in η is much greater for BK-62. Consequently, within a short time the viscosity for BK-62 is larger than that for BK-60. It is clear therefore that the two ink formulations have very different curing behaviors.

Oscillatory Shear:

Very similar trends are seen in the oscillatory data. Figures 11 and 12 show the stress curves associated with a sine wave strain for ink samples cured various lengths of time. As shown previously, the initial

stress levels in BK-62 are much lower than in BK-60. The changes associated with curing, however, are substantially larger for BK-62 and within a short time the stress levels in BK-62 are larger than those in BK-60. In view of the correlation that was found between the oscillatory and short term steady flow experiments on the uncured inks, the similar trends in the curing tests are a logical result. With both inks there is a decrease in non-linearity as the inks cure; i.e., the stress curves become more sinusoidal. The angle by which the stress leads the strain (sine wave) also decreases with curing indicating that although both the elastic and viscous components of the response increase, the elasticity increases more rapidly at least in the initial phases of cure.

Analysis of Cure:

A simple analysis of the cure results for short term steady flow can be performed by noting that for a number of polymerization reactions, the early stages of cure can be described by a first order type equation. In the simplest case this would mean that log (η) would vary linearly with time. To examine this possibility the data for various shear rates were analyzed by plotting log (η) vs. time (Figures 13 and 14). If the initial points (zero cure time data) are excluded, the data for each shear rate can be fit, to a first approximation, with a straight line. The fact that the zero cure time points do not fall near the lines suggests that the mechanical property results show an initiation time just as was found previously in thermal experiments.[2]

The slopes, k, of the lines in Figures 13 and 14 provide a measure of the rate of change of viscosity with time during curing. The initiation period can also be characterized by determining the time, t_o, corresponding to the point on each straight line where the viscosity equals the zero cure time viscosity of the ink at that shear rate. Values of k and t_o for the

various shear rates and inks are given in Table II. Over most of the measured shear rate range, the slopes are quite similar. At the two highest shear rates the slopes are less as would be suggested by the data in Figures 9 and 10. It should be noted, however, that the initiation times are greater at these shear rates, and as a result the data points at the shortest non-zero cure time may be in the initiation region. If straight lines are fit to the data for the shear rate of 55.6 sec^{-1} without including the results for either zero cure time or the shortest non-zero cure time, the slopes are greater although still not as large as the values obtained at lower shear rates (Table II). Consequently, although the data here are limited, the changes do appear to be somewhat slower at the higher shear rates.

The results in Table II help quantify the differences in cure behavior between BK-60 and BK-62. Previous experiments[2] using thermal analysis techniques have found that the initiation period for BK-62 is shorter than that for BK-60. This same trend is seen in the mechanical properties data. Moreover, the rate at which the properties change once curing has begun is approximately 50% greater for BK-62 than for BK-60. When these results are combined with the observation that a major problem with the performance of BK-62 on the press is excessive drying on the plate, the inescapable conclusion is that the differences in curing behavior are a major source of the problems with BK-62.

It is easy to see how these differences in curing could lead to excessive drying on the plate. Even under conditions where excessive drying on the plate is not observed, however, there will still be significant differences in the mechanical properties of the two inks formulations due to the curing behavior. This would affect transfer on the

feed rollers, wiping of the plate, and pick-up of ink by the paper and thus other problems with BK-62 may also be related to the cure behavior. In general it would appear that the changes in ink properties during cure must fall within a given range if proper performance on the press is to be achieved. Unfortunately, the original BK-62 ink fails to meet this criterion.

CONCLUSIONS

The rheology of two intaglio ink formulations with very different performance on the press was examined prior to and during the early phases of cure. The uncured inks exhibit complex viscoelastic properties with stress overshoot, time dependence, and non-linearity. A major aspect of the non-linearity is a large shear rate dependence of the viscosity. Curing of the inks produces changes in both the viscosity and elasticity of the inks. After a short initiation period, the increase in the logarithm of the short term steady flow viscosity is linear with respect to time so the slopes of the best-fit straight lines at various shear rates can be used to characterize the rate of change in properties. Over a wide range of shear rates the slopes of these lines show only a small variation. A comparison between the two formulations, however, reveals significant differences: BK-62 has a shorter initiation period than BK-60 and a rate of increase in viscosity during curing that is 50% greater than BK-60. These differences in curing behavior play a major role in the poor performance of BK-62.

ACKNOWLEDGEMENT

The equipment utilized in this work was developed and used in cooperation with the Naval Research Laboratory. Without their assistance this work would not have been possible.

References

1. "Production of Government Securities", Public Brochure, P.15 - REV 9-80, Bureau of Engraving and Printing.

2. W. R. Newitt, B. Lipman, and B. A. Vaudreuil, Bureau of Engraving and Printing Research Report BEP-81-013, February, 1982.

3. K. Hirayama, Research Bulletin Printing Bureau, Ministry of Finance, Japan, 47, 1 (1979).

4. J. Shurz and T. Kashmoula, Papier, 30, V52 (1976).

5. P. Oittinen, Acto Polytechnica Scandinavica, No. 131, 1 (1976).

6. T. Amari, et al., Prog. Polym. Phys. in Japan, 22, 101 & 105 (1979).

7. D. Hunston, et al, Adhesion and Adsorption of Polymers, Vol. 12A, Ed. L. H. Lee, p.321 (Plenum Press, New York, 1980).

Table I Composition of Ink Formulations

Ingredients	BK-60	BK-62
Pigments	51.4	36
Barytes	-	30
Calcium Carbonate	17.4	17
Linseed Oil Vehicle	16.5	-
Varnish	6.5	9
Bodied Tung Oil	-	8
Amorphous Silica	5.7	-
Driers	1.9	-
Petroleum Solvent	0.6	-
Total	100	100

Table II Cure Parameters

Shear Rate (sec^{-1})	BK-60		BK-62	
	$kx10^4$	t_o(sec)	$kx10^4$	t_o(sec)
0.56	6.1	330	9.4	150
1.76	6.4	360	9.6	180
5.56	6.1	410	9.8	270
17.60	5.6	410	8.8	280
55.60	4.7	420	6.4	340
55.60[a]	5.0	500	7.2	530

[a] Does not include data point for shortest non-zero cure time.

Figure Captions

Figure 1: The stress associated with the initiation of steady shear flow in BK-60 at shear rates of 55.7 sec^{-1} (A) and 5.6 sec^{-1} (B).

Figure 2: Viscosity of BK-62 as a function of time for steady shear flow at shear rates of 1.76 sec^{-1} (Δ), 5.57 sec^{-1} (X), and 17.6 sec^{-1} (□).

Figure 3: Short term steady flow viscosity vs. shear rate for two samples of BK-62: X & ◇ and two samples of BK-60: □ & + .

Figure 4: The stress curves for BK-60 associated with a sine wave strain at an amplitude of 1.5 x 10^{-3} radians and frequencies of 6.0 HZ (A), 0.6 Hz (B), and 0.06 Hz (C).

Figure 5: The stress curves for BK-60 associated with a sine wave strain of amplitude 1.5 x 10^{-3} radians and frequency of 0.06 Hz before (A) and after (B) shearing with steady shear flow (shear rate 60 sec^{-1}) for 1 minute.

Figure 6: The stress curves for BK-60 (A) and BK-62 (B) associated with a sine wave strain of amplitude 1.5 x 10^{-3} radians and frequency 0.06 Hz.

Figure 7: Comparison between the measured stress curve (overlapping data points appear as heavy line) and calculated curve (thin line) for BK-60 at frequency of 6 Hz and sine wave strain of amplitude 1.5x10^{-3} radians.

Figure 8: The dependence of log (η_1') on time average shear rate for BK-60 at amplitudes of 4.5x10^{-4} rad (Δ), 2.2x10^{-3} rad (□), 6.4x10^{-3} rad. (◇), 9.8x10^{-3} rad. (+), 2.2x10^{-2} rad. (△), and 4.5x10^{-2} rad. (X). Short term steady flow viscosity vs. shear rate (□).

Figure 9: Short term steady flow viscosity vs. shear rate data for samples of BK-62 cured for 0 min. (X), 7.5 min. (□), 20 min. (◇), and 30 min. (+).

Figure 10: Short term steady flow viscosity vs. shear rate data for samples of BK-60 cured for 0 min. (X), 10 min. (◇), 20 min. (□), and 30 min. (+).

Figure 11: The stress curves for BK-62 associated with a sine wave strain of amplitude 1.5 x 10^{-3} radians and frequency 0.06 Hz cured for 0 min. (A), 5 min. (B), 10 min. (C), 20 min. (D), and 30 min. (E).

Figure 12: The stress curves for BK-60 associated with a sine wave strain of amplitude 1.5x10^{-3} radians and frequency 0.06 HZ cured for 0 min. (A), 10 min. (B), 20 min. (C), and 30 min. (D).

Figure 13: Short term steady flow viscosity of BK-62 vs. cure time at shear rates of 0.56 sec^{-1} (X), 1.76 sec^{-1} (□), 5.57 sec^{-1} (◇), 17.6 sec^{-1} (+), and 55.6 sec^{-1} (Δ).

Figure 14: Short term steady flow viscosity of BK-60 vs. cure time at shear rates of 0.56 sec^{-1} (X), 1.76 sec^{-1} (□), 5.57 sec^{-1} (◇), 17.6 sec^{-1} (+), and 55.6 sec^{-1} (Δ).

Stress X 10^-5 (dynes cm^2)
1.0
0.5
0
10
8
6
4
2
0
Time (sec)
A
B
A
7
6
5
4
3
2
1
0
Stress X 10^-5 (dynes/cm^2)

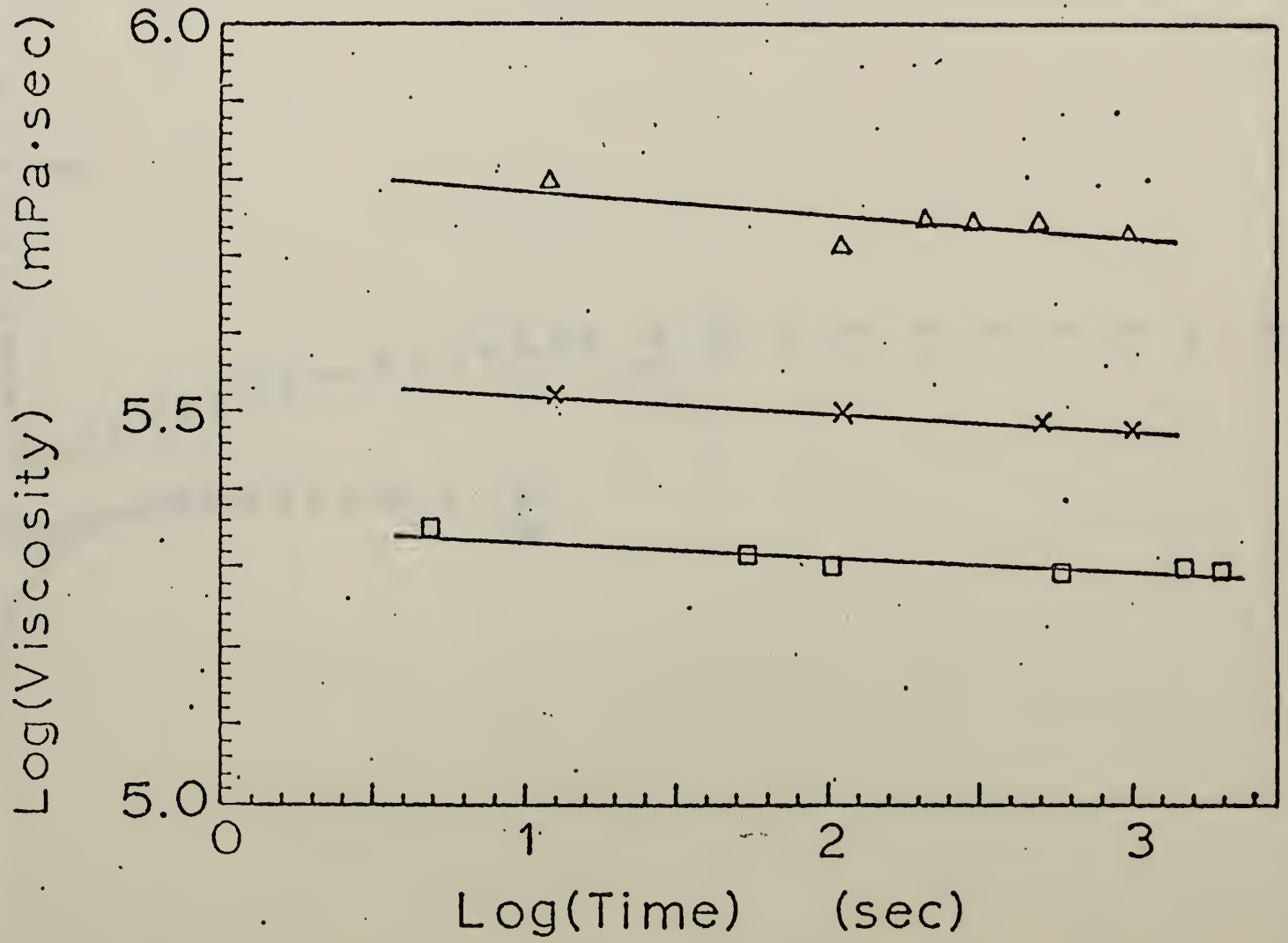
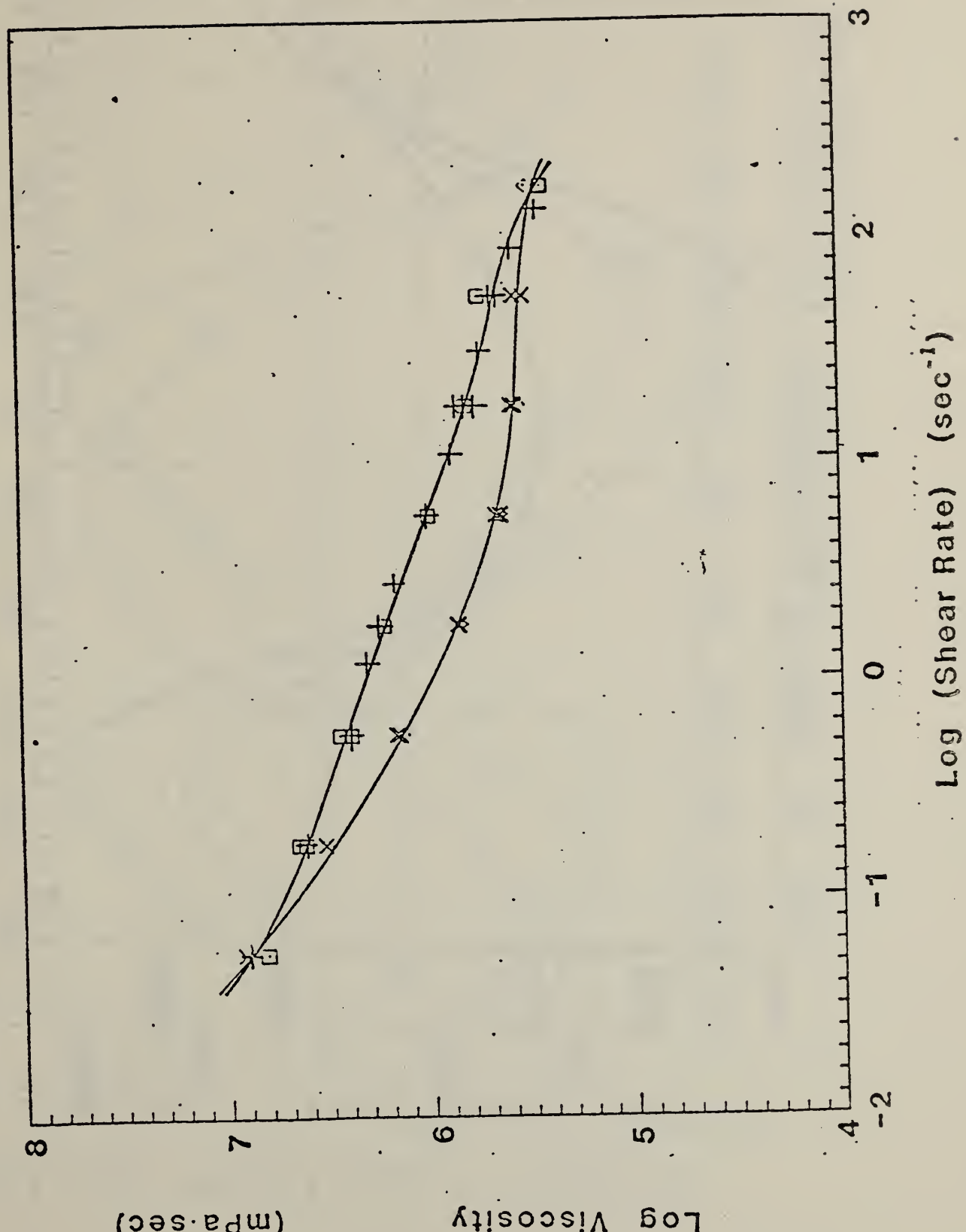


Figure 2

Figure 3



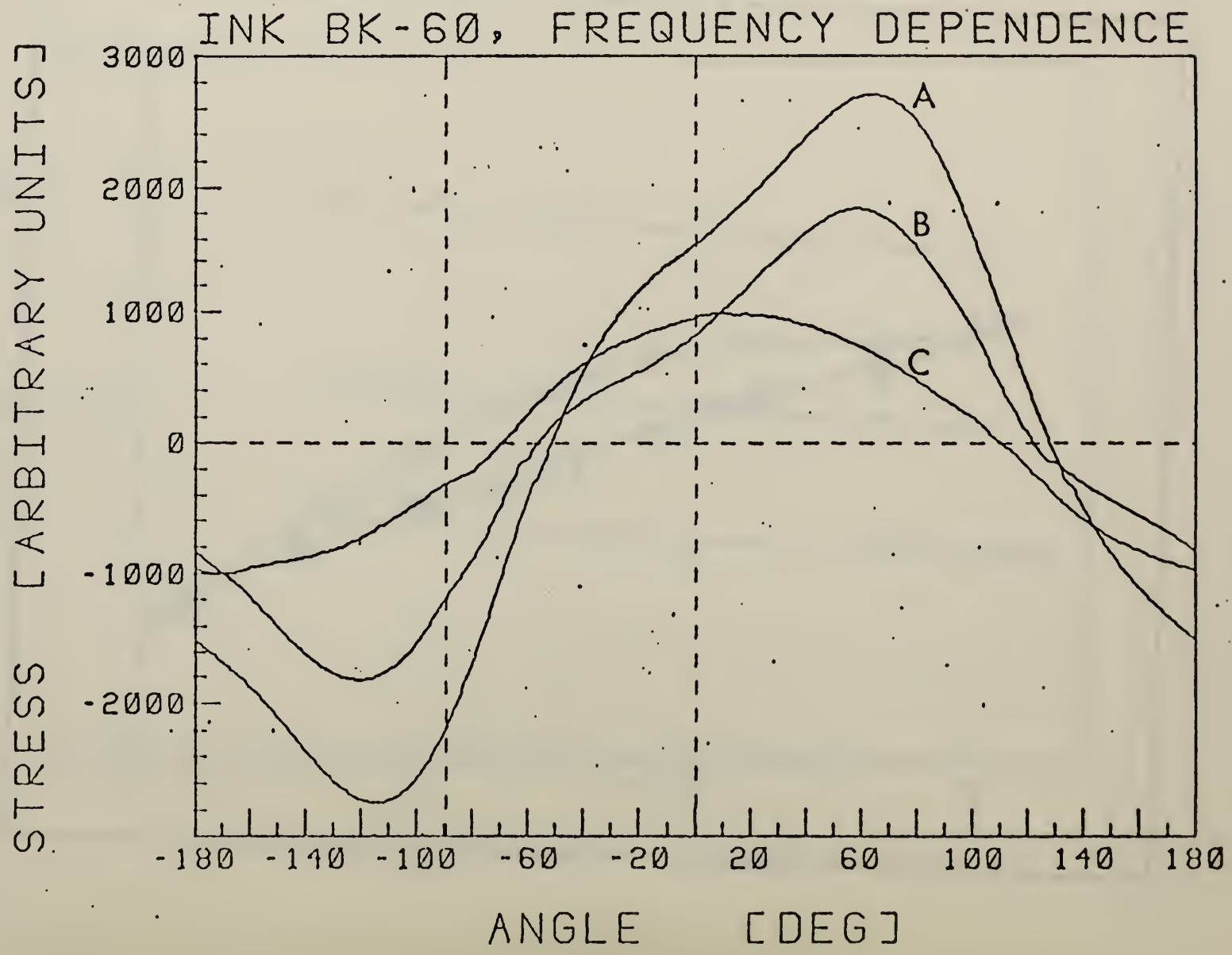

INK BK-60, FREQUENCY DEPENDENCE
STRESS [ARBITRARY UNITS]
3000
2000
1000
0
-1000
-2000
A
B
C
-180
-140
-100
-60
-20
20
60
100
140
180
ANGLE [DEG]

Figure 4

Figure 5

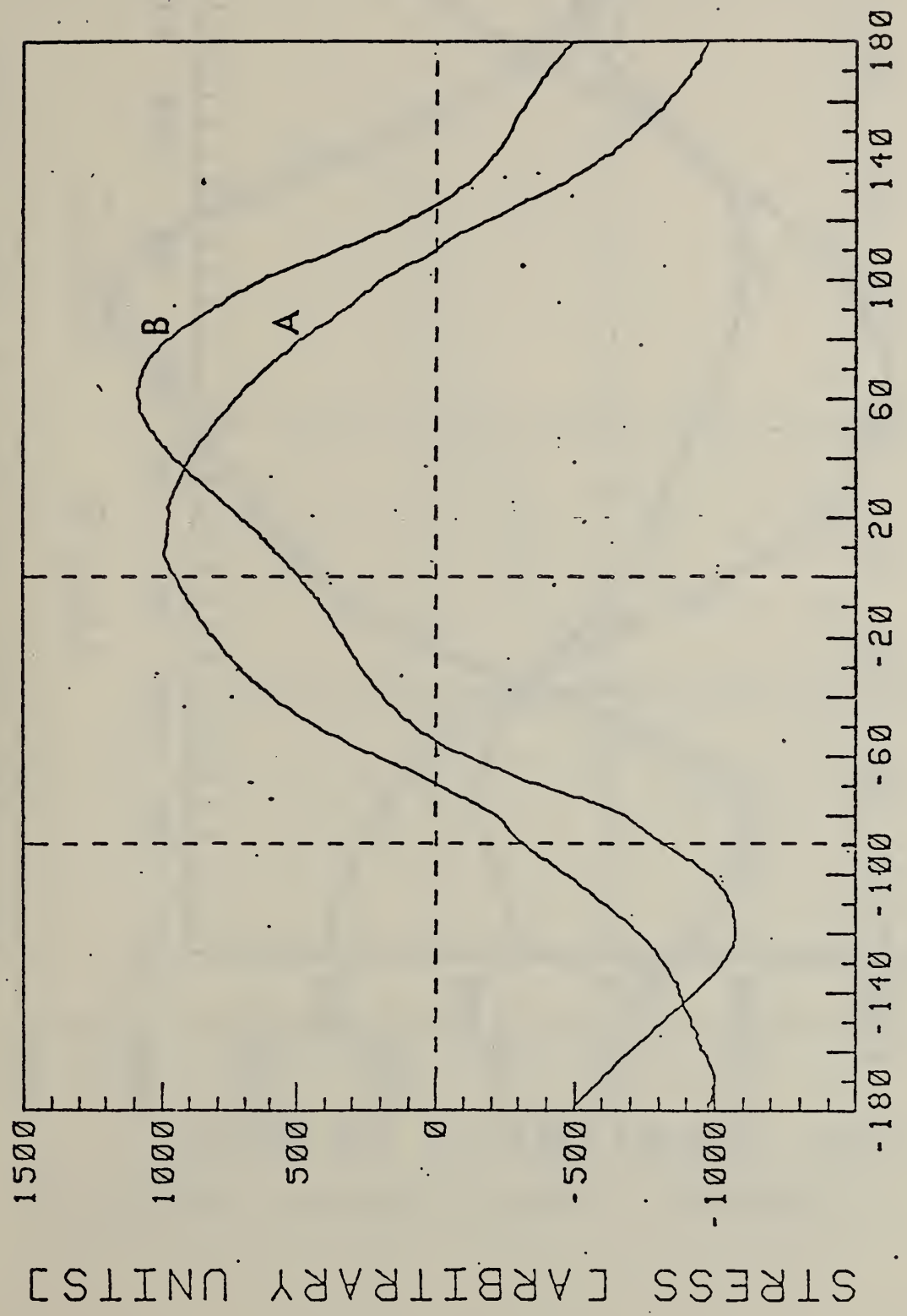

STRESS [ARBITRARY UNITS]
1500
1000
500
0
-500
-1000
-180 -140 -100 -60 -20 20 60 100 140 180
ANGLE [DEG]
A
B

Figure 6

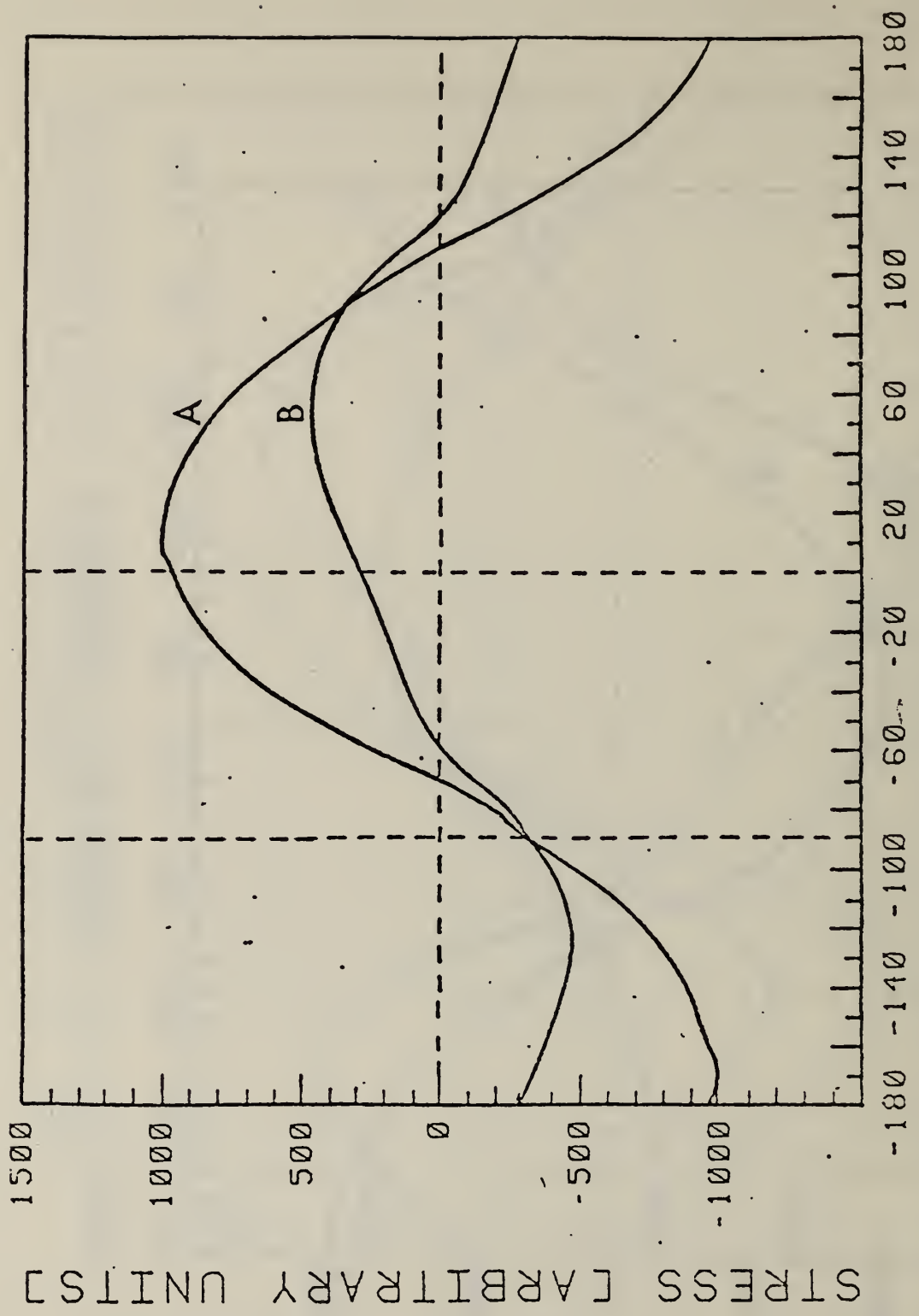
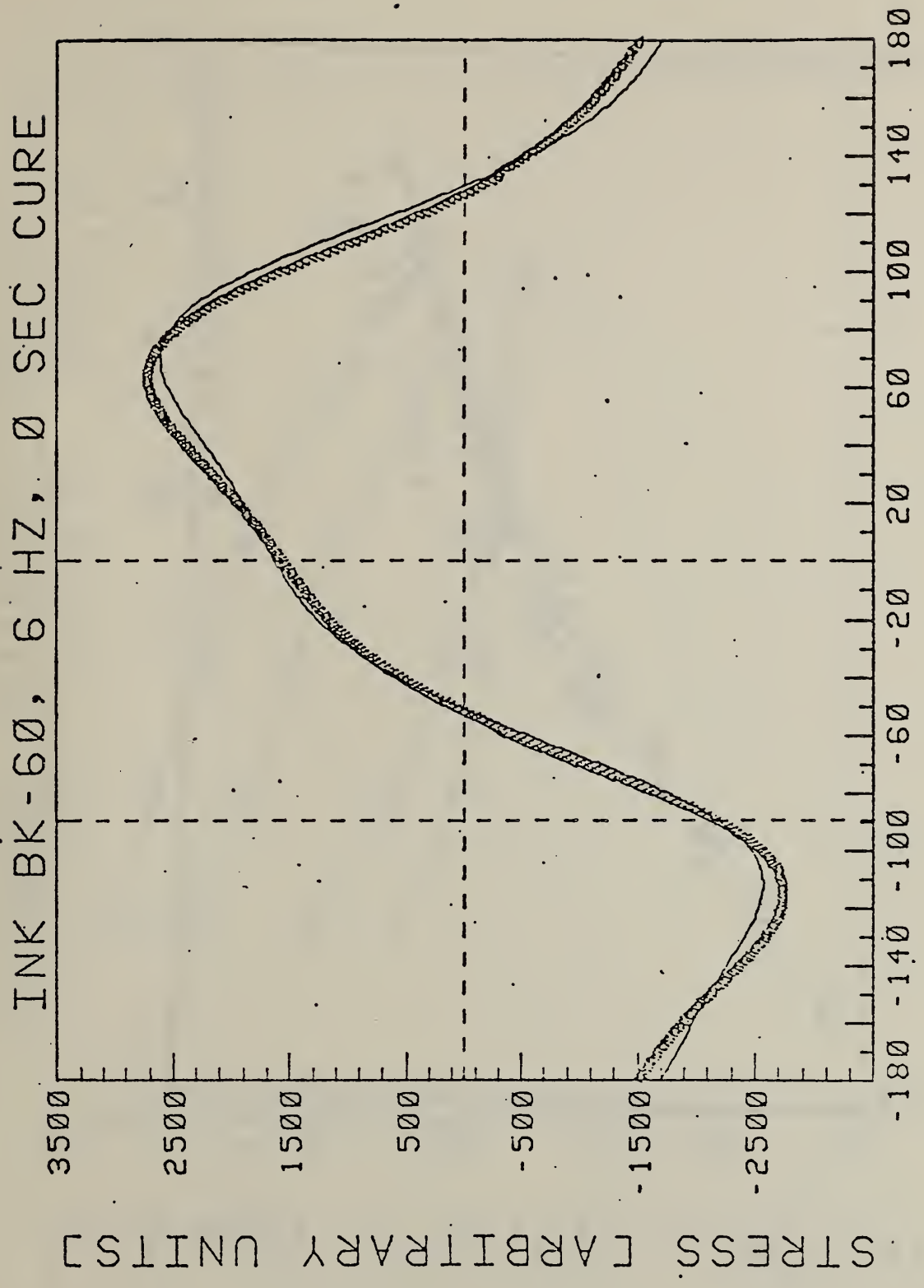

STRESS [ARBITRARY UNITS]
1500
1000
500
0
-500
-1000
-180 -140 -100 -60 -20 20 60 100 140 180
ANGLE [DEG]
A
B

Figure 7


INK BK-60, 6 HZ, 0 SEC CURE
STRESS [ARBITRARY UNITS]
3500
2500
1500
500
-500
-1500
-2500
-180 -140 -100 -60 -20 20 60 100 140 180
ANGLE [DEG]

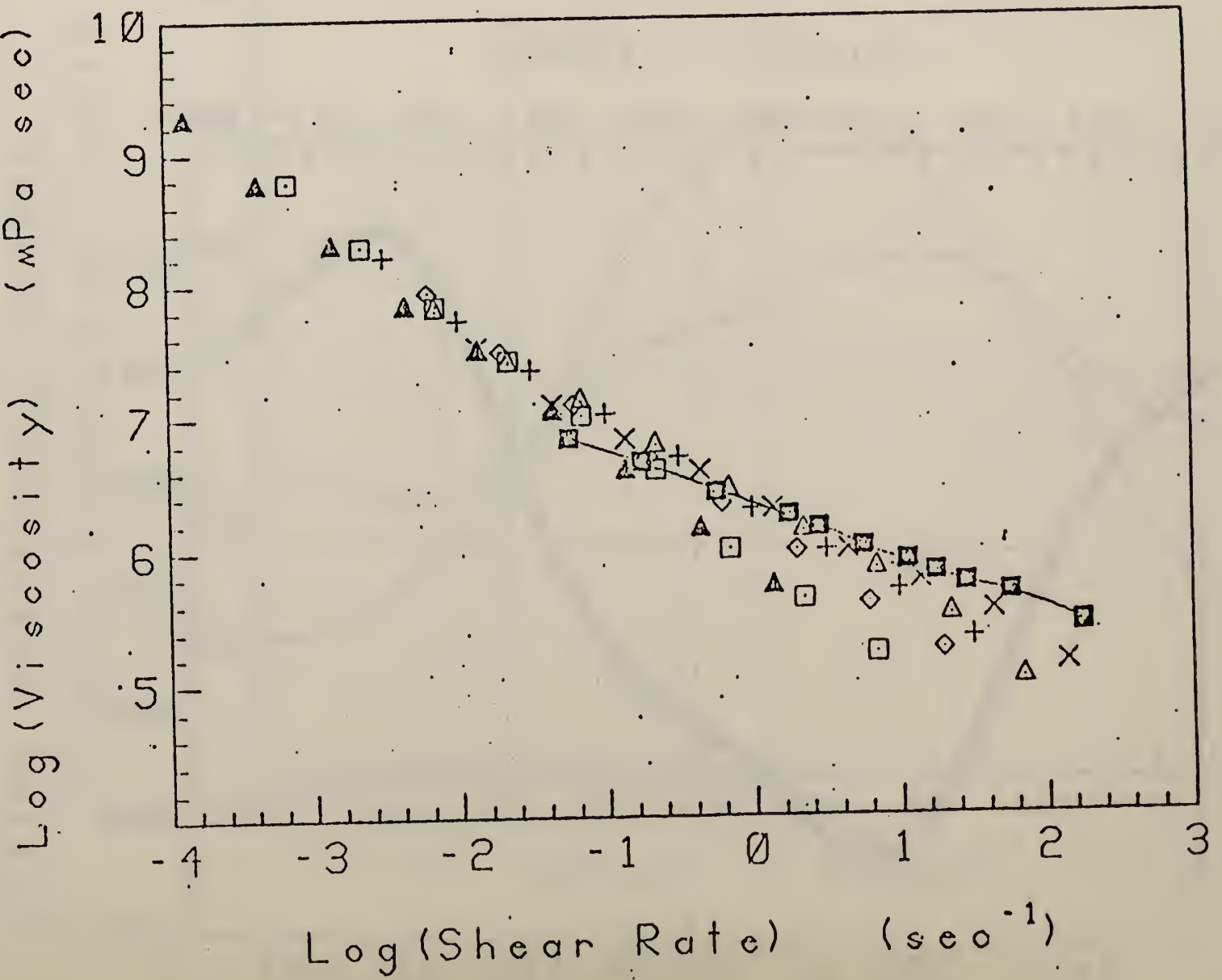


Figure 8

Figure 9

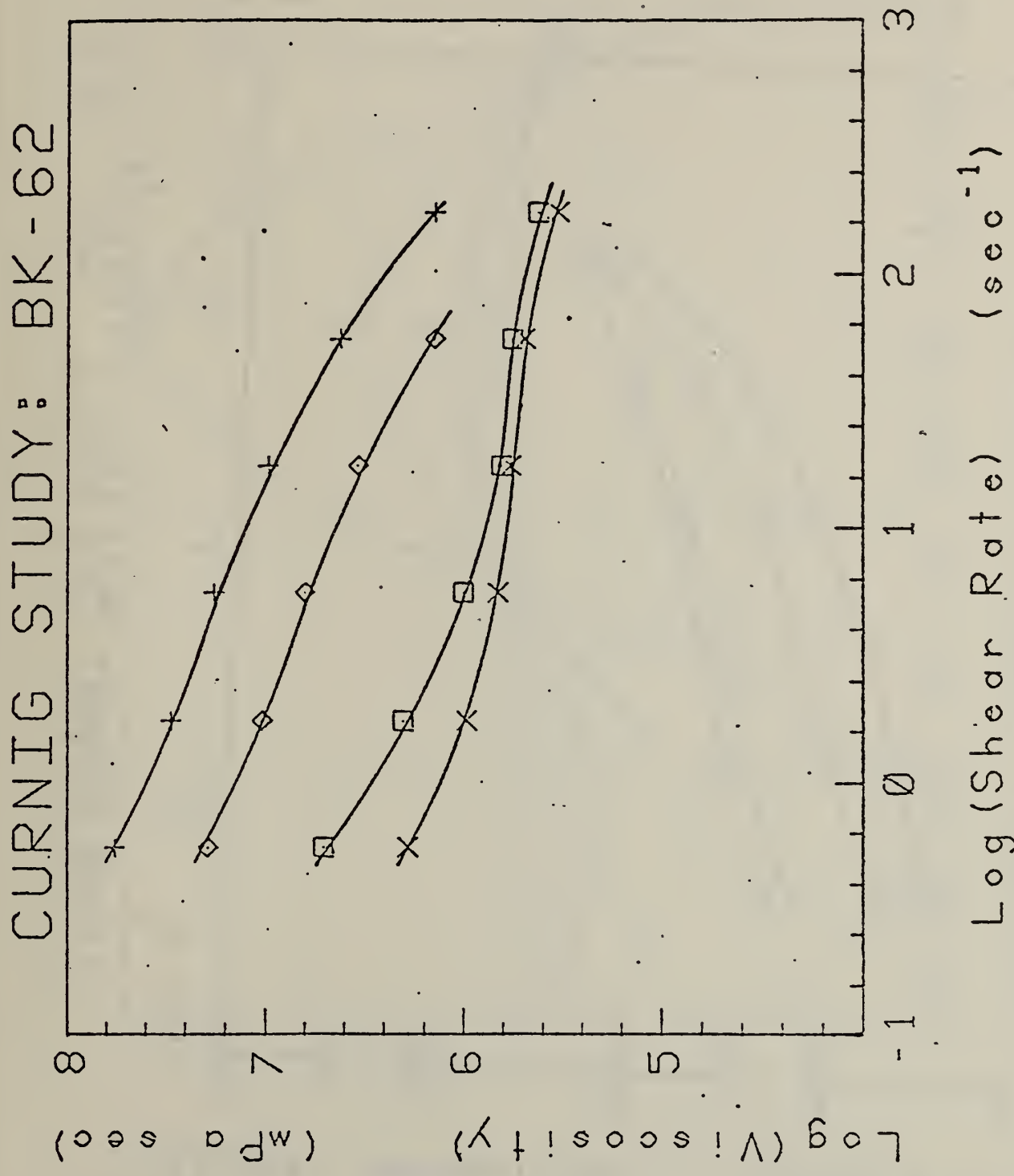
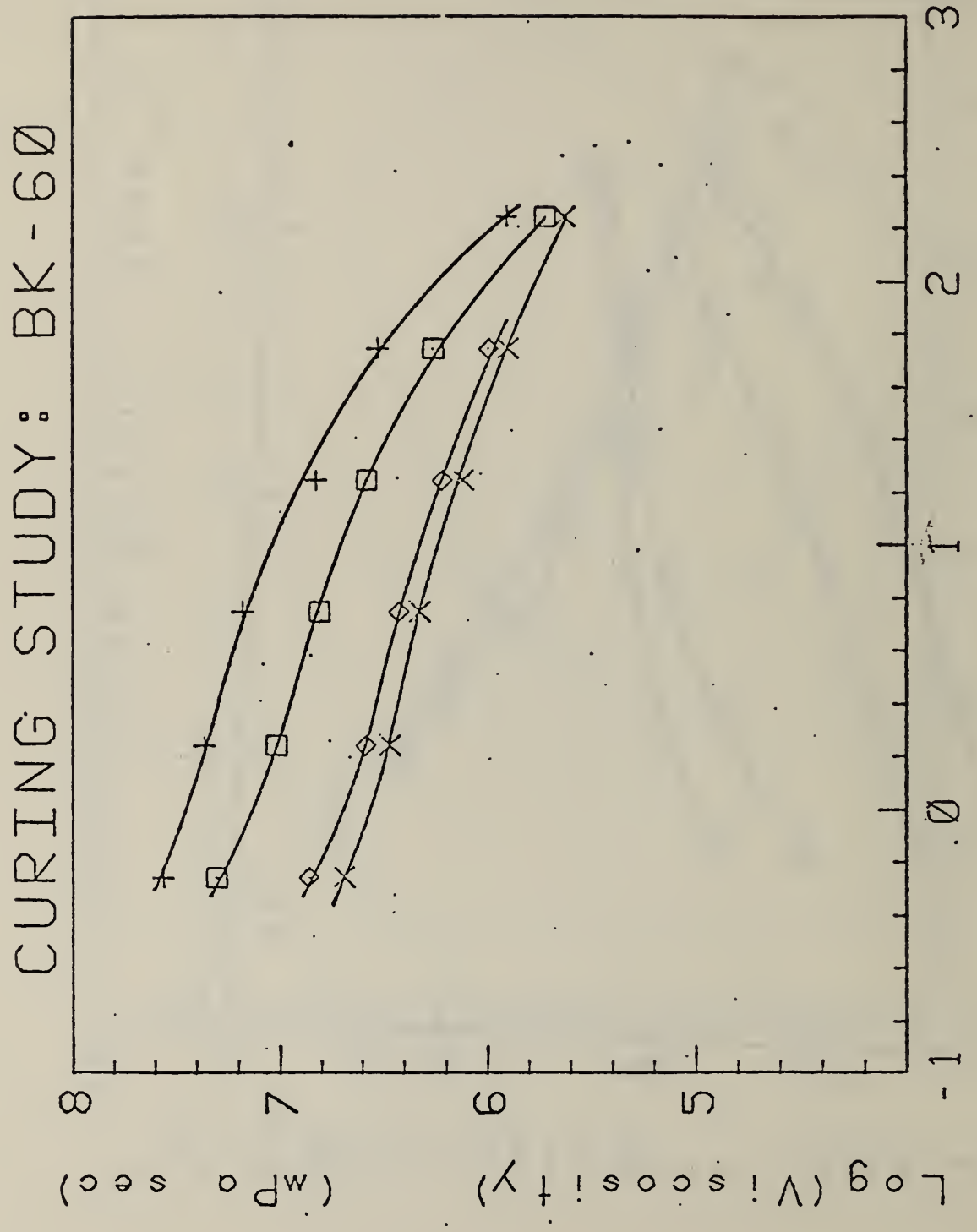

CURNIG STUDY: BK-62
Log (Viscosity) (mPa sec)
8
7
6
5
-1
0
1
2
3
Log (Shear Rate) (sec-1)

Figure 10


CURING STUDY: BK-60
Log (Viscosity) (mPa sec)
8
7
6
5
-1
0
1
2
3
Log (Shear Rate) (sec-1)

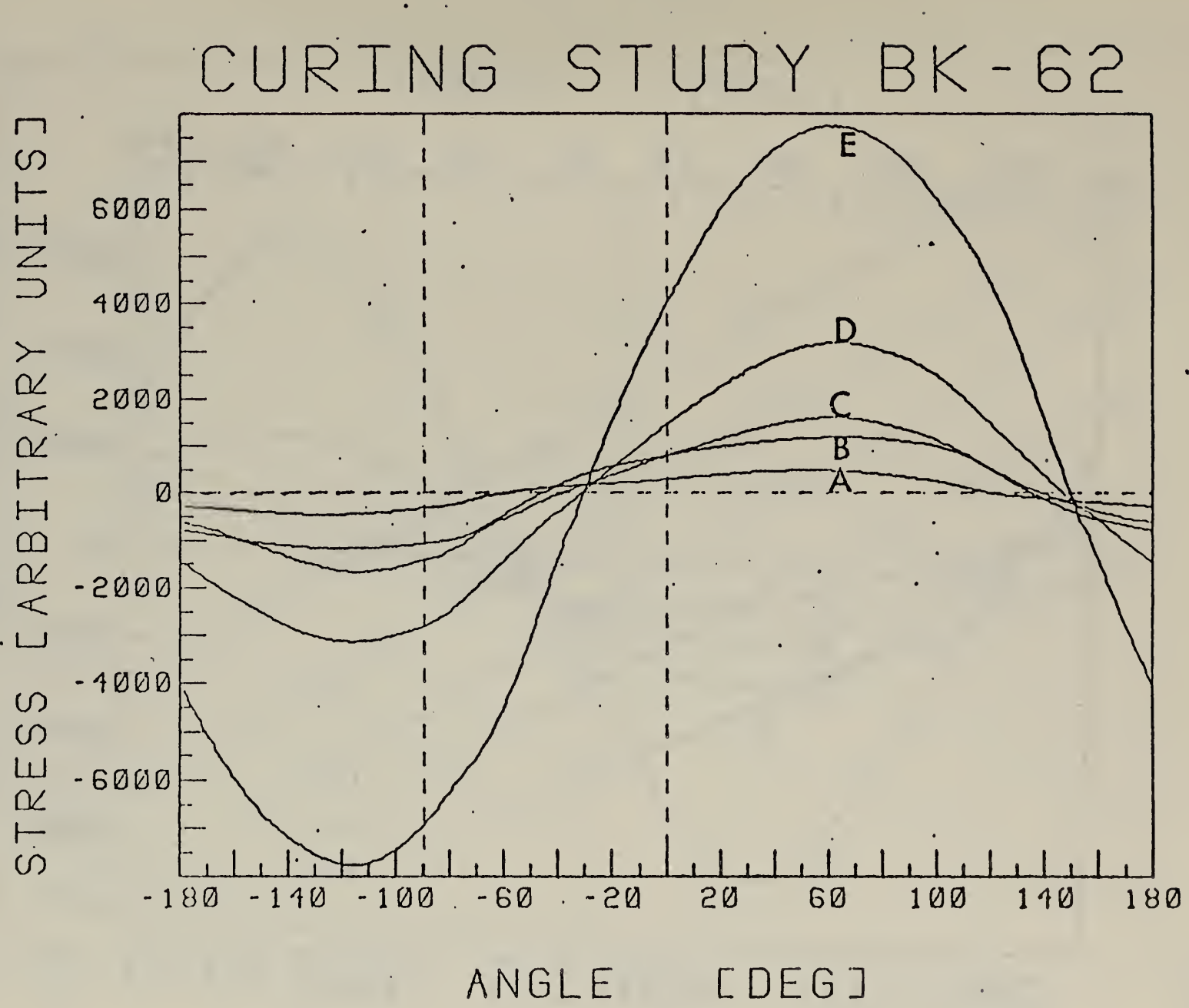

CURING STUDY BK-62
STRESS [ARBITRARY UNITS]
6000
4000
2000
0
-2000
-4000
-6000
E
D
C
B
A
-180
-140
-100
-60
-20
20
60
100
140
180
ANGLE [DEG]

Figure 11

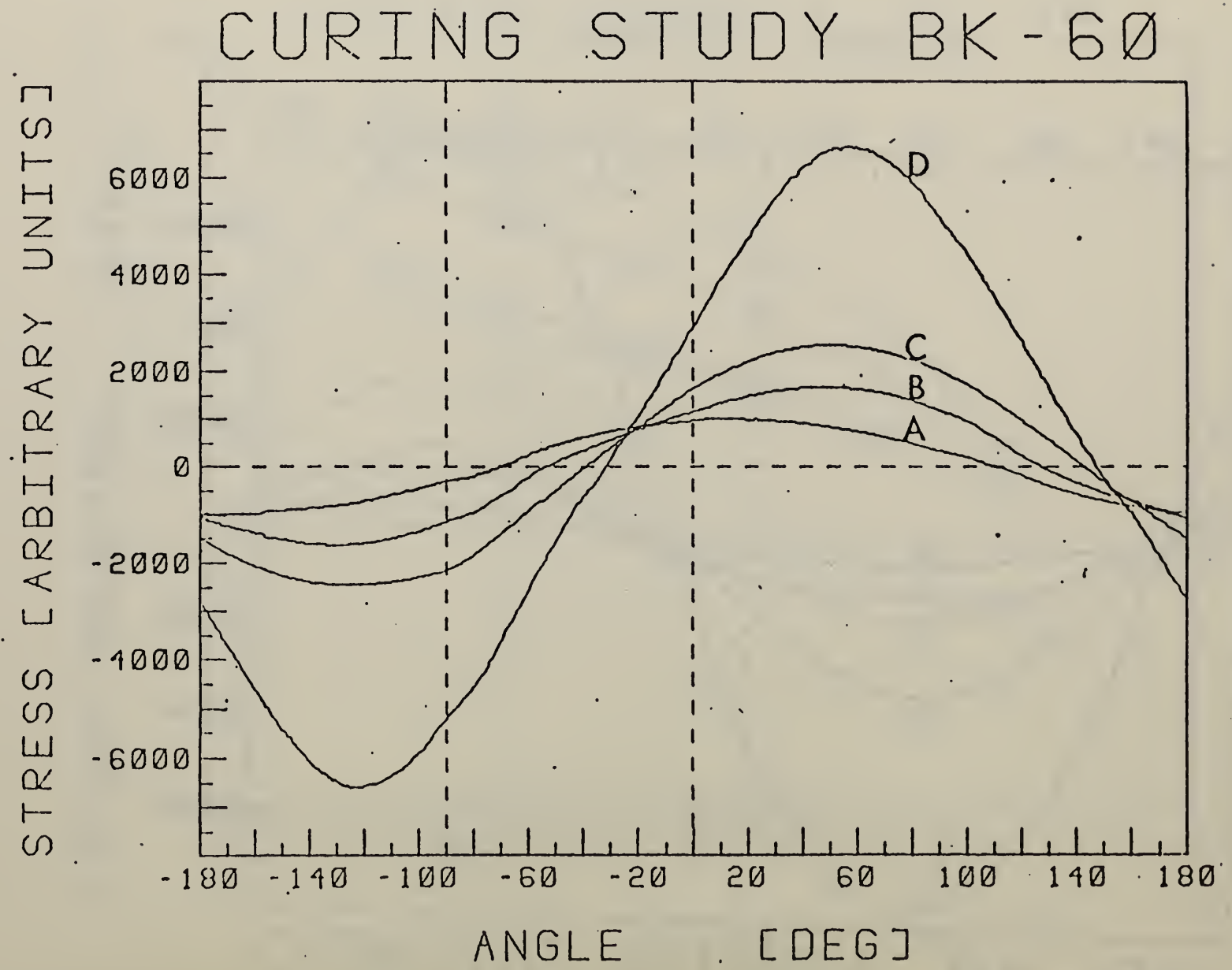
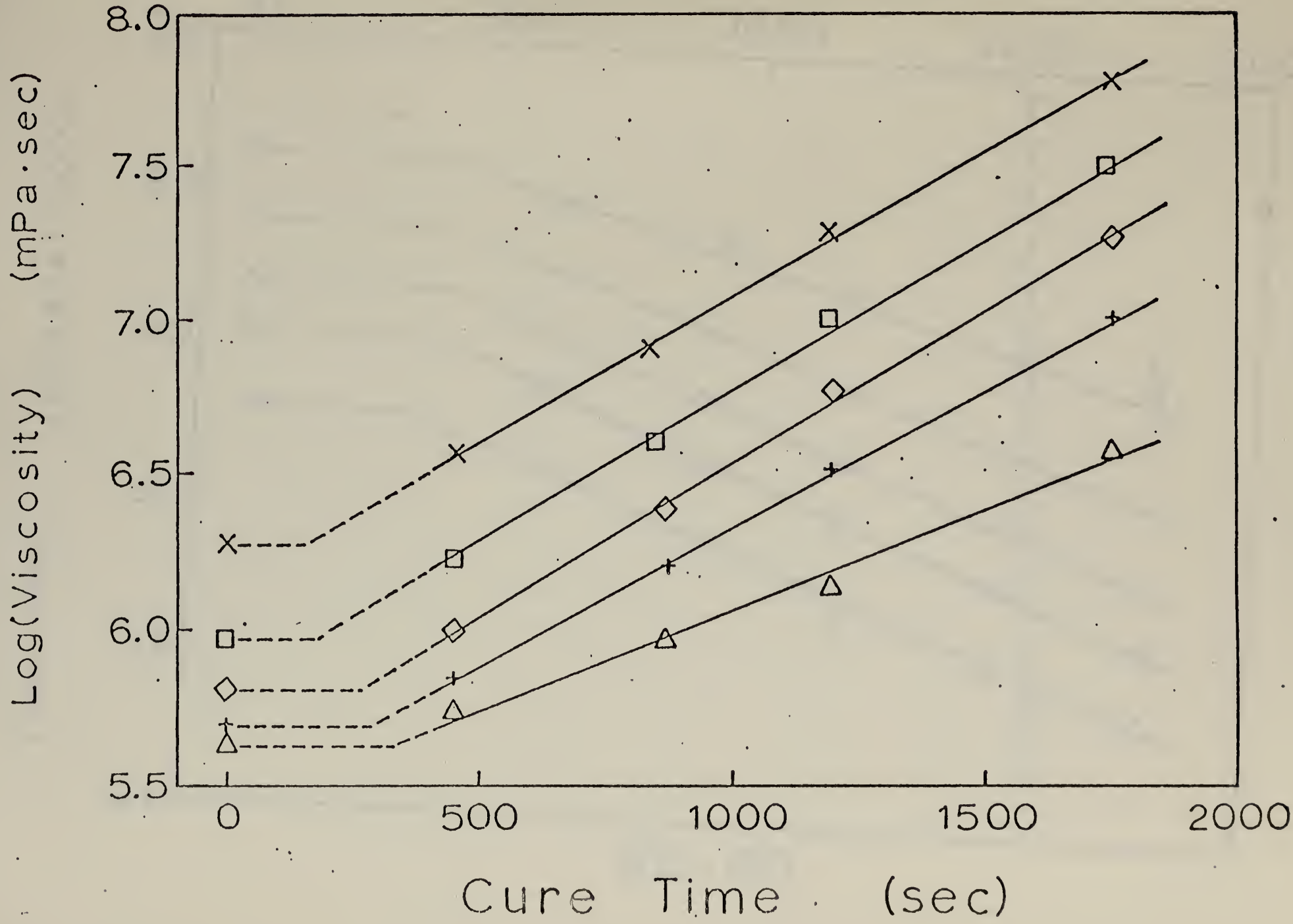

CURING STUDY BK-60
STRESS [ARBITRARY UNITS]
6000
4000
2000
0
-2000
-4000
-6000
D
C
B
A
-180
-140
-100
-60
-20
20
60
100
140
180
ANGLE [DEG]

Figure 12

BK-62


8.0
7.5
7.0
6.5
6.0
5.5
Log(Viscosity) (mPa·sec)
0
500
1000
1500
2000
Cure Time (sec)

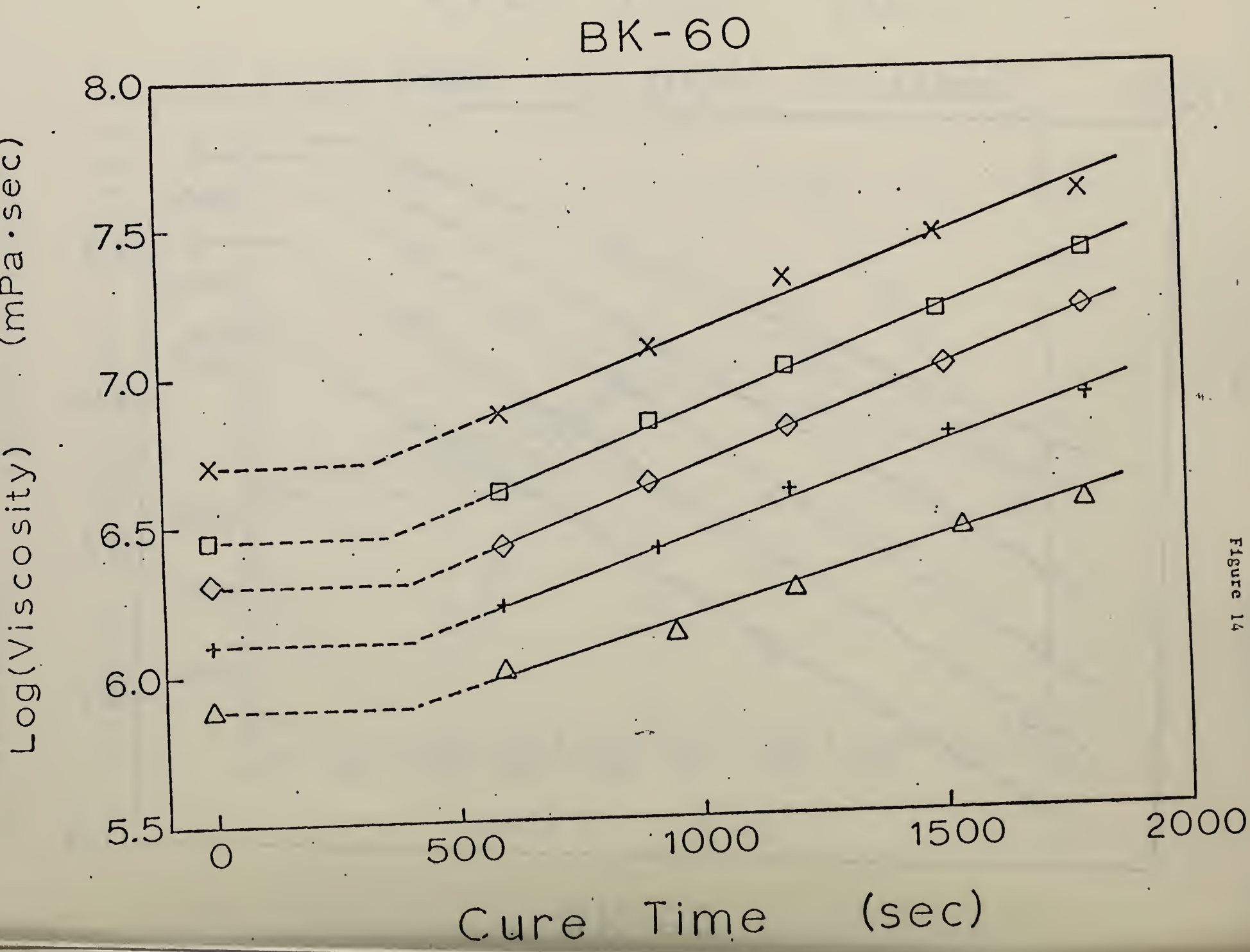

BK-60
8.0
7.5
7.0
6.5
6.0
5.5
Log(Viscosity) (mPa·sec)
0
500
1000
1500
2000
Cure Time (sec)

Figure 14

Appendix II

Non-Destructive Characterization of Polymer Films via Ultrasonics

Non-Destructive Characterization of Polymer Films via Ultrasonics

D. L. Hunston
Polymer Science and Standards Division
Center for Material Science

In applications such as adhesives, fiber-reinforced composites, paints, coatings, etc. the polymer must be fluid in the early stages of fabrication so that the proper flow, leveling, wetting and spreading at interfaces, etc. can be achieved. The polymer must then harden by cooling, solvent loss, or chemical reactions to form a rigid material. In most cases the successful fabrication of a final product requires that associated changes in mechanical properties take place at the appropriate times and rates. It is desirable therefore to have nondestructive techniques that can monitor these changes as they occur. Unfortunately, this is generally very difficult, particularly since many of the applications involve thin films, whose mechanical properties are difficult to measure and can not usually be predicted from experiments on bulk samples.

To address this problem, an effort is being made to develop new methods for nondestructively characterizing thin films. The work to date has focused on the investigation of an ultrasonic shear wave propagation technique. A shear deformation was chosen because the shear properties of liquids and solids are very different. Ultrasonic frequencies were selected because in this range the attenuation of shear waves in many polymers is so high that a thin film can be treated as if it were infinitely thick and this greatly simplifies the analysis. The devise consists of a thin strip of aluminum or quartz in which a shear wave is propagated. When the surface is coated with the polymer to be tested, the wave in the strip generates a shear wave in the coating. Although the high attenuation in the polymer makes it impossible to observe this wave directly, its generation causes changes in the wave in the strip, i.e., an increase in attenuation and a decrease in velocity measured along the strip. By examining the wave in the strip before and after the coating is applied, the shear mechanical properties of the coating can be determined. Although a quantitative evaluation requires the measurement of changes in both velocity and attenuation, it is sometimes useful simply to follow changes by monitoring attenuation.

During the last year the apparatus necessary to implement this technique has been set up and tested by examining several model polymer systems. The measurements are made using the pulse-echo technique, and to assist in the data acquisition and analysis, the apparatus has been interfaced to a minicomputer. The first samples tested were based on an epoxy-type polymer that cures by free radical initiation. Figure 1 shows a plot of attenuation vs. curing time for two formulations containing the same epoxy but with different concentrations of accelerator. The experiments clearly show that there is an initiation period prior to the onset of cure. The rate of cure influences the width of the transition while the ultimate attenuation level depends on the structure of the cured film among other factors. When the accelerator concentration is changed both the reaction rate and the induction period are altered but the ultimate attenuation level remains the same. This type of information can be crucial in designing epoxy-based adhesives and composites.

The second model system studied this year involved natural-product based drying oils that are used in some printing inks (1). Thin films of these liquids harden by polymerization when exposed to oxygen. The rate of hardening must be correct if proper performance is to be achieved. Figure shows the results of a very simple test in which a thin film of the sample was placed on the quartz strip and the attenuation was monitored as a function of time. The initial increase in attenuation is rapid but eventually the attenuation approaches a limit when the film becomes fully cured. The curve in Figure 2 represents the best fit with a simple first order rate equation. Data of this type can be very helpful in optimizing the design of polymer systems.

The results to date indicate that this technique can be used to qualitatively monitor changes that occur during the liquid-to-solid transition in important polymer systems. During the next year an effort will be made to quantify this test. As part of this effort the measurement capability will be expanded to permit the determination of velocity change as well as attenuation. In addition the program will investigate the possibilities for coupling this technique with other methods such as dielectric tests so that both can be used simultaneously. The information provided by this coupling would make both measurement techniques more useful.

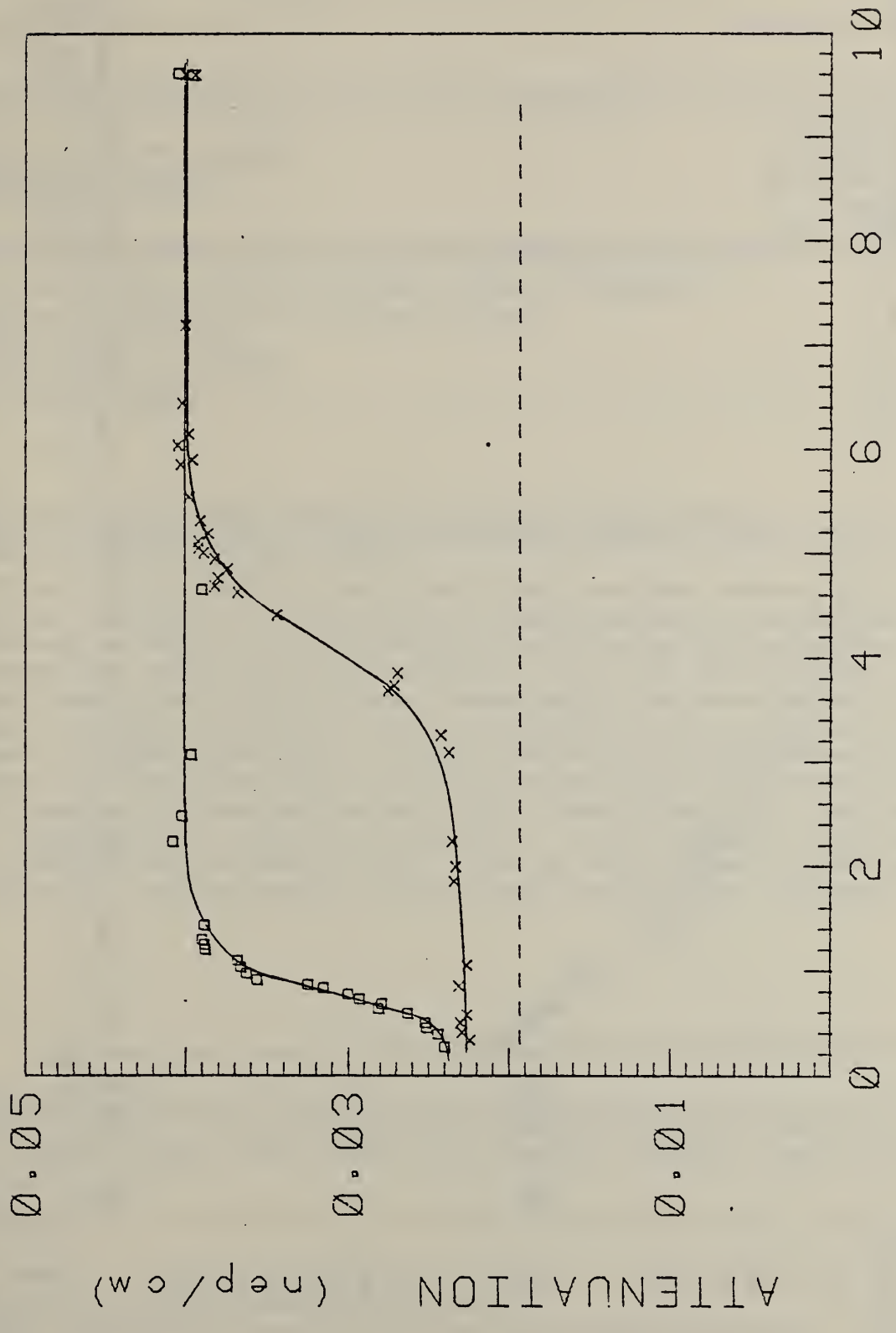
(1) D. L. Hunston, J. L. Rushford, W. R. Newitt, and B. A. Vaudreuil, "Rheology of Cure for Intaglio Printing Inks", Organic Coatings and Plastics Preprints, in press.

Figure Captions

Figure 1: Cure data for the epoxy/accelerator system: dashed line for uncoated strip, X for 0.25% accelerator, and □ for 0.35% accelerator.

Figure 2: Attenuation vs. time plot for the curing of a drying oil based polymer system. The curve represents the best fit with a first order rate equation.

Figure 1



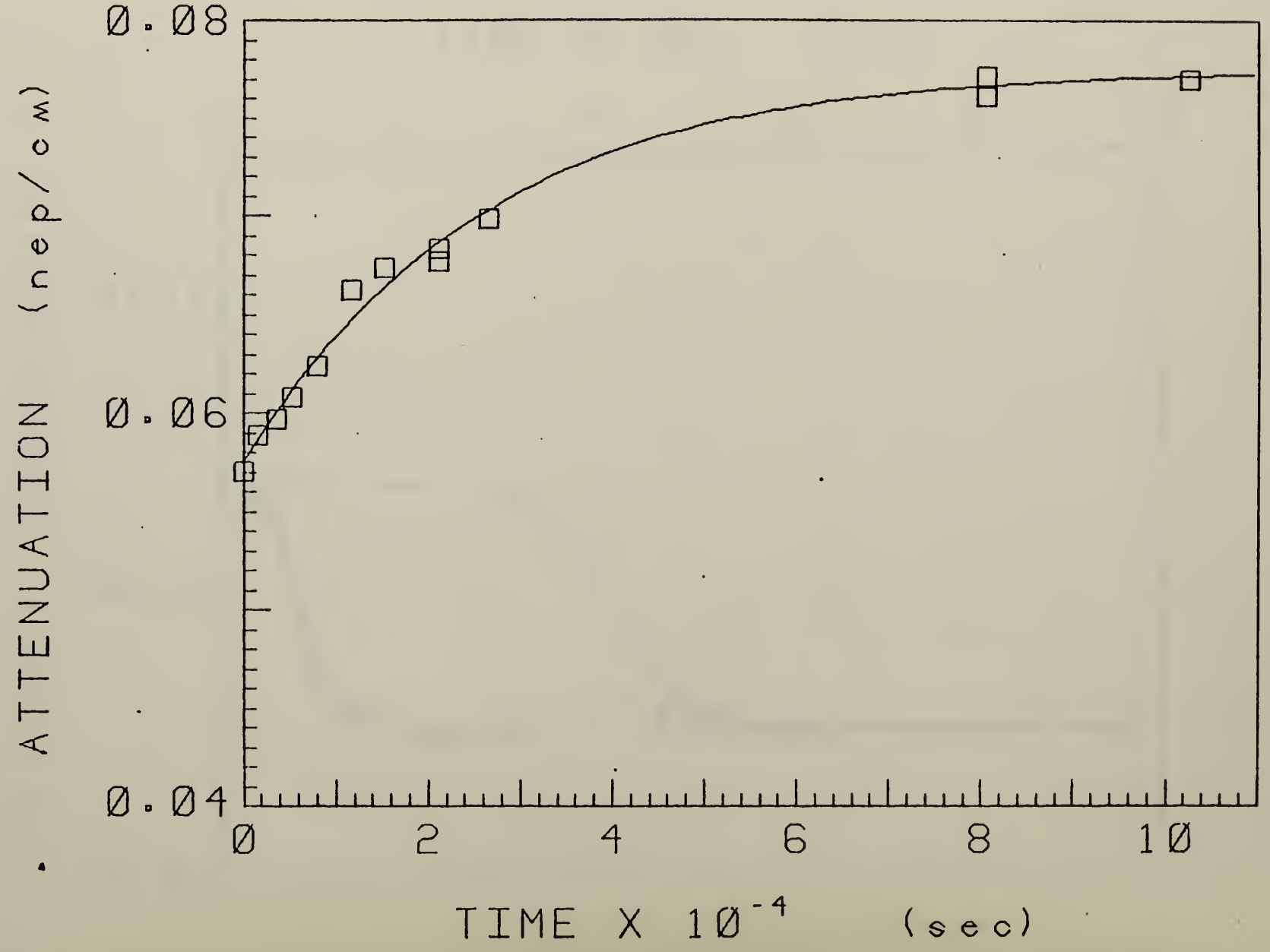


Figure 2

NBS-114A (REV. 2-80)

U.S. DEPT. OF COMM. **BIBLIOGRAPHIC DATA SHEET** (See instructions)	1. PUBLICATION OR REPORT NO.	2. Performing Organ. Report No.	3. Publication Date

4. TITLE AND SUBTITLE

Relationships Between Mechanical Properties and Performance of Inks As the Basis for Quality Control Techniques

5. AUTHOR(S)

Donald L. Hunston

6. PERFORMING ORGANIZATION (If joint or other than NBS, see instructions)

NATIONAL BUREAU OF STANDARDS
DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20234

7. Contract/Grant No.

T-0283-02

8. Type of Report & Period Covered

Progress Report
Oct. 1, 1981 to Sept 30, 1982

9. SPONSORING ORGANIZATION NAME AND COMPLETE ADDRESS (Street, City, State, ZIP)

Bureau of Engraving and Printing, Treasury Department,
Office of Research and Technical Services
14th and C St., S.W.
Washington, D.C. 20226

10. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)

Three different intaglio ink formulations have been examined to determine their mechanical properties. In all cases the properties share a strong shear rate and time dependence. In addition, the behaviors of the different formulations vary substantially at intermediate shear rates but are similar at the very high and very low shear rates that are seen on the printing press. Consequently, the shear behavior has importance for ink fabrication but does not explain the differences in printing performance that are seen for these formulations. The ink samples were then examined for the changes in mechanical properties that occur during drying (curing). Distinct differences in curing behavior are observed for the various formulations and it was determined that these differences can influence performance. It was also found that direct exposure to air (oxygen) will produce curing. The major implications of these results in terms of fabrication, quality control, and printing procedures are discussed.

12. KEY WORDS (Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)

cure; drying; intaglio ink; linseed oil; printing; rheology; tung oil; viscoelasticity; viscosity

13. AVAILABILITY

☒ Unlimited

☐ For Official Distribution. Do Not Release to NTIS

☐ Order From Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.

☒ Order From National Technical Information Service (NTIS), Springfield, VA. 22161

14. NO. OF PRINTED PAGES

15. Price