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

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

SUMMARY

This report summarizes the results obtained during 1984 in the joint program between the National Bureau of Standards (NBS) and the Bureau of Engraving and Printing (BEP) to study the mechanical properties of printing inks as the basis for developing quality control tests and procedures. Eight specific research topics will be covered: rubber mill cure experiments, ultrasonic tests, poker-chip experiments, squeeze flow tests, a review of black ink test results, recent data obtained for green inks, ink uniformity tests, and results of laboratory ink experiments.

The results from experiments using the rubber mill to study cure suggest that it is the early phases of cure that are most important in performance of the ink on the press. In addition, although the amount of data is very limited, the cure kinetics measured in the rubber mill experiments appear to be the same over the range of film thicknesses and temperatures that were examined. These test conditions include both those where the cure rates are relatively slow and those designed to more nearly simulate the conditions actually present on the press. This is useful because in the latter case the cure rates are too rapid to permit convenient study.

Construction of the BEP ultrasonic cure monitoring apparatus is complete by the addition of the items needed to make the system self sufficient. Experiments show that this test is sensitive to the effects of temperature and film thickness on cure rate and, to at least some degree, can follow surface and subsurface drying. Both cure rates and induction times were found to change with curing parameters, and since no simple relationship between these two properties was found, it was concluded that both must be measured to characterize cure. Without agitation, subsurface drying was found to proceed for days even in thin films.

The poker-chip test results show that the film splitting behavior of the inks is highly rate dependent. Like viscosity measurements, however, when the film splitting test is used for cure monitoring, similar results are obtained over a wide range of low and intermediate rates. A comparison of the poker-chip test and viscosity measurements as cure monitoring methods reveals that although the former may be more sensitive to initiation, in general, the latter is the preferred method and by itself provides a reasonable characterization of relative cure rate.

Results for the squeeze flow test suggest that, as a cure monitoring method, it gives data similar to the viscosity tests

Consequently, the squeeze flow experiment provides a simple alternative to viscosity measurements for characterizing cure.

The report reviews the data obtained previously for 8 black ink samples with known performance on the press. These results indicated that inks with short cure times generally gave poor performances while inks with long cure times usually performed well. Inks with intermediate cure times gave a wide variety of performances, and it was concluded that in these cases other factors, such as the set-up of the press, influenced performance. The inks tested also exhibited a wide variation in cure times. This variation was not anticipated and is suspected to be a major contributing factor to the spoilage obtained for these inks. Spoilage is defined as the percentage of printed sheets that are unacceptable due to ink related problems.

To examine this hypothesis, 17 batches of green ink were obtained. These inks were examined for cure behavior and the results showed that there were large batch-to-batch variations even when consecutive batches were compared. In general, the cure times were found to be somewhat slower than those typical of the black inks, and since longer cure times generally mean a better chance for good press performance, this result may explain why spoilage has been less of a problem with the green inks. Nevertheless, the batch-to-batch variations are very large and must therefore be viewed as a problem and probably a major contributing factor to spoilage. As a result, it was concluded that the need to identify and control the sources of this variation is crucial to reducing ink spoilage levels for both the green and black inks.

To further study these variations, three production inks were examined by taking samples from the top and bottom of each batch and measuring the drying behavior. The results show that variations within a batch contribute significantly to those differences found between batches. For the three inks examined no consistent trend was found for the variation in drying properties with position in the batch. Although still preliminary, these data suggest that the differences result from a random variable such as poor mixing rather than a factor such as a systematic segregation of ingredients induced by processing. Variables of this second type might be expected to introduce position dependent variations in properties within a batch.

To determine if controlled and reproducible inks could be fabricated, three ink samples were carefully prepared in the laboratory at BEP. When tested at NBS, these three inks showed very little difference in behavior relative to the variations observed in production batches. This result is encouraging since it suggests that systematic studies can be performed with laboratory inks to analyze the effects of variations in formulation and processing on the drying properties. This offers the best hope for identifying the sources of the variations in ink properties and from this identification developing methods and procedures to minimize this unwanted variability.

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

In cooperation with the Bureau of Engraving and Printing (BEP), NBS is studying the rheological properties of printing inks, particularly properties associated with drying behavior, in an effort to develop a better basic understanding of the factors that control ink performance. The goals in this work are to use the information developed to generate test methods and guidelines for improved ink quality control. In addition the results will be valuable in formulating improved inks. This report describes the work performed during 1984. It covers progress in eight research areas: (1) the use of a rubber mill as an ink cure device, (2) the further development of the ultrasonics test device, (3) the evaluation of the poker-chip test as a method to monitor ink curing, (4) the continued development of the squeeze flow experiments as a method to study ink curing, (5) a review and evaluation of results previously obtained for black inks with known performance, (6) an analysis of results obtained for 17 new samples of green ink, (7) an examination of ink batch uniformity with production lots, and (8) an evaluation of reproducibility for ink samples prepared in the laboratory. Each of these topics will be discussed in detail below.

RUBBER-MILL EXPERIMENTS: As discussed in the previous Annual Report (1), the rubber mill provides an excellent and versatile device for curing inks under circumstances that simulate some of the conditions present on the printing press. The advantages of the rubber mill as compared to other roller devices are that both rolls are heated for more uniform temperature control and the film thickness can be varied in a controlled manner.

By using the rubber mill, there are two important questions related to the study of ink curing behavior that can be addressed: (1) what part of the cure is most important in ink performance on the press, and (2) are the kinetics measured in the mill studies the same as those operating on the press? Although complete and definitive answers to these questions would require a long and detailed study of kinetics, the tests performed here provide some valuable insight into these questions.

A series of experiments was conducted on a sample of black ink using different cure temperatures and film thicknesses. The times required for solidification were measured and the results are listed in Table I. Solidification was defined as the point where the ink was completely dry and no flow could be obtained. This point could easily be estimated by noting that all of the ink transferred to the back roll on the mill when dry. Based on the data from these tests, an estimate could be made for the corresponding time to solidification under press conditions, i.e., preheated ink, < 100 μm thickness, and 80 C. Such an estimate indicates the ink would completely harden in significantly less than 1 minute. The actual residence time of the ink on the press rollers is much less that 1 minute. This suggests that it is the early stages of the drying that are most important for proper press performance. Of course, the later phases of cure may be of concern for other aspects of spoilage, such as the smearing and sticking together of printed sheets. Nevertheless, in light of the apparent importance of the early phases of cure on press performance, future work will focus on this aspect.

A second interesting and important result was also obtained from these cure data. When the logarithm of the time to solidification was plotted against reciprocal temperature, the points were found to fall roughly along parallel straight lines for each thickness (Figure 1). Obviously, the data are limited and the uncertainties in the time to solidification measurement are significant so only a first impressions can be obtained. Nevertheless, within these limits, there is no indication of a major change in kinetics over the range of conditions studied. More experiments are planned but, for the moment at least, it appears that the standard test conditions used in this work (60 C and 0.3 mm film thickness) should provide a good indication of the relative reaction rates on the press

ULTRASONIC EXPERIMENTS: The details of the ultrasonic test apparatus being developed for BEP (see Figure 2) have been described previously (1,2). Since last year's Annual Report (1), several additional components have been added to make the apparatus a stand-alone system: an oscilloscope, a recorder and an attenuator. A prototype temperature control chamber has been completed and tests to evaluate this preliminary design are now underway. The results of the first experiments, which evaluated temperature and film thickness effects, will be reported here.

Figure 3 shows the drying curves obtained by measuring the increase in attenuation as a function of time in the ultrasonic apparatus as different film thickness samples of the same ink cure at 60 C. These curves indicate that both the cure rate and the induction time changed as the film thickness was decreased although the major change was in the cure rate. A five fold reduction in the thickness increased the drying rate by roughly 25 fold while decreasing the induction time by only about 20%.

The effects of increasing temperature at a fixed film thickness (0.007 cm) showed similar trends, Figure 4. The differences in rates observed here, however, were less than those seen in Figure 3. Nevertheless, an increase in cure temperature of 20 C still produced roughly a 3 fold increase in rate. The induction period also seemed to decrease as the temperature was increased although the particular curve shown here for 40.7 C does not show this trend.

Many of the curves obtained in these experiments exhibited a distinct hump (see Figure 4). This hump is believed to be an indication that there were two drying processes: surface drying and subsurface drying. The general observation was that when the hump was reached, the surface was dry but the ink below the surface was not (even in thin films). Thus, the ultrasonic technique shows promise as a measurement tool for both surface and subsurface drying, and the latter is difficult to monitor by other techniques. The measurements indicated that the subsurface drying is very slow and continued for days. This could be an important problem if the ink thickness in printing were to be too large.

The results shown in Figures 3 and 4 also clearly demonstrate that both the induction times and cure rates changed significantly as a function of temperature and film thickness. No simple correlation between the two properties was observed in these tests, however, and thus a major result of this study is that both must be measured to characterize the ink curing. If only one is measured, the reliability of the test as a quality control tool will be severely limited. The Figures also suggest that without agitation the drying rates are very low. Conditions which produced complete drying on the rubber mill in 40 min. gave measurable changes associated with drying in the ultrasonic apparatus for days. Additional experiments to investigate this difference are planned.

<u>POKER-CHIP TEST</u>: The poker-chip test (Figure 5) has also been described in the previous Annual Reports (1,2). With the completion of the computerization of the NBS tensile test machine, it was possible to examine the poker-chip test over a very wide range of film splitting rates (cross-head speeds) as shown in Figure 6. As pointed out in the previously (1,2), the results show that, like viscosity, the failure loads for film splitting are a strong function of rate. This is an important result and raises questions with regard to what rate should be used in cure monitoring tests. To study this question, a

particular ink sample (batch 9 prepared on 1/16/82 in the BEP quality control program) was cured on the rubber mill, and periodically during the cure, samples were removed and characterized with the poker-chip test. The NBS test device made it possible to examine the partially cured inks over a wide range of rates. The results, which were first presented in last years Annual Report (1), are shown in Figure 6. When these results are compared to cure data curves obtained previously (1,2) for other inks using viscosity experiments (Figure 7), two important similarities (in addition to the high rate dependence) are observed. First, over most of the range of rates examined, curing produces a roughly vertical shift in the curves obtained with both techniques. Second in both measurements there is a tendency for the curves to come together at high rates. This means that in using either test to monitor cure, there are a variety of intermediate or low rates where the choice of a testing rate will have little effect on the results.

Since both the poker-chip and viscosity tests have now been developed into potential cure monitoring tools, it is of interest to compare them. The first such comparison was presented in last year's report (1). Since then a number of additional experiments of this type have been conducted. In these experiments samples of various inks were cured to various degrees on the rubber mill and characterized with the two tests. The viscosities were measured at a shear rate of 5 sec^{-1}, and the poker-chip tests were conducted at a cross-head speed of 0.0008 cm/sec. The resulting data were then compared, and a typical plot is shown in Figure 8. The vertical scale in this Figure represents the viscosity in mPa sec divided by 10^6 for the shear flow tests and the failure load in kg for film splitting tests. Such plots reveal a clear similarity between the two experiments. The poker-chip results are perhaps more sensitive to the onset of cure. Once cure is well underway, however, the poker-chip test loses accuracy in that it shows a good deal of scatter and, on average, little change with curing. In this range the film tends to split rather cleanly and exhibits a grainy structure. The viscosity test on the other hand gives a clear indication of curing over most of the drying range. This indicates that the viscosity test is a more complete, overall cure measuring procedure.

Data such as that shown in Figure 8 are now available for a number of different ink samples and the trends are quite consistent. Based on this data base, it is now felt that although the poker-chip test provides some additional insight into curing, this information is not sufficiently valuable from a quality control point of view to make it worthwhile to utilize both a viscosity type test and the poker-chip test when characterizing the curing of an ink. To state this another way, the results show that for the ink formulations tested here a viscosity test will probably detect any ink cure problems that show up in the poker-chip test. Consequently, future experiments will focus on the viscosity test or a suitable substitute evaluation procedure.

<u>SQUEEZE FLOW TEST</u>: As mentioned previously (1), the squeeze

flow test is being considered as a quick and easy experiment that can be used in place of the more complex and time consuming viscosity measurement method to follow cure. This test is conducted by placing an ink sample between two plates and applying a compressive load to the top plate (Figure 9). The plate separation then decreases as a function of time with the major change occurring in less than 30 seconds. As a result a relatively reproducible measurement can be obtained after 60 seconds. Although this experiment is much simpler to perform than a careful shear viscosity test, the flow involved is more complex. On the other hand, shear viscosity plays an important role in the squeeze flow test, and the technique has the advantage that it can be performed quickly and easily with inexpensive, off-the-shelf equipment. For the experiments performed here, a simple hardness tester was used, and thus the results are expressed in terms of hardness numbers; higher hardness numbers mean a larger plate separation at 60 seconds or a higher viscosity.

Since the flow pattern in the squeeze flow test is not well defined for a complex, nonlinear viscoelastic fluid such as the inks, it is useful to conduct a detailed comparison between the results of this test and those for a well defined shear flow viscosity test. This will help determine if the results for the squeeze flow tests can be interpreted in a manner equivalent to the results of the viscosity tests. Such experiments are now underway. Meanwhile, a series of tests was performed using the squeeze flow experiments to follow the cure behavior of a wide range of black and green inks. The results of these tests will be reported in detail below, but it is worth noting here that the data from these experiments clearly demonstrate the ability of this test to easily monitor cure behavior in inks. Moreover, the general shape of the cure curves obtained by squeeze flow measurements is remarkably similar to that for the curves obtained by viscosity tests. Consequently, the results are very encouraging with regard to the possibility of substituting squeeze flow measurements for viscosity tests.

REVIEW OF RESULTS FOR BEP'S QC INKS: Before discussing the new results for tests conducted with the 17 batches of green inks, it is useful to review one set of experiments presented and discussed in last year's Annual Report (1). These experiments involved the evaluation of a specially selected set of black inks. During a period of 4 weeks in early 1982, samples were taken from every batch of black ink formulated at BEP and these samples were stored in freezers. For all of these inks detailed spoilage figures were obtained at BEP by tracking the printing performance of each batch. Based on these figures, eight inks were selected for further study: four with very low spoilage (less than 1.7%) and four with very high spoilage (greater than 9.8%). The stored samples of these selected inks were then retrieved and subjected to detailed characterization experiments Although variations in a number of properties were found, the only parameter that correlated with spoilage was the cure behavior. The drying curves for the eight inks were measured by curing on the rubber mill and monitoring changes in properties with the squeeze flow test. The results are shown in Figure 10. Solid curves are drawn through the points for the low spoilage inks while dashed lines are used for the high spoilage inks. Each ink curve is designated by a letter, and Table II lists the batch numbers and fabrication dates (in 1982) for these inks. Table II also lists the spoilage figures and the cure rates determination (Fast or Slow) made in tests at BEP using IR experiments.

Based on an examination of these results, last year's Annual Report (1) concluded that the cure rates could be divided into three regions: fast, intermediate, and slow. The inks with fast cure rates inevitably gave poor performance, those with slow cure rates almost always gave good performance, and those with intermediate cure rates could have a wide range of performance levels. The evidence suggests that in this third case, the performance depended on other factors in addition to the ink quality, for example, the set-up of the press. One simple way to compare cure rates is to determine the time required for the squeeze flow test results to reach a hardness number of 30. Unlike the previously used time-to-solidification measurement, this procedure has the advantage that the time can be determined quite accurately since both the times to lower hardness and the times to higher hardness can be used for interpolation. Moreover, like the previous method, this technique includes the influence of both the induction time and the cure rate. For these reasons, it was concluded in the previous Annual Report (1) that this evaluation method represents a good choice for characterizing the inks when only a single parameter is to be used.

Table II lists the values of this parameter for the eight inks tested. By using these results, the previous work (1) suggested that inks with time to 30 hardness values less than 32 min. had a cure rate that was too fast and hence these inks gave poor press performances; inks with values greater than 38 had sufficiently slow cure rates to give good performances; and inks which had intermediate values of this parameter involved the risk of unsatisfactory performance. Although these conditions included all of the test results obtained, it is reasonable to assume that there must also be a lower limit to the acceptable range of cure rates, i.e., cure times that are beyond some limiting value will indicate cure rates too slow to give adequate performance on the press. The results to date in this program, however, suggest that this end of the scale is generally not the major problem.

Since these results were reported in last year's Annual Report (1), one new observation has been made; i.e., the degree of batch-to-batch variation that was found in these tests was surprisingly large. The cure times (time to 30 hardness) varied by almost a factor of 2. This seems disturbingly high and is clearly undesirable although it must be admitted that these inks represent extremes over a 4 week period. The inks undoubtedly involve different lots of starting materials, different people performing the formulation, and possibly variations in storage times and histories. As a result, it is difficult to determine how typical these variations are. In the new experiments conducted recently with the green inks, these potential complications were considered in designing the test plan.

RESULTS FOR NEW INK SAMPLES: The recent studies employed a series of 17 batches of green ink. All of the samples were taken in a 4 day period and in many cases involved samples from consecutive batches made by the same people with the same starting materials. The samples were stored in a freezer for only a minimal time period before testing. The tests involved characterizing the cure rate using the rubber mill-squeeze flow procedure. The results are shown in Figures 11 to 14 where each Figure contains data for batches formulated on a given day. Table III lists the formulation date (in 1983), batch number, and corresponding symbol used to represent the results in the Figures.

Despite the fact that most of the uncertainties involved in the tests on the black inks were controlled in these recent experiments, the batch-to-batch variations in the green inks continued to be very large. Here again, the cure times differed by almost a factor of 2, and in some cases, these large differences were seen in consecutive batches made of the same day. Moreover, these variations were not isolated to a single day but were typical of the results obtained all 4 days. This same trend can be seen in Table III which lists the time to 30 hardness values for the 17 batches of green ink.

Although the spoilage figure for these inks were not available, it is instructive to compare their characteristic times to cure with those obtained previously for the black inks.

This is done in Figure 15 with dashed lines separating the fast, intermediate, and slow cure regimes. Interestingly enough, all but one of the green inks fell into the slow cure region where good press performance was normally obtained for the black inks. The single green ink batch falling outside this range had an intermediate cure rate which could well give good performance if other factors are properly controlled. The data here is obviously limited but they do suggest that the green ink formulation shows large batch-to-batch variations just as was found for the black inks. For the green inks, however, the cure rates were, on average, significantly slower that those for the black inks and this may explain why the spoilage figure for the green inks have generally been lower than those for the black inks.

The final and most important conclusion from the test conducted here concerns the possible consequences of the batch-to-batch variations. Previous work has concluded that the press and other factors can be adjusted to compensate for a wide range of ink parameters so long as the variations in these parameters occur slowly over a time period of months or years. Rapid and unpredictable variations such as those seen in Figures 10-14, however, represent a serious problem that can clearly lead to spoilage if not properly controlled. At the present time, there is no explanation for these variations, nor any reason to suspect that they must be present. As a result, there is a need to develop an understanding of the factors that are responsible for these batch-to-batch differences.

UNIFORMITY OF PRODUCTION INKS: In view of the above results, there are two important questions that must be addressed. First, to what extent are the apparent batch-to-batch variations really reflections of non-uniformity within each batch. The degree to which this is true will have a great influence on what must be done to minimize such variations. The second question concerns the ability to prepare laboratory ink batches with minimal variations both within and between batches. Only if well-controlled, reproducible laboratory samples can be fabricated will it be possible to study the origins of the variations in properties for production ink batches in a simple and systematic way. In an effort to address both of these questions, ink samples were obtained from BEP and tested at NBS.

To judge the homogeneity of ink batches, tests were conducted with samples from three different production batches. In each case two samples were obtained: one from the top of the batch and the other from the bottom. The drying behavior of each sample was then measured using the rubber mill-squeeze flow test. The results are shown in Figure 16. A different symbol is used to designate each batch with the open symbols indicating the samples from the top of each batch and the filled symbols for the samples from the bottom.

The results in this Figure represent only three batches and thus the conclusions must be taken as tentative; nevertheless, three important observations can be made. First, very significant variations in cure behavior were found to occur within two of the three batches. To compare these within batch differences with the variations measured previously between batches, the curing behavior of these samples was characterized by determining the time to 30 hardness values. These results were then plotted in Figure 17 together with the results from Figure 15. Clearly the within-batch heterogeneity represents a significant factor contributing to the batch-to-batch variations. Consequently, correlations between the spoilage figures for various batches of ink and their performances can only be established when the differences are large enough to overcome the influence of the within-batch variations.

The second observation that can be made from the data in Figure 16 concerns the shape of the drying curves. Here again the limited number of results must be noted but for these cases at least it appears that samples from the same ink batch give drying curves with similar shapes but different induction times. This is in contrast to curves for samples from different batches where both the shape and induction times can be different. This would suggest that the batch-to-batch variations may in some cases be qualitatively different than the within batch heterogeneity.

A third important observation can also be made from the drying curves. It is of interest to see if the inhomogeneity within a batch exhibits any systematic trends. The existence or absence of such trends provides an important clue as to the source of the variations An examination of the results in Figure 16 clearly shows that, for these samples at least, no consistent trends are present; i.e., in one case the sample from the top of the batch gave a shorter cure time while in another case the reverse was true. It might be speculated, therefore, that the variations within a batch are random inhomogeneities attributable to factors such as inadequate mixing rather than some type of segregation of ingredients produced by the processing itself. The latter circumstance might be expected to produce the same effect each time thus leading to a consistent trend and property variations that depend on location in the batch. Additional studies are needed to test this speculation, but these results provide a very useful indication with regard to what future experiments should be conducted.

VARIABILITY TESTS ON LABORATORY INKS: In view of the large variations in ink properties, it is important to determine if laboratory samples can be produced with controlled and reproducible properties. To examine this question, three ink batches were fabricated in the laboratory at BEP using starting materials from the same lots and taking care to minimize variations in the processing. These samples were tested at NBS for drying behavior again using the rubber mill-squeeze flow technique. The drying curves are shown in Figure 18. These results can be compared with the data for production inks shown in Figure 16. From this comparison it is clear that the laboratory samples were very similar relative to the production inks.

This same observation can be made in another way by again using the time to 30 hardness values as characterization parameters for cure. These times were determined and the results plotted together with the data from Figure 17 in Figure 19. This graph shows that controlled and reproducible inks can be made in the laboratory.

Although these experiments involved only one set of laboratory inks, the results are very encouraging because they suggest that systematic studies can be performed with laboratory inks to analyze the effects of variations in formulations and processing on the drying properties. This offers the best hope for identifying the sources of the variations in ink properties and, from this identification, developing methods and processes to minimize the variability.

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TABLE I: CURING OF INKS OF RUBBER MILL

TEMPERATURE (C)	FILM THICKNESS (mm)	TIME TO SOLIDIFICATION (min)
40	0.3	65
40	~0.1	26
50	0.3	31
50	~0.1	15
60	0.3	21
60	~0.1	9
70	0.3	12
70	~0.1	5
80	0.3	8

TABLE II: COMPARISON OF INK CURE RESULTS

INK BATCH	DATE	DESIGNATION	SPOILAGE (%)	TIME TO 30 HARDNESS (min)	EEP CURE RATE
9	1-16-82	A	22.8	37	S=SLOW
10	1-22-82	B	11.2	31	F=FAST
3	1-26-82	C	9.9	29	F
17	1-28-82	D	13.5	27	F
7	1-12-82	E	0.74	33	S
5	1-25-82	F	1.64	42	S
13	1-27-82	G	1.19	41	S
9	2- 2-82	H	0.95	52	S

TABLE III: CURE DATA FOR GREEN INKS

BATCH NUMBER	SYMBOL	TIME TO 30 HARDNESS (min) FOR INKS FABRICATED ON			
		11-14-83	11-15-83	11-17-83	11-18-83
1	□	49	--	62	44
2	+	54	--	38	54
3	△	55	--	58	35
4	◇	60	--	55	54
5	×	52	--	--	--
6	▲	50	--	--	--
14	■	--	--	--	56
15	◆	--	45	--	--
16	●	--	51	--	--

FIGURE CAPTIONS

Figure 1: Arrhenius type plot of time to solidification data at two different film thicknesses: □ = 0.3 mm, △ = ~0.1 mm. The lines correspond to activation energies of about 12 kcal/mol.

Figure 2: Diagram of the ultrasonic test apparatus with typical oscilloscope display (test frequency is 3 or 5 MHz).

Figure 3: Drying curves from ultrasonic apparatus at three film thicknesses: ——— 5, — — 13, and ----- 25 x 10^{-3} cm.

Figure 4: Drying curves from ultrasonic apparatus for film of thickness 7 x 10^{-3} cm at three temperatures: ——— 40.7, — — 50.8, and ----- 60.4 C.

Figure 5: Diagram of poker-chip test and sample of data output.

Figure 6: Film splitting force measured at various rates for samples of ink batch 9 (1/16/82) cured on mill for times of: 0 min. ◆, 7 min. ■, 15 min. +, 25 min. △, 32 min. X, 37 min. ◇, and 43 min. □.

Figure 7: Viscosity as a function of shear rate for samples of ink BK-60 cured on mill for 0 min. X, 10 min. ◇, 20 min. □, and 30 min. +.

Figure 8: Comparison of poker-chip, □, and viscosity, △, cure data on same ink: batch 17 (1/28/82). Vertical bars on poker-chip data represent scatter range found with 8 tests.

Figure 9: Diagram of squeeze flow test and schematic of data for uncured ———, and partially cured ---- ink.

Figure 10: Squeeze flow results for 8 specially selected black inks cured on the rubber-mill. Dashed curves correspond to inks with high spoilage while solid curves are for low spoilage inks. Letters designating particular ink samples are defined in Table II.

Figure 11: Squeeze flow results for green inks fabricated on 11/14/83 and cured on the rubber-mill. The symbols used in this graph designate the batch number and are defined in Table III.

Figure 12: Squeeze flow results for green inks fabricated on 11/15/83 and cured on the rubber-mill. The symbols used in this graph designate the batch number and are defined in Table III.

Figure 13: Squeeze flow results for green inks fabricated on 11/17/83 and cured on the rubber-mill. The symbols used in this graph designate the batch number and are defined in Table III.

Figure 14: Squeeze flow results for green inks fabricated on 11/18/83 and cured on the rubber-mill. The symbols used in this graph designate the batch number and are defined in Table III.

Figure 15: Comparison of ink cure times for ink samples including data from Figures 10 to 14, △. Data for the Black inks, □ , comes from Table II, and based on the black ink results, vertical dashed lines are drawn to separate the data into performance regions according to press behavior.

Figure 16: Drying curves for production samples of BK-62-RCA Mod. 3A inks made on 7/9/84: Sample number 5 - ■, 6 - □, 9 - △, 10- ▲, 11 - ◇, and 12 - ◆. Open symbols indicate samples from the top of the batch; filled symbols from the bottom.

Figure 17: Time to 30 hardness values for a variety of black and green inks. Data from Figure 16 is plotted at the top of the graph using the same symbols as in Figure 16. The other points are taken from Figure 15.

Figure 18: Drying curves for laboratory samples of BK-62-RCA inks fabricated on 6/30/84: Sample number 1 - □, 2 - △, and 3 - ◇.

Figure 19: Data for laboratory inks added to Figure 17; same symbols as Figure 18.

Figure 1

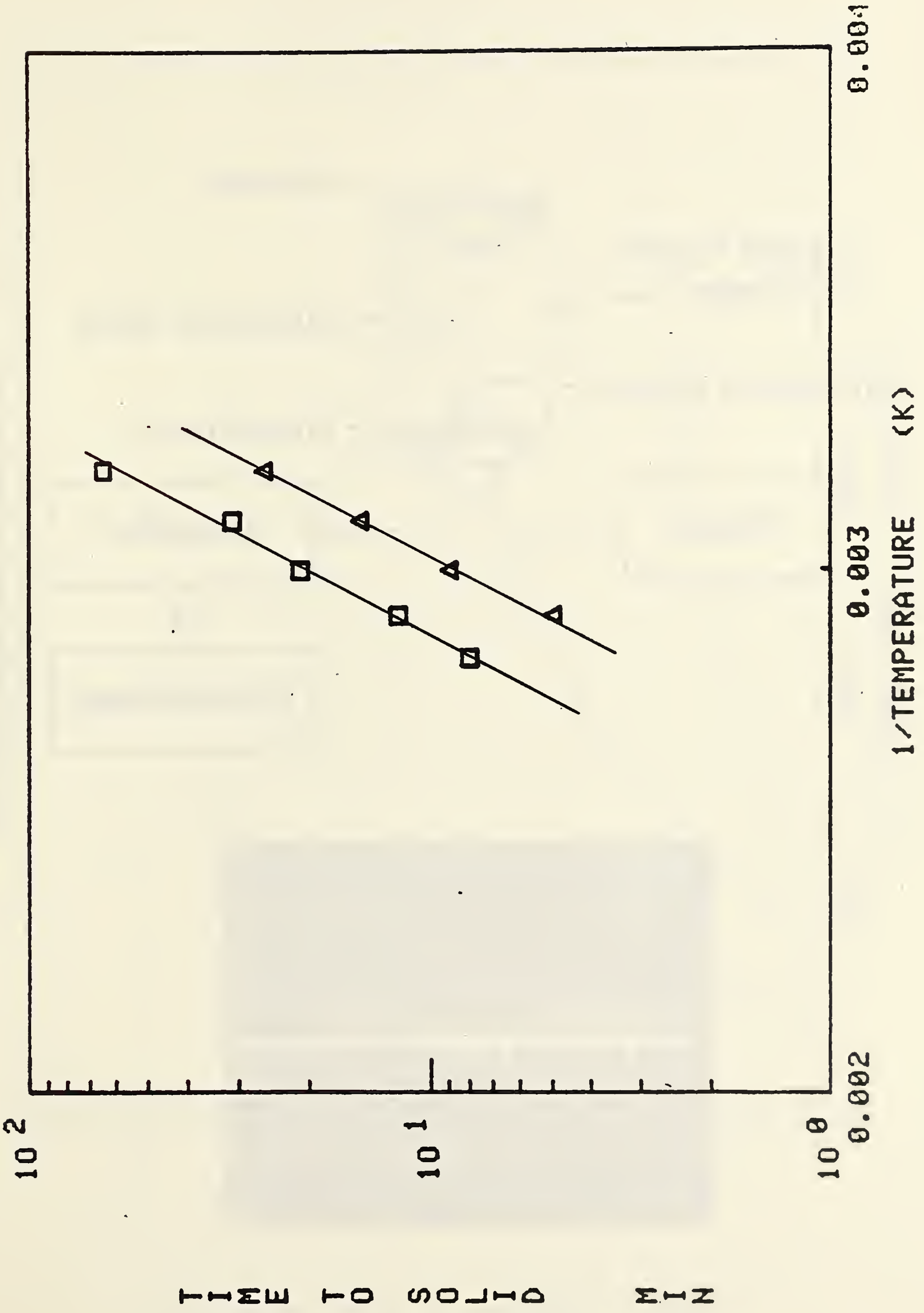


Figure 2

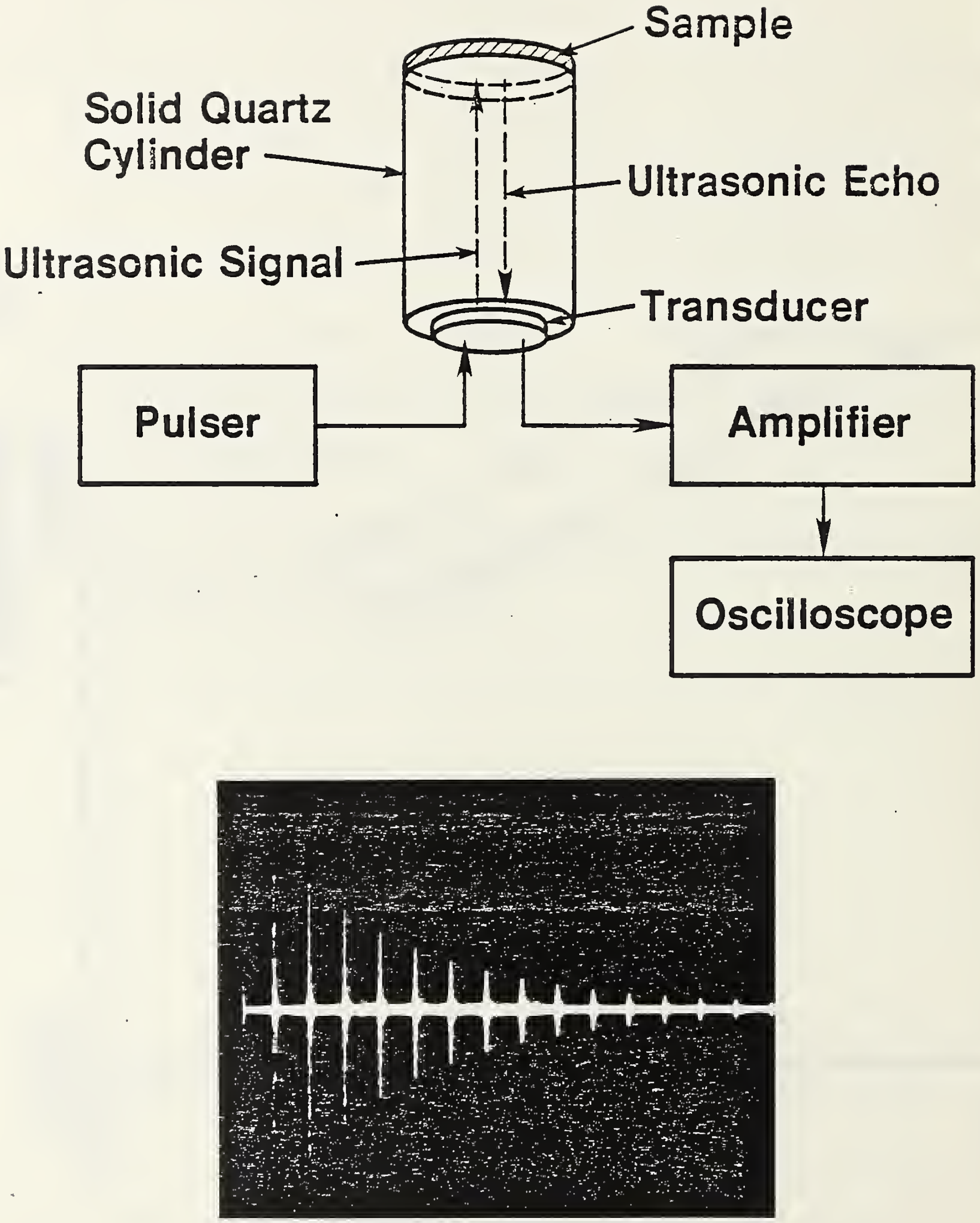

Sample
Solid Quartz Cylinder
Ultrasonic Echo
Ultrasonic Signal
Transducer
Pulser
Amplifier
Oscilloscope

Figure 3

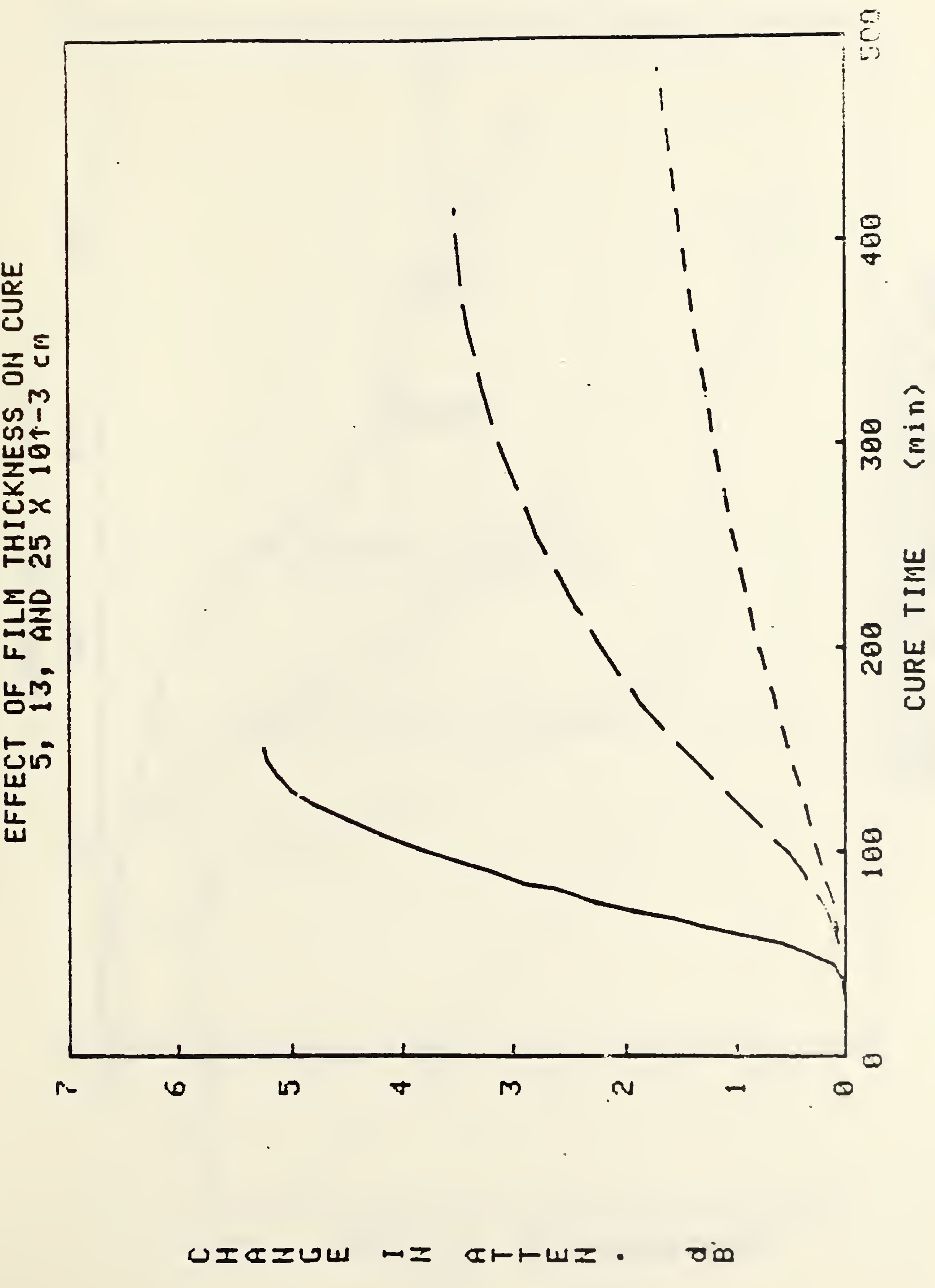

EFFECT OF FILM THICKNESS ON CURE
5, 13, AND 25 X 10↑-3 cm
CHANGE IN ATTEN. dB
0
1
2
3
4
5
6
7
CURE TIME (min)
0
100
200
300
400
500

Figure 4

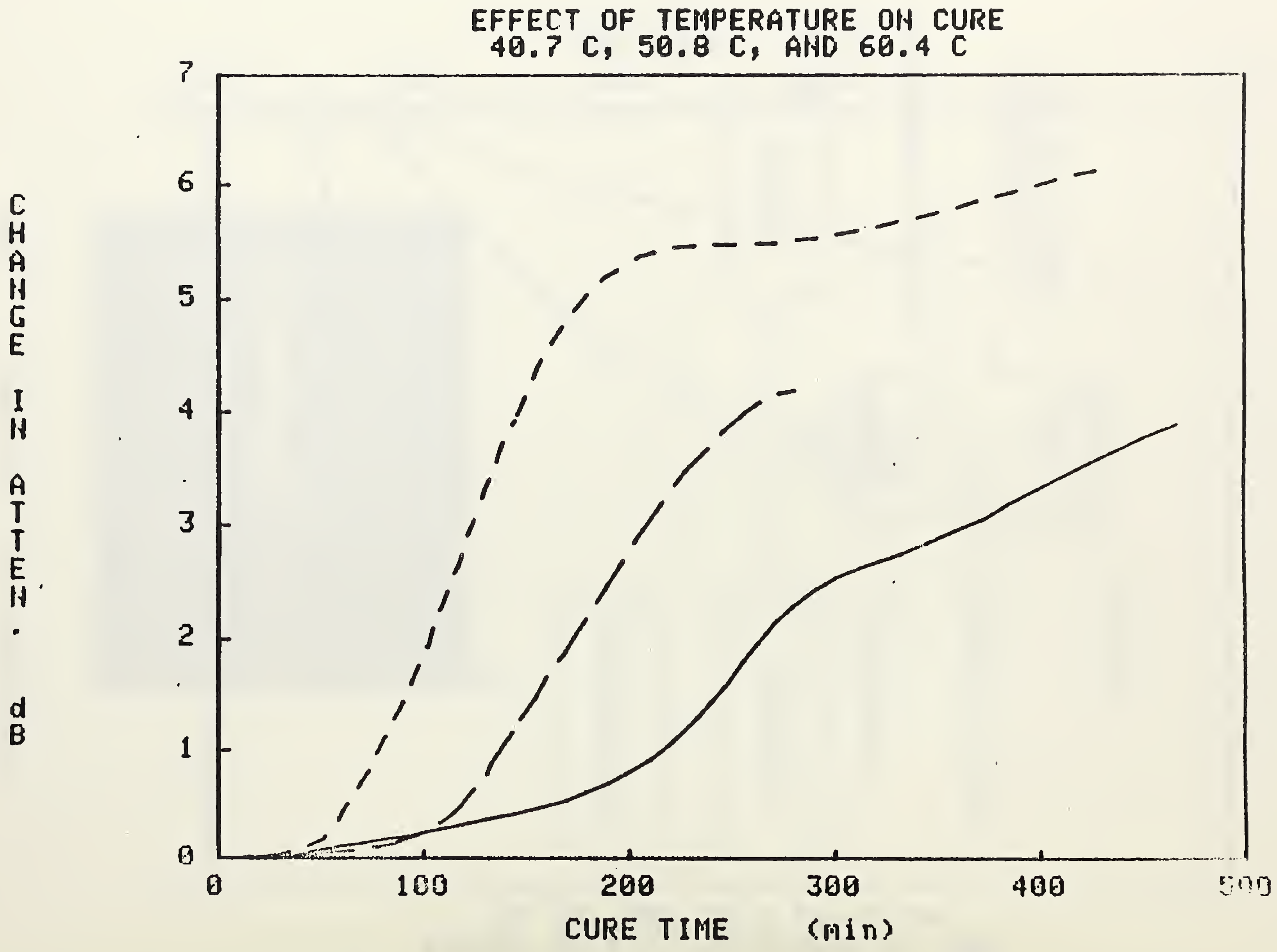
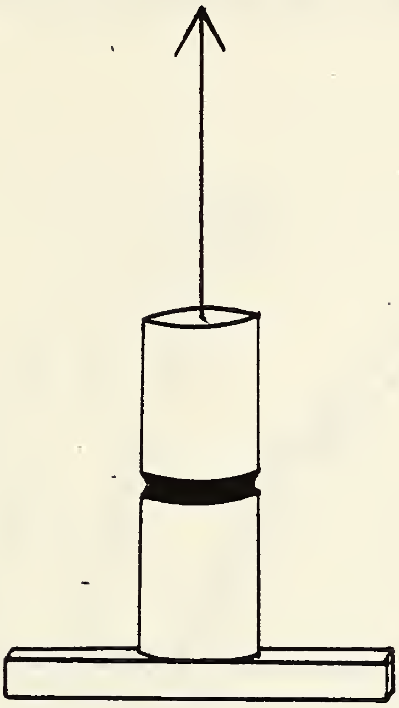
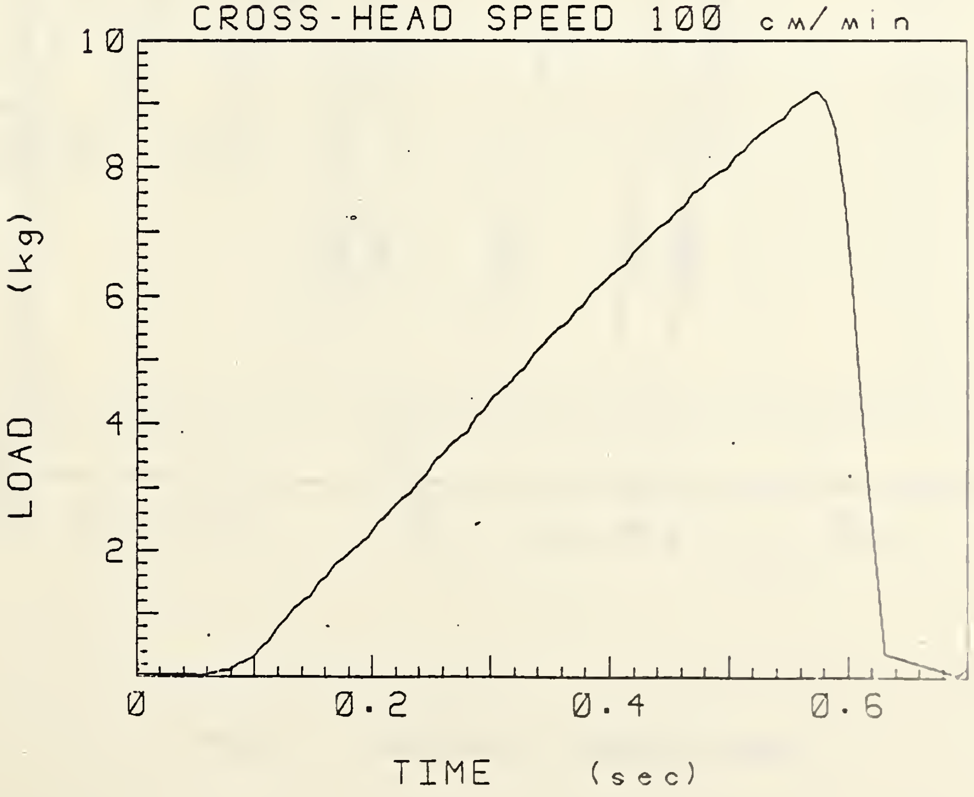

EFFECT OF TEMPERATURE ON CURE
40.7 C, 50.8 C, AND 60.4 C
CHANGE IN ATTEN. dB
0
1
2
3
4
5
6
7
0
100
200
300
400
500
CURE TIME (min)

Figure 5

POKER-CHIP TEST





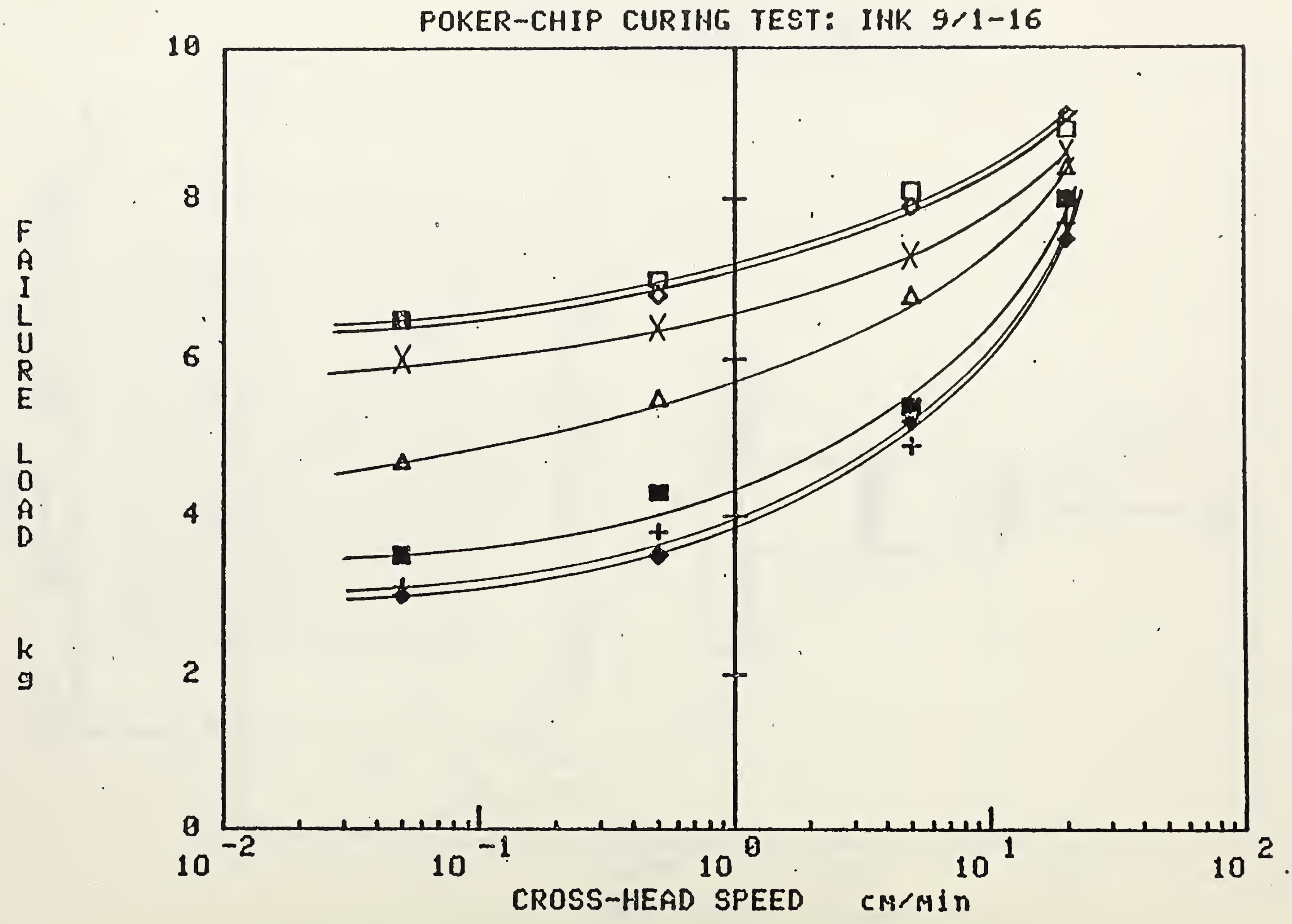

POKER-CHIP CURING TEST: INK 9/1-16
FAILURE LOAD kg
0
2
4
6
8
10
10^{-2}
10^{-1}
10^{0}
10^{1}
10^{2}
CROSS-HEAD SPEED cm/min

Figure 6

Figure 7

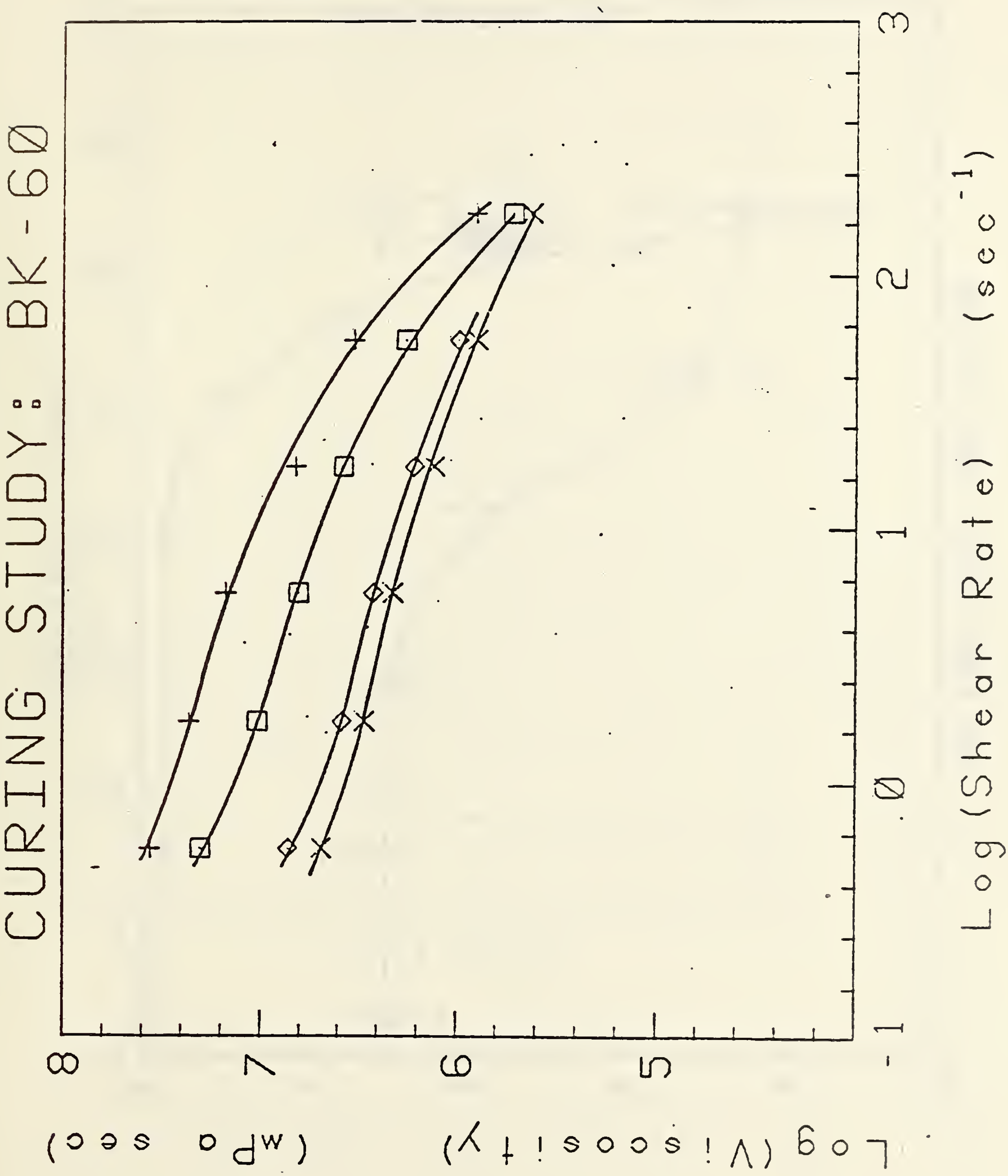
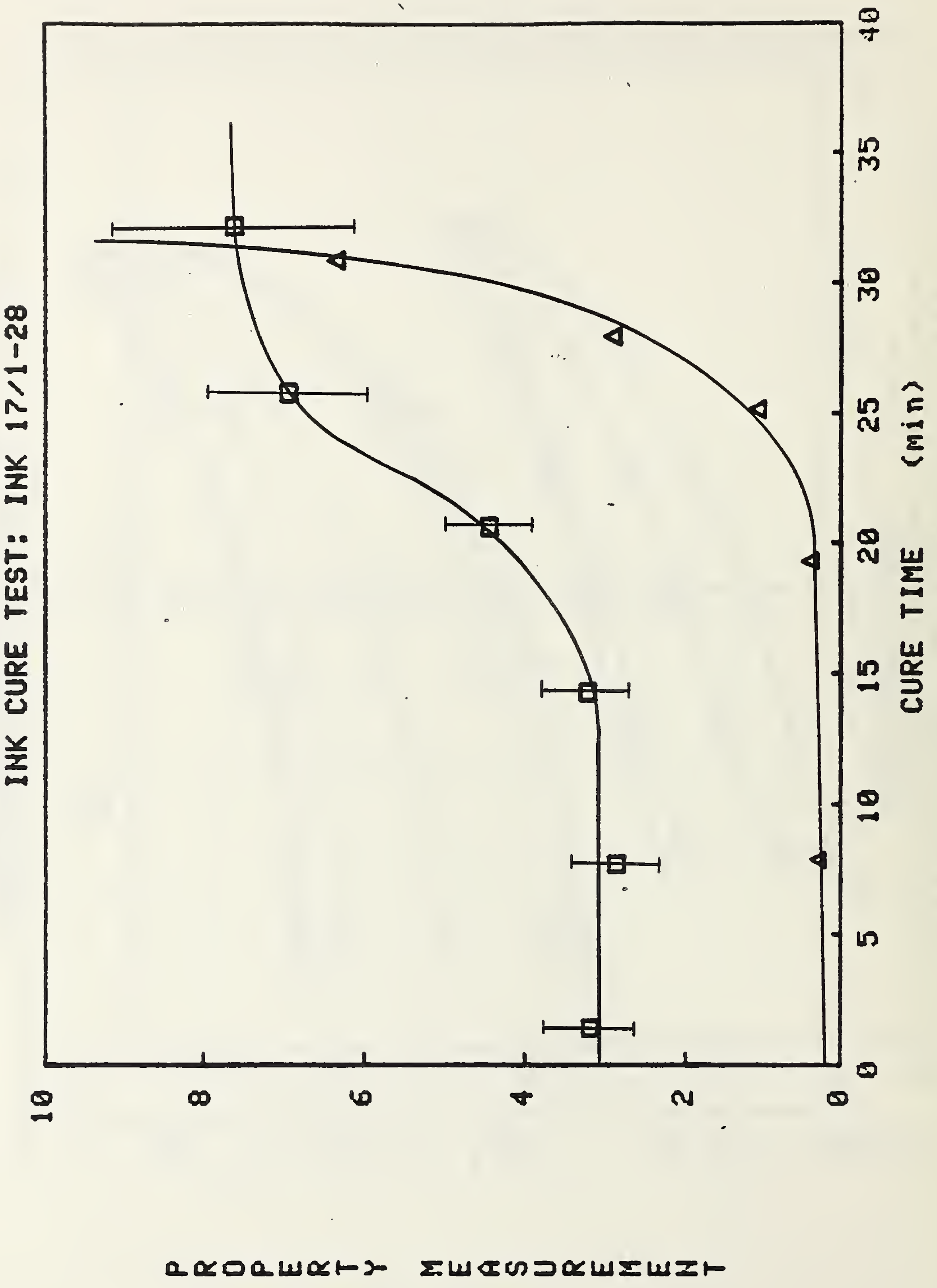

CURING STUDY: BK-60
Log (Viscosity) (mPa sec)
8
7
6
5
Log (Shear Rate) (sec^{-1})
-1
0
1
2
3

Figure 8


INK CURE TEST: INK 17/1-28
CURE TIME (min)
PROPERTY MEASUREMENT
0
5
10
15
20
25
30
35
40
0
2
4
6
8
10

SQUEEZE FLOW TEST

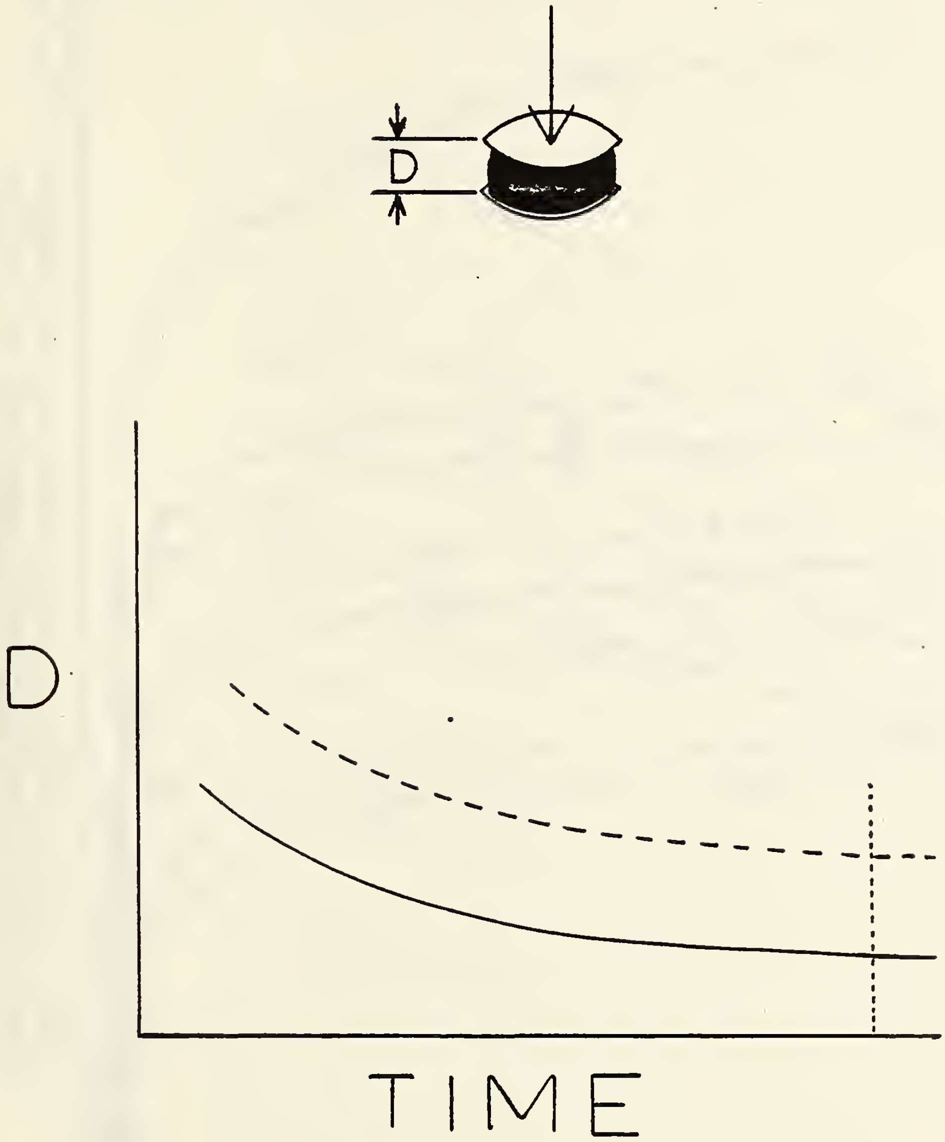


Figure 10

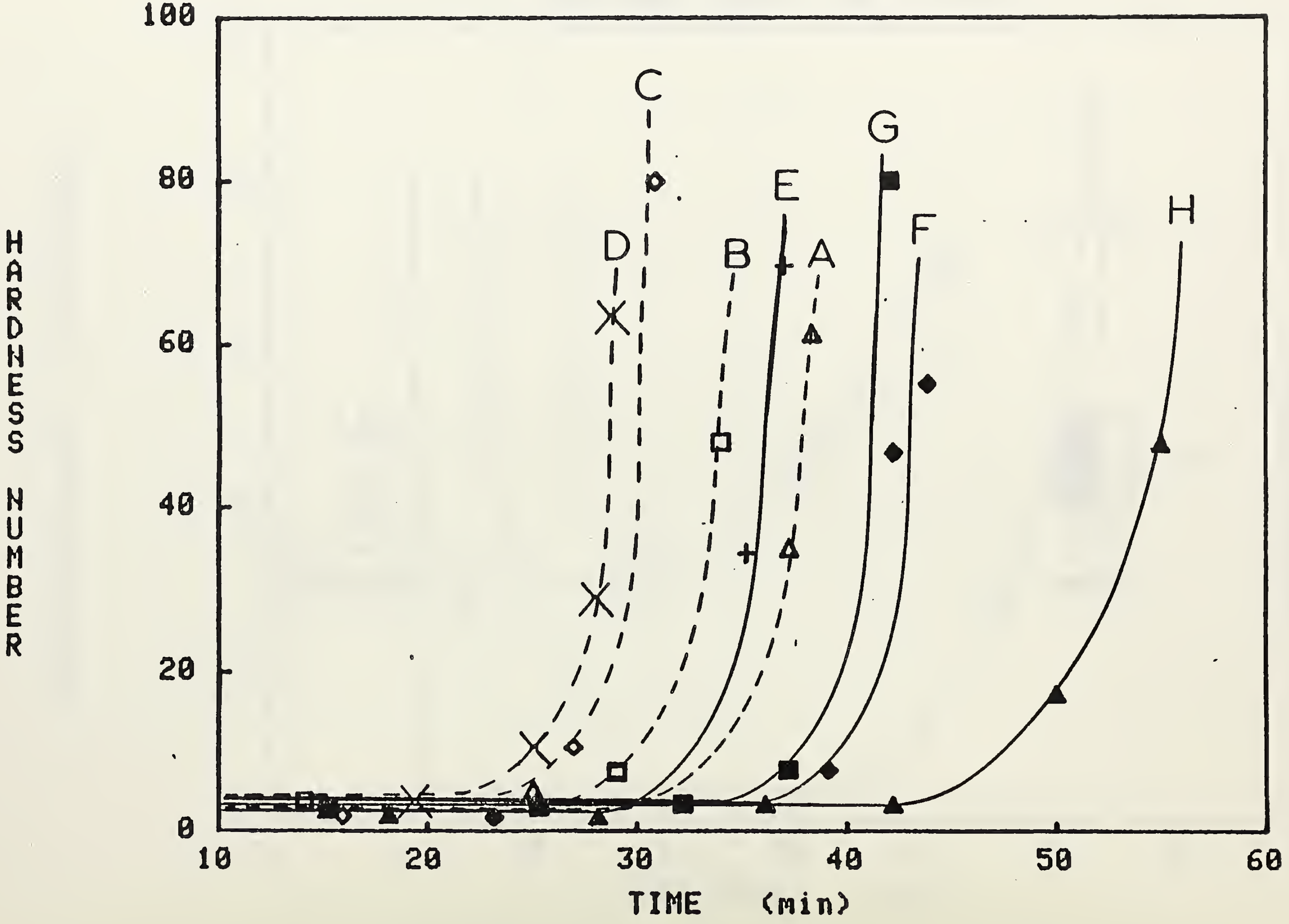

HARDNESS NUMBER
TIME (min)
0
20
40
60
80
100
10
20
30
40
50
60
A
B
C
D
E
F
G
H

Figure 11

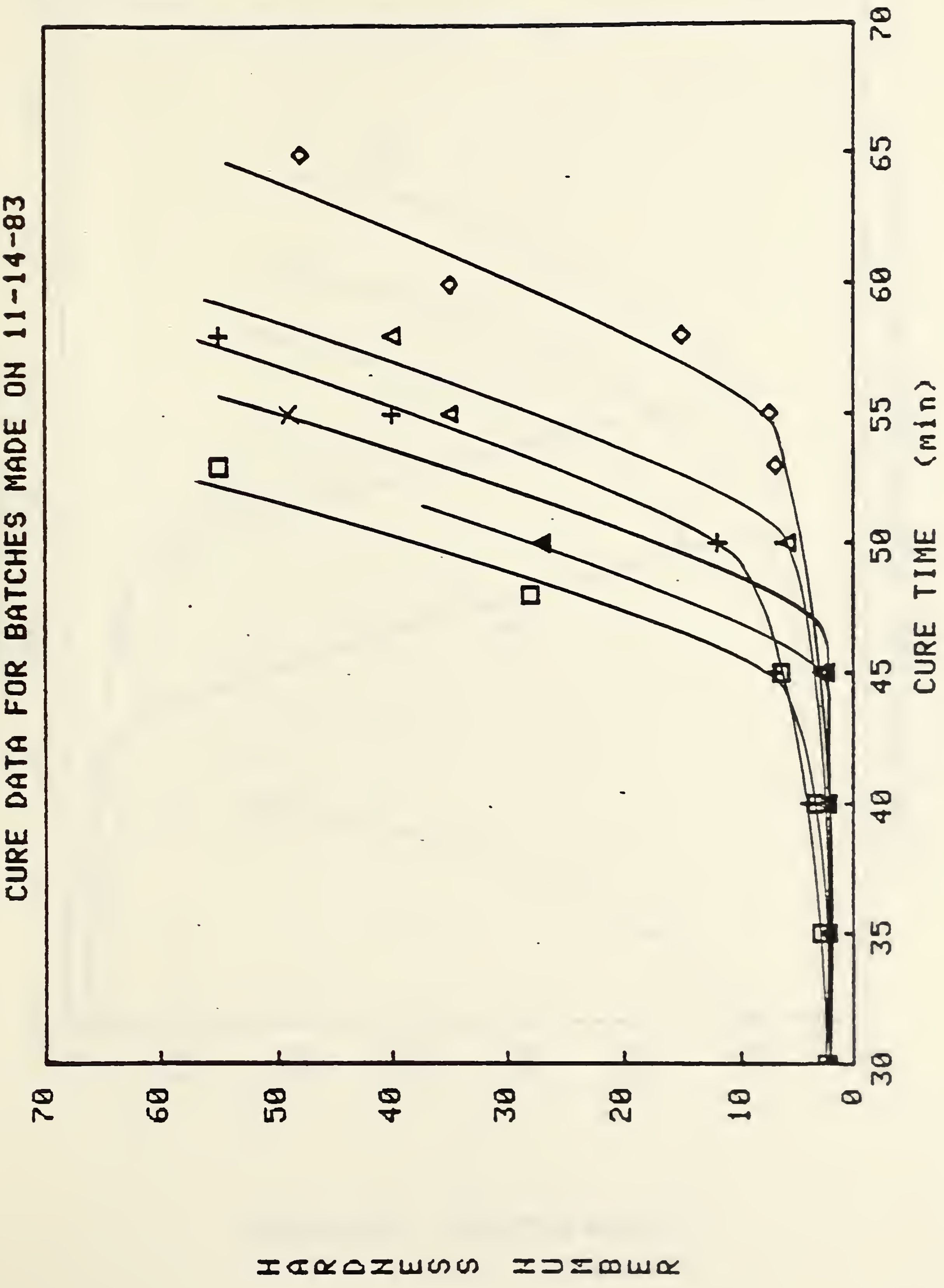

CURE DATA FOR BATCHES MADE ON 11-14-83
HARDNESS NUMBER
CURE TIME (min)
0
10
20
30
40
50
60
70
30
35
40
45
50
55
60
65
70

Figure 12

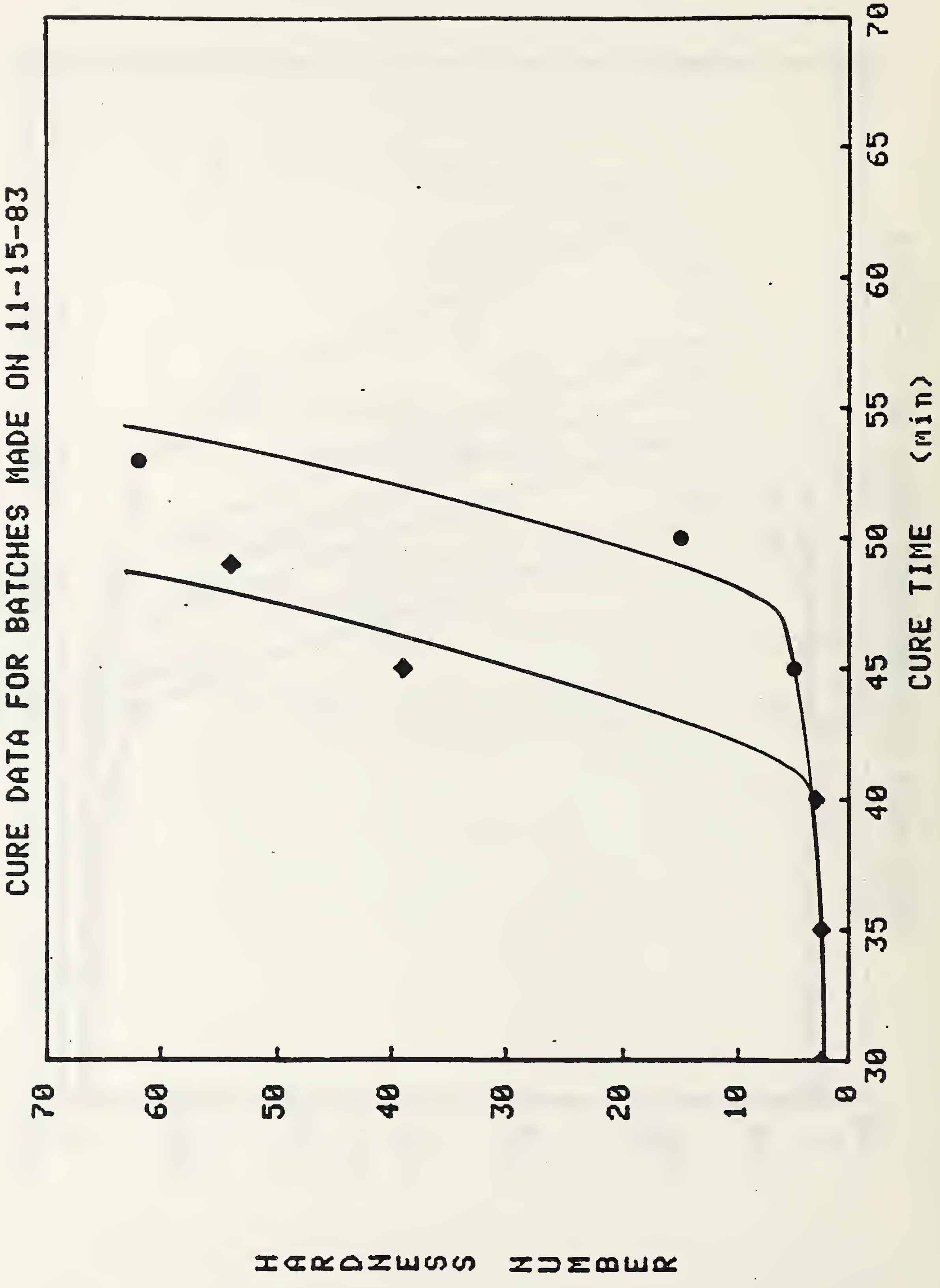

CURE DATA FOR BATCHES MADE ON 11-15-83
HARDNESS NUMBER
0
10
20
30
40
50
60
70
CURE TIME (min)
30
35
40
45
50
55
60
65
70

Figure 13

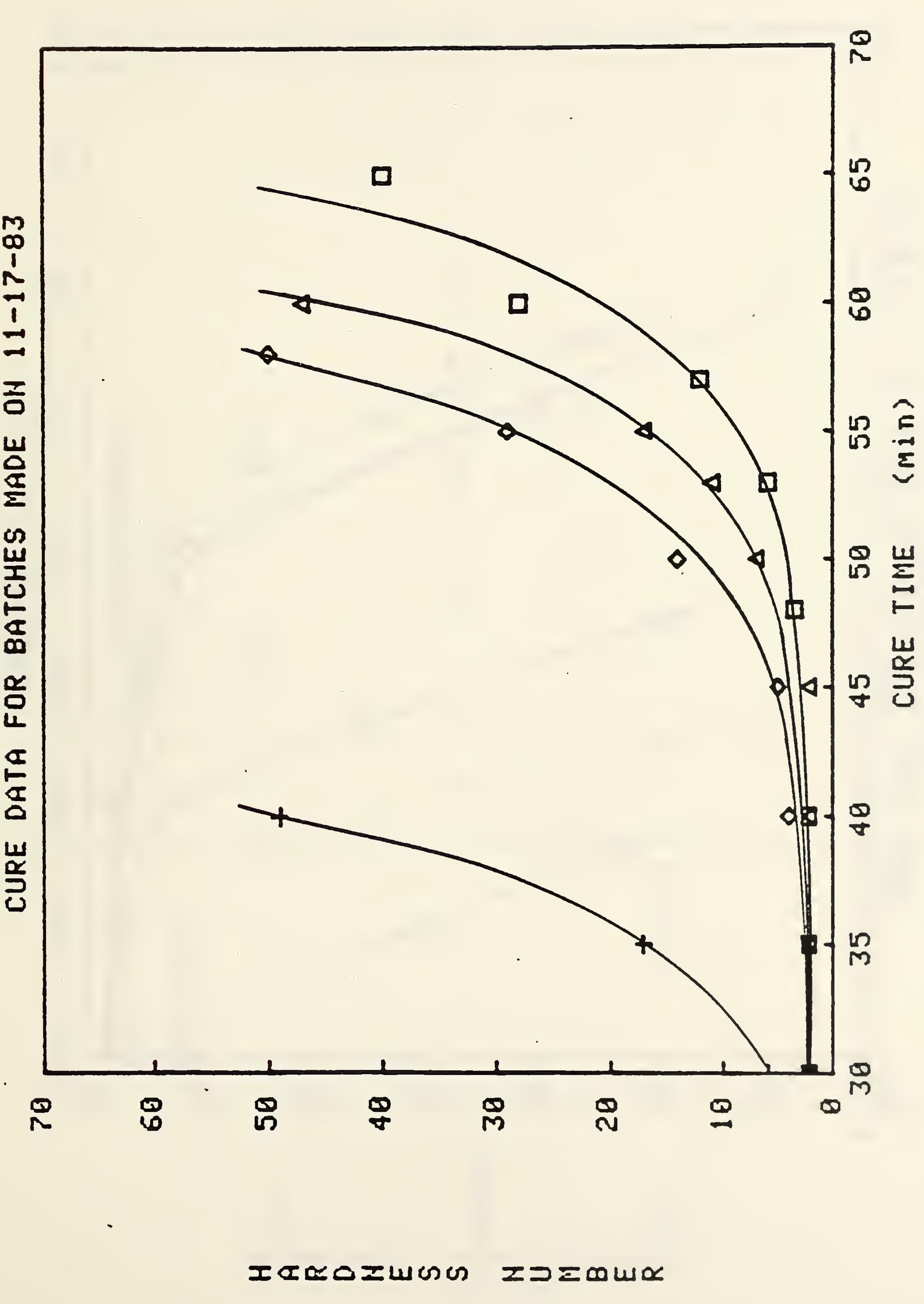

CURE DATA FOR BATCHES MADE ON 11-17-83
HARDNESS NUMBER
CURE TIME (min)
0
10
20
30
40
50
60
70
30
35
40
45
50
55
60
65
70

Figure 14

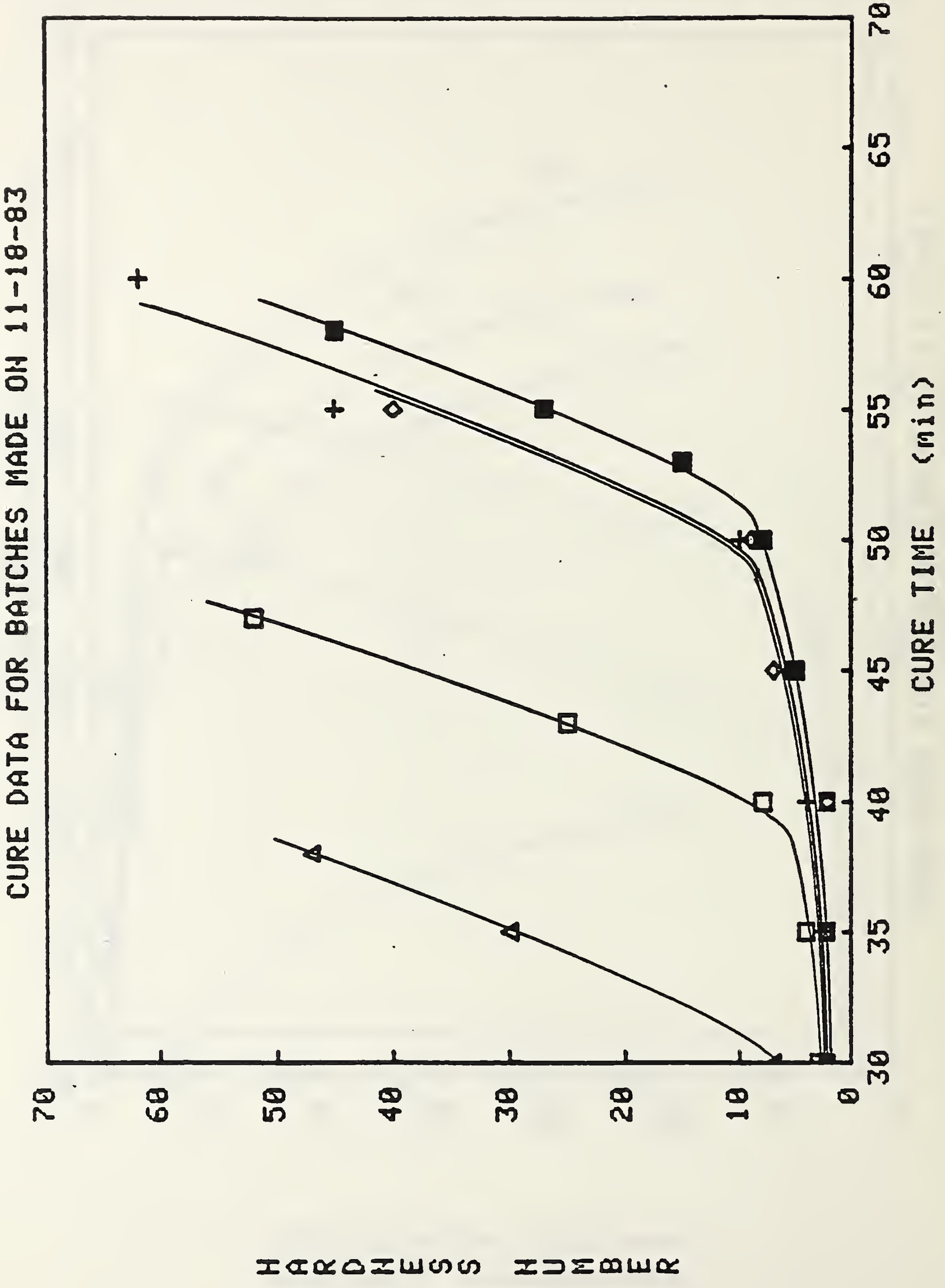

CURE DATA FOR BATCHES MADE ON 11-18-83
HARDNESS NUMBER
0
10
20
30
40
50
60
70
CURE TIME (min)
30
35
40
45
50
55
60
65
70

Figure 15

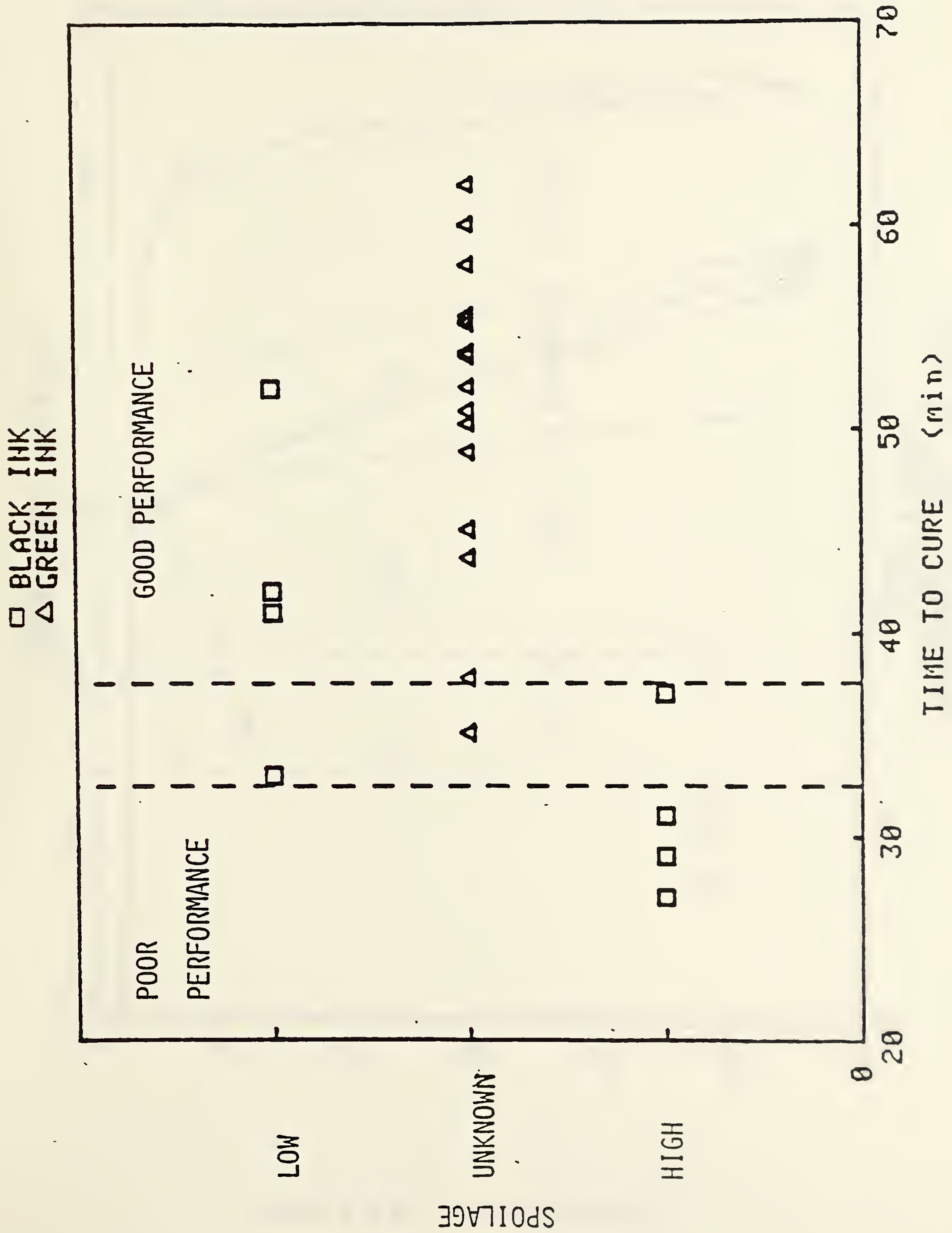

□ BLACK INK
△ GREEN INK
GOOD PERFORMANCE
POOR
PERFORMANCE
LOW
UNKNOWN
HIGH
SPOILAGE
0
20
30
40
50
60
70
TIME TO CURE (min)

Figure 16

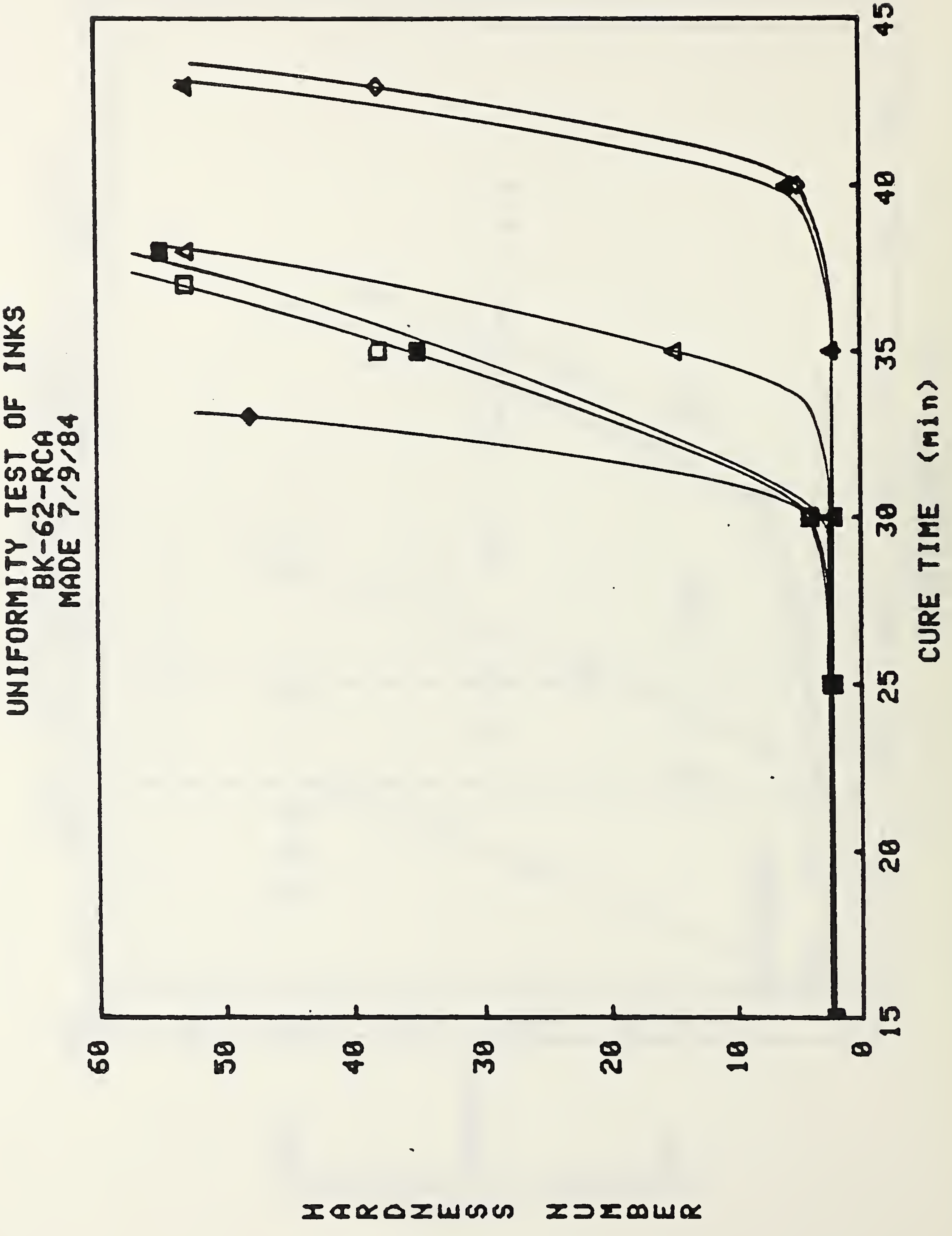

UNIFORMITY TEST OF INKS
BK-62-RCA
MADE 7/9/84
HARDNESS NUMBER
0
10
20
30
40
50
60
CURE TIME (min)
15
20
25
30
35
40
45

Figure 17

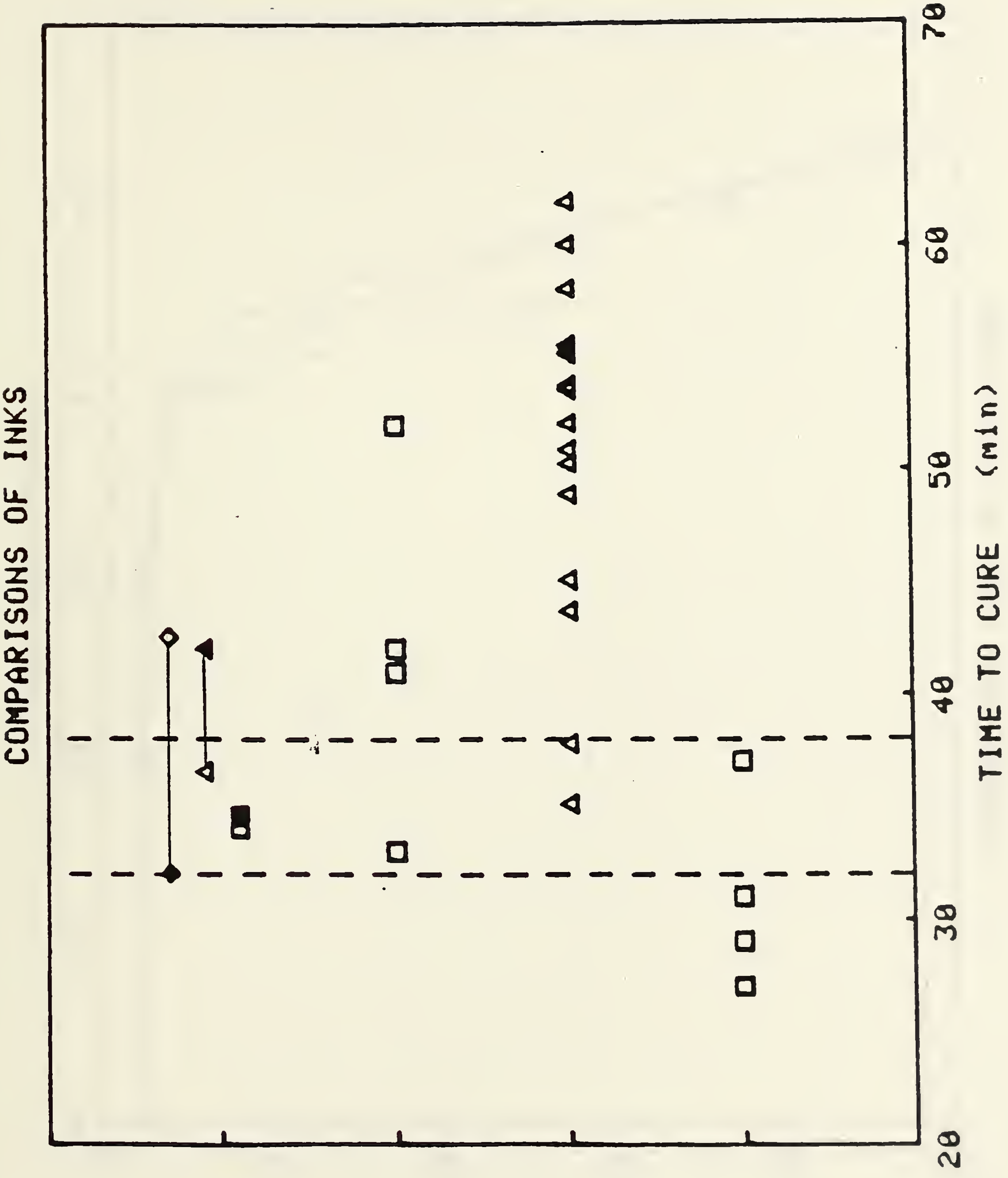


Figure 18

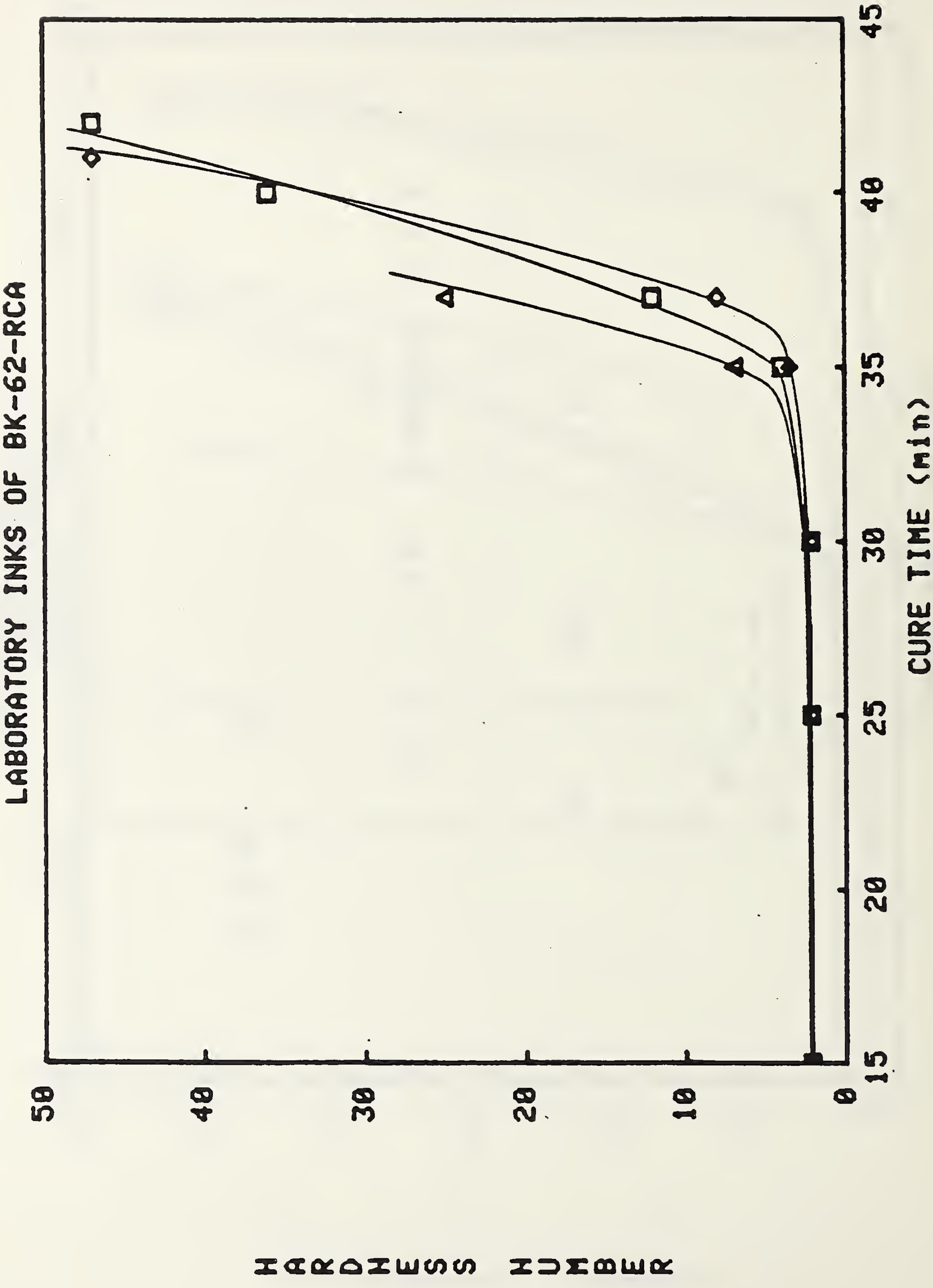
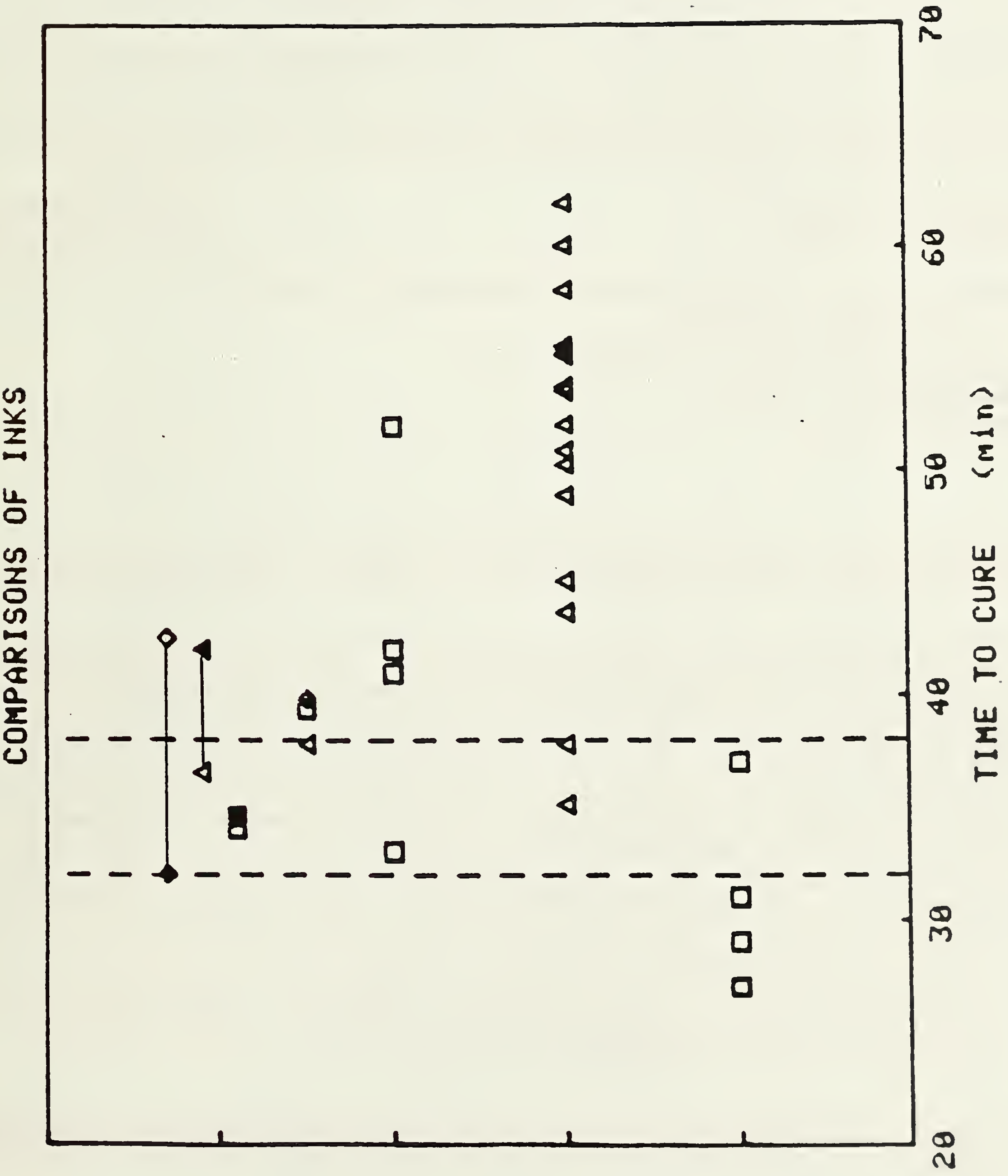

LABORATORY INKS OF BK-62-RCA
HARDNESS NUMBER
0
10
20
30
40
50
CURE TIME (min)
15
20
25
30
35
40
45

Figure 19



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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)*

This report reviews the progress of a joint program with the Bureau of Engraving and Printing (BEP) designed to study the mechanical properties of ink both before and during curing. The objectives are to develop quality control tests and guidelines for improved ink formulations. This report covers progress in a number of specific research areas. First, the development of a variety of test methods is discussed. These methods include shear viscosity measurements, squeeze flow experiments, and the poker-chip test. Second, the correlation that was developed previously between ink drying behavior and press performance is examined further. Large batch-to-batch variations in drying behavior were found for production inks, and this is concluded to be a major contributor to poor ink performance since the press can not be adjusted to compensate for these rapid and unpredictable variations. Third, the variations in properties within an ink batch were studied and found to be a significant fraction of the between batch variations. Finally, Laboratory inks were prepared and studied. These inks exhibited relatively little variation either within or between batches. Consequently, the results indicate that model inks can be prepared in the Laboratory for systematic studies of property-performance relationships.

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

curing; drying; intaglio ink; printing; quality control; rheology; viscoelasticity; viscosity

13. AVAILABILITY

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