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ALGINATE ADDITIVES
AND
COATING MIGRATION CONTROL

by

Peter B. Bradshaw

A Thesis to be submitted to the
Faculty of the Department of Paper Technology
in partial fulfillment
of the
Degree of Bachelor of Science

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ABSTRACT

In this study the feasibility of using alginate compounds in latex coating slurries to control migration so as to improve the coating properties of the latex is discussed. In the past, starch and casein have been used in an attempt to alleviate streaking, blade build-up and premature drying, but they have not performed in an entirely satisfactory way, particularly with higher concentrations of solids. Considerable evidence is presented to indicate that the use of alginate additives will enhance both the coating ability and the coating properties of latex, even when high concentrations of solids are present.

In addition, a new method, using the Perkins-Elmer infrared spectrascope, for measuring migration is introduced. The greatest asset here is that the method can be used without other special equipment and can be applied after the coatings have been completely processed.

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HISTORICAL BACKGROUND

The literature on this subject is rather limited. An extensive review revealed that it falls roughly into two categories: various means of measuring migration control; and chemicals added to coating slurries to control migration.

Techniques of Measurement

Many measurement techniques have been tried. As yet, no satisfactory method of quantitative measurement exists. The problem must be solved, therefore, by qualitative measurement of properties which one would expect to be present in the sheet if a certain compound were also present. No methods for a sufficiently precise qualitative analysis of coating migration have been devised so far, but a few have been used which give indication of migration measurement.

Barber,[1] comparing alginates to hydrocolloids, states that the highest percent of coating solids could be run with sodium alginates, but failed to back his data by migration tests on the hydrocolloids that he used. In Part I of an article on coating color migration, Beazley and Climpson[2] tried to correlate two types of migration measuring instruments, electrical and optical. The electrical instrument they analysed measured the conductivity of a sheet and the time the coating took to reach a certain penetration. There should be better methods than theirs available, and further research should be done on this. In fact, in an article immediately following (Part II),[15] Beazley and Climpson question the correctness of their own measurements.

Bohmer and Lute[4] used essentially the same measurement procedures as those cited above, refining the procedure a bit by trying to eliminate the mechanical defects of the machine with the use of AC instead of DC to supress the capacitor effect of DC on a paper sheet. They did not, however, sufficiently discuss the problems caused by variations in paper quality. Had they done so, they would have run into the same difficulties as Beazley and Climpson.[2] Both articles[2&4] mentioned the importance of the contact angle between the coating and the paper as a parameter for migration properties. This is most significant in the capillary region since only capillary action is a force for migration at the time the coating is applied to the sheet at the blade nip. As the contact angle decreases, the capillary action increases as described by Washburn's modification of Poiseuille's equation. (See "Adhesive Migration and Water Retention With Reference to Blade Coating,"[4] Bohmer and Lute.)

Bohmer and Lute ran tests on the machine speed and available penetration time of four different coating machines, and with the data obtained on alginates in the process it would be possible, theoretically, to calculate the distance between the flooded nip and the blade of the coater. Actually, however, the data were never correlated by them on a blade coater.

Also writing on migration, Clark, Windle and Beazley[6] assumed that in the capillary region, water migrated out of the binder and the pigment and into the capillaries of the sheet. They theorized further that binder and pigment migrated into the sheet during the blade nip. To prove this, they studied four different techniques of migration measurement:

Electrical conductivity
Roller and inclined plane
Ultrasonic techniques
Optical techniques

Of these, they picked the optical technique because the electrical had too much variation with the different base stocks; the roller and inclined plane had too much variation with the viscosity of the coating; and the ultrasonic was not easy to relate to true penetration, and also air in the sheet would contribute to gross error. The optical technique, however, was applicable under both high and low pressure situations which relates closely to the actual mechanics of a blade coater. Clark, Windle and Beazley went through tests on various base stocks, grades of coating and binder makeups and discussed the behavior of each and explained the parameters for the results they obtained. Their conclusions support Boher and Lute's, above. That is, alginates give the least amount of migration during the capillary phase.

Chemical Compounds Used to Control Migration

Smidsrød[13] gives a rundown on viscosities of different molecular-weight alginates and tries to correlate them with a formula where viscosity is a function of molecular weight. He also does work with different ion concentrations. This information possibly could be used in developing coating makeups.

Ogaard[12] gives basic history on the use of alginates as a migration retardant. He states that basically, as of 1966, there was little use of alginates by the industry on blade coaters, but demand was rising and thus additional research should be forthcoming. He gives an extensive discussion of the use of alginates in pigment coatings and states that alginates have pseudo-plastic flow properties and, when plotted on a shear-stress graph, produce no hysteresis curve. The addition of alginates, he says, can change the rheological properties of the coating mixture. He attempts to explain why alginates retard water migration in the coating mixture. He says:

> "The ability to retain water depends on at least three factors:
>
> 1. Reduced penetration due to increase in the viscosity;
> 2. Physical-chemical absorption of water in the polymer, for example by constructing a hydrogen bridge, etc.;
> 3. Reduced penetration due to the effect of an insulating layer formed on the surface of the paper (e.g., by means of the formation of aluminium alginate, etc.)"

In conclusion, he states that low viscosity alginates are more beneficial to migration control than the higher viscosity ones, and discusses the migration mechanics of coating pigments during blade coating operations; i. e., streaking and blade build-up. Tests were run on compatibility of alginates with other substances used in the industry and few were found with which alginates were not compatible. Satin white, or most cation active substances, were among these. He also explains how hard water can be treated so that the alginates will not be affected. This could be important for tests run in Michigan and other hard-water areas.

Other compounds which have been used to control migration include soya protein, hydroxyethyl cellulose, carboxymethyl cellulose,[1] none of which appears to be superior to sodium alginates.

EXPERIMENTAL DESIGN

Introduction

The object of this experiment is basically two-fold: 1) to test the feasibility of using alginates in different latex coatings; and 2) to develop a new and more accurate method of measuring migration.

Coating Makeup and Application

The test coatings were run on the Black-Clawson air-knife coater on two different types of base stocks. The base stocks were unsized, semi-mechanical stock and a latex-impregnated stock. Coating speed was 250 feet per minute and air-knife pressure was set to achieve a 12 pound coat-weight on a 3300 square foot ream.

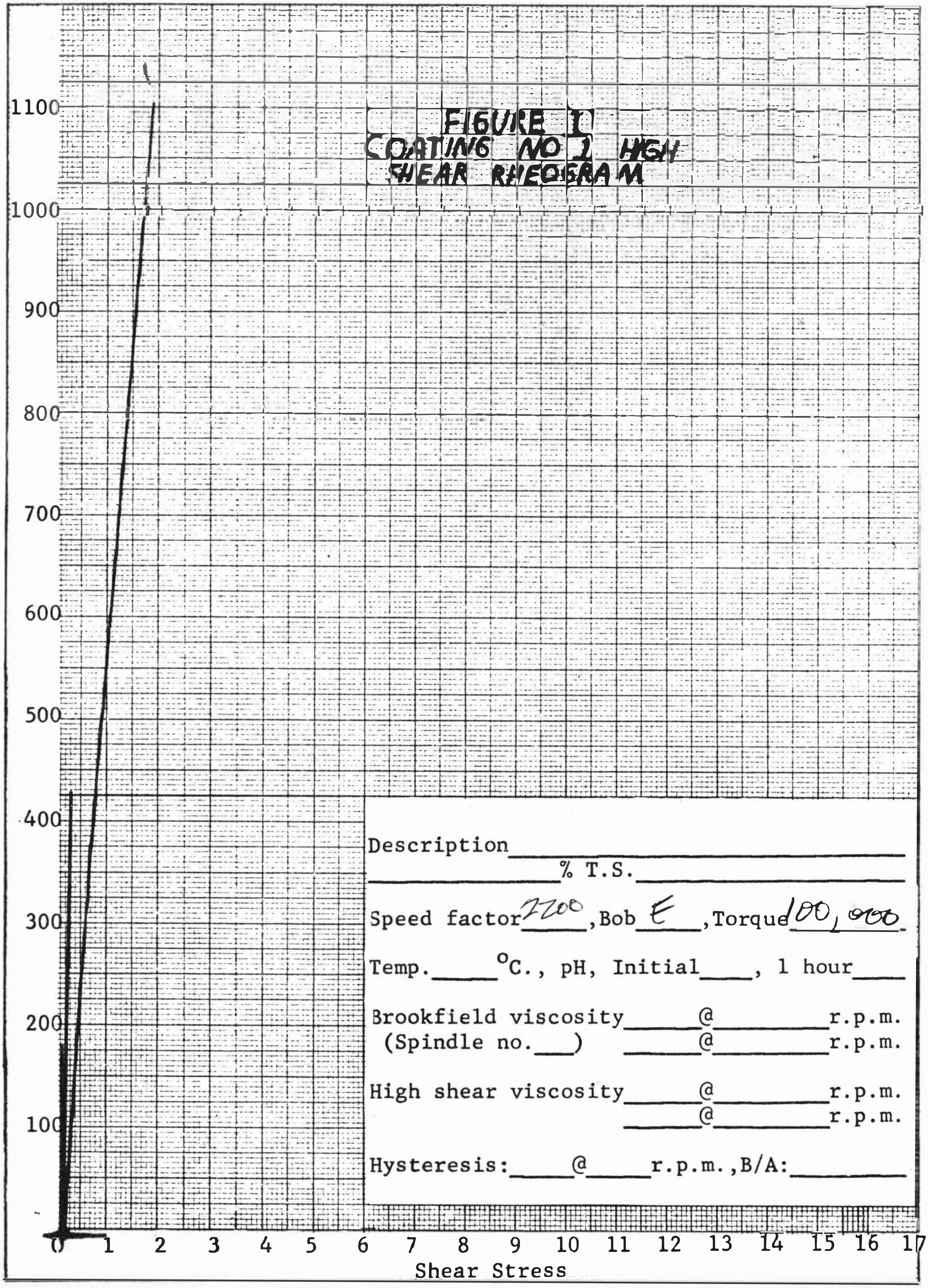
Two-hundred and fifty pounds of coating were made up the night before at 70% solids; and the next day, four different coatings were made up using the basic formula of 20 parts latex to 100 parts clay and these were diluted down to 50% solids with water. The latexes used were acrylic latex and a butadiene acrylonitrile. The latter was supposed to have a strong infra-red spectrascope band. The Kelgin Q alginate was added in coatings 2 and 4 at 0.6% of total dry weight. Coatings 1 and 2 used acrylic latex and 3, 4 and 5 used butadiene acrylonitrile. Coatings 1, 2, 3 and 4 were run on the semi-mechanical base stock, and coating 5 was run on latex impregnated base stock. Samples of all the coatings were taken and rheograms were run on the five coatings. (See figures 1, 2, 3 and 4.)

The drying of the coatings was accomplished as follows:

1. The first two zones of the dryer were set at 250° F. and the third zone was set at 350°.

2. The first zone and the last zone were set at 250° and the middle zone at 350°.

FIGURE I
COATING NO 1 HIGH
SHEAR RHEOGRAM



Description ________________

________ % T.S. ________

Speed factor 2200, Bob E, Torque 100,000

Temp. ____ °C., pH, Initial ____, 1 hour ____

Brookfield viscosity ____ @ ________ r.p.m.
(Spindle no. ___) ____ @ ________ r.p.m.

High shear viscosity ____ @ ________ r.p.m.
____ @ ________ r.p.m.

Hysteresis: ____ @ ____ r.p.m., B/A: ________

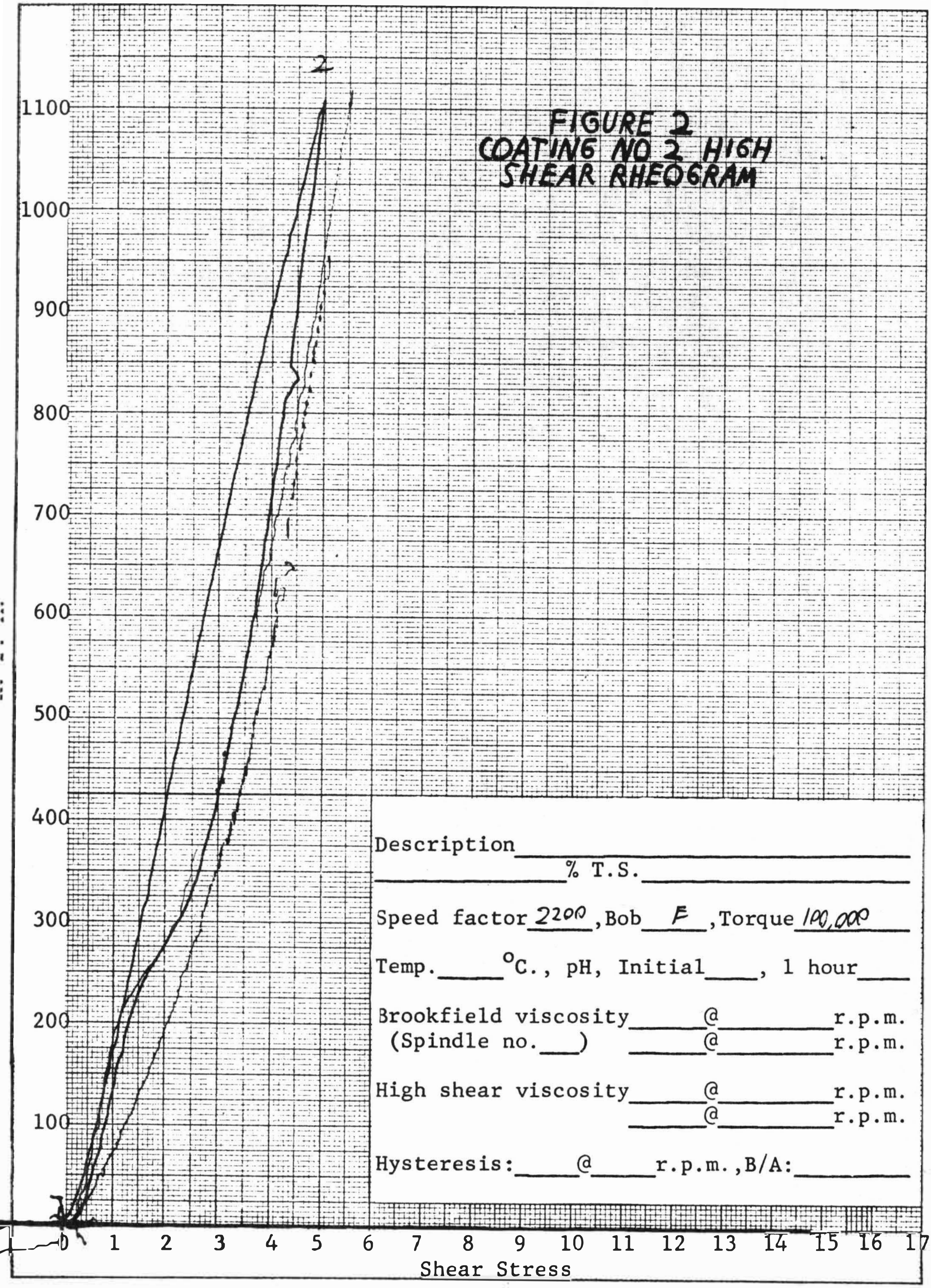


FIGURE 2
COATING NO 2 HIGH
SHEAR RHEOGRAM

Description____________________________________

_______________% T.S.________________________

Speed factor 2200, Bob F, Torque 100,000

Temp._____°C., pH, Initial____, 1 hour____

Brookfield viscosity_____@________r.p.m.
(Spindle no.___) _____@________r.p.m.

High shear viscosity_____@________r.p.m.
_____@________r.p.m.

Hysteresis:_____@_____r.p.m.,B/A:_________

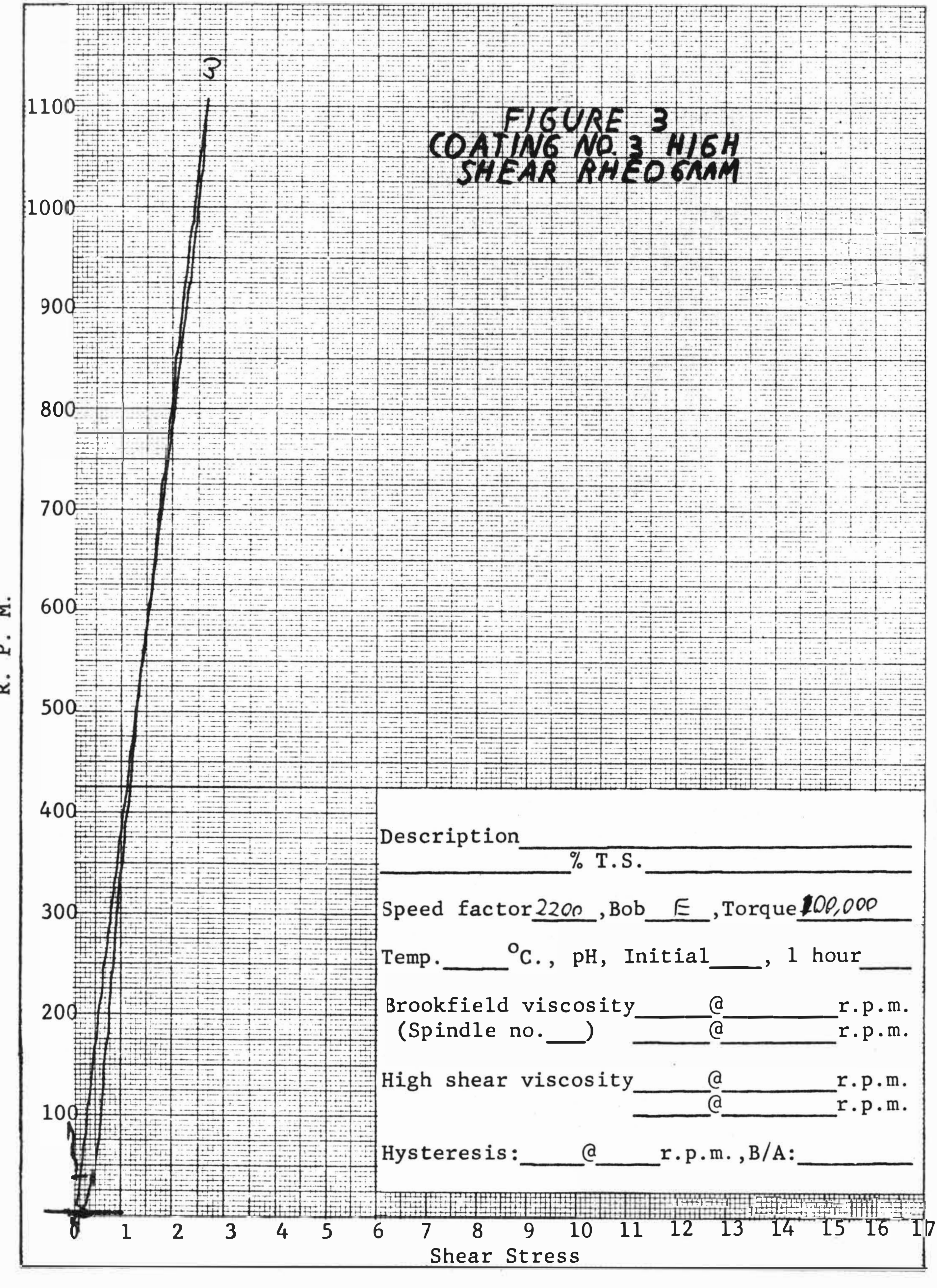


FIGURE 3
COATING NO. 3 HIGH
SHEAR RHEOGRAM

Description_________________________

________________% T.S.______________________

Speed factor 2200, Bob E, Torque 100,000

Temp._____ °C., pH, Initial____, 1 hour____

Brookfield viscosity_____@_________r.p.m.
(Spindle no.___) _____@_________r.p.m.

High shear viscosity_____@_________r.p.m.
_____@_________r.p.m.

Hysteresis:_____@_____r.p.m.,B/A:_________

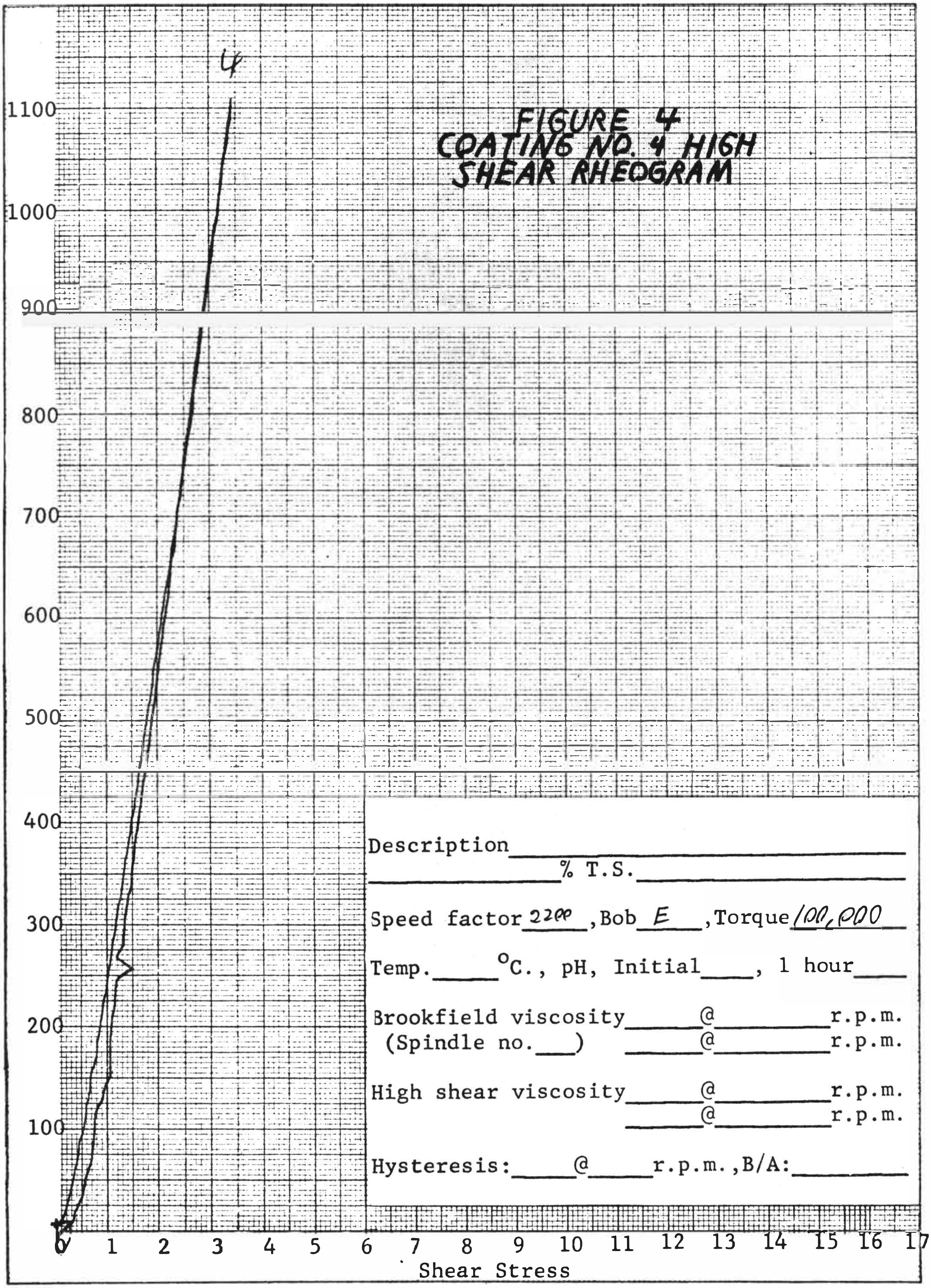


FIGURE 4
COATING NO. 4 HIGH
SHEAR RHEOGRAM

Description ____________________

____________ % T.S. ____________

Speed factor 2200, Bob E, Torque 100,000

Temp. _____ °C., pH, Initial ____, 1 hour ____

Brookfield viscosity _____ @ ________ r.p.m.
(Spindle no. ___) _____ @ ________ r.p.m.

High shear viscosity _____ @ ________ r.p.m.
_____ @ ________ r.p.m.

Hysteresis: _____ @ _____ r.p.m., B/A: ________

3. The first zone was set at 350°, and the other two zones at 250°.

4. The infra-red unit was placed between the air-knife and the dryer tunnel and was used as the fourth drying condition with the other three zones turned off.

Preparing Samples for Testing

The coating rolls were slabbed down and samples were taken of the five different coating combinations:

1. Semi-mechanical base stock; acrylic latex with no alginate
2. Semi-mechanical base stock; acrylic latex with alginate
3. Semi-mechanical base stock; butadiene acrylonitrile without alginate
4. Semi-mechanical base stock; butadience acrylonitrile with alginate
5. Latex impregnated stock; acrylic latex with alginate

At this time, it was noticed that sample #5 was mottled and not suitable for further analysis, and this sample was discarded.

A variety of printing tests was run as follows:

1. Tappi brightness
2. K & N glass ink holdout
3. IGT pick test
4. Tappi opacity
5. Ash coat weights

Another set of samples was prepared for testing in the Perkins-Elmer multiple internal spectrascope. These samples were super-calendered at 2000 pli to get better contact between our testing apparatus and the sheets, and cut into 1½" x 9/16" samples. Each sample was then placed in the sample holder of the Perkins-Elmer spectrascope and a multiple internal reflectance reading was made. It was noted at this time that the butadiene acrylonitrile latex did not give a clear infra-red band, and sample coatings 3 and 4 were discarded. Samples 1 and 2, however, gave a good infra-red band, and these samples are the ones on which the final tests and analyses were run.

Next, samples were prepared for the internal measurement of migration. This was done by using the same super-calendered samples and grinding away the coating at different depths with reference to the surface. (See Appendix A for sketch.) Depths of grinding were from 2/10,000" to 16/10,000" at increments of 2/10,000" each. At grinding, the sheets were held to a flat steel surface by means of a vacuum and the grinding wheel was lowered to obtain the different depths. The machine was a standard toolmakers' surface grinder, and the wheel a 60-grit aluminum oxide wheel dressed with a diamond dresser.

Sixty-four samples were prepared, eight for each of the four coating zones, multiplied by the two different coatings. These were then tested in the Perkins-Elmer for internal migration.

From previous work with the Perkins-Elmer,[16] a calibration curve was made, giving percent acrylic latex from 0% to 50%, based on the amount of clay in the coating.

Measurement of Graphs

A method of measuring from the infra-red reading had to be devised to eliminate as much mechanical and human error as possible between readings. To do this, extinction coefficients were computed of both clay and latex. The extinction coefficient of the latex, divided by the extinction coefficient of the clay, gave a number less than 1, which was read against the calibration curve so that the percent latex could be determined. Further detail is available in Appendix B.

EXPERIMENTAL FINDINGS

Advantages of Adding Alginates to Clay Coatings

It was expected that the addition of alginate would increase the viscosity of the clay coating. (See Fig. 1, Fig. 2) Therefore, the air-knife pressure had to be raised accordingly to compensate for the higher viscosity, from 1.25 psi to 1.75 psi.

The standard Tappi tests were run, and these indicated that the alginate additive did control migration to an appreciable extent. Because a poor choice of base stock had been made, it was impossible to run a successful pick test as the base stock failed before the coating did. The results of the other tests are as follows:

Brightness

Alginate tended to increase the brightness of the sheet (see Fig. 5) by an average of 2.5 points.

K and N Gloss Ink Holdout

The alginate decreased the amount of ink absorbed into the sheet as compared to coatings without alginate. This became more pronounced as the time between the application and drying of the coating increased.

Opacity

Opacity stayed much the same in both instances, due to the fact that samples with and without alginate contained the same amounts of clay and fiber. Therefore, it is expected that opacity would remain constant.

The above results can be attributed, at least in part, to deflocculation and coating porosity. It can be assumed that sodium alginate gave closer pigment packing and produced and maintained a higher degree of pigment deflocculation than the coating without alginate.

In addition, alginates have a tendency to keep migration constant through different drying conditions, whereas variation in drying conditions in coatings without alginates causes drastic change in migration. (See Figs. 8, 9, 10, 11) It is likely that coatings with alginate require a longer drying time to set completely, and therefore migration is apt to be constant under a variety of drying conditions due to the fact that alginates produce a more stable homoginization of the various ingredients in the coating.

Our results also indicate that coatings without alginate tend to have relatively more binder at the surface and internally in the sheet than at the coating and base stock interface. In other words, the binder tends to form a sandwich with a filling of clay. Upon the addition of alginate, the binder is found to be homogenized throughout the coating. This, of course, explains the decrease in the amount of ink absorption. (See Fig. 6)

Had our base stock held up, it could be expected that a higher pick number would be obtained as a result of the addition of alginate to the coating because more binder throughout the coating would yield a stronger coating-to-base-stock interface.

Accuracy of Migration Measurement Method

As stated before, the extinction coefficient measuring method was adopted in order to minimize as much as possible both human and mechanical error. Even so, error still was a factor in determining the amount of coating in the sheet. For instance, it was found that readings would vary slightly in absolute percent acrylic latex in the coating from one day to the next. (See Figs. 11, 12) The reading in Fig. 12 was made 3 days after the reading in Fig. 11, and though the curves are relatively the same, the calibration varies somewhat. As experience was gained, it became evident that the positioning of the mirrors and crystal were crucial to obtaining constant values.

Even though absolute percentages may vary from day to day, it was found that the over-all trends were consistent. To minimize further the possibility of error, a new calibration curve for percent acrylic was made each time a series of samples was to be run. This calibration curve is linear with respect to percent acrylic vs. the extinction coefficient.

Of all methods cited in the literature, this method is the most adaptable to use by the industry because production coatings can be measured without the need for special coating and measuring devices. Migration can be measured after the coating is dried. Ease of testing and immediate results also enhance the practicability of this method.

FIGURE 5

BRIGHTNESS

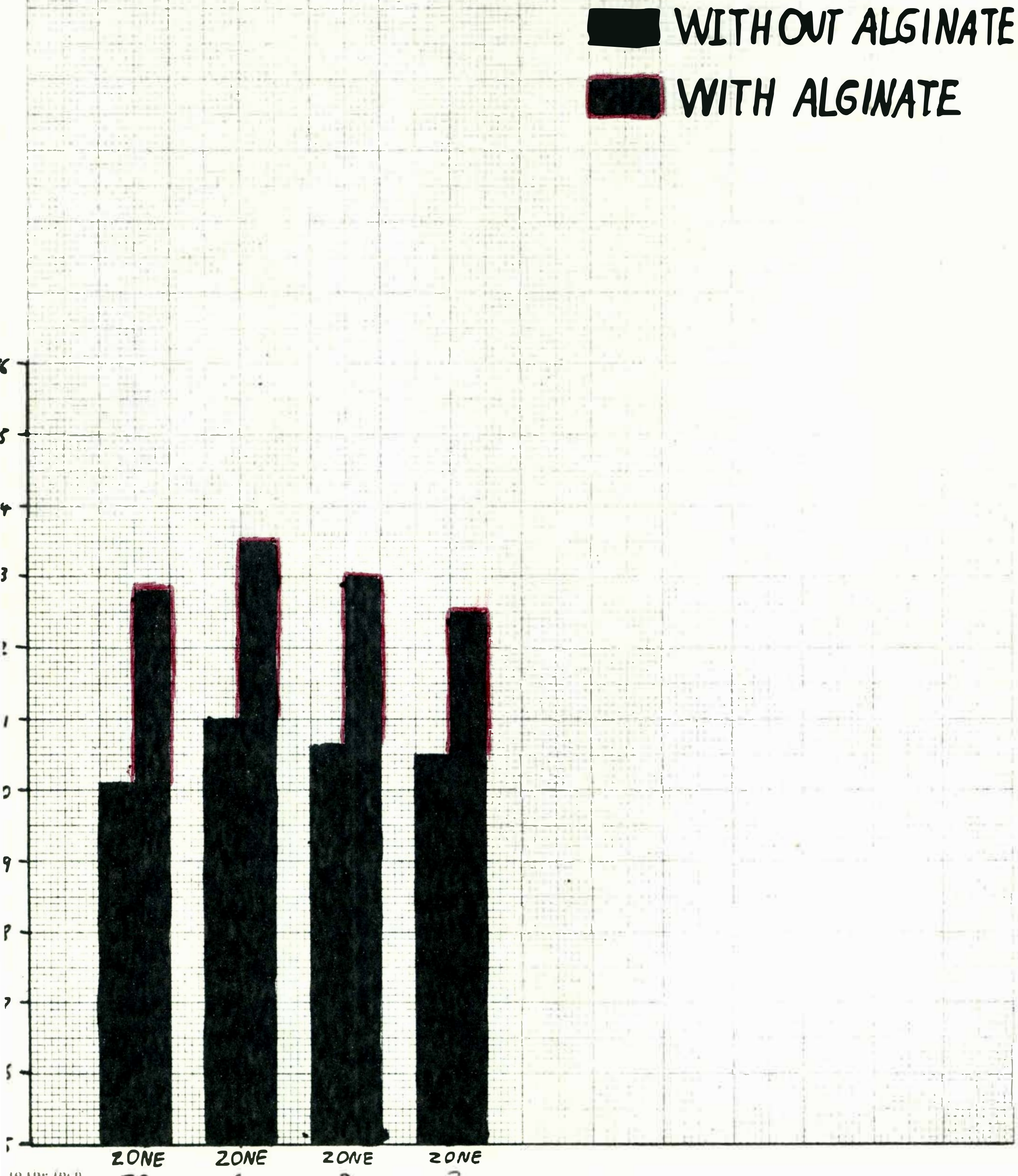


FIGURE 6

K AND N GLOSS INK HOLD OUT

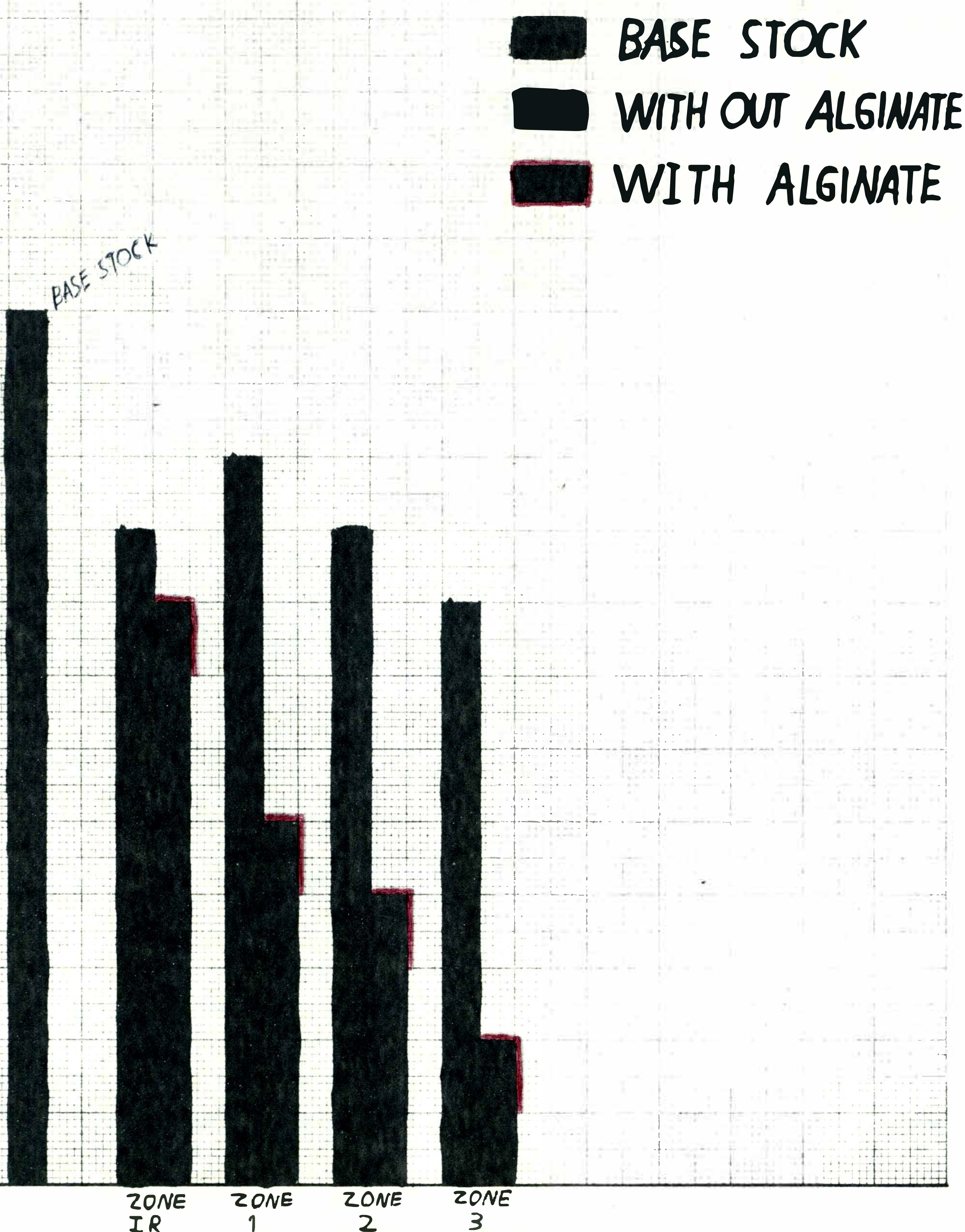


FIGURE 7

OPACITY

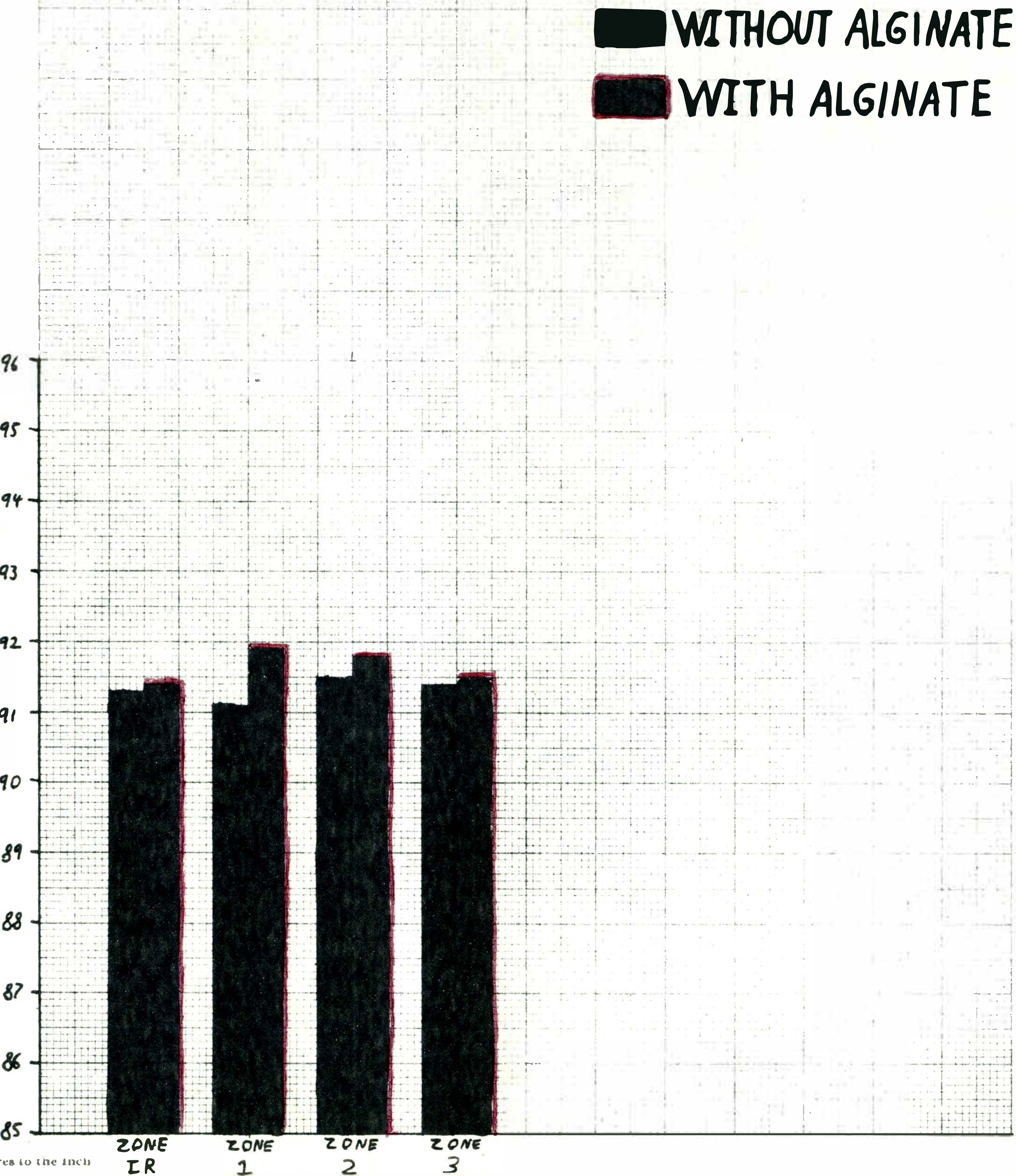


FIGURE 8

% ACRYLIC TO CLAY vs. DEPTH

IR ZONE

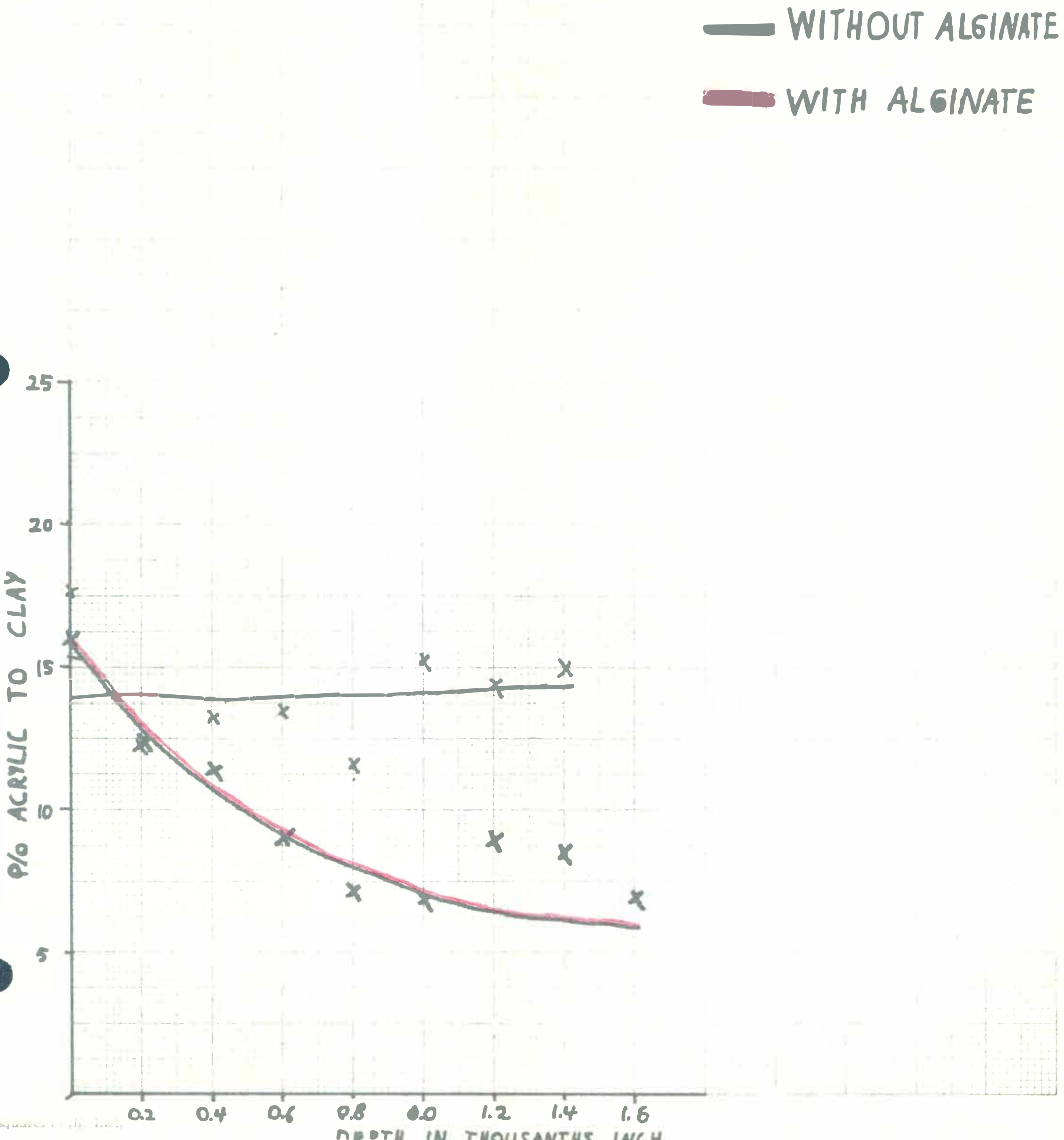


FIGURE 9

% ACRYLIC TO CLAY vs. DEPTH

ZONE 1

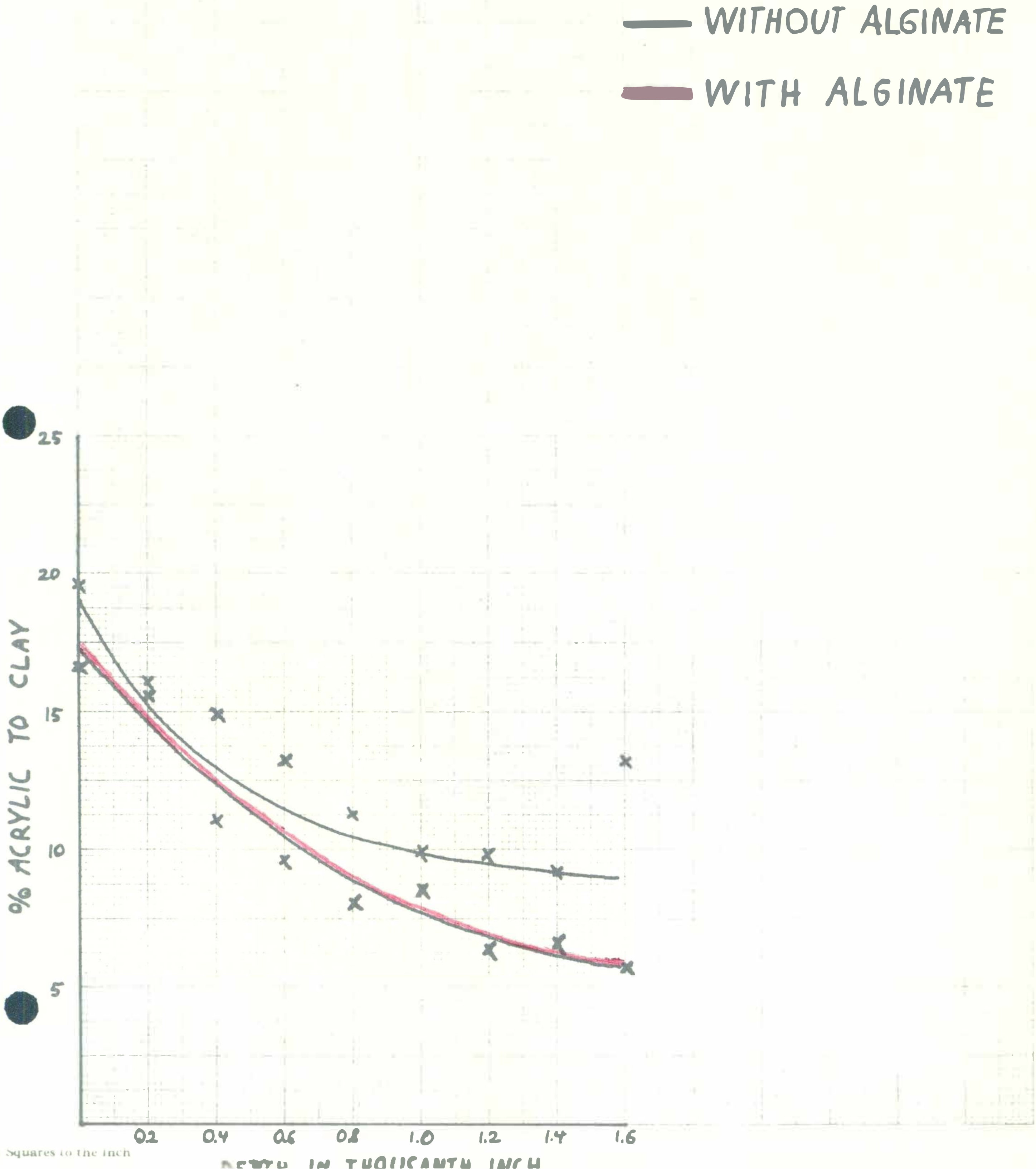


FIGURE 10

% ACRYLIC TO CLAY vs. DEPTH

ZONE 2

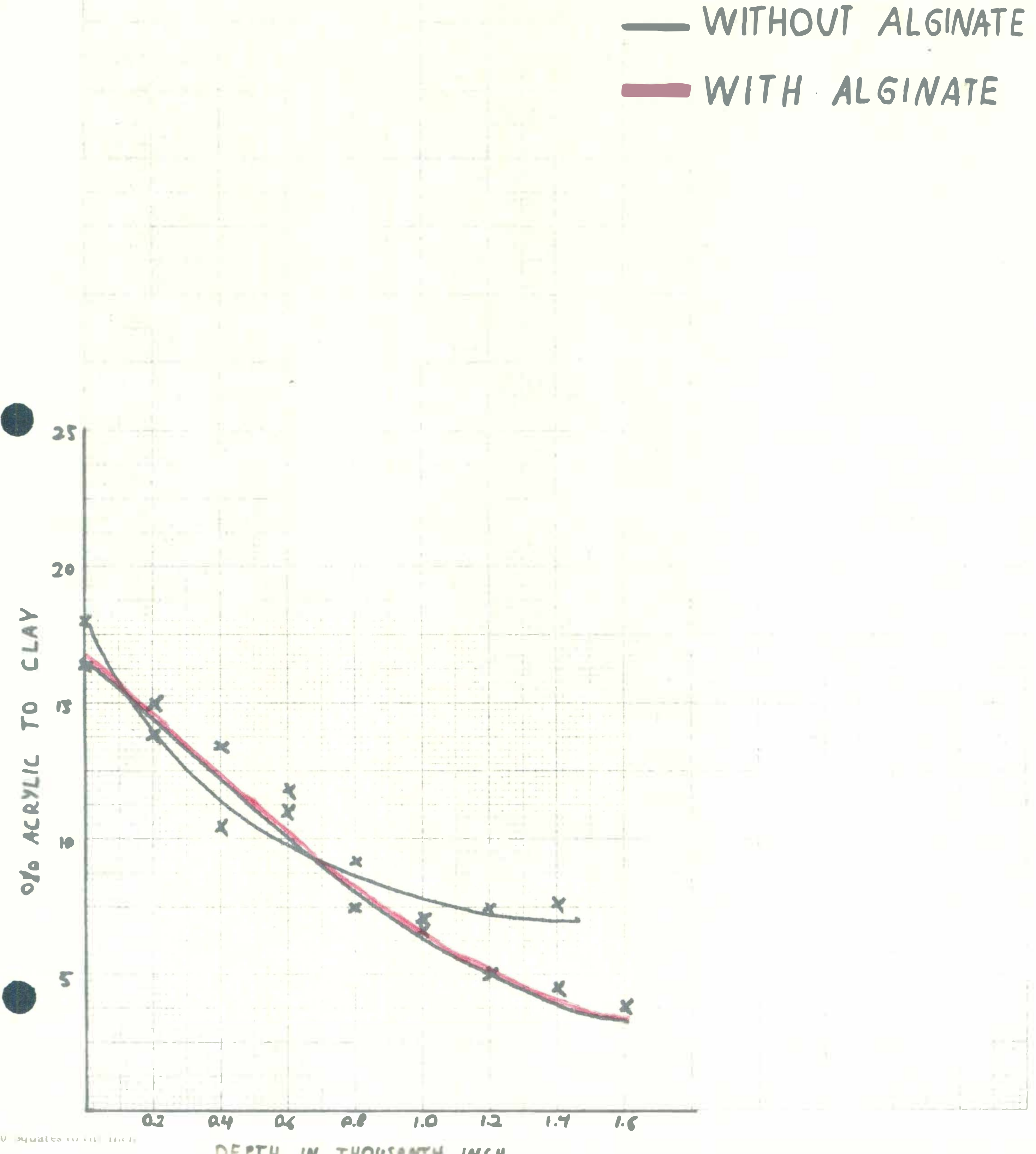


FIGURE 11

% ACRYLIC TO CLAY vs. DEPTH

ZONE 3

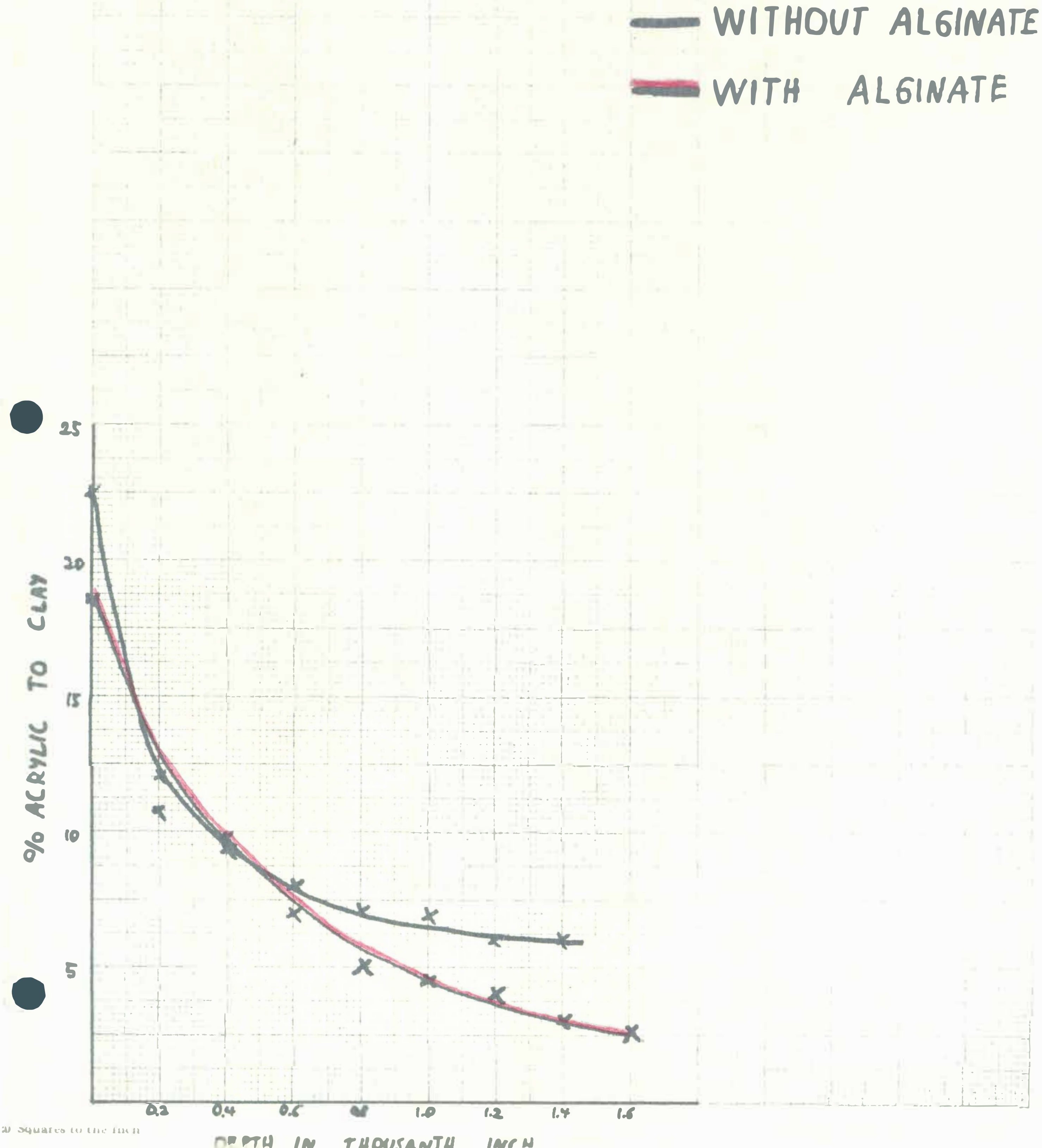
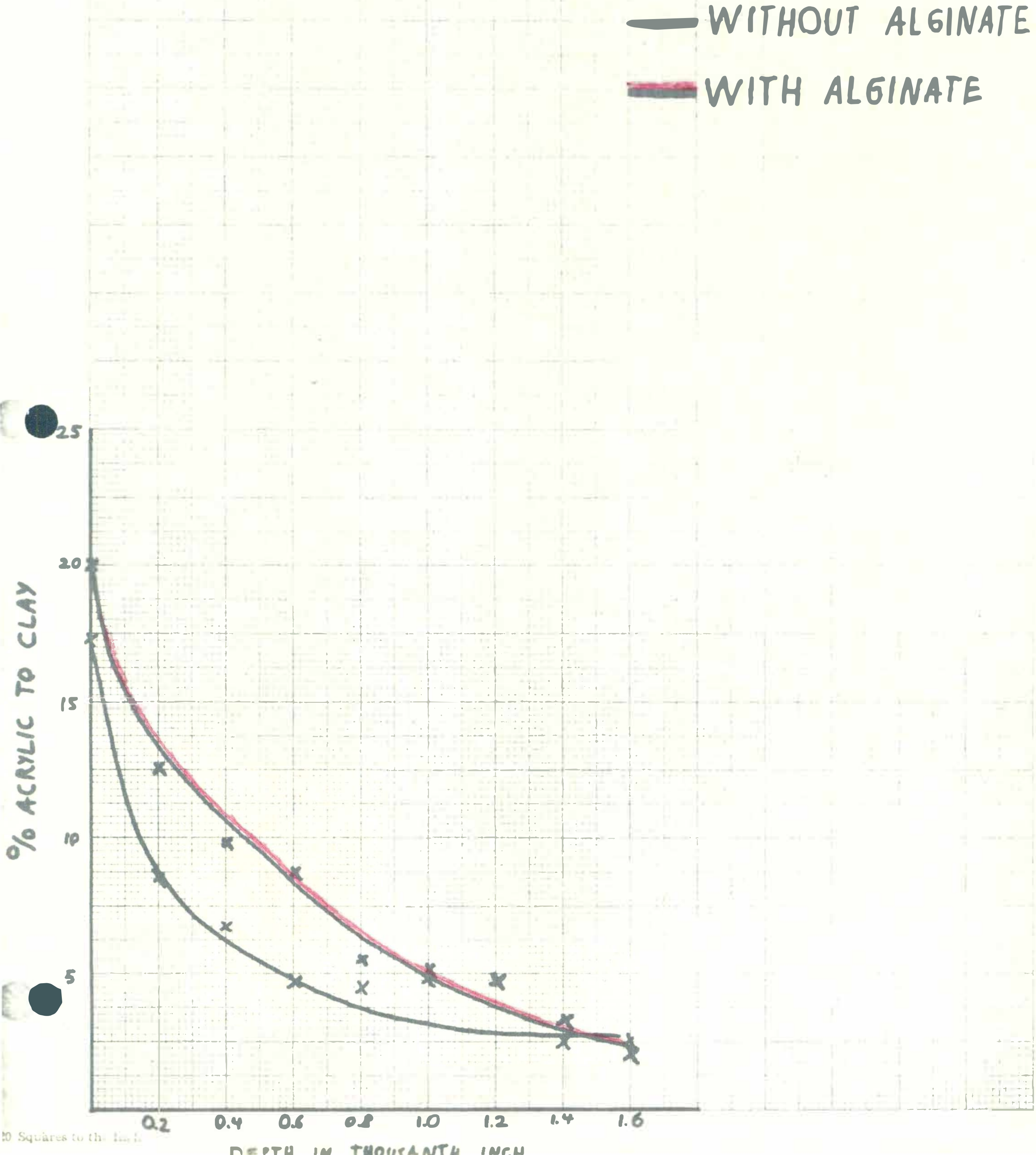


FIGURE 12

% ACRYLIC TO CLAY vs. DEPTH

ZONE 3



SUGGESTIONS FOR FURTHER RESEARCH AND CONCLUSIONS

Facilities available were inappropriate for testing the use of alginates with different binders. It is possible that the addition of alginates to such binders as styrene buta-diene and possibly starch or casine along with many other latex binders currently on the market would be fruitful subjects for further testing. The major benefit derived from the use of alginates in the paper industry is that higher solids and faster speeds can be run with blade coaters. Due to lack of time, this characteristic of alginate additives was not investigated as it seemed more beneficial to devise ways of measuring migration. This area, however, should be investigated more fully, since there is no doubt that binder coating migration plays a significant part in the application properties of the coating.

Possibly it would be instructive to test coatings with varying amounts of alginate additive with respect to runability and coating properties.

It would also be of significant value if a way of obtaining better contact between the measuring sheet and the crystal could be devised for the Perkins-Elmer infra-red spectrometer. This would not only increase the accuracy of the machine, but would also enable us to test a variety of substances in the coatings.

In conclusion, first, if this study were to be run again, it would be beneficial to make sure that a stronger base stock, possibly one that had been super-calendered before the test coatings were applied, was used. It would also be desirable to include a number of coating make-ups in the study, as discussed above.

In general, even with the above defects in method, it can be concluded that the perkins-Elmer is an excellent device with which to obtain an accurate analysis of migration. In addition, now that latex binders are becoming a major ingredient in industrial coatings and the cost of starch has risen, the increased use of alginate additives is clearly beneficial to the industry. It is evident that, with their use, coatings require less dilution with water which saves drying time and energy; higher coating speeds are feasible; and migration is beneficially influenced so as to produce a product of higher quality.

BIBLIOGRAPHY

1. Barber, E. J. Effect of Hydrocolloids on Coating Color Operability and Coated Paper Properties. TAPPI, 56 No. 1; 52-5. January 1973.

2. Beazley, K. M. and Climpson, Margaret. Liquid Migration From Coating Colors. I. Correlation Between Electrical and Optical Measurements. TAPPI, No. 12, 2232-6, December 1970.

3. Blood, C. T.; Hilton, K.A. Alginates Improve Blade Coating. PULP PAPER INTERN. 9, No. 4; 90. April 1967.

4. Bohmer, E; Lute, J. Adhesive Migration and Water Retention With Reference to Blade Coating. SVENSK PAPPERSTID, 69, No. 18; 610-18. September 30, 1966.

5. Cerma, E.; Baradel, P.; Lokar, A. Rapid Determination of the Average Viscometric Molecular Weight of Alginates By Viscosity Measurements of One Percent Solutions. RASS. CHIM., 22 No. 1; 3-8. Jan./Feb. 1970

6. Clark, N. O.; Windle, W.; Beazley, K. M. Liquid Migration in Blade Coating. TAPPI, 52, No. 11; 2191-2202. November 1969.

7. Dobromyslova, G. A.; Kazakova, A. A.; Kin'kov, P. I. Reducing the Migration of Latex in Bonded Nonwovens. TEKSTIL. PROM., 30 No. 8; 63-4. August 1970.

8. Dyck, A. W. J. Focus on Paper Coating. AM. PAPER IND., 51, No. 7; 14-16. July 1969.

9. Fairchild, W. P.; Kelco Co. Paper-Coating Compositions and Processes. U. S. pat. 3,351,479. Issued Nov. 7, 1967.

10. Fairchild, W P.; Robison, J. E. Controlling Migration in Paper and Board Coatings. INVEST. TEC. PAPER. S No. 15; 53-72. January 1968.

11. Hiemstra, Pieter; Vandermeeren, Joseph. Coatings for Offset Printing Made With Different Adhesives. TAPPI 52, No. 2; 263-9. February 1969.

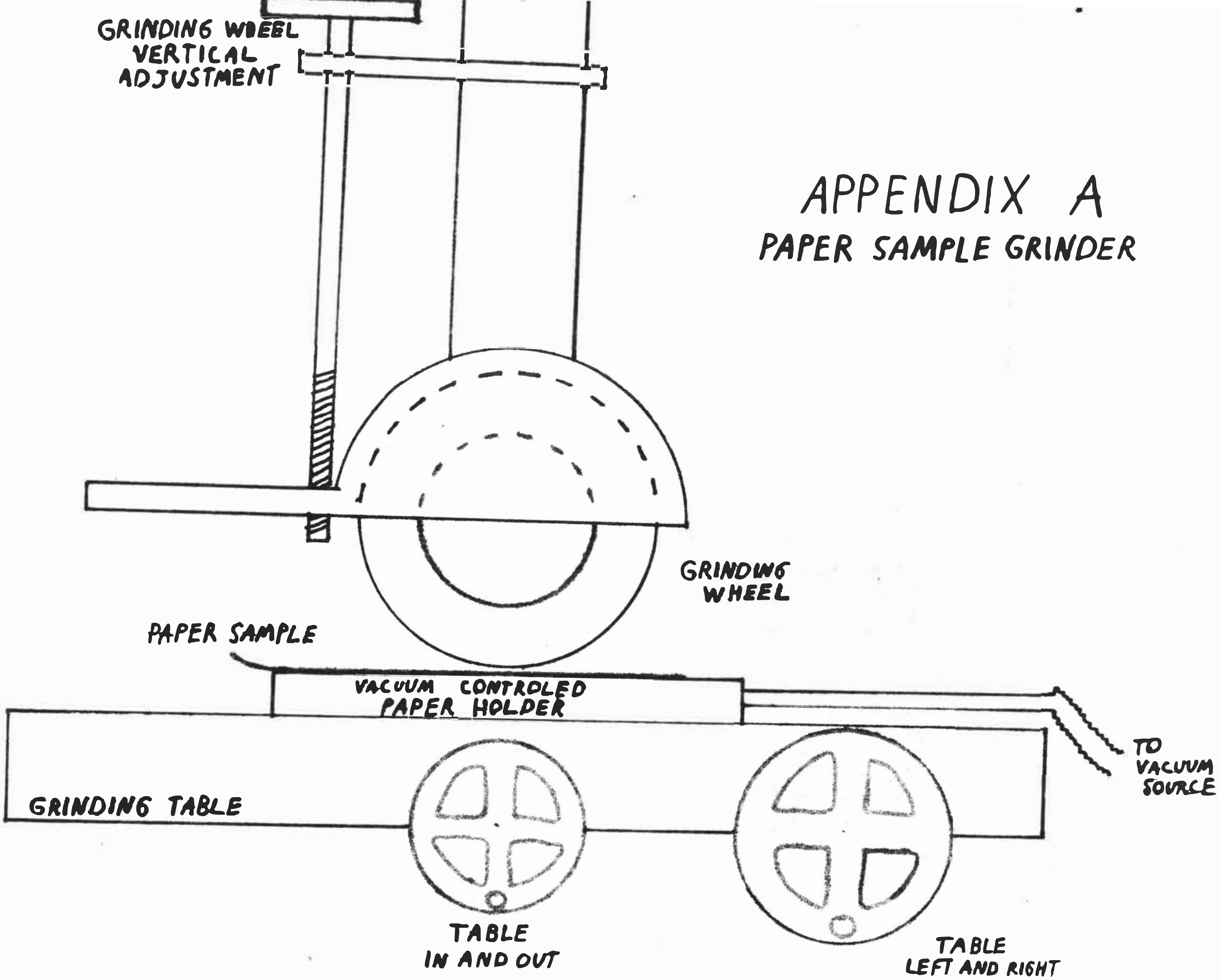
12. Ogaard, E. A. H. Alginates in the Paper Industry. DEUT. PAPIERWIRTSCH, No. 7; 32-4, 36, 38. 1966.

13. Smidsrød, Olav. Solution Properties of Alginate. NORWEGIAN INSTITUTE OF SEAWEED RESEARCH, N. T. H., Trondheim, Norway. (Received October 17, 1969.)

14. Society of Chemical Industry. Chemistry and Rheology of Water-Soluble Gums and Colloids. Read March 28, 1966. London Soc. of Chem. Ind. (S. C. I. Monograph No. 24), 1966, 131 pp.

15. Windle, W.; Beazley, K. M. and Climpson, Margaret. Liquid Migration From Coating Colors. II. The Mechanism of Migration. TAPPI No. 12; 2232-6, December 1970.

APPENDIX A
PAPER SAMPLE GRINDER



APPENDIX B
% ACRYLIC LATEX CALCULATIONS

% LATEX TO CLAY = $kC_o = \left(\frac{\mathrm{Ln}\, I_A - \mathrm{Ln}\, I_o}{\mathrm{Ln}\, I_c - \mathrm{Ln}\, I_o}\right)k$

$$C_o = \frac{\mathrm{Ln}\frac{I_A}{I_o}}{\mathrm{Ln}\frac{I_c}{I_o}}$$

$$E_A = \mathrm{Ln}\frac{I_A}{I_A}$$

$$E_c = \mathrm{Ln}\frac{I_c}{I_o}$$

I_A, I_c, AND I_o FROM IR READ-OUT, NEXT PAGE

$$C_o = \frac{E_A}{E_o}$$

% LATEX = kC_o

k IS A CONSTANT FROM THE SLOPE OF THE CALIBRATION CURVE MADE WITH 0 TO 50% LATEX SAMPLES

PERKIN-ELMER
MODEL 700

REMARKS
2Z 3
.0002

% C = .307

ORIGIN
PURITY
PHASE
CONCENTRATION
THICKNESS .0002 cut out
DATE 4/8/75
OPERATOR

SPECTRUM NO.
SAMPLE 1
SAMPLE 2

SAMPLE

SPECTRUM NO.