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# Rheology of Coating Adhesives

Ryan A. Smith
*Western Michigan University*

# RHEOLOGY OF COATING ADHESIVES

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RYAN A. SMITH


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# ABSTRACT

Many compounds, "flow modifiers", have been used to change the flow properties of coating adhesives. Thiourea, ammonium thiocyanate,and urea were used in this work to find out what effect they would have on the coating adhesives, starch and alpha protein. It was found that they all lowered the viscosity a great deal. Also it was found that the resulting flow curve in most cases was pseudoplastic.

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## INTRODUCTION

High speed on the machine coating has made it necessary for the paper coater to increase the per cent solids of the coating color. One of the best means of doing this is to change the flow properties of the coating adhesive to allow an increase in the solids content of the coating color to be made. There are many types of flow modifiers now being used and being tried on experimental coating colors.

Before any attempt can be made to describe the effect of the various flow modifiers on adhesives used in the preparation of coating colors it is important for one to understand the different types of flow, and why knowledge of the type of flow is important.

Rheology is the science of the deformation and flow of matter. There are many types of flow. Those of importance to the paper coater include Newtonian, plastic, pseudoplastic, dilatant, and thixotropy.

## TYPES OF FLOW

One of the first men to apply physical considerations to the flow of liquids was Sir Isaac Newton(1). The Newton model of flow consists of two parallel plates with the space between them filled with the test liquid. A tangential shearing stress, F, is applied to the top plate which then moves with respect to the bottom plate and carries with it innumerable parallel planes of the test liquid. The top plane moves the greatest distance and the bottom plane remains stationary. If v is the velocity of the top plane and r is the distance between the top and the bottom planes, then $\frac{dv}{dr}$ is the velocity gradient or rate of shear. For a constant value of F, $\frac{dv}{dr}$ must be constant throughout the test material. Newton assumed that the shearing stress per unit area, F, was directly proportional to the rate of shear as shown in equation 1:

$$F = n \frac{dv}{dr} \qquad (1)$$

where the proportionally constant, n, is the coefficient of viscosity which is defined as the tangential shearing force per unit area that will induce a unit rate of shear.

Another type of system which exhibits flow is one known as a plastic of which a clay-water suspension is typical. In such a system flow will start once a sufficient shearing stress has been exerted upon it to overcome the internal resistance to flow. The stress necessary to initiate flow is the yield value, f. Once such a system begins to flow, it proceeds linearly as in Newtonian flow. Equation 2 describes plastic flow:

$$F - f = n\frac{dv}{dr} \qquad (2)$$

A third type of flow, pseudoplastic, is characterized by a nonlinear flow curve where the rate of shear increases more rapidly than the shearing stress and where there is no yield value. This type of flow is described by equation 3;

$$\frac{dv}{dr} = ae^{b \ln F} \qquad (3)$$

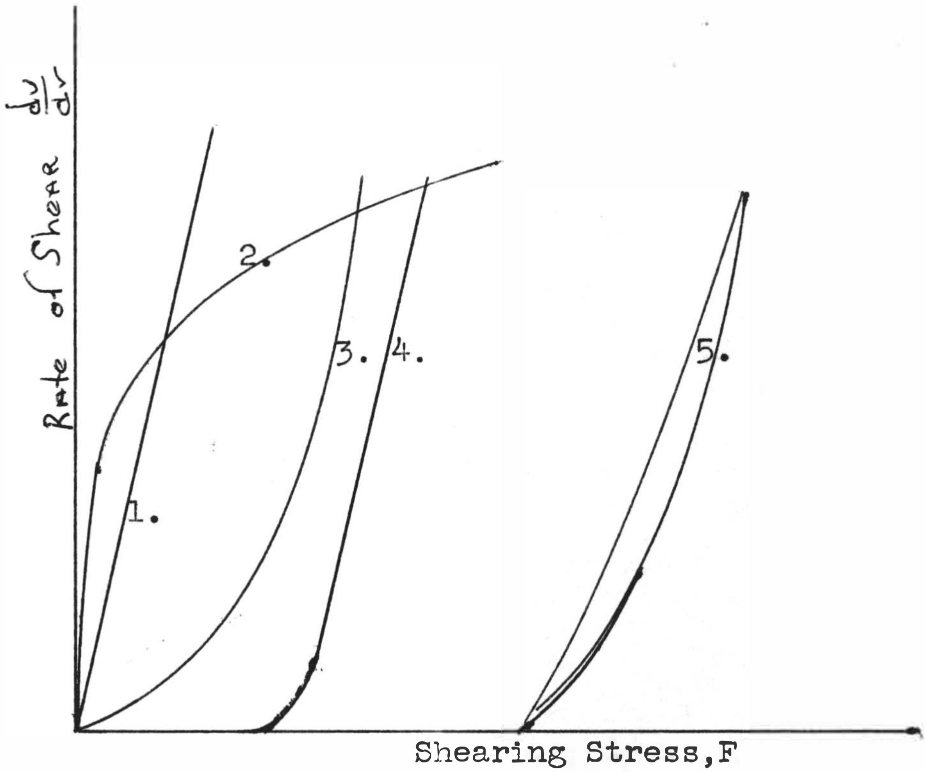
an example of this type of flow is a dispersion of high polymers such as casein.

Dilatant flow is characterized by a nonlinear flow curve where large increases in the shearing stress are required to produce small increases in the rate of shear. High solids, closely packed pigment dispersions exhibit dilatant flow.

Thixotropic systems give nonlinear flow curves where the rate of shear increases more rapidly than the shearing stress as the shearing stress is increased. Once the structure of the system has been broken, the flow curve will conform to either that of a plastic or pseudoplastic system and will require less shearing stress to produce a unit change in the rate of shear than orginally. Thus if a plot is obtained of the rate of shear versus the shearing stress from minimum to maximum and back to minimum shearing stress, an hysteresis loop is obtained. This breakdown in structure can best be explained as a liquidation of a gel to form a sol when the stress is applied and when the stress is released, the sol will revert to a gel (1).

The graph on the following page shows the flow curve obtained on a rotational type viscometer for the types of flow described above.

It has been shown (1) that some materials exhibiting Newtonian flow at low rates of shear give nonlinear flow curves when the rate of shear is sufficiently high. Most, if not all, coating colors give nonlinear flow curves. Because the rate of shear on the coating color when used with on the machine coating is high, it is important for the paper coater to use a viscometer that is able to apply a high rate of shear to the coating color.




TYPES OF FLOW
1. Newtonian
2. Dilatant
3. Pseudoplastic
4. Plastic
5. Thixotropic

## TYPES OF VISCOMETERS

There are many different test used to control coating colors in the mill. They include a determination of per cent solids, a measure of viscosity, and, of course, visual inspection of the finished sheet. There are over 25 different methods (2) of estimating viscosity and these use over 100 different modifications of viscometers. The most common viscometers, and they are the ones to be used in this thesis, include the Stormer, Brookfield. Hercules, and Mac Michael. They are all concentric cylinder type with the exception of the Brookfield. The Mac Michael and Hercules measure the amount of torque transmitted by the coating color while varying rates of shear are applied. The Stormer measures the time required for a certain number of revolutions when the material is sheared under a constant load is measured. A direct viscosity reading can be obtained by using the Brookfield.

However, due to the high shearing rate applied to paper at high speed on the machine coaters, attempts have been made to increase the rate of shear in the viscometer. This is in order to more closely simulate the conditions at the nip.

## FLOW MODIFIERS USED ON COATING ADHESIVES

There have been a number of different compounds used to modify the flow characteristics of a coating adhesive. Sodium sequisilicate, urea, dicyandiamide, acetamide, thiocyanates, latices, and other compounds have been used to alter the flow of a coating adhesive.

The use of urea (4), (6) as a fluidifying agent for paper coating adhesives appears attractive for the following reasons:

1. Small amounts of urea are required for large reductions in viscosity.
2. It has a stabilizing effect on the coating adhesive.
3. Solubility of urea makes its addition to high solids adhesive dispersions simple.

Urea is cheap and very plentiful.

Dicandiamide has been found to be an effective stabilizer on the viscosity of starch adhesives. It will also reduce the viscosity of the starch adhesive a great deal(4).

The use of sodium sequisilicate as a flow modifier can be used to great advantage with casein. With the proper amount of sodium sequisilicate the apparent viscosity can be modified to less than 30 per cent of the unmodified color (3) In addition, the solids content can be increased to more than 65 per cent. Colors modified with sodium sequisilicate are usually pseudoplastic.

Latices have often been used to modify the flow of coating adhesives. Dow Latex 512-R has been studied in great detail by Jahn (5). The conclusions reached in this experiment included that 512-R is a valuable modifier for casein, alpha protein, and starch bound coatings. This is due to the fact that its initial viscosity is lower than that of the adhesive , and partially substituting 512-R for the adhesive will result is a lower final viscosity.

There are many variables that one encounters when working with flow modifiers. The per cent of the flow modifier that is added to the adhesive has a very definite affect of the final viscosity. It is usually found that there is an upper limit to the amount that is economically wise to add. Beyond this point there is a small viscosity change in relation to the amount added. The effectiveness of the modifier can be influenced by its order of addition to the adhesive, adding either before cooking the adhesive or after cooking (3).

The final viscostiy that will result from the addition of the flow modifier will be due to a large degree to the type of viscometer used (2). The rate of shearing has a large effect on the final viscosity, as has been mentioned before, and the resultant type of flow will largely depend on the viscometer used.

## LITERATURE CITED

1. TAPPI Monograph-11, Preparation of Paper Coating Colors, TAPPI. (1953)

2. Chase, R. C., and Gorham, J. F., Some of the Variables Affecting Flow Properties of Paper Coating Colors. TAPPI. (Aug 1956) vol 39 #8.

3. Smith, J., Terlfe, R.T., and Ware, H., Casein Adhesives in Roll Coating, TAPPI. (May 1950) vol 33 #5.

4. Ritson, D. D., Landes, C. G., Use of Dicyandiamide in Paper Coatings, TAPPI. (May 1955) vol39 #5

5. Jahn, R.G., Effect of Dow Latex 512-R on the Rheological Properties of Casein, Alpha Protein, and Starch Bound Clay Coatings, TAPPI. (Oct 1956) vol 39 #10

6. Belihe, J.R.Jr., and Ellis, G.C., Viscosity Control of Paper Coating Adhesives with Urea., TAPPI (Feb 1957) vol 40 #2

## EXPERIMENTAL DESIGN

The adhesives to be tested were cooked in the following manner;

STARCH- Stayco M starch was used, being cooked at 40 per cent solids. The flow modifier was added as a percentage of dry adhesive, and was added in the following percentages, 0%, 5%, 10%, and 25%. The starch was heated to 85°C and cooked for 15 minutes. It was then colled to room temperature and the viscosity determined.

ALPHA PROTEIN- Alpha Protein was cooked at 18.18 per cent solids. The flow modifier was added as a percentage of dry adhesive, and was added in the following percentages, 0%, 5%, 10%, and 25%. The protein was soaked for 15 minutes before a cutting agent was added. The protein was cut with 10% $NH_3$ based on the weight of the protein. It was then heated to 58°C and cooked for one hour. The protein was cooled to room temperature and the viscosity determined.

The viscosity of the adhesives was determined with a Stormer and Brookfield viscometer. The directions with the instrument were followed in determining the viscosity.

## RESULTS

The results from this thesis are presented on the following 12 graphs. The object of this thesis was to determine the type of curve we can obtain with a certain combination a flow modifier and adhesive. The degree of reduction of the viscosity of the adhesive was also to be noted.

The graphs obtained with the Stormer are plots of the driving force ( X axis) versus the Revolutions Per Minute on the Y axis.

With the Brookfield, the Revolutions Per Minute was plotted versus the reading on the 100 scale on the Brookfield. One spindle was used on a certain combination of adhesive and flow modifier.

FIGURE 1.

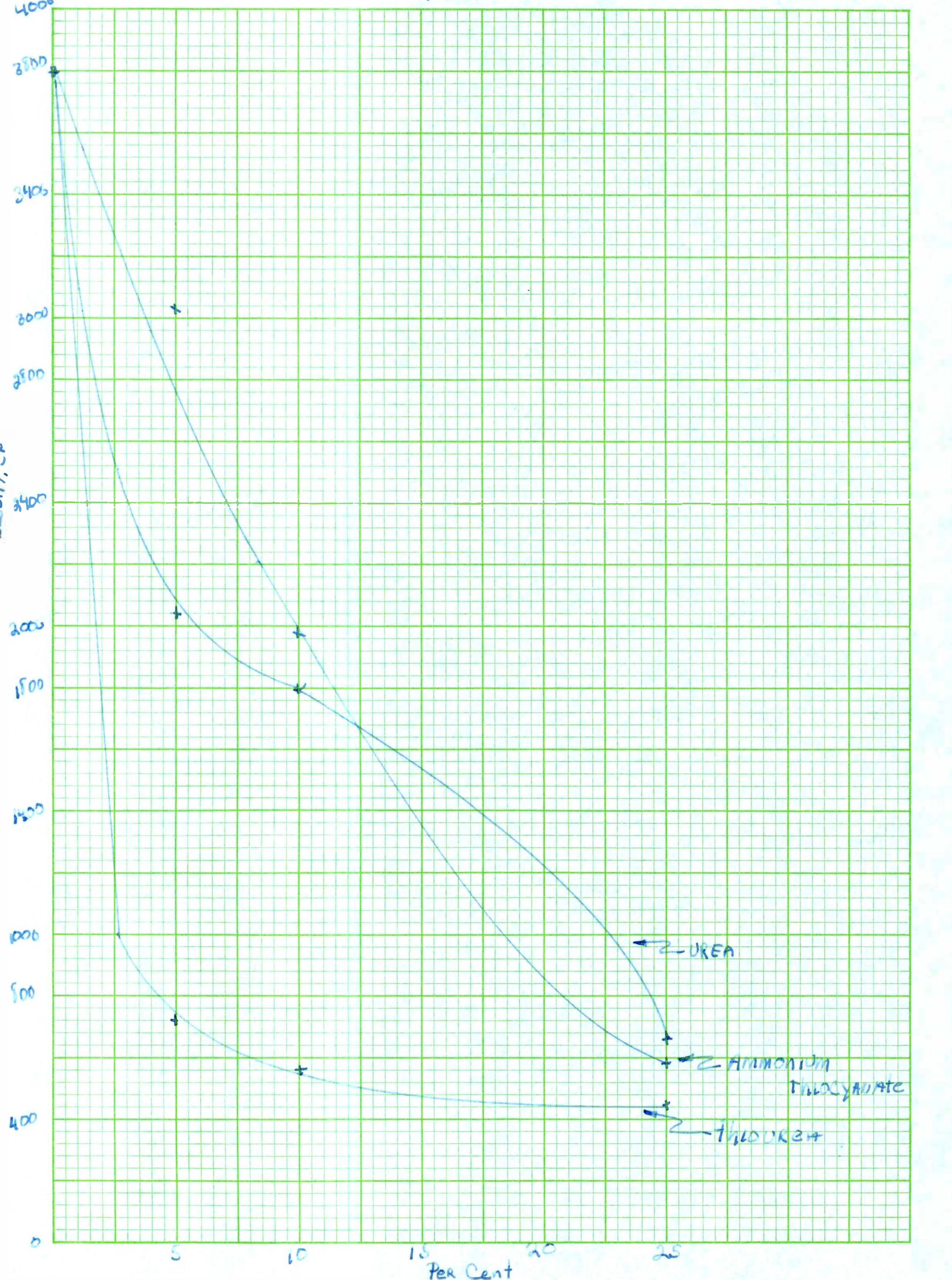
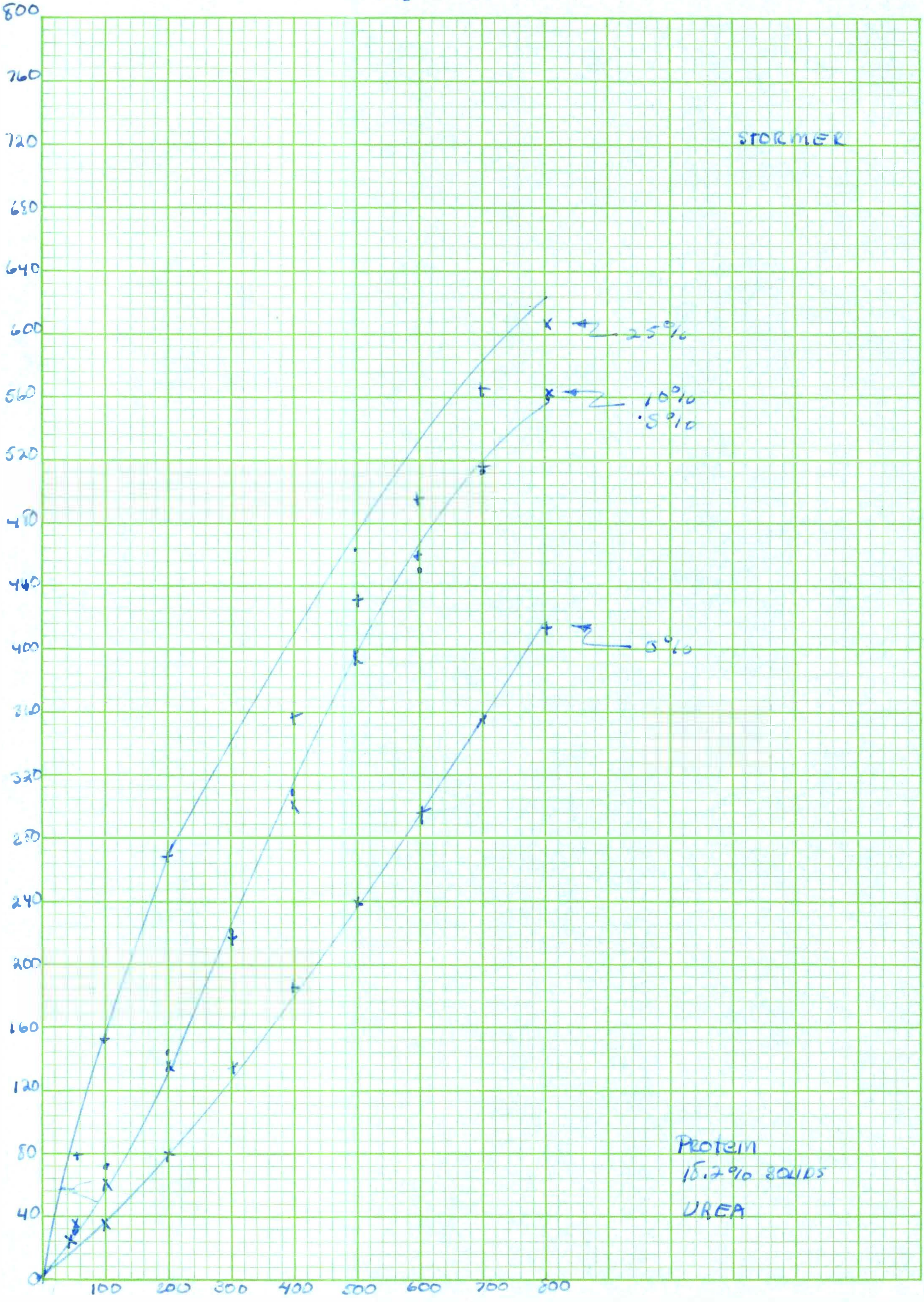

4000
3800
3400
3000
2800
2400
2000
1800
1400
1000
800
400
0
5
10
15
20
25
Per Cent
UREA
AMMONIUM THIOCYANATE
THIOUREA

Figure 2



800
760
720
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640
600
560
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440
400
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280
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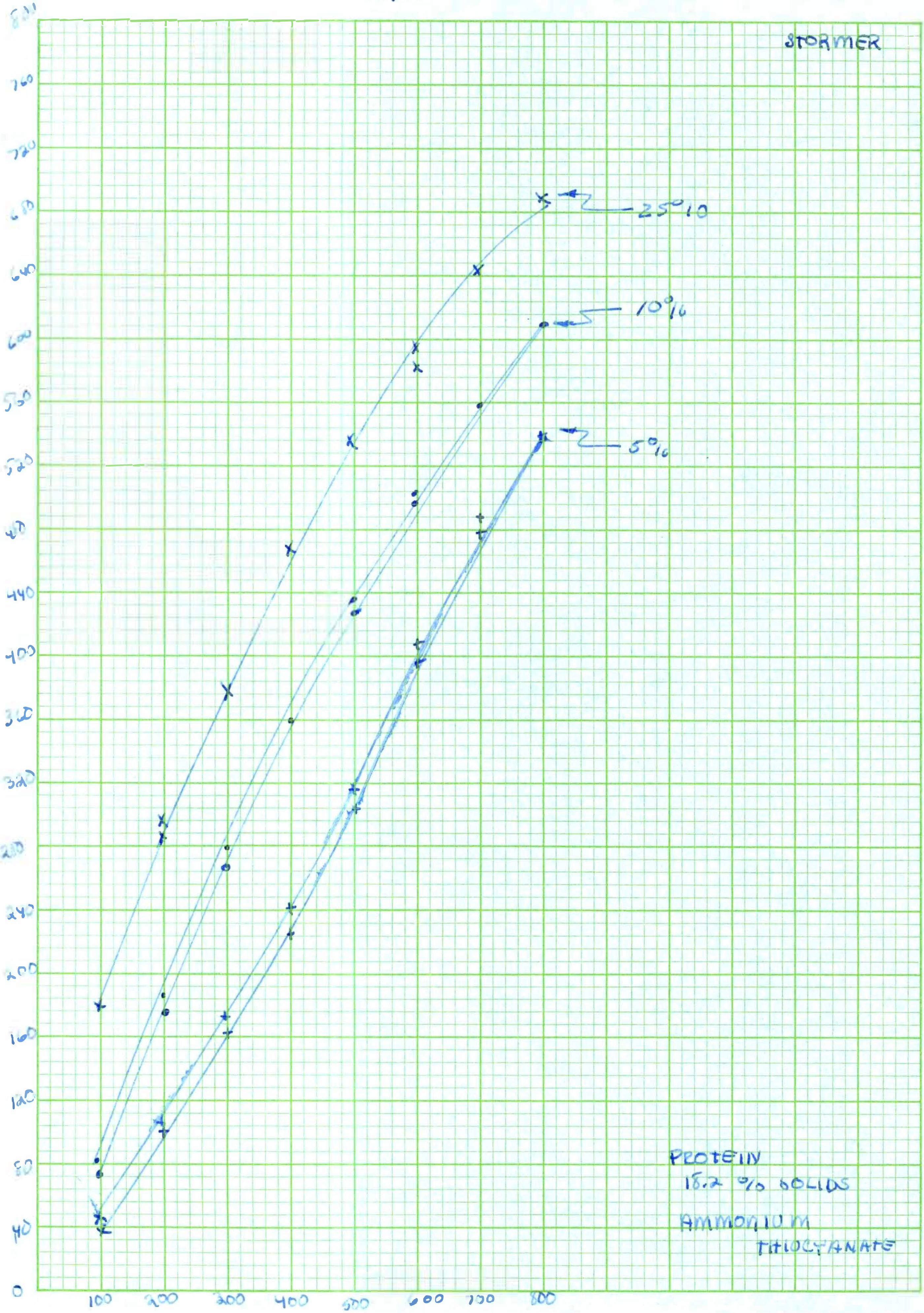
120
80
40
0
100
200
300
400
500
600
700
800
STORMER
25%
10%
5%
0%
Protein
15.2% SOLIDS
UREA

FIGURE 3


STORMER
25%
10%
5%
PROTEIN
18.2 % SOLIDS
AMMONIUM
THIOCYANATE
0
40
80
120
160
200
240
280
320
360
400
440
480
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560
600
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680
720
760
800
100
200
300
400
500
600
700
800

FIGURE 4

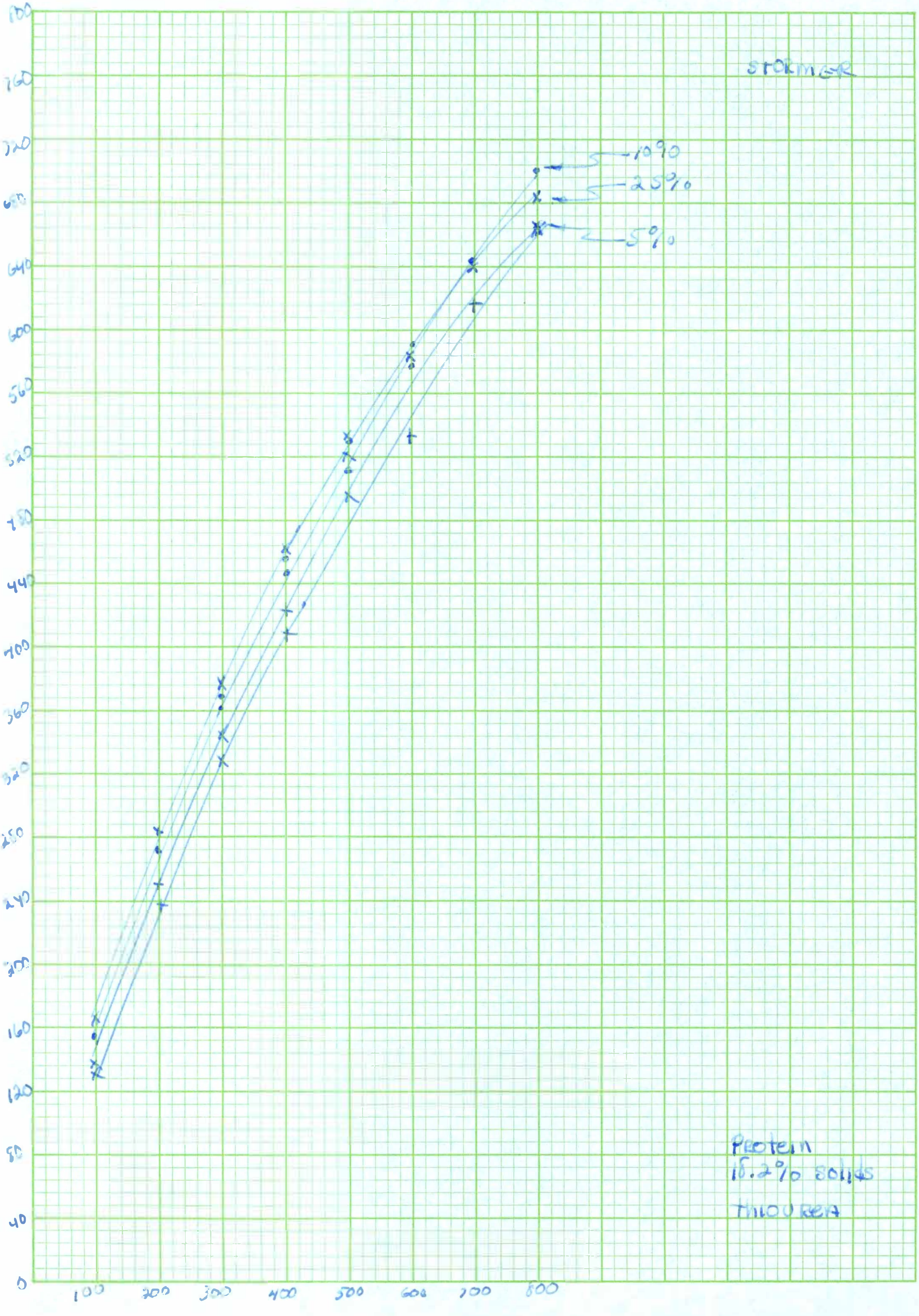
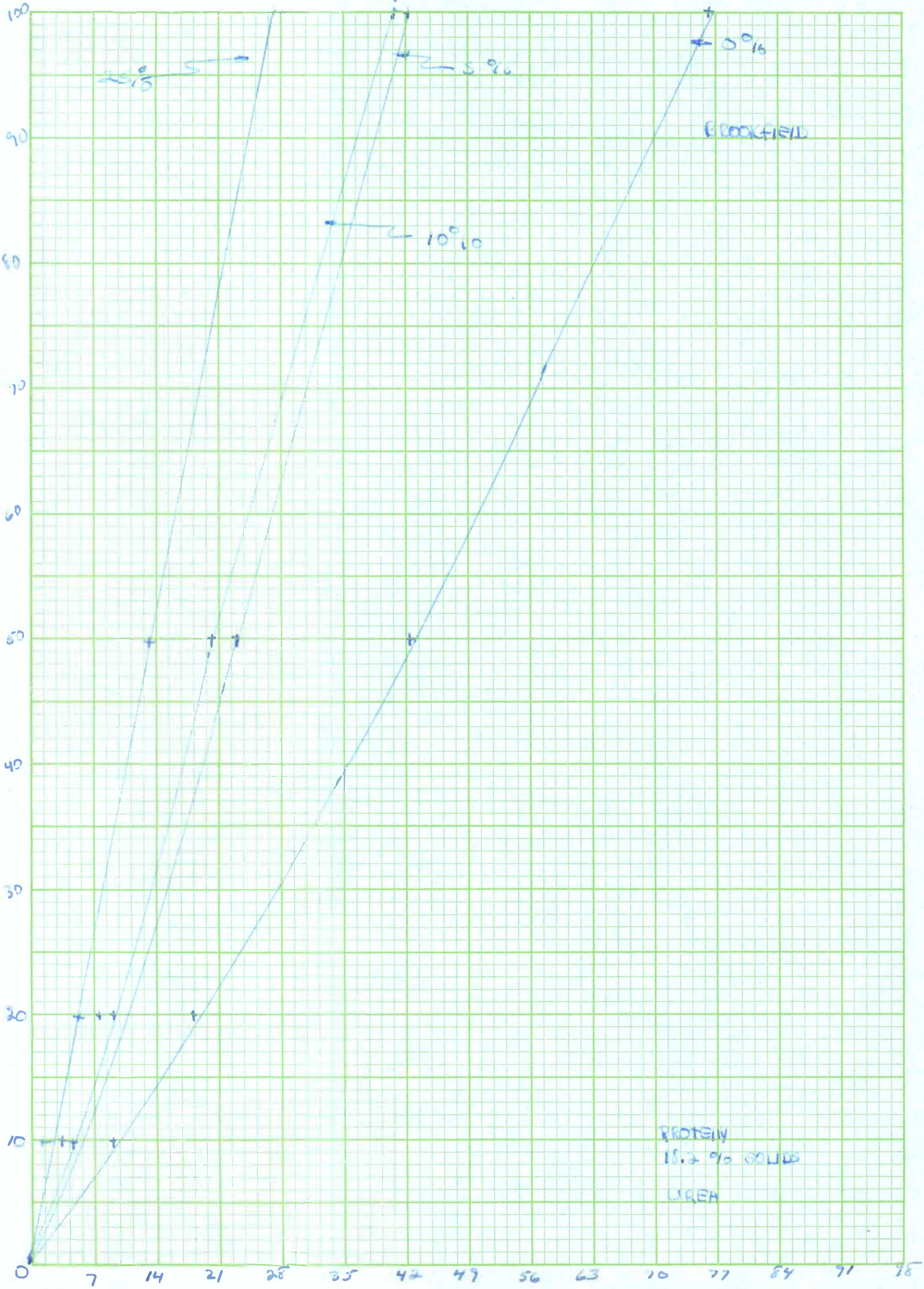


FIGURE 5



100
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10
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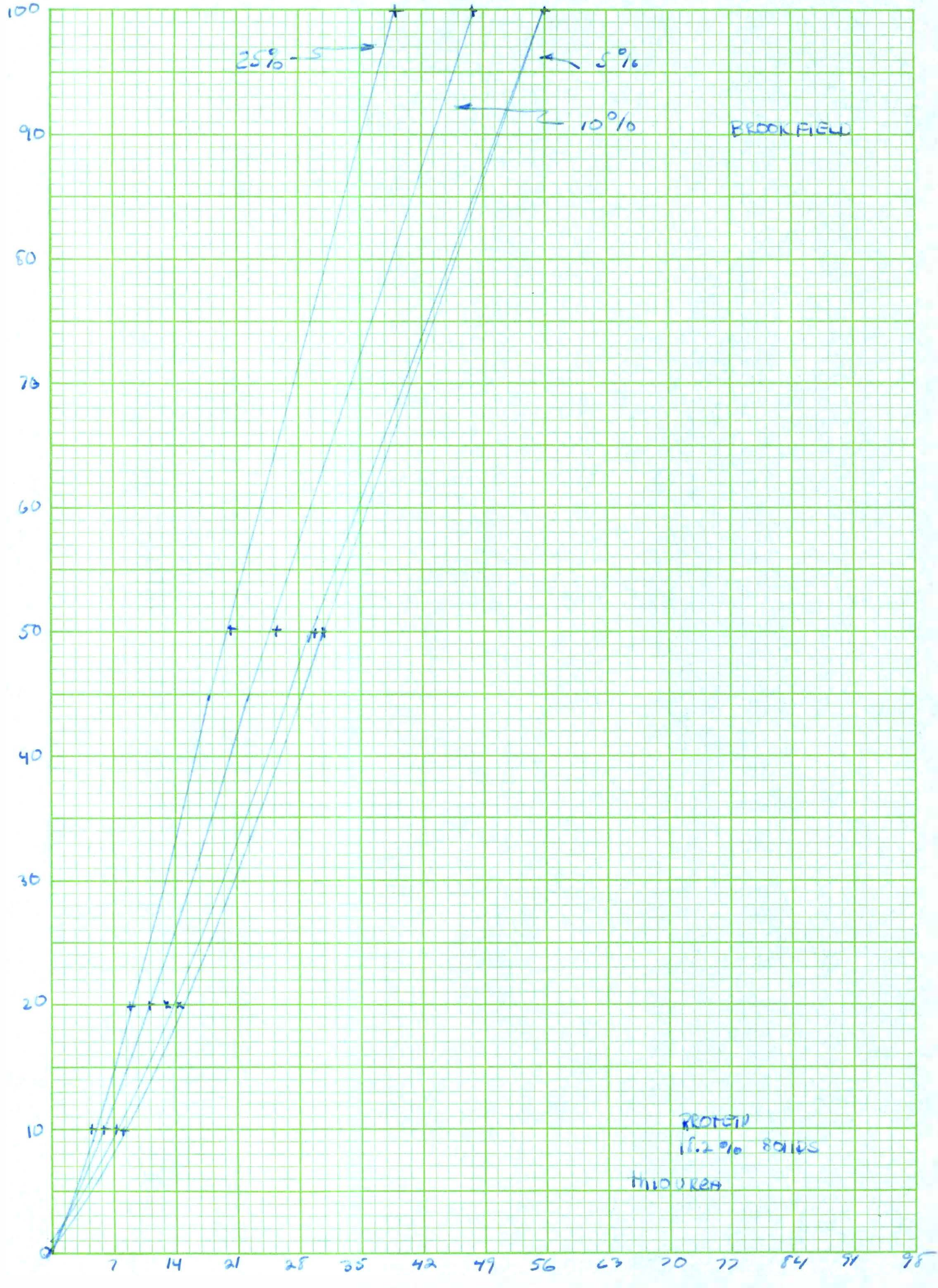
7
14
21
28
35
42
49
56
63
70
77
84
91
98
25%
5%
10%
0%
BROOKFIELD
PROTEIN
18.2 % SOLIDS
UREA

Figuee 6



100
90
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25%
5%
10%
BROOKFIELD
PROTEIN
THIOUREA
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28
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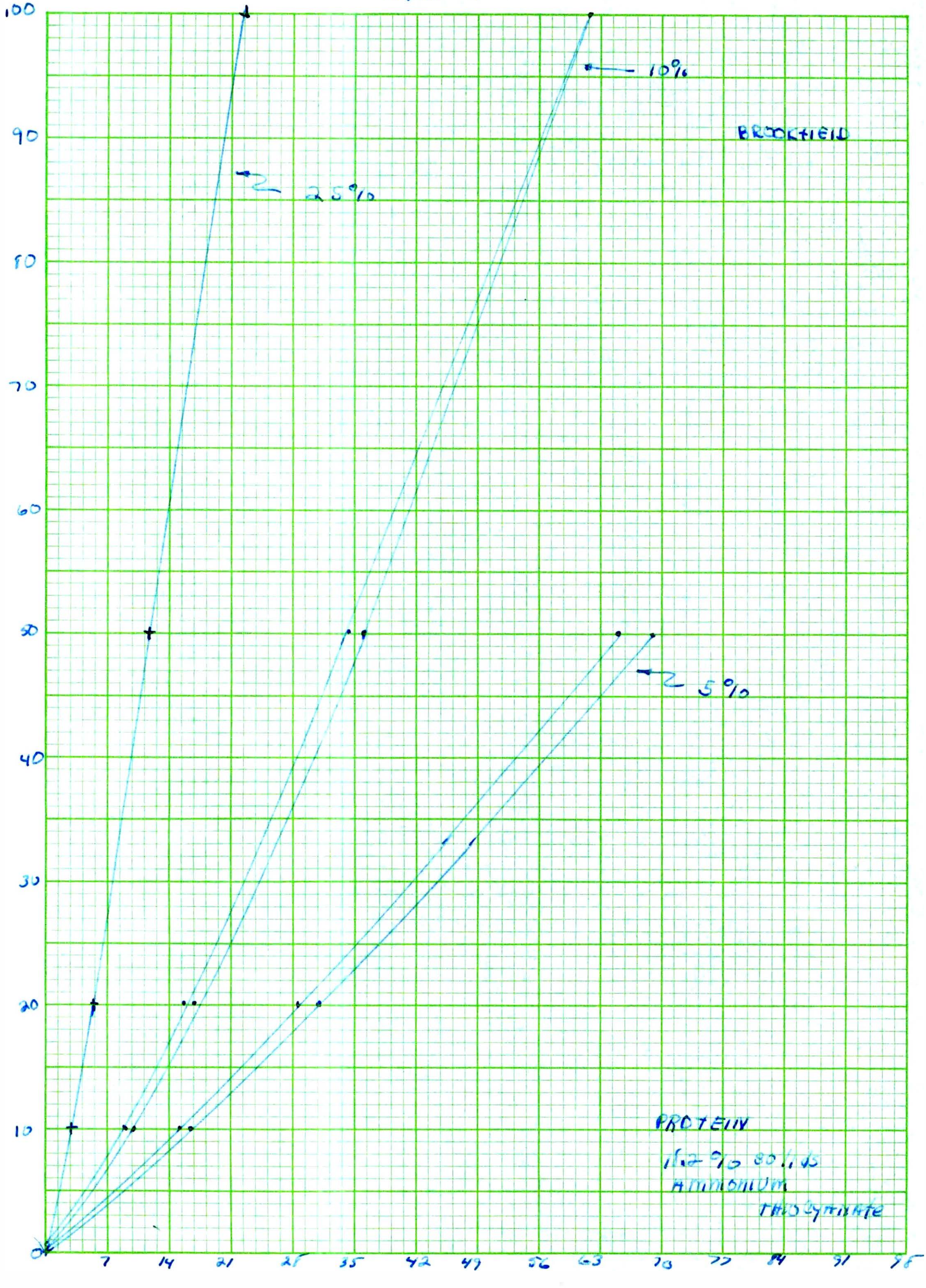
42
49
56
63
70
77
84
91
98

Figure 7



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10%
5%
BROOKFIELD
PROTEIN
11.2 % SOLIDS
AMMONIUM
THIOCYANATE

Figure 8

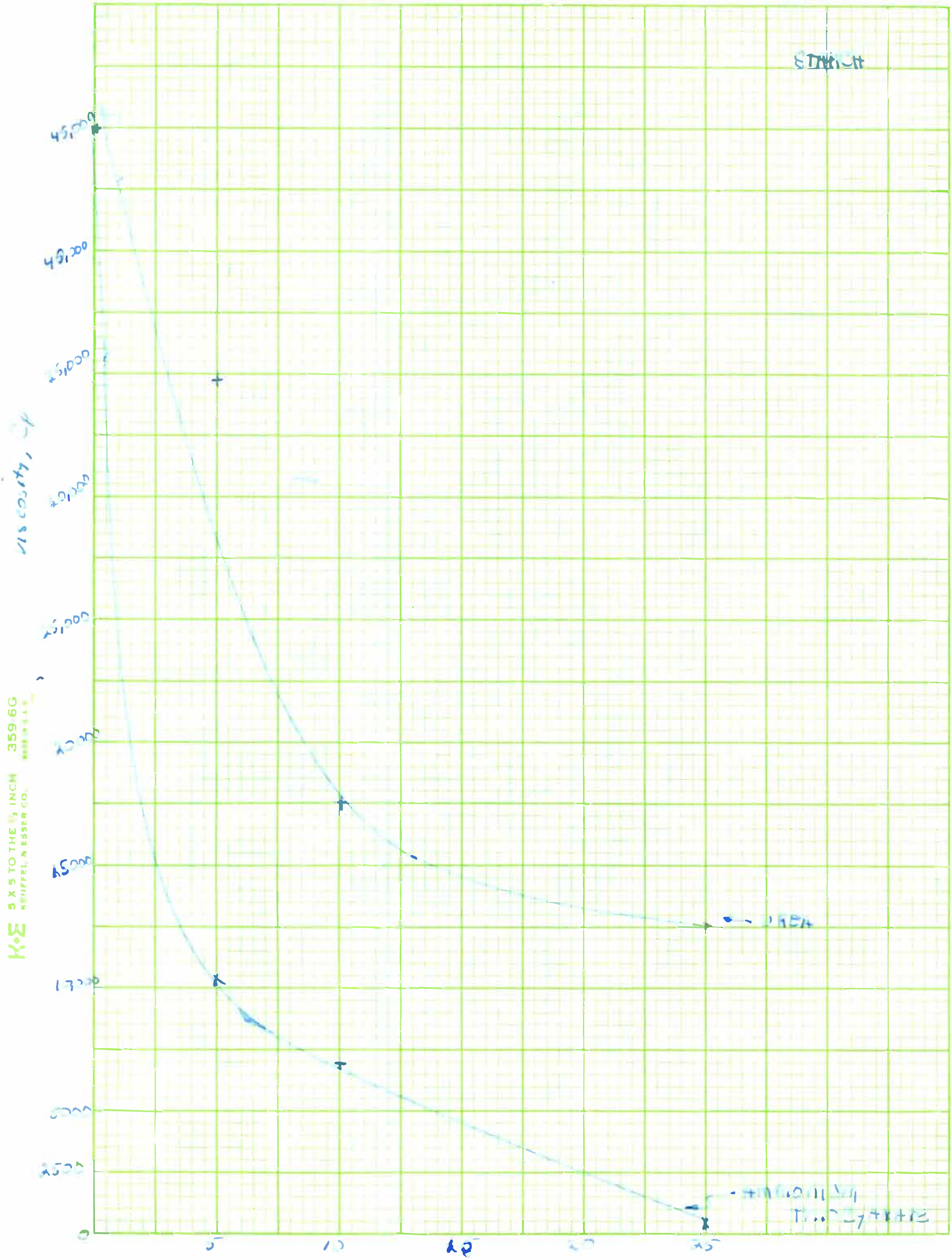
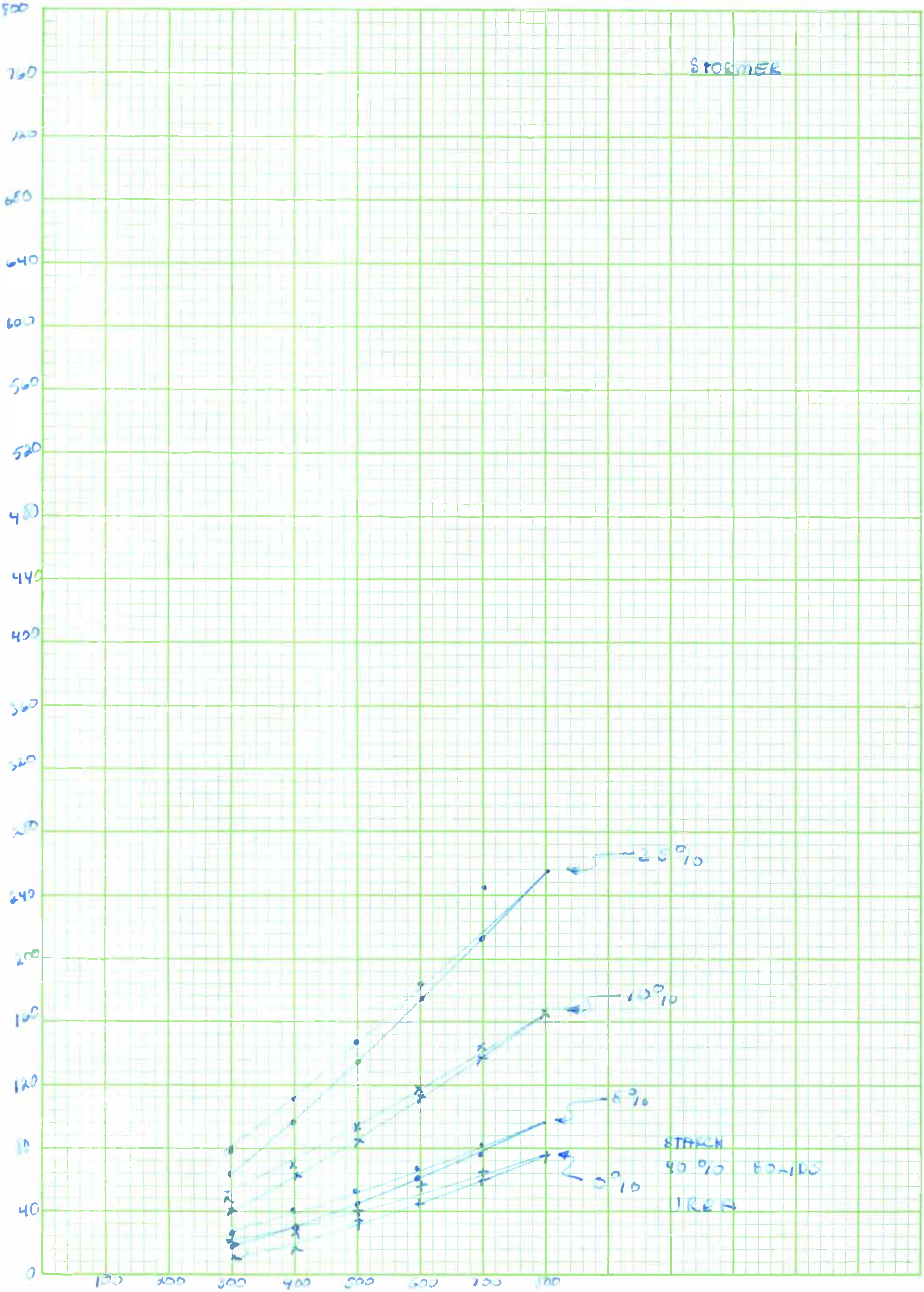


Figure 9



# Figure 10

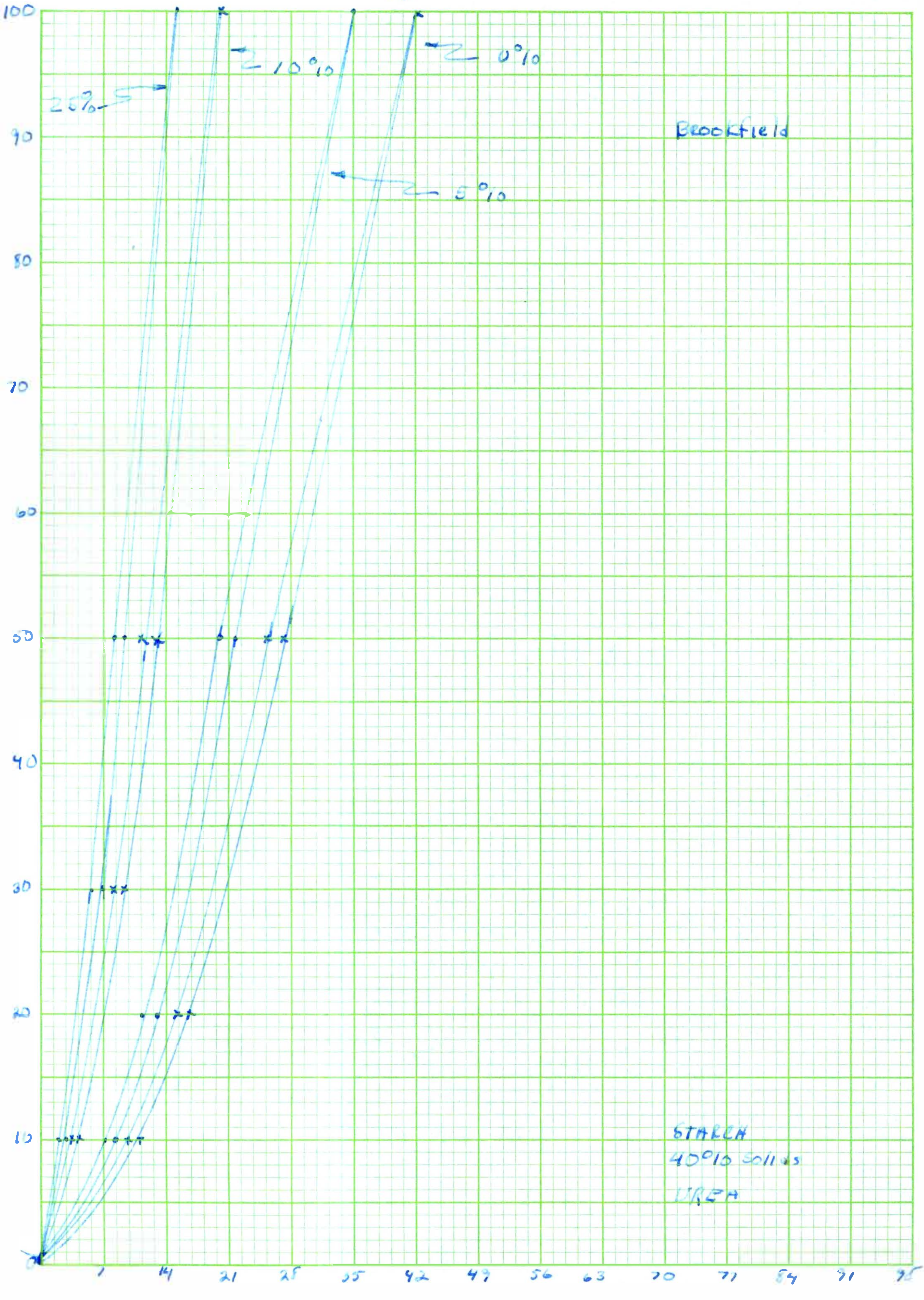
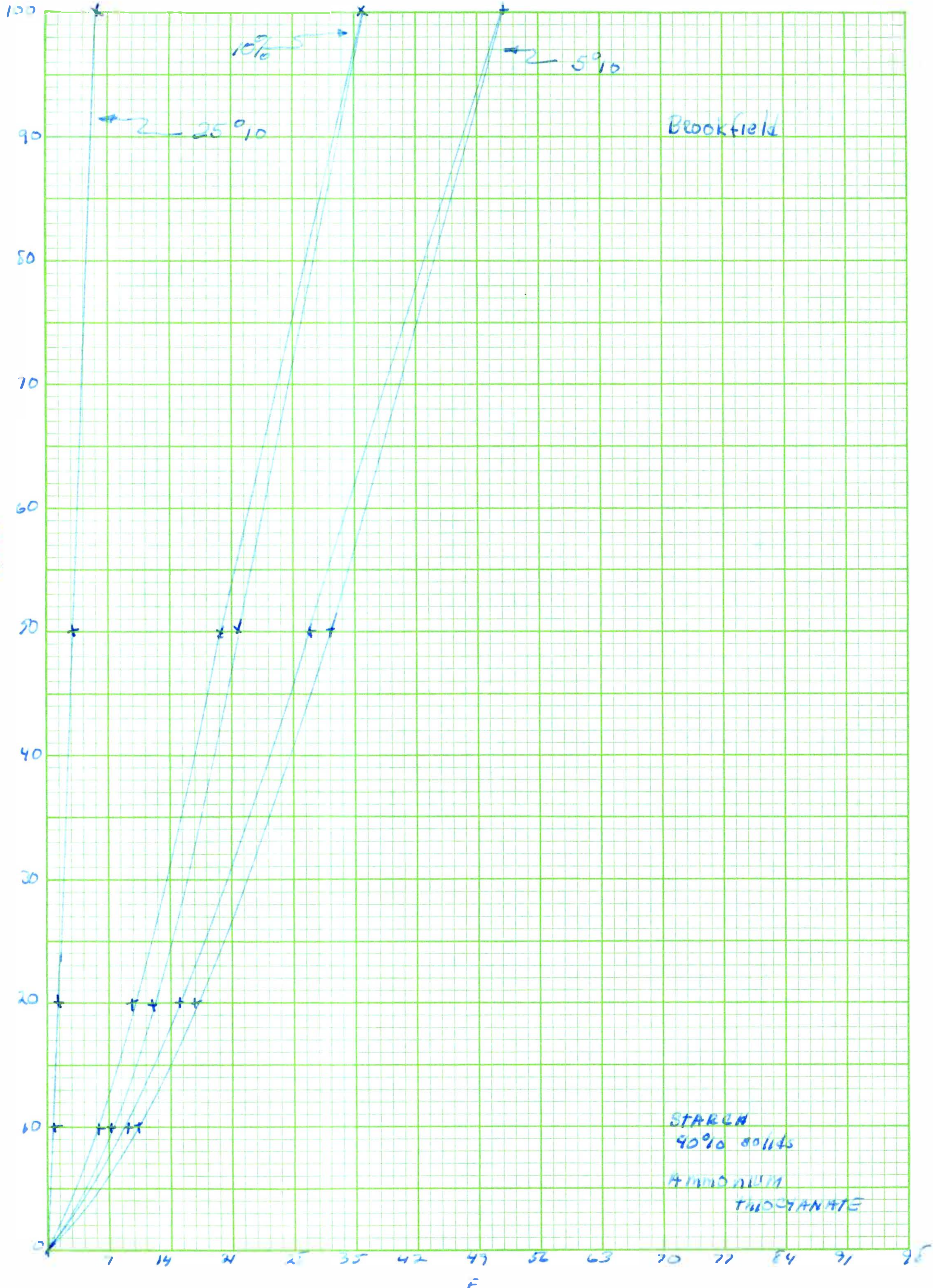
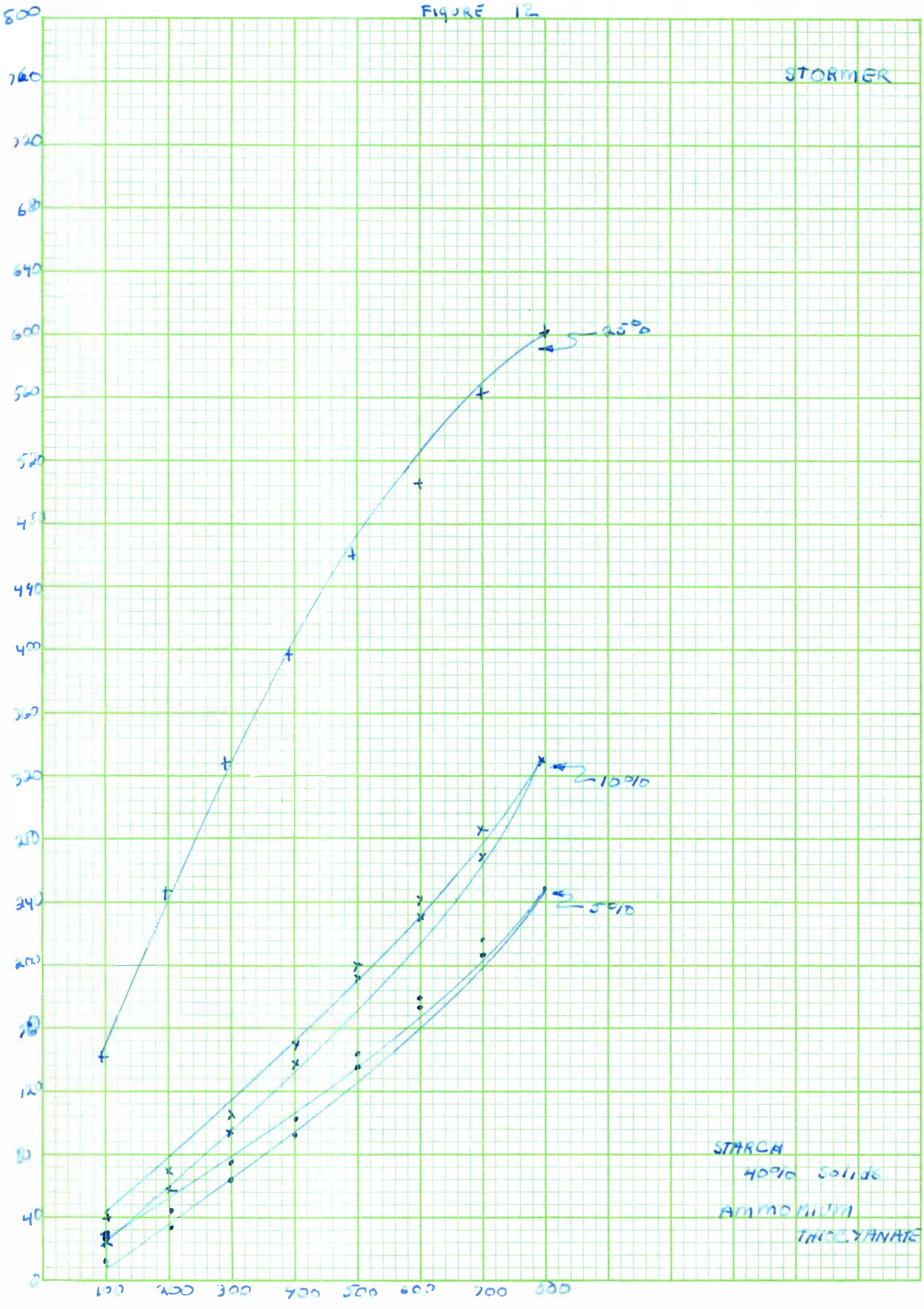


Figure 11



10%
5%
25%
Brookfield
R.P.M.
STARCH
90% solids
AMMONIUM
THIOCYANATE
F

# FIGURE 12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280
240
200
160
120
80
40
0
100
200
300
400
500
600
700
800
STORMER
25%
10%
5%
STARCH
40% Solids
AMMONIUM
THIOCYANATE

## DISCUSSION OF RESULTS

In the experiments, starch was modified with urea and ammonium thiocyanate.

In figures 9 and 10 it can be seen that the type of flow curve obtained with both the Stormer and Brookfield show pseudoplastic-thixotropic curves with the larger amount of "flow modifier" having the greatest effect in lowering the viscosity of the starch. Both viscometers show the same type of flow curve.

In figure 8, where the actual viscosity in centipoises is plotted versus the per cent "flow modifier" added, it can be seen that ammonium thiocyanate has a much greater effect on the viscosity than does the urea. It also shows that the initial 5 per cent "flow modifier" has the greatest effect on the viscosity and as more is added, the reduction in viscosity is much less.

With alpha protein as the adhesive, urea, thiourea, and ammonium thiocyanate were used as "flow modifiers".

In figure 2 it can be seen that the type of flow is almost Newtonian with urea, but has very slight dilatant characteristics.

With ammonium thiocyanate, as can be seen in figure 3, the curves show dilatant flow. In fact with 5 per cent ammonium thiocyanate the curve shows thixotropic-dilatant flow.

With thiourea, figure 4, the curves again show dilatancy with the 25 per cent thiourea being more dilatant than the 10 per cent. This and the above curves were obtained with the Stormer viscometer, and in the type of flow we do not normally expect.

With the Brookfield, we obtain a type of flow that does not correspond with the type of flow curve obtained with the Stormer. Here in figure 5 using urea as the "flow modifier" a pseudoplastic flow curve is obtained.

Again with ammonium thiocyanate and thiourea, figures 6 and 7, pseudoplastic flow is obtained, although with 5 per cent and 10 per cent "modifier" thixotropic flow can also be noted.

Therefore it can be seen that the two types of viscometers, Brookfield and Stormer, do not give the same type of flow curve when alpha protein is the adhesive. The Stormer shows dilatant flow while the Brookfield shows thixotropic-pseudoplastic flow.

From figure 1, we can see that thiourea has the greatest effect on the viscosity of the alpha protein adhesive while urea has the least effect on the viscosity. Ammonium thiocyanate lies between the two.

Also the initial 5 per cent "flow modifier" added again has the greatest effect on the viscosity while the continued addition of the "modifier" does not have as much effect on the viscosity of the adhesive.

## CONCLUSIONS

From the results of the experiments we can see that "flow modifiers" such as urea, thiourea, and ammonium thiocyanate can be used to lower the viscosity of coating adhesives a great deal. The type of flow curves obtained is usually pseudoplastic, and the initial five per cent of the flow modifier added has the greatest effect in lowering the viscosity of the adhesive.