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Historical and Theoretical Survey of the Effect of a Cationic Starch on the Hygroexpansivity of Paper

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Historical and Theoretical Survey

of

The Effect of a Cationic Starch

on the

Hygroexpansivity of Paper

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Abstract

The effect of a cationic starch as an additive on the hygroexpansivity of paper was made. It was found that the hygroexpansivity of the paper increases as the freeness of the stock is lowered. Small additions of cationic starch gave a substantial strength increase with approximately the same expansitivity as the lower strength paper made with pulp alone.

TABLE OF CONTENTS

Historical and Theoretical Survey

Dimensional Stability

A well known feature of paper is the dimensional changes which occur when there is a change in the moisture content of the paper. In many converting processes, as well as in other fields of use, it is impossible to maintain a constant moisture content in paper. The moisture content of paper is dependent upon the humidity of the surrounding air, and thus it is not necessary for paper to come into direct contact with free water in order for it to cause difficulties in applications where dimensional stability is of importance.

Tongren (1) states that the dimensional stability of paper or paper products made from cellulosic parent material is related to changes in the relative humidity of the atmosphere surrounding that paper. Cellulose, being a hygroscopic material, takes up moisture from the surrounding atmosphere until an equilibrium has been established. Conversely, cellulose will give up moisture to a dry atmosphere. In either case the cellulosic material paper will tend to change its dimensions, to expand as it takes up moisture vapor, or to contract as it gives up moisture vapor.

Stamm (2) says that water is held within the cell walls of cellulosic materials in three distinct ways: 1) as water of constitution, 2) as surface-bound or surface adsorbed water, and 3) as capillary condensed water.

Nance (3) says that not only water, but water vapor can also have drastic effects upon the rheological characteristics of paper.

Griffin (4), and others, using a relative humidity range of zero to one hundred per cent found for a wide variety of papers a cross directional change of 1.1 to 1.8% and a machine direction change of 0.35 to 0.85%. In addition, the change from 80 to 100% relative humidity was greater than from 60 to 80% relative humidity.

Hamburger (5) found an offset paper to change two and one-half times as much in the cross direction as in the machine direction.

Calkins (6) states that there are two causes of changes in dimension of paper with changes in moisture content. First, the dimensions of the individual fibers change. Thus, cotton fibers conditioned from zero to ninety per cent relative humidity increase in their diameter from twelve to fifteen per cent, although showing only a very slight increase in their length.

More important, however, as a cause of dimensional instability, is the relaxation of strains put into paper during manufacture where moisture content is increased. A sheet of paper is not a homogeneous material, but is composed of individual fibers which have been formed together in a wet mass, in a reasonably random orientation. As this mass is being formed, the fibers are bent and twisted, and then dried under tension. As the fibers

dry they shrink, they become stiffer and as water is removed they are pulled toward one another by surface tension effects and form bonds-presumably hydrogen bonds-between hydroxyl groups on areas on various fibers close enough for this phenomenon to take place. Differential shrinkage takes place; strains formed by fibers drying, bending, and being placed under tensions are "frozen in" by conditions on the paper machine - machine direction tension from the pull of the reel, and tension caused by the forces of internal shrinkage being resisted by felt pressure. This sheet, when subjected to higher humidity, will show greater expansion because the moisture will tend to release the bonds that hold the sheet together.

The following points are given by Calkins to support this approach:

1) Soft, unbeaten papers show low expansivities. (There is plenty of space to expand and little bonding). Conversely, a dense sheet tends to have higher expansivity, even with the same internal bonding.

2) Paper recycled several times between high and how humidities show lower expansivity because some strains are permanently removed.

3) Paper from the edges of a paper machine shows greater expansivity than paper from the center.

4) Fillers or plasticizers reduce expansion. Besides reducing effective amounts of fiber, they reduce bonding.

Glover (7) has suggested that the water expansibility of paper

is controlled by the swelling of the interfiber bonds, rather than by the swelling of the fibers as such.

It is also stated by Rance (8) that possibly the water-accessibility of the cellulose can affect the hygroexpansivity of the sheet only if the cellulose has been made accessible by removal of, or damage to, the outer skin which protects the water accessible material.

Lorey and Libby (9) investigated methods for dimensionally stabilizing paper. They found that basis weight had no effect on the expansion of handsheets with increases in humidity nor did fiber size, except when the fibers were very coarse and greater expansion occurred. Freeness also had no effect except at high freeness where the pulp was bulky and expansion greater, but sheets subjected to high pressures showed less expansion. The application of heat to wet handsheets decreased the expansion of the dried sheets with increases in humidity, but beater addition of clay filler had no effect. Dimensional changes of sheets formed from sulfite pulp increases as the purity of the pulp increased, and sheets made from hardwood pulps expanded to the same extent as sheets made from softwood pulps. Silicone and rosin sizes, added by beater addition, did not decrease the dimensional changes of handsheets with changes in humidity. Neoprene-treated handsheets showed decreases in expansion with increases in humidity as the addition of neoprene was increased above 20%. When thermosetting resins were applied by impregnation,

the handsheets showed less expansion with increases in humidity, and of the resins investigated, phenol-formaldehyde, thio-urea-formaldehyde and glyoxyl-cellosize exhibited optimum effects in the order listed. Urea, a plasticizing agent, showed a negative effect and increased the dimensional changes with changes in humidity.

George (10) summarized the effect of several papermaking variables on hygroexpansivity.

1) Of the pulps derived from wood, unbleached coniferous sulfite gave the greatest dimensional stability.

2) A major factor influencing expansivity of paper is the stock freeness. A slow stock results in a dense paper with numerous fiber to fiber bonds. In the more open sheet produced from free-stock there is an opportunity for some internal expansion and fiber realignment which is not transmitted to the edge of the sheet.

3) Beater additives may have an effect on dimensional stability, but, in general, it is an adverse effect. However, if the beater additive replaces pulp refining, improvement in dimensional stability may result.

4) The expansion and contraction of paper is closely related to fiber orientation. This is because there is little change in the length of a fiber, but substantial change in its diameter.

5) The amount of tension during drying is a major factor in determining the dimensional stability.

Rance has also stated (11) that the hygrosensitivity of the formed paper sheet is directly influenced by the degree of beating to which the pulp stock has been subjected and more specially so when that beating involves mainly "wetting" as opposed to "cutting"..... Dimensional change due to humidity change is correspondingly affected by beating, though at a rather lower level.

Swanson (12) claims that papers of lower density, higher porosity, and better formation might be expected to show lower changes in external dimensions with changes in humidity because of the greater opportunity for expansion and contraction of the fibers within the voids of the sheet. He also adds that a decrease in the dimensional changes of paper may be effected by decreasing mechanical refining.

Stamm (13) gives four different types of treatments which may reduce the swelling and shrinking of wood and other cellulosic materials.

1) coating the external or the microscopically visible internal structure with paints or water-repellant chemicals.

2) depositing bulking agents within the cell-wall structure.

3) blocking or replacing the hydroxyl groups of cellulose and lignin with less polar groups.

4) forming cross bridges between the structural units.

Calkins (6) suggests the following to obtain lower expansivities.

1) Using fibers that don't expand.

2) Running a bulky sheet to minimize fiber expansion effects.

3) Reducing the internal bonding of the sheet by various means.

4) Putting in bonds that are not susceptible to moisture.

5) Treating the paper so that the fibers are impervious to water and hence don't expand because the moisture doesn't penetrate them.

6) Treating the paper with some material that has the strength to hold stable dimensions even if fiber bonds are relaxed.

Starch

Swanson (12) states that starch is used in the papermaking process for two reasons: a) to increase the strength properties, and b) to supplement the beating operation, which would mean chemical hydration. He also believes that a chemically hydrated material would preserve the natural fiber structure, and papers could be made which have a high strength as well as a higher opacity, porosity, better formation, better compressibility for printing, lower hygroexpansivity, and less tendency to curl and cockle.

Steffens (14) says that starch is chemically and physically similar to cellulose. In its cooked form it acts like a highly-hydrated cellulose.

Pacsu (15) stated, and Kerr and Geverson (16) have confirmed that cellulose fibers will adsorb up to 1% of their weight of corn amylose, which is the straight chain fraction of corn starch. Strasser, (17) supported by Steffens (14), believes that starch is never adsorbed by the fiber but that

it adheres to the fiber by mechanical means.

Leech (18) believes that beater additives which increase paper strength must accomplish the improvement by affecting one or more of the factors contributing to paper strength. He gives these four factors as contributing to paper strength: 1) the strength of the fibers, 2) the strength of fiber-to-fiber bonds, 3) the number of bonds, and 4) the distribution of bonds.

Lewis (19) states that little is known about the mechanism by which starch added to the pulp increases the strength of the formed sheet or board. It is generally believed, however, that the starch acts as a binder, forming strong bonds with the fibers of the pulp. The resulting fiber-to-fiber bonds are stronger than the fiber-to-fiber bonds without starches or other binders added, such as newsprint and blotter papers.

Casey (20) feels that the chief function of starch in paper is to increase the fiber-to-fiber bond by acting as a cementing agent between adjacent fibers at their point of contact. Casey (21) also believes that starch is one of the factors influencing the expansiveness of paper.

The so-called "cationic" starches are of relatively recent origin. These starches are chemically modified with substituted groups that impart a positive electro-chemical charge to the starch molecule. Of the "cationic" starches, Cato 8 is typical.

Cato 8 (22) is the most recent product in a series of corn

starch derivatives in which the parent starch has been modified so that its molecules and molecular aggregates are cationic, carrying a positive charge. If its solution is placedin an electrophoresis cell, the molecular aggregates will migrate toward the cathode causing a rise in viscosity and concentration near the cathode. Cato 8 was developed specifically for wet end addition on the paper machine and is designed to meet the requirements of internal starch additives.

The cationic groups of Cato 8 are attracted by the relatively anionic cellulose fibers. The added benefit of a difference in molecular charge results in stronger fiber bonding properties than through the action of natural adhesion alone.

Physical characteristics of Cato 8

Physical form	Pearl
Color	White
pH (approx.)	4
Moisture (approx.)	12%
Solubility in cold water	nil.

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Experimental Procedure

Materials Used

The pulp used in this investigation was a high quality bleached sulphite pulp. Cato 8 starch was taken as a typical cationic starch and was used wherever starch additions were made.

Preparation of Starch

Twenty grams of Cato 8 starch were dispersed in 980 cc. of cold distilled water and heated to 190° Fahrenheit.

Refining

The bleached sulphite pulp was soaked in tap water for three and one half hours. The pulp was then placed in a Valley laboratory beater, the consistency adjusted to 1.55%, and allowed to mix for five minutes with no weight on the beater roll. At the end of this time a four killogram weight was placed on the roll and refining was started. Pulp samples were taken for handsheets at Canadian standard freenesses of 608, 508, 398, 295, and 204 ml.

Forming, Pressing and Drying of Handsheets

At each of the above freenesses six handsheets were made with zero, one, two, and three per cent Cato 8 starch on the British sheet mold according to Tappi standard T205 M-58 with the following exception: The stock from the beater was diluted to .12 per cent consistency and 1000 cc. of this stock was used for each 1.2 gram handsheet. The Cato 8 starch was added to the diluted stock with

a pipette and stirred vigorously.

The sheets were pressed and dried according to Tappi standard T205 M-58.

Strength Tests

Tear, tensile, and mullen tests were made on the handsheets following Tappi standards T403 M-53, T404 M-50, and T414 M-49.

Expansion

Two samples from each set of sheets were run in the Neenah expansiometer to determine the per cent expansion of the samples. In each case the sample was five inches in length and one inch in width. By using the following saturated salt solutions three readings were taken from the expansiometer in a relative humidity range of 95 to 50 per cent relative humidity. The saturated salt solutions were potassium chromate, sodium nitrite and potassium carbonate in that order. By using this method a plot of expansiometer readings vs. per cent relative humidity gave a straight line and the per cent expansion was calculated from the following formula:

$$X = 15C/H_2-H_1$$

where

X = expansion

C = the difference in the expansiometer readings at relative humidities of 65 and 50 per cent

H_2 = 65 per cent relative humidity

H_1 = 50 per cent relative humidity

The expansion divided by the length of the test speciman, five inches, gave the per cent expansion of the handsheets.

Results and Conclusions

Table I gives the tear, tensile, and mullen strengths of the sheets made. Also included in this table are the per cent expansion of the handsheets made.

In figures 1 through 5 expansiometer readings are plotted against per cent relative humidity. From these graphs, and the formula given in the procedure, the per cent expansion was calculated.

Figure 6 shows a plot of the per cent expansion against the freeness. The per cent expansion is plotted against per cent Cato 8 starch at the various freenesses in figures 7 through 11. In figure 12 tensile strength is plotted against freeness and per cent of Cato 8 starch.

TABLE I

50-65% RH.

Sample	Freeness	Tear	Kg/15mm Tensile	Mullen	% Expansion
Blank	608	84	9.6	24.0	.14
1%		72	13.5	36.6	.15
2%		68	14.1	37.7	.15
3%		56	14.4	41.3	.16
Blank	508	32	12.2	33.0	.16
1%		26	15.6	44.0	.154
2%		24	16.4	48.2	.136
3%		36	17.8	56.0	.19
Blank	398	20.8	13.8	33.4	.17
1%		21.2	16.9	45.9	.174
2%		21.2	17.3	46.1	.19
3%		21.2	18.3	52.0	.166
Blank	295	34	15.5	35	.18
1%		22	18.0	41	.196
2%		21.2	18.4	45.6	.19
3%		17.2	18.5	45.6	.19
Blank	204	42.0	15.1	35	.19
1%		26.4	16.6	41	.17
2%		16.0	18.0	46	.17
3%		16.8	19.4	46	.15

FREENESS 608 EXPANSIOMETER READINGS vs. % R.H.

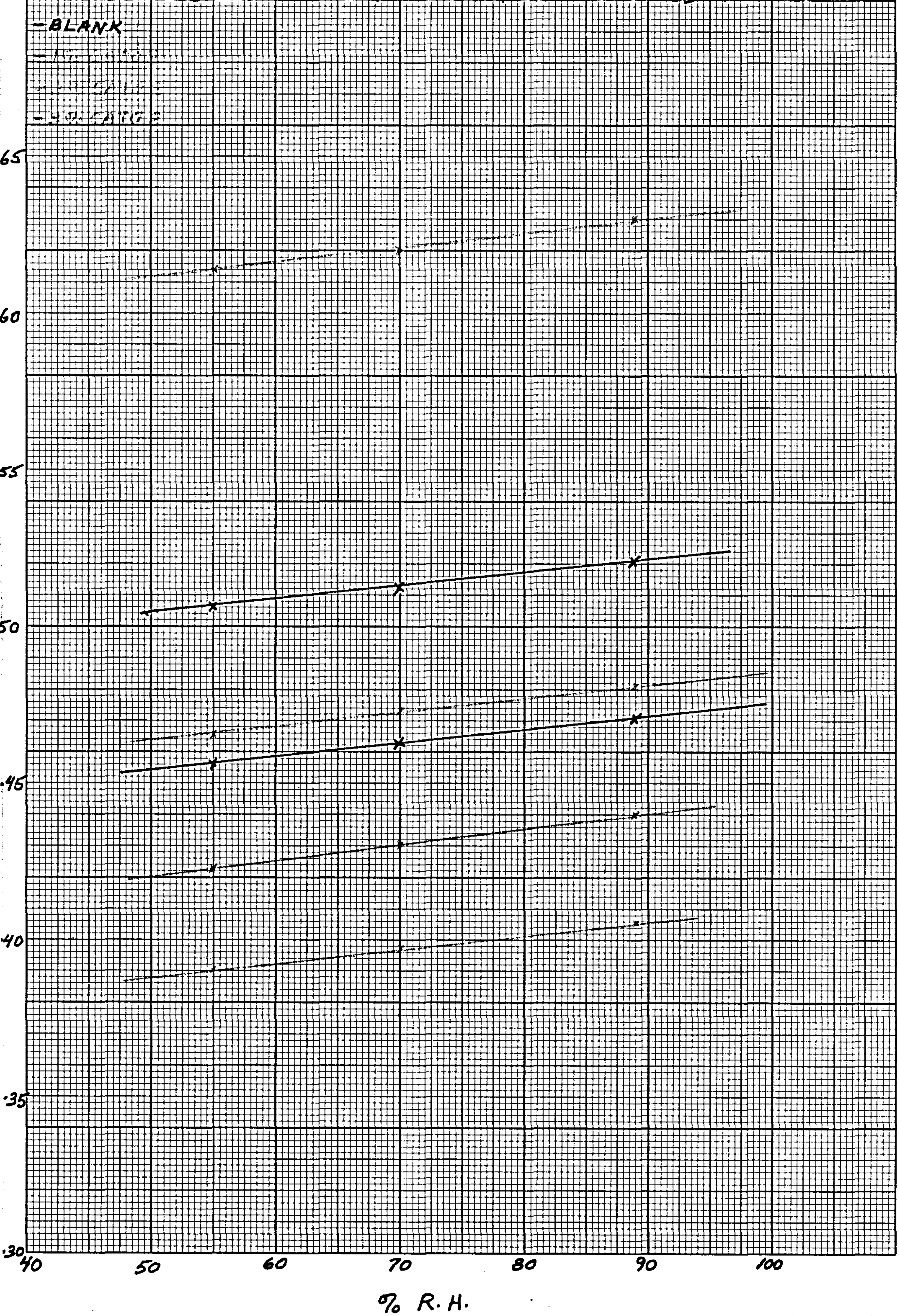
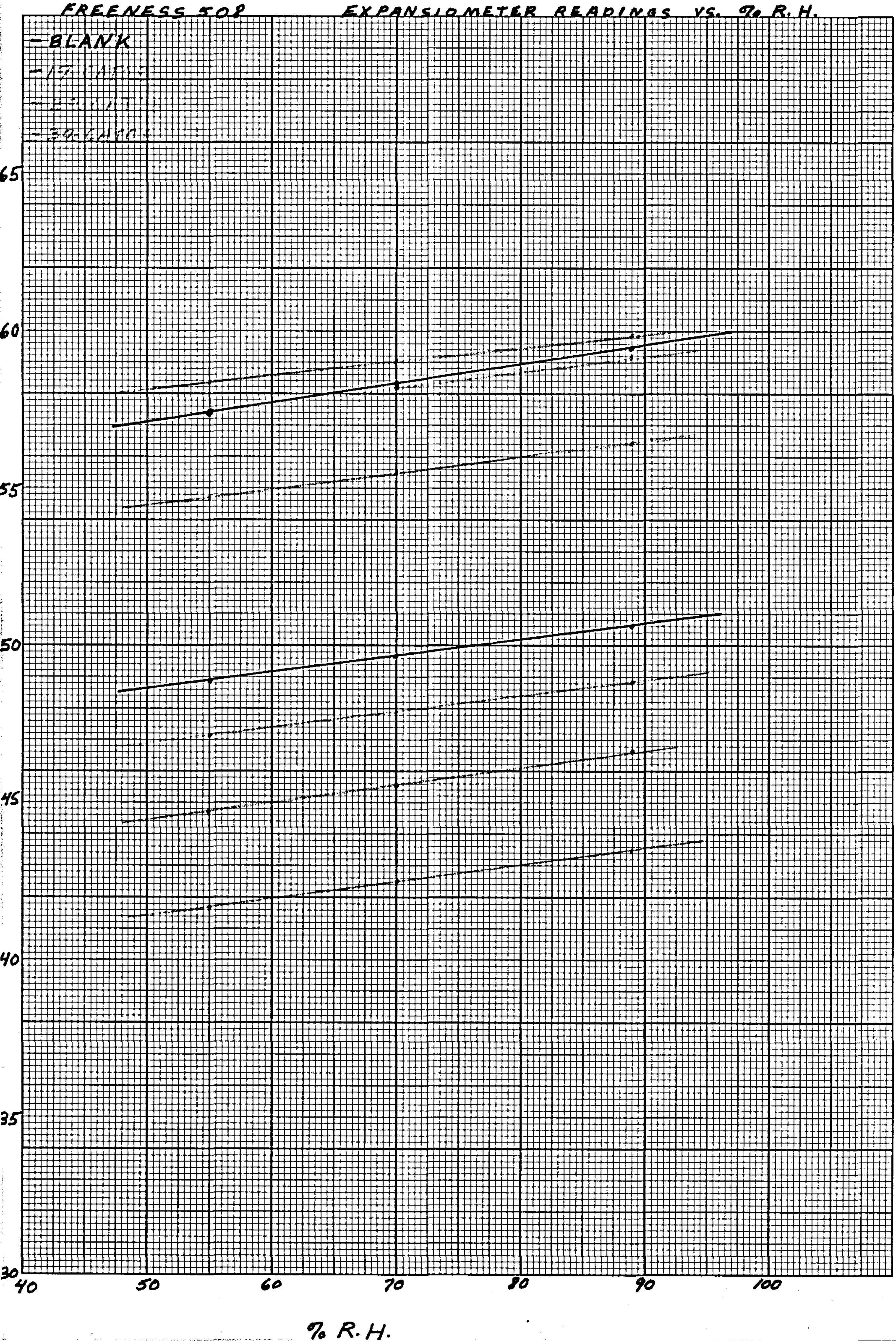


Figure 2



FREENESS 508
EXPANSIOMETER READINGS VS. % R.H.
—BLANK
65
60
55
50
45
40
35
30
40
50
60
70
80
90
100
% R.H.

Figure 3

FREENESS 398 EXPANSIOMETER READINGS VS. % R.H.

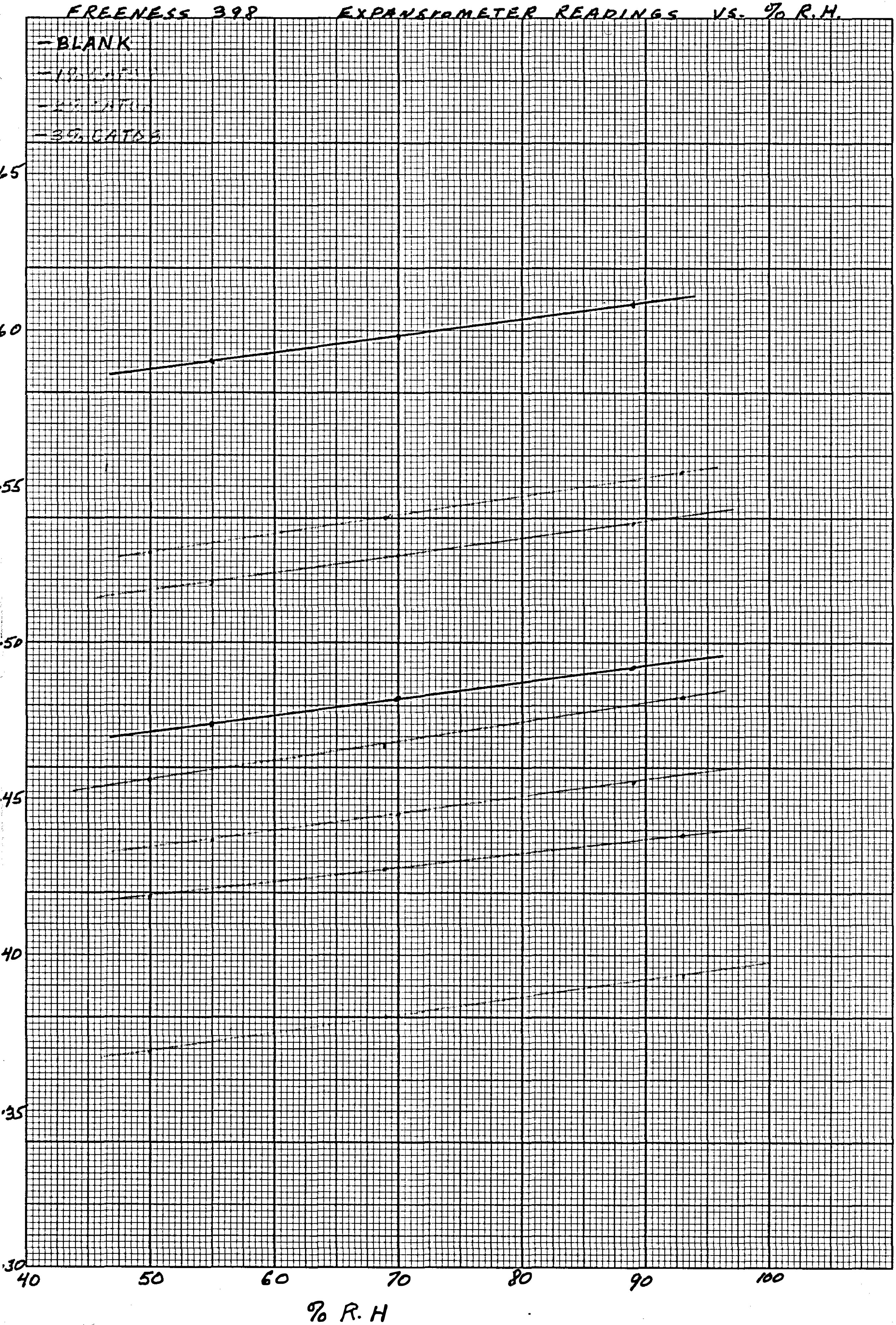


Figure 4

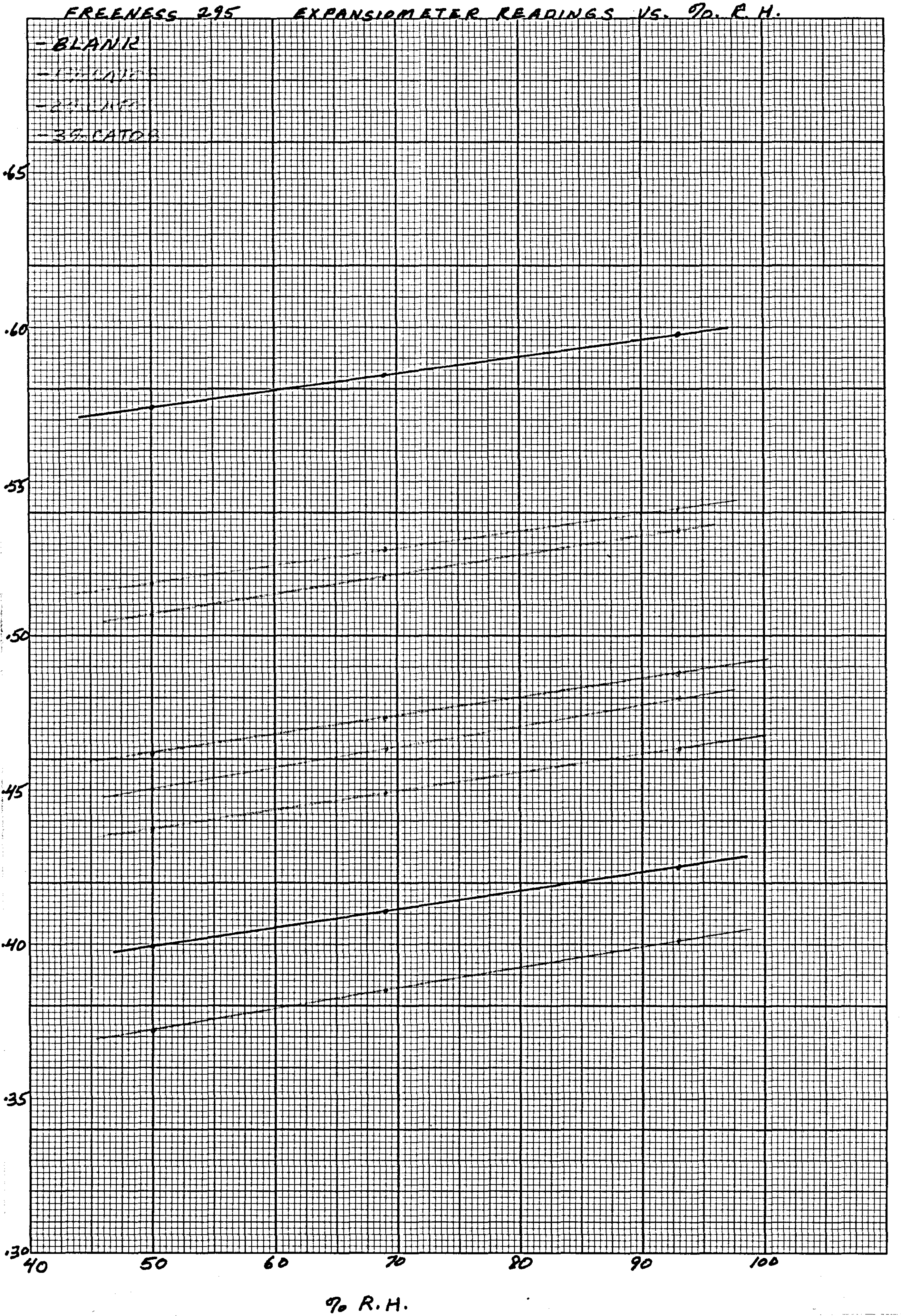

FREENESS 295 EXPANSIOMETER READINGS VS. % R.H.
-BLANK
.65
.60
.55
.50
.45
.40
.35
.30
40
50
60
70
80
90
100
% R.H.

Figure 5

FREENESS 204 EXPANSIOMETER READINGS VS. % R.H.

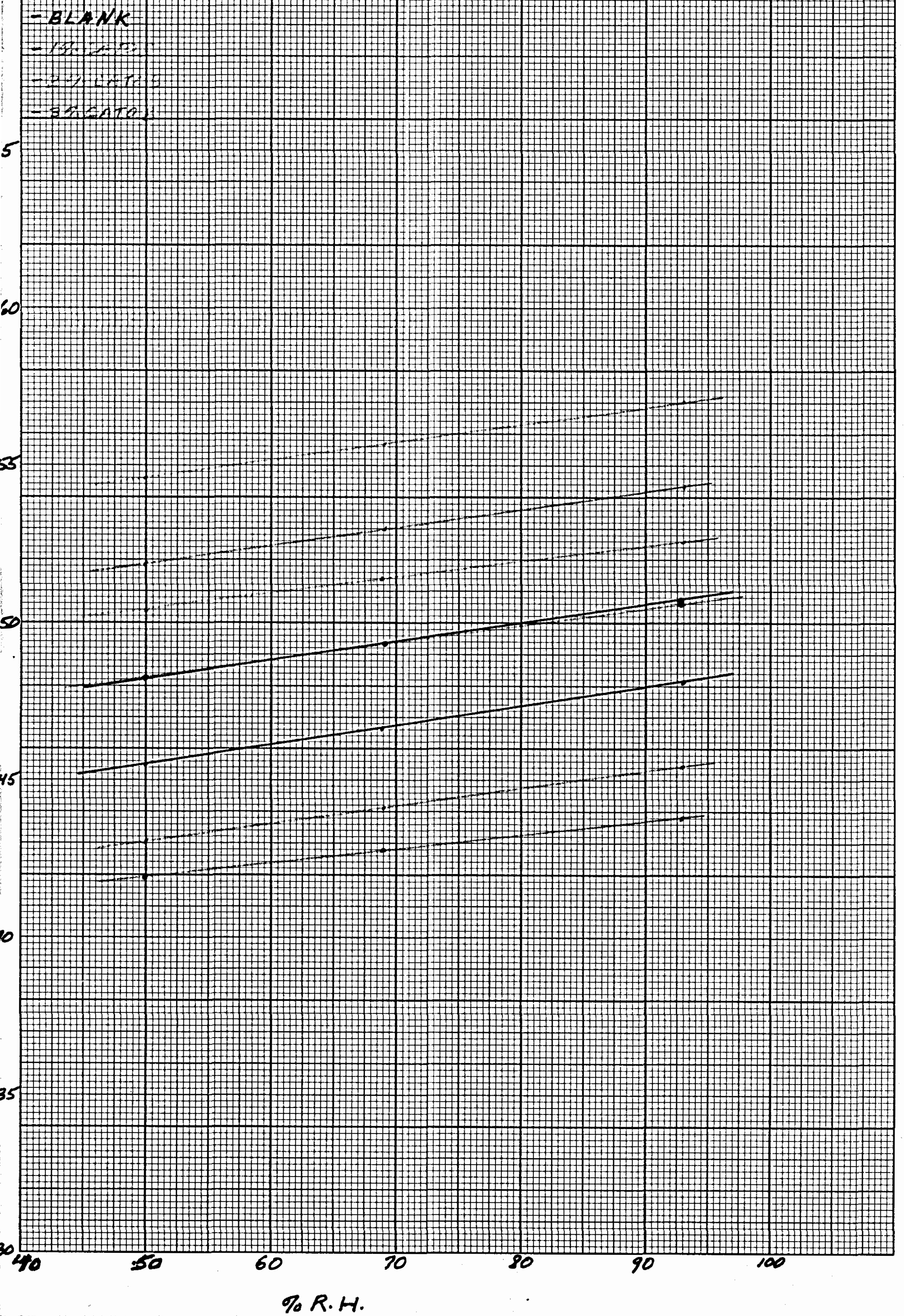
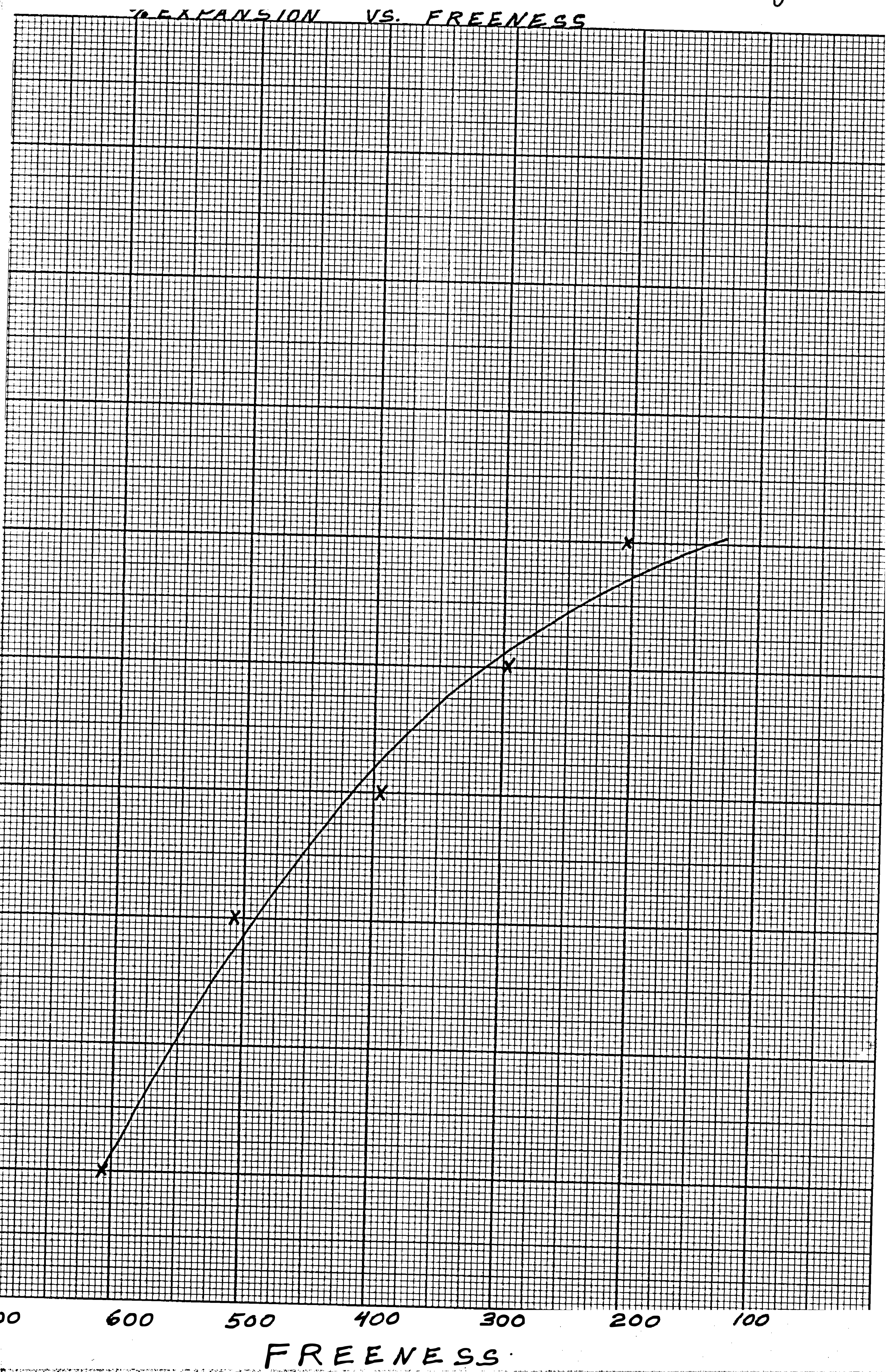


Figure 6



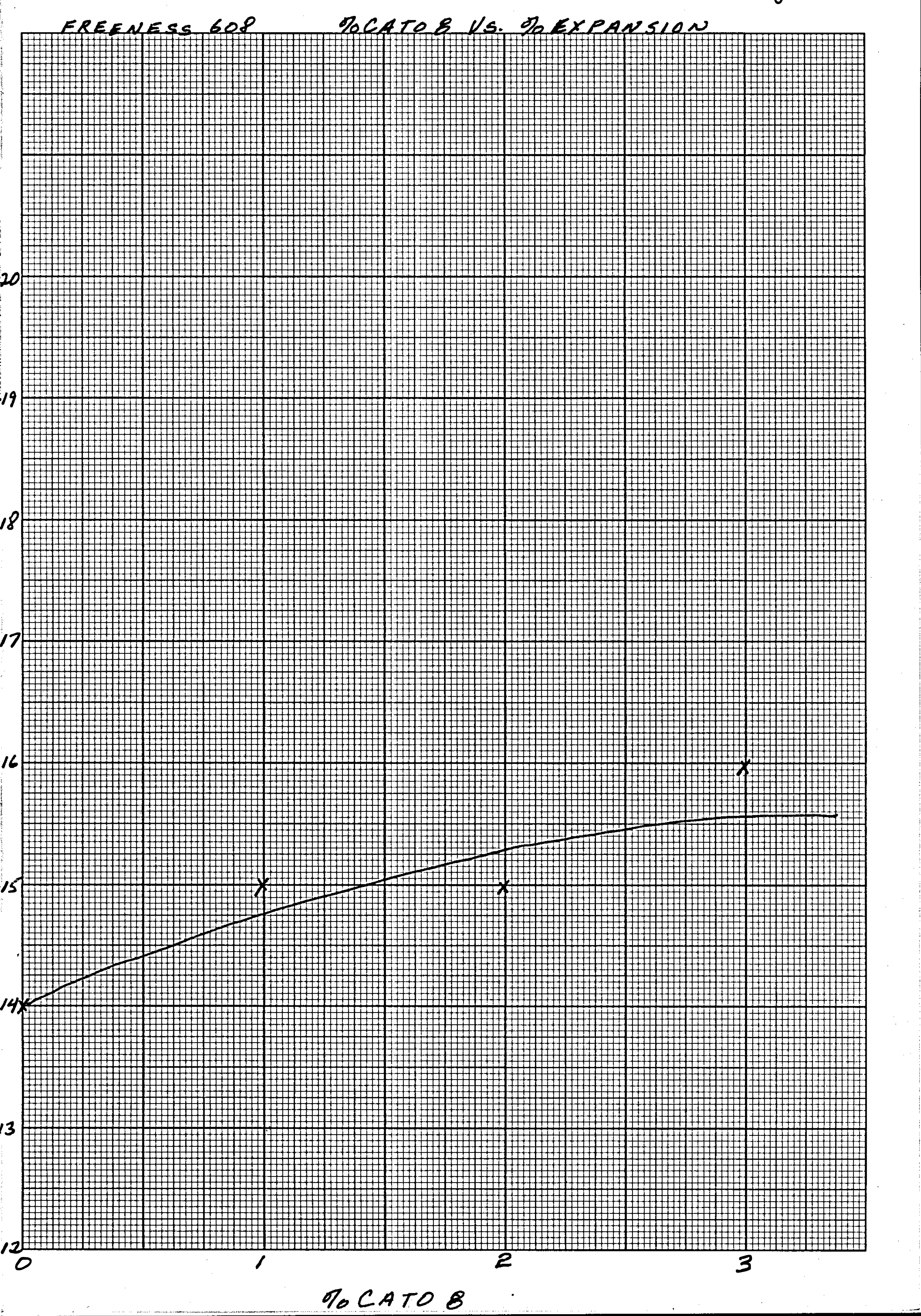
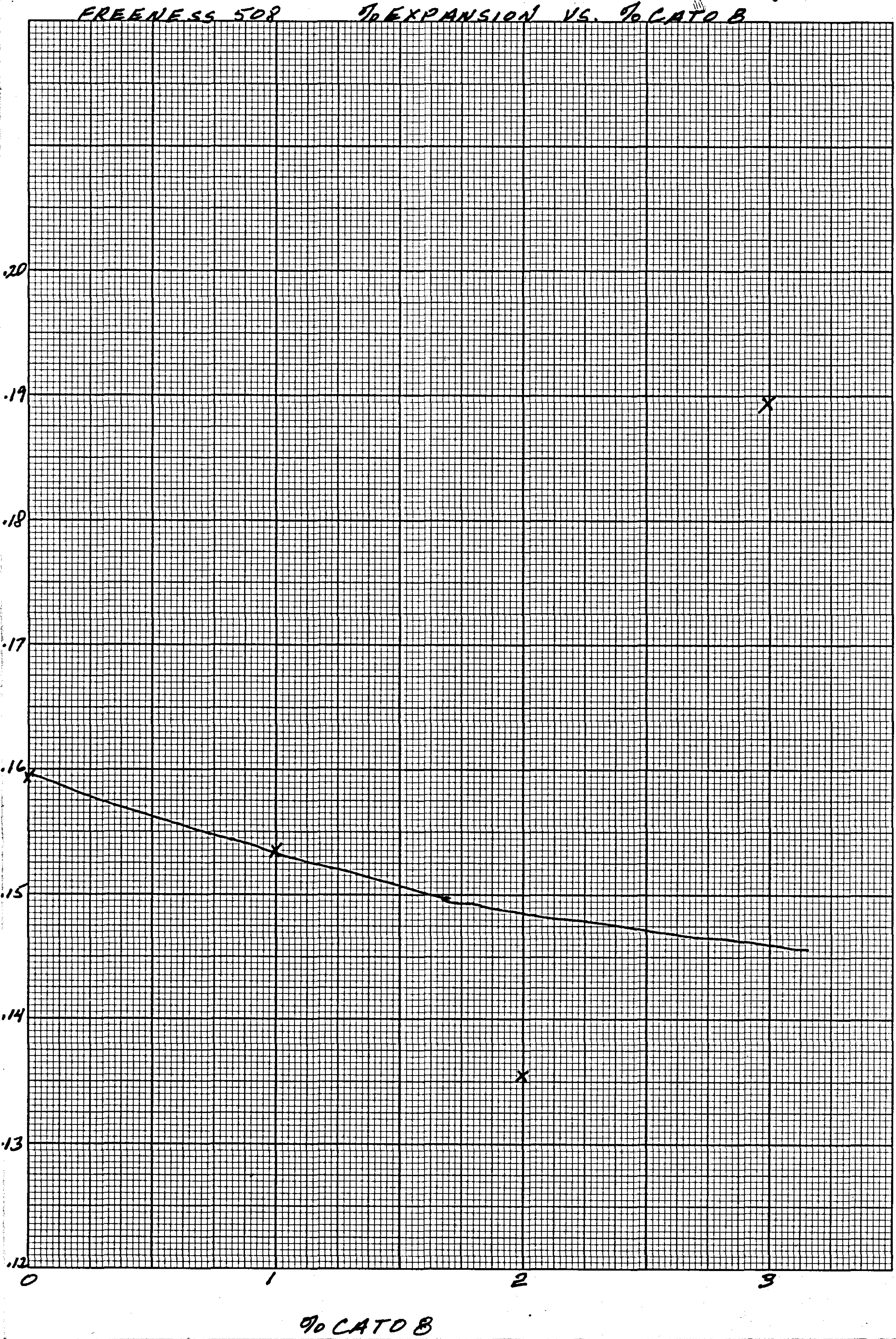

FREENESS 608
% CATO 8 VS. % EXPANSION
20
19
18
17
16
15
14
13
12
0
1
2
3
% CATO 8

Figure 8


FREENESS 508 % EXPANSION VS. % CATO B
.20
.19
.18
.17
.16
.15
.14
.13
.12
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1
2
3
% CATO B

Figure 9

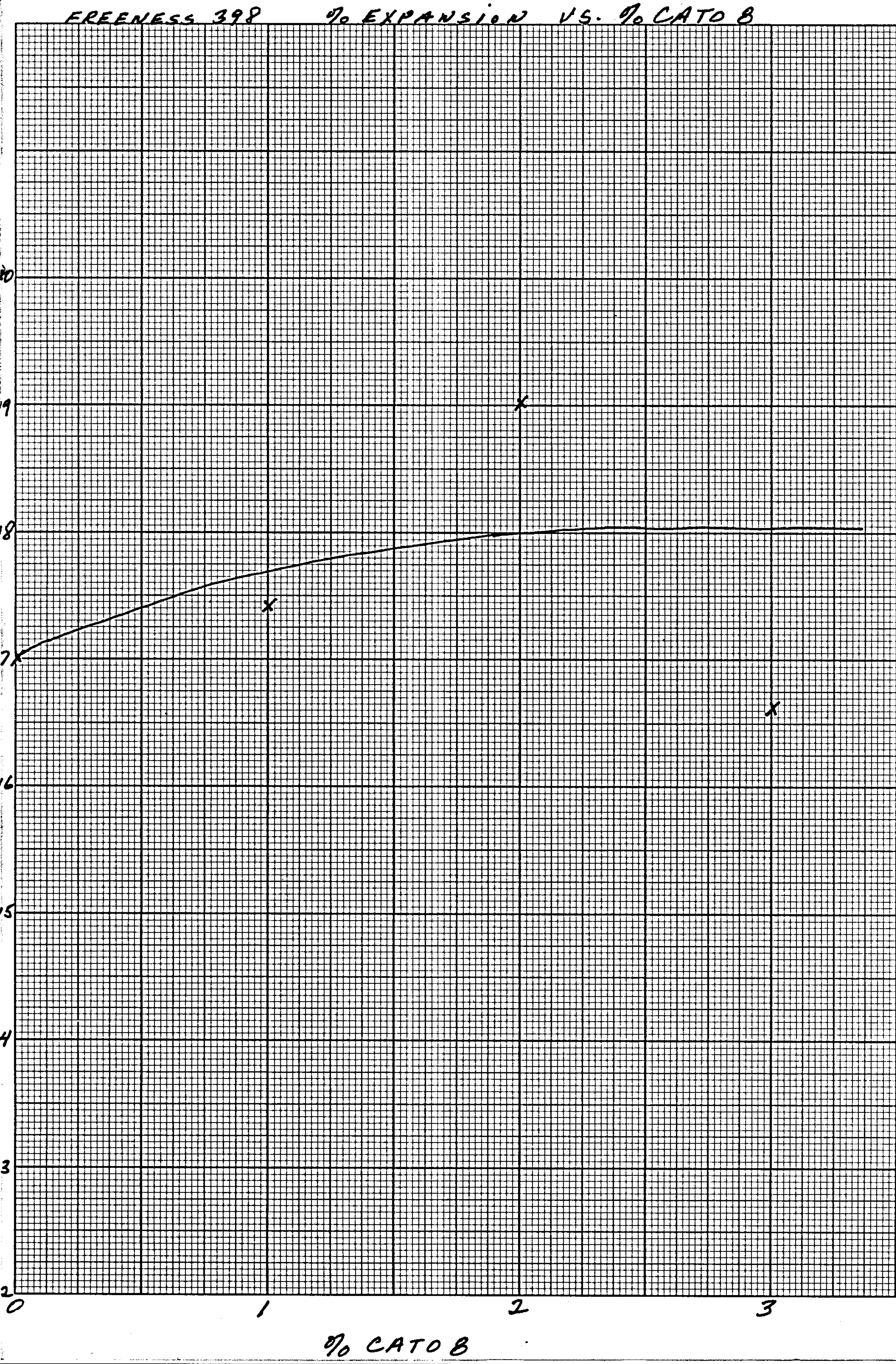
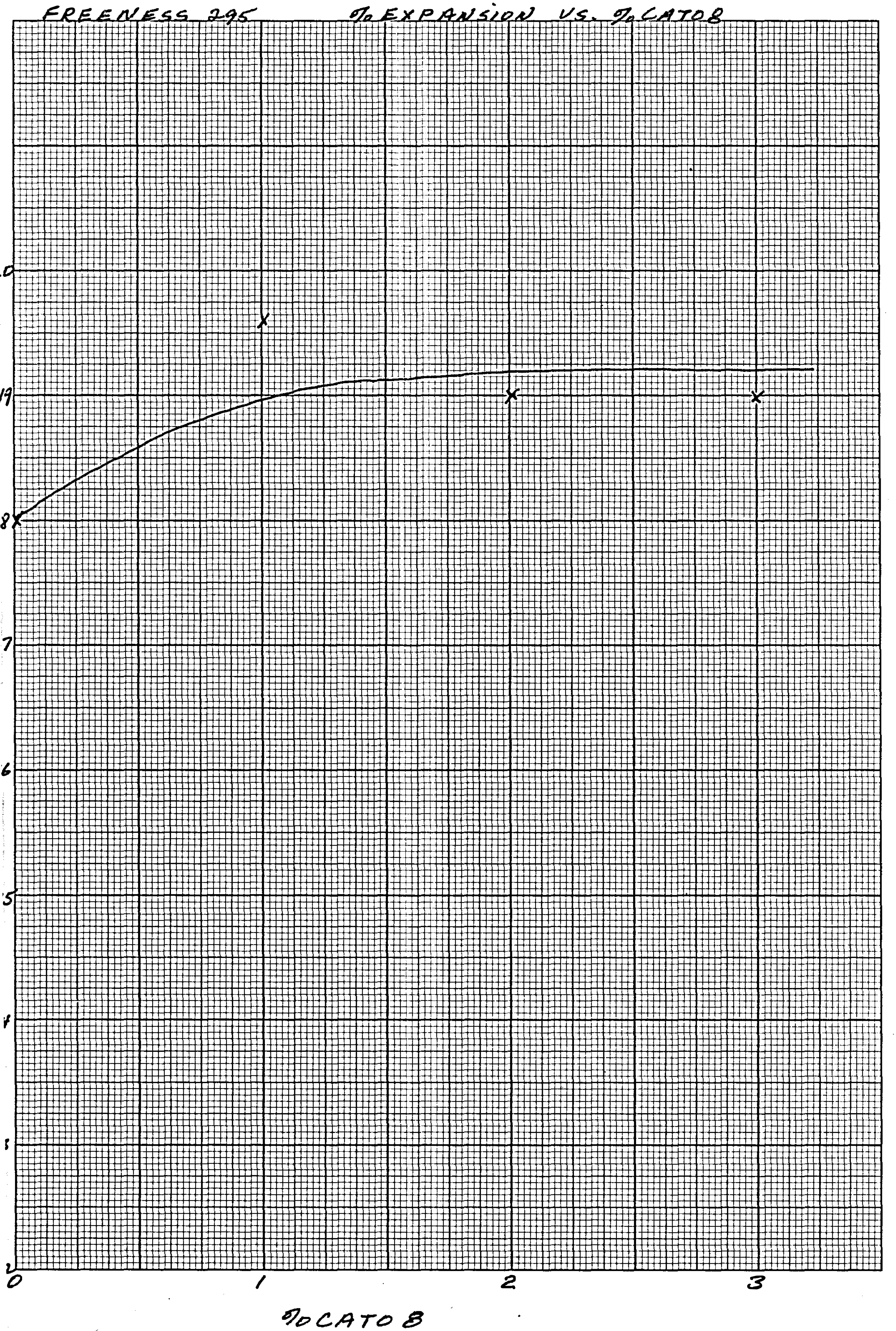
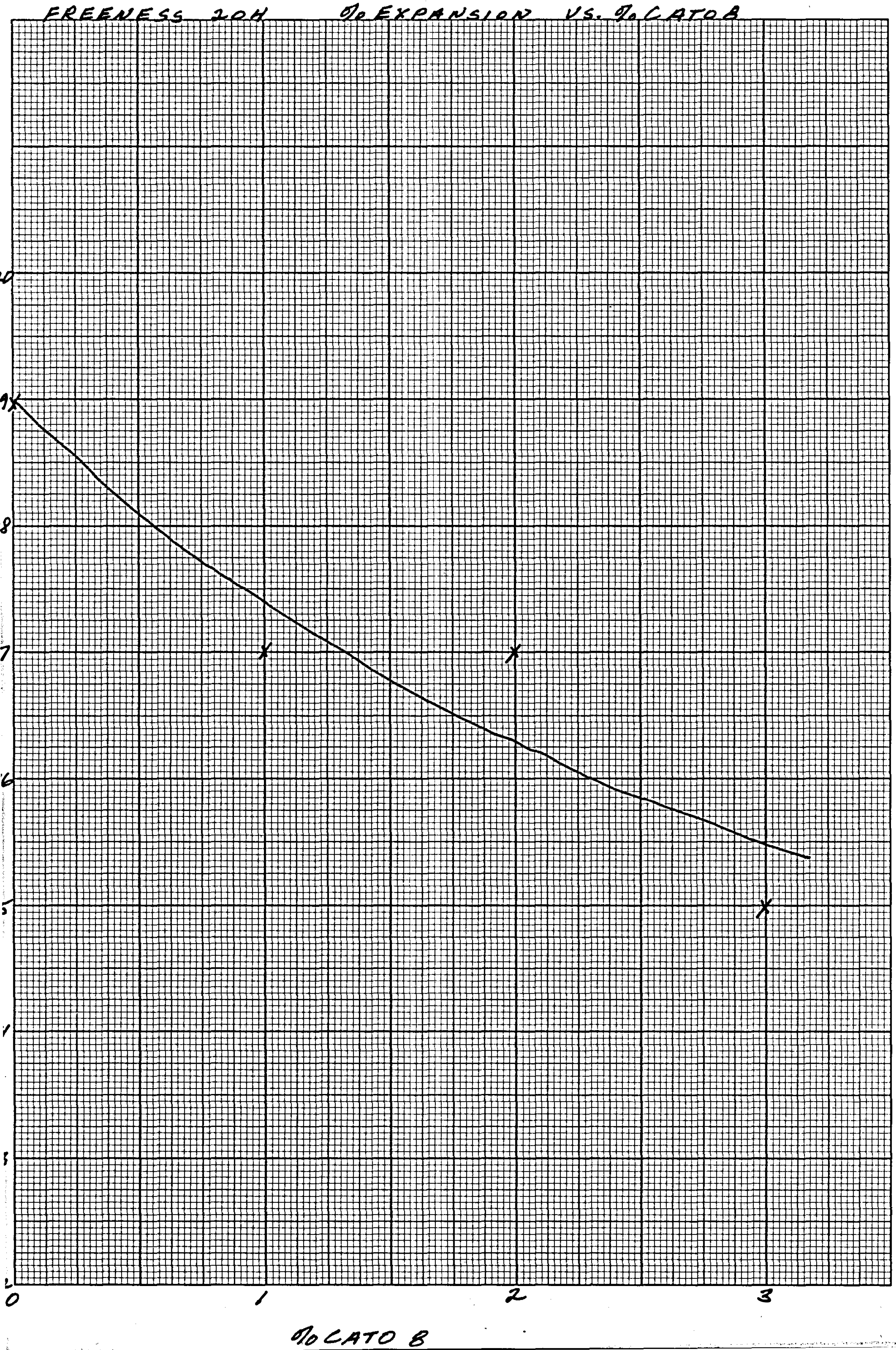


Figure 10




FREENESS 20H %EXPANSION VS. % CATO 8
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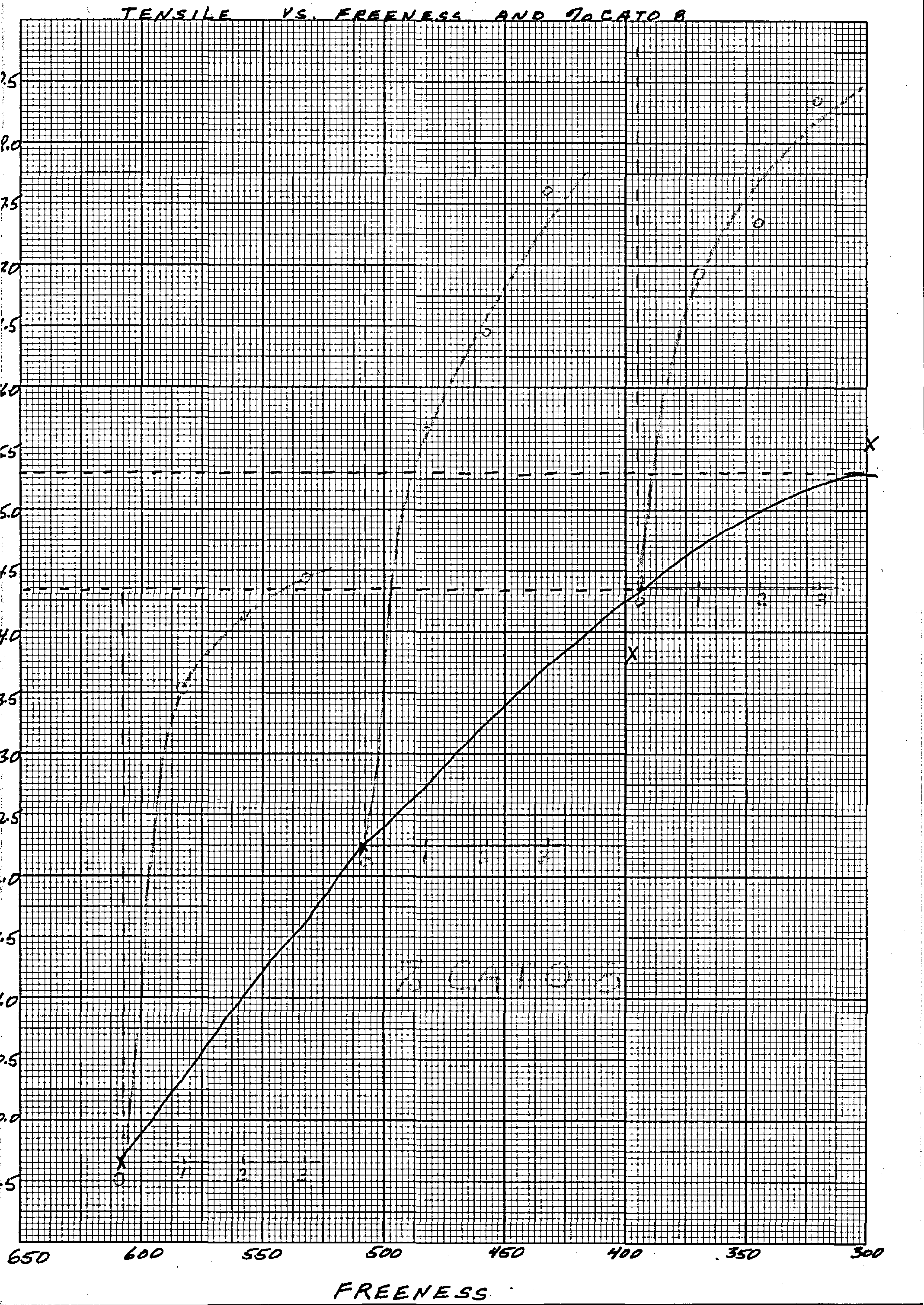
8
7
6
5
0
1
2
3
% CATO 8


TENSILE VS. FREENESS AND % CATO 8
.5
.0
.5
.0
.5
.0
.5
.0
.5
.0
.5
.0
.5
.0
.5
.0
.5
0
1
2
3
% CATO 8
650
600
550
500
450
400
350
300
FREENESS

From Table I it is seen that the addition of Cato 8 gave a substantial increase in the mullen and tensile strengths of the sheets to which it was added. By adding one per cent Cato 8 to the stock at freeness 608 a higher mullen was obtained than by beating to a freeness of 204. The tensile strength increased as the amount of Cato 8 starch was increased at each freeness.

The tear tests show a general decrease as the freeness is lowered and the amount of starch increased.

The per cent expansion of the sheets was varied and these will be discussed later.

In figures 1 through 5 the expansiometer readings were plotted against the per cent relative himidity. In each case this plot yielded a straight line. From this figure and the formula:

$$X = 15C/H_2-H_1$$

where

X = expansion

C = difference in the expansiometer readings at 65 and 50 per cent relative humidity

H_2 = 65 per cent relative humidity

H_1 = 50 per cent relative humidity

The values of X, divided by the length of the test speciman, give the per cent expansion of the sheets and these values are shown in Table I.

From figure 6 it is seen that as the freeness is lowered, or

beating increased, the per cent expansion of the sheets increased. This was expected from the literature survey which showed that as the freeness was lowered the expansion increased.

In figures 7 through 11 the per cent expansion is plotted against the per cent of Cato 8 added at the various freenesses. The curves show a general increase in expansion as the amount of Cato 8 is increased at freeness values of 608, 508, and 398. At freeness 295 the curve is almost a horizontal line and the expansion decreases as the amount of starch increases at freeness 204. It appears that the addition of Cato 8 increases the hygroexpansitivity at high freenesses and tends to lower the per cent hygroexpansitivity at lower freenesses. However, not enough is known about starch-fiber bonding to draw any definite conclusions.

Tensile strength is plotted against freeness and per cent Cato 8 starch in figure 12. By drawing a horizontal line from one freeness value to its tensile strength and observing the per cent Cato 8 that was added to a lower freeness stock to reach this tensile strength, the effect of Cato 8 starch on the hygroexpansitivity of the paper can be observed. The expansion at the percentage of starch needed to cross this tensile line was found from figures 7 through 11.

The handsheets showed a maximum tensile strength of 15.25 kg. per mm., with no starch additions, at a freeness of 300. The expansion was .18 per cent.

At freeness 395 and 0.3 per cent Cato 8 the tensile strength of

15.25 was obtained. The expansion was .171 per cent which is lower than the .18 per cent expansion obtained by increasing strength by beating alone, and is essentially that of the sheet made at freeness 395 with no Cato 8 addition.

At freeness 508 and 0.8 per cent Cato 8 the tensile strength was 15.25 and the expansion .15 per cent. This is much lower than the expansion when strength was developed be beating alone.

A tensile strength of 15.25 was not obtained with up to 3 per cent Cato 8 addition at freeness 608 so no conclusions can be drawn.

By beating to a freeness of 395 a tensile strength of 14.3 Kg. per mm. was realized with an expansion of .17 per cent.

At freeness 508 and 0.4 per cent Cato 8 a tensile strength of 14.3 was developed and an expansion of .158 per cent. This is lower than the .17 per cent expansion when the tensile strength was developed by beating alone.

At a freeness of 608 and 2.6 per cent Cato 8 the tensile strength of 14.3 was attained and the expansion was .155 per cent. This is lower than the expansion by building strength by beating alone.

From this investigation these conclusions can be drawn:

1) As the freeness is lowered, or beating increased, the dimensional stability is decreased or the per cent expansion is increased.

2) In general small additions of Cato 8 starch, while giving a substantial strength increase, give approximately the same expansions as the pulp to which the starch was added.

3) Greater dimensional stability can be attained by supplementing mechanical refining with Cato 8 starch.

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Acknowledgment

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