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THE INFLUENCE OF FINES ON AN ALKYL KETENE DIMER SYNTHETIC SIZING AGENT

by

Andrea S. Coyle

A Thesis submitted
in partial fulfillment of
the course requirements for
The Bachelor of Science Degree

Western Michigan University
Kalamazoo, Michigan

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ABSTRACT

It is the purpose of this thesis to attempt to evaluate the influence of fines on an alkyl ketene dimer (AKD) synthetic sizing agent and to study the role of fines on sizing.

It was found that the addition of fines lowered the degree of sizing in the sheet. Since there was more surface area available when fines were increased, more sizing agent was necessary in order to obtain the same level of sizing with a Hercules or Cobb Size Test. Since the amount of sizing agent was held constant, sizing decreased as a result of the addition of fines.

A sheet produced from longer fibers reacted with the sizing agent prior to the fines addition resulted in a lower degree of sizing than a sheet made from reacting the sizing agent with the fines first. It is believed that the unsized fines had a greater ability to block off the hydrophobic ends of the sized longer fibers and therefore decreased sizing efficiency.

In a sheet containing an insignificant amount of AKD, fines tended to increase sizing in the sheet. The Washburn equation predicts the rate of penetration since rate of penetration is proportional to pore size. By increasing the amount of fines the pore size of the sheet was decreased and therefore, rate of liquid penetration decreased.

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INTRODUCTION

The objective of this thesis is to determine the influence of fines in a white water system on a synthetic sizing agent. It is believed that fines play a significant role in a synthetic sizing system. Synthetic sizing agents react with the hydroxyl groups on a cellulose molecule. Since the fines have a large surface area per unit weight of fibers, the fines consume a significant portion of the sizing chemical. Most papermills are closing up their white water systems, thus more fines are being recirculated at the wet end of the paper machine which is the point of addition for synthetic sizing agents.

A variety of synthetic sizing agents are available, however, this thesis will discuss only alkyl ketene dimers which do not require the addition of retention aids.

SIZING THEORY

Sizing can be defined as the process in which a chemical additive provides paper with resistance to wetting and penetration, usually by aqueous liquids (5).

Cellulose itself is a very hydrophilic substance. The fiber surface has a high specific energy, thus water will readily wet a fiber surface. Various chemical additives have been developed to produce repellency of water, ink, and milk.

Davidson (5) explains that many different processes occur when the paper surface is wet. It must first wet the fibers, after which it is drawn into the sheet structure by capillary action of the pores between the fibers. The liquid also tends to spread out on the surface by a process called feathering. The liquid can also penetrate into the paper along its surface by paths through the cellulose material. The rate of flow of a liquid through a thin tube or capillary is represented by the Washburn equation: (5,8)

$$\frac{dl}{dt} = \frac{(Pr^2 + 2r\gamma\cos\theta)}{8\eta l}$$

where l is the length of capillary; r is the radius of the capillary; P is the external pressure; γ is the surface tension of the liquid; θ is the contact angle between the liquid and the capillary wall; and η is the viscosity of the liquid.

A sizing agent should make the fiber surfaces hydrophobic so that the contact angle with aqueous liquids will be high (7). The sizing molecule should be oriented on the fiber surface so

that the hydrophobic group is exposed. In addition, the sizing agent should be attached to the fiber surface so that it cannot be easily dislodged by liquid penetration. It is also desirable to have the sizing material evenly distributed over the fiber surface. Less than a complete monolayer coverage is sufficient to give a high contact angle for water repellency (5).

Sized paper may have a contact angle of over 100° which indicated that the sheet is water repellent, however, after a short period when the liquid contacts the paper, the contact angle drops considerably and the water droplet spreads and penetrates the paper (26).

Beginning as early as 1807, alum/rosin system has been the traditional method to achieve sizing in the sheet (5). This method requires a certain chemical environment, namely acidic pH (4.0-5.0), which can cause various disadvantages. Alum/rosin sizing is accomplished by forming chemical aggregates which precipitate on the fiber surfaces.

In the 1950's, synthetic sizing agents were developed which were chemically bound to the fiber surfaces under neutral or alkaline condition (6).

NEUTRAL SIZING

The use of synthetic sizing has increased significantly within the past ten years and still continues to grow. Neutral sized calcium carbonate filled paper have opened a new realm of papermaking that is producing paper for lithography, industrial papers, chart papers, archive text, photocopying, and coated stock (14). Neutral size, as compared to an alum/rosin system, is

producing better paper at a lower cost.

A changeover from an alum/rosin system to a neutral sizing system must be done at one time (18). A slow incremental change may be disasterous due to the complications involved. Other changes that would result would include internal loadings, dyestuffs, wet strength resins, and physical changes in the sheet.

The main components one would expect to find in any wet end additive system for neutral or alkaline papermaking are: (4)

1) filler
2) neutral sizing agent
3) retention agent-necessary for certain sizing agents

Retention agents are either included in the sizing emulsion or should be added to the sizing chemical.

Various synthetic sizing agents have been introduced that will react with the hydroxyl groups on the cellulose molecule and thus become permanently anchored. In principle, the monomolecular layer of a firmly bound sizing agent with its hydrophobic end oriented away from the cellulose molecule should provide excellent water repellency (5). In practice, chemically reactive sizing agents are generally more effective than the rosin/alum sizing system, per pound added, due to the stronger (chemical) bonding and better distribution (5). Improved sizing can be obtained with additions as low as 0.05 percent (5). These sizing materials are generally more expensive than rosin, however, they do not require alum as a co-reactant, retention aid or as a bonding link with the cellulose fibers.

The synthetic sizes can be used in a neutral to alkaline papermaking system thus reducing equipment corrosion, and

increasing long term strength of the sheet due to less aging (16). Many chemical additives can react with cellulose more rapidly under alkaline conditions. In alum/rosin systems, excess alum or insufficient alum can upset the ionic and electrochemical balance of the paper machine's wet end system (13).

Some of the most commonly encountered synthetic sizing agents are listed in Table I (8,17).

Chemical Reaction

Of the cellulose reactive sizes the alkyl ketene dimer (AKD) is the most common. These AKD's are made from fatty acids, namely mysteric, palmitic, stearic, and oleic. The AKD consists of two hydrocarbon chains attached to a 4-membered lactone ring. At a neutral pH this ring reacts with the cellulose hydroxyl group to form a stable ester linkage (6,8,25).

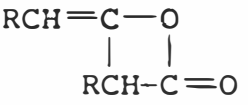
The alkly ketene dimers are believed to have the following structure,

Table I (8,17)

Chemical functionalities of common cellulose-reactive sizing systems

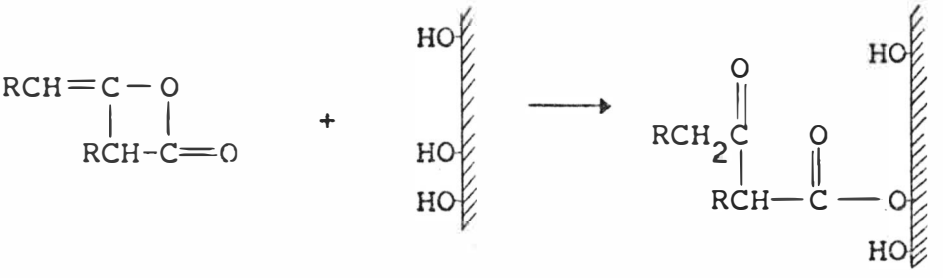
Water Resistant functionality	Cellulose Reactive Group	Size Complex
Stearic acid	anhydride	Distearic-anhydride
Alkylated succinic acid	anhydride	Alkenyl succinic-anhydride
Styrene copolymer	anhydride	Styrene maleic anhydride
Stearic acid	alkylated ketene	Alkyl ketene dimer

Fig. 1



where R represents an alkyl group such as $-C_{16}H_{33}$. The reaction of alkyl ketene dimers with paper fibers involves mainly esterification of surface hydroxyl groups as represented by the following equation (6).

Fig. 2



Although the ketene dimer molecule will also react with water, its long hydrocarbon chains seem to protect the very active lactone ring. When the dimer is added internally about two-thirds of the retained material will react with cellulose rather than form the hydrolysis product, a ketone (5).

It appears that only the surface hydroxyl groups on the cellulose molecule react with the AKD and only the surface characteristics of the fiber are affected. Davis (6) concluded that the amount of AKD that can readily be made to react with the fiber is of the order of magnitude required to form a monomolecular layer on the fiber surface. As evidence that a chemical reaction has taken place can be shown that after the reaction the AKD can no longer be extracted from the fiber by organic solvents and that the fibers retain its size after the extraction.

Like most organic chemical reactions, the reaction between

AKD and fibers require certain favorable conditions. The reaction is not instantaneous but does proceed at a finite rate; heat and time are required for the development of sizing after the sheet is made. In most cases, heat and time to sufficiently dry the sheet are also sufficient to cure the AKD (6). Therefore, sizing is usually developed under paper machine operating conditions.

Fiber reactivity is important and treatments which tend to decrease the reactivity of the cellulose surface makes it more difficult to size. Previously drying the fibers at a low pH tends to reduce its reactivity and makes it more difficult to size. The reaction between the AKD and fiber takes place for the most part after the fiber is dry (6). While the sheet is still wet, the fiber is swollen and tends to repel the AKD which is hydrophobic in nature. Whem the contact with water at high temperatures is too long, the reaction of the AKD with water is a competing reaction which tends to decrease sizing efficiency. Drying conditions are, therefore, important.

FINES

Fines are fragmentary particles found in pulps, mostly produced by mechanical treatment. With softwood pulps, they are primarily debris from fibrous materials. In the case of hardwood pulps, fines are made of fibrous debris plus non-fibrous materials such as ray cells and vessel segments (9).

Most papermaking furnishes contain a large amount of fines. These fines play an important role in drainage and retention. They also contribute to the development of strength and other

sheet properties. Since a major part of paper mill white water and discharge contain fines, improved use and retention of fines is of both economical and environmental interests.

Fines can be defined as the fibrous portion of a furnish that can pass through a 200 mesh screen. Pulp fines are rod-shaped, semicrystalline, fibrillar material with widths of 0.1 - 0.5 m and lengths reaching several tens of microns (13). Their structure and high surface area classifies them separately. There is no major difference in chemical composition. Pulp fines tend to swell considerably, retaining 2-3 times as much water as the longer coarser fibers, and tend to behave somewhat as a gel (13).

Britt (2) shows a general comparison of the distribution of fines content on papmaking wet ends (Table II). This shows the tray water is mainly composed of fines, these fines are consuming large amount of chemical additives, namely synthetic sizing agents, are being filtered through the sheet and not being retained.

Table II (2)

Stock fines content on papermachine wetends

Sampling Point	Tissue Fourdrinier % fines	Newsprint Fourdrinier % fines	Newsprint Twin-wire % fines
Stuffbox	25	36.3	35.2
Headbox	60	49.4	64.1
Tray	95	98.7	90.0
Couch sheet	12	25.4	25.0

The fines particles, with their large surface area, require greater polymer concentrations to achieve better efficiency. The projected area per unit volume of fiber can be calculated from the following equation (9),

$$\frac{A}{V} = \frac{nLD}{v}$$

where A is the projected fiber area; V is the fiber volume; n is the number of fibers per unit mass; L is the fiber length; D is the fiber diameter; and v is the specific volume.

Polymer or particle adsorption is primarily a function of hydrodynamic surface area (12). Therefore, fines with their larger hydrodynamic surface areas can adsorb a larger amount of chemical additives when compared against long fibers. The hydrodynamic surface area of the pulp fines is found to seven times as large as the surface area of the longer fiber fraction (13). By using the silvering technique to determine surface area, the pulp fines were found to be only five times as large as the surface area of the fibers (13). The silvering technique usually produces a lower surface area than other surface area techniques.

Other methods used to determine surface area other than hydrodymanic and silvering methods are dye adsorption, geometric method, filtration resistance (liquid permeability), gas adsorption, and optical methods (23). Ingmanson and Thode (10,23) found that the filtration resistance method is the best precise technique to obtain the surface area of beaten pulps containing fines. Neither the silvering technique or the dye adsorption method accounts for the surface area contribution of fines (19,23).

FINES AND SIZING INTERACTIONS

Fines are of great importance in a neutral sizing system because of their large surface area. Since the effective surface area of the fines are greater than the fibers, the fines have more reactive sites per unit of weight. The hydroxyl groups on the cellulose fines react with the synthetic sizing agent and as an effect, the fines consume a majority of the sizing chemical.

Marton (13) extensively compared the fines interaction with various chemical additives. In a fines/alum system, it was determined that the alum concentration was more than four times higher on the pulp fines than on the fiber fraction in a white water system. In a rosin size system, the fines captured about 80 percent of the total size added, while the surface of the fibers may have been only partially covered with size, thus creating a rather unstable sizing situation (Table III) (13). Hence, there seems to be a definite relationship with fines and particle interaction.

Table III (13)

Distribution of alum and rosin size

	Headbox furnish			
	Total filtrable solids	Fiber faction	Fines fraction (18%)	Base stock
Al as alum, %	1.3	0.8	2.4	1.1
Rosin, %	0.5	0.05	2.2	0.4

By comparing the difference in adsorbing properties of fines and fibers, it can be found that objectionable non-uniformity may exist in sheet propertoes. Marton (13) found that pigment fillers usually accumulate on the top side of a single wire sheet. The increased adsorption of fines may lead to a two sidedness in sizing, in receptivity of coating color, in smoothness, or in dyestuff application.

The presence of alum in a fiber furnish tends to prefer fines and, therefore, leads to alum starvation of the surface of long fibers (13). Increasing the rate of alum addition may serve as a temporary solution, however, excessive alum concentrations lead to other undesireable problems. Improvements of first pass retention is usually the best method to reducing the accumulation of fines and to minimize the materials lost through the suspended solids in the discharge (13).

RETENTION

Retention of fines and sizing agent are important in a paper making system. Walkush (24) investigated the effect of shear rate of fines retention at constant fines concentration and various pulp solids content. The results are shown in figure 3. As can be seen, the maximum retention decreases as the shear rate increases and as the pulp solids decrease.

Griggs (8) found that differences in mixing agitation itself may alter the sizing response, especially as it affects the adsorption of the sizing complex. The anionic surface charge of cellulose becomes increasingly electronegative as the time of agitation increases. This can be directly related

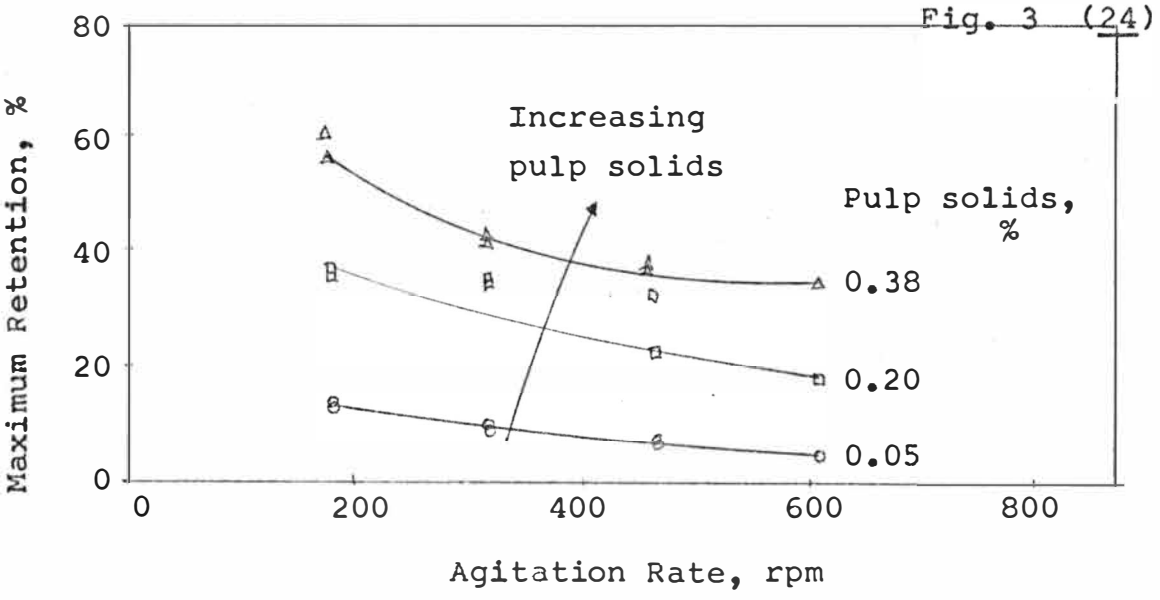


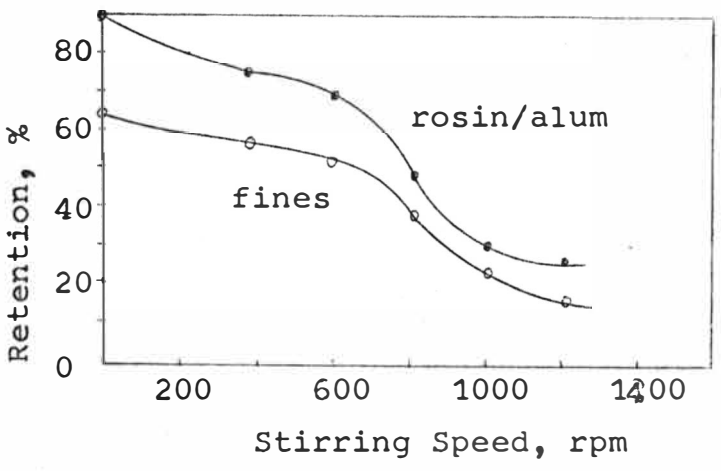
Fig. 3 (24)

to the amount of refinement where the more highly beaten pulps have increasingly higher anionic charges because of their increased surface areas. In terms of size affinity or other polymer needs of the cellulose, the amount of cationic material needs to satisfy the electronegative charge of the fiber renders it isoelectric (20).

Once the polymer-fiber bridges or sizing bonds have been established, hydrodynamic shear forces within the papermaking system may interfere with the established sizing networks. Because of this limitation, many of the synthetic sizing agents are introduced into the papermaking system in areas beyond severe agitation (15).

Figure 4 (3) shows the effect of the addition of 0.5% rosin size and 2.5% alum in a stock system. It will be noted that the retention (or flocculation) of fines is improved at low degrees of turbulence. With the rosin/alum/stock system, retention is greater than the fines system. This is due to the

Figure 4 (3)



formation of a floc as a result of electrokinetic forces (3,11).

Good retention of synthetic size is accomplished with a retention aid, which is either included with the purchased size or will be added when the sizing agent is added. The American Israeli Paper Mills, Ltd. (22) used an octadecenyl succinic anhydride sizing agent that was retained with either a cationic starch or a cationic polyacrylamide. It was found that the additions of starch had to be kept as low as possible to prevent deterioration of sheet formation and increased trouble with slime. It was later found that the higher the bicarbonate content of the machine white water, the lower the retention of the sizing agent using cationic starch. A high concentration of dissolved carbonate blocks active cationic sites of the cationic starch, thus reducing its effectiveness in size retention.

Information on the retention of alkyl ketene diner sizing agents is not available at this time.

CONTACT TIME

Because of the relatively short contact times available in the papermaking process, Nelson (15) found the absorption and surface conformation of polymeric additives would not be expected to go to completion. It was found that efficiency decreased at longer contact times, while the control showed a slight improvement. A time optimum could be based on the concept of "best balance" between absorption on the fiber surface to provide stability and extension into the liquid phase to promote bridging.

TEMPERATURE

It is generally recognized that increasing the headbox temperature improved drainge by reducing the viscosity. In a study done by Nelson (15), cationic starch, cationic polymer and anionic polymer were analyzed for any temperature effects. Neither the cationic starch or the cationic polymer were influenced by temperature changes over the range of 20-40^{o}C.

The effect on the anionic polymer showed a significant positive association with both temperature and time-temperature interactions. It is believed that the effectiveness of the anionic polymer is related to adsorption phenomona. The different responses of the cationic and anionic polymers to temperature change may be either charge related or from a difference in molecular weight.

The alkyl ketene dimer is cationic, however, the effect of temperature in the aqueous system with fines is inconclusive.

SUMMARY

Synthetic sizing agents, which are used in neutral or alkaine conditions, are able to chemically react with the cellulose fibers. Of the synthetic sizing agents available, the alkyl ketene dimer is the most common. The fines portion of the paper stock furnish has a larger surface area per unit weight than fibers and therefore has more reactive sites available for the reaction with the alkyl ketene dimers. Studies have shown that the fines interact with various chemical additives (such as alum, rosin, and fillers) more so than the fibers. Synthetic sizing agents are also believed to interact with the fines in the same manner, although no studies have confirmed this theory. Retention, contact time, and temperature also play an important role in the fines/synthetic sizing interaction.

STATEMENT OF THE PROBLEM

The purpose of this thesis is to study the influence of fines on an alkyl ketene dimer synthetic sizing agent. Previous studies reported the role of fines in an alum, rosin, filler and various polymer systems, however, synthetic sizing agents have not been studied until this time.

It is believed that sizing will decrease as fines are increased primarily due to the fines consuming a large portion of the sizing agent due to its greater surface area. Therefore, sizing will decrease due to the fines consumption of the sizing agent.

The influence of adding the synthetic sizing agent to the fines or longer fibers will be studied to determine if order of addition is an influencing factor.

EXPERIMENTAL DESIGN

The purpose of the experimental portion of this thesis is to show the effect of fines, if any, on the alkyl ketene dimer (Hercon 40). Four different levels of fines will be tested in addition to four levels of sizing agent. The order of addition of the sizing agent to the fines and fibers will also be observed to determine if there is any influence in the sizing test results.

The fines will be separated from the long fibers by using a Clark Classifier and only the long fibers will be retained. The fines fraction will be obtained from the white water from the pilot plant paper machine at Western Michigan University from the same pulp. The fines fraction will be allowed to react with the sizing agent for a given amount of time then the longer fibers will be reacted, and vise-versa to test the influence of order of addition of the sizing agent.

The sheets will be made using a buchner funnel to keep the consistency of the stock at headbox consistency (approximately 0.5% consistency) to avoid forming the hydrolysis product from the AKD, a ketone. A second reason for using a buchner funnel is to attempt to obtain 100 percent retention of the pulp. A pH of 8.3 will be held constant in addition to contact time with the sizing agent prior to making the sheet.

The sheet will be placed in an oven in order to cure the sizing agent in the sheet.

The effect of two-sidedness in the sheet will be considered and only the top side (opposite the filter paper side) will be tested.

EXPERIMENTAL PROCEDURE

The fines-free fibers were obtained from a bleached 50% softwood and 50% hardwood kraft (Espanola) pulp beaten at 1.75% consistency to 500 ml C.S. freeness in a 1½ lb. Valley Beater with a 5400 g. load. Fines were removed in a Clark Classifier using a 100 mesh screen to retain the long fibers.

To prepare the fines necessary for this experiment, the same pulp was refined for 35 minutes at approximately 2.0% consistency in a 01-Claflin refiner to a 500 ml C.S. freeness. The white water was collected while a 40 lb. sheet was made (at 85 fpm) on the 30 inch-wide pilot plant fourdrinier at Western Michigan University. The fines were settled for five days and collected at 0.24% consistency. The fines were stored in wet form with a trace of formaldehyde.

The alkyl detene dimer, Hercon 40, was added in levels of 0.375, 0.75, 1.50, and 4.50 lbs. per ton of O.D. pulp. All sheets were made at room temperature (21^{o}C) and constant pH (between 8.1 - 8.3) which was adjusted with $NaHCO_3$.

The four levels of fines (10, 20, 30, and 40% based on total fiber weight) were allowed to react in a beaker for 5 minutes with the various levels of Hercon 40. After the initial 5 minute period, the long fibers were added to the fines/Hercon 40 mixture and allowed to react for an additional 5 minutes. The order of addition was reversed,

thus reacting the Hercon 40 with the long fibers first.

After the completion of the contact time, a handsheet was made using a buchner funnel and coarse filter paper. The sheet was dried on the cylinder dryer.

Prior to testing, all sheets were cured in an oven at 105^{o}C for 5 minutes.

The sheets were tested via the Cobb Size Test (TAPPI Standard T-441) at a two minute contact period with the filter paper side opposite the water. The Hercules Ink Penetration Test was also used with the Hercules Test Solution #2 (lot #K-4776-56-1).

DATA AND RESULTS

Most of the sheets produced for this thesis contained an insufficient amount of sizing agent due to a calculation error. The first three levels of sizing agent (0.375, 0.75, and 1.50 lbs/ton O.D. pulp) contained an insufficient amount of sizing and only the influence of fiber fines on sizing could be studied on these sizing levels. The last level of sizing agent addition (4.50 lbs/ton O.D. pulp) was able to size the sheet, therefore, the effect of fines and the influence of order of addition could be studied. The data is shown in exact figures in Appendix 1, and graphically on the following pages in Figures 1-10.

The graphs are divided into groups as follows: The effect of fines on sizing is shown in Figures 1-4. For the Hercules Size Test (Figures 1,2) sizing increased (shown as an increase in seconds) as fines were increased. Both sets of data follow the results for the sheet containing no sizing agent. Figures 3,4 also show the effect of fines on sizing only this time the Cobb Test was used. Sizing increased (shown as a decrease in weight) as fines increased for the first three levels of sizing agent. For the fourth level of sizing agent addition the sizing increased as fines were increased.

Figures 1 thru 4 show the influence of order of addition of the sizing agent to the fines and fibers. For Figures 1 and 3, the sizing agent was reacted with the

fines prior to the addition of the longer fibers. Figures 2 and 4 show the results of reacting the sizing agent with the longer fibers prior to the addition of the fines.

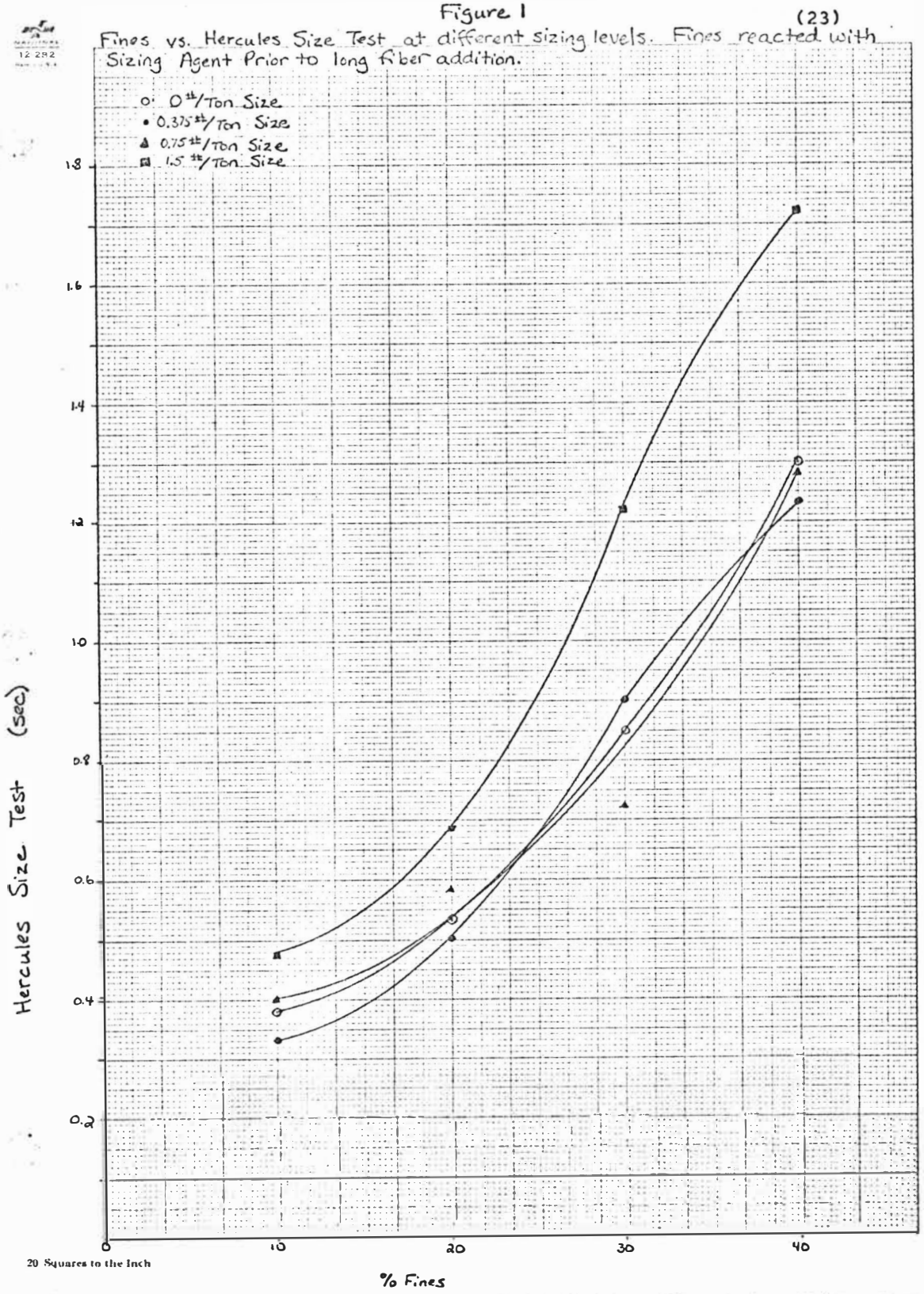
Figures 5 thru 8 show the effect on sizing by varying the amount of sizing agent for different levels of fines. In Figures 5 and 6, the Hercules Size Test was used to measure the degree of sizing. In all cases, sizing increased as the amount of sizing agent increased. For the Cobb Size Test, again sizing increased as the chemical increased, however, the data was scattered more with the Cobb Test than for the Hercules Size Test. Again, order of addition of the sizing chemical to fines was plotted with similar results.

Figures 9 and 10 show the effect of fines in a sized sheet and the two different orders of addition of the sizing agent to the fines/fibers. For the Hercules Size Test, sizing decreased as fines contact was increased. The same is true for the Cobb Size Test results, however, sizing increased at the 40% fines level.

In Figures 9 and 10, the sheets with the longer fibers reacted with the sizing agent prior to the addition of the fines had a lower degree of sizing that the sheets made with the fines reacted with the sizing agent prior to the addition of the longer fibers.

Figure 1

Fines vs. Hercules Size Test at different sizing levels. Fines reacted with Sizing Agent Prior to long fiber addition.



20 Squares to the Inch

Figure 2

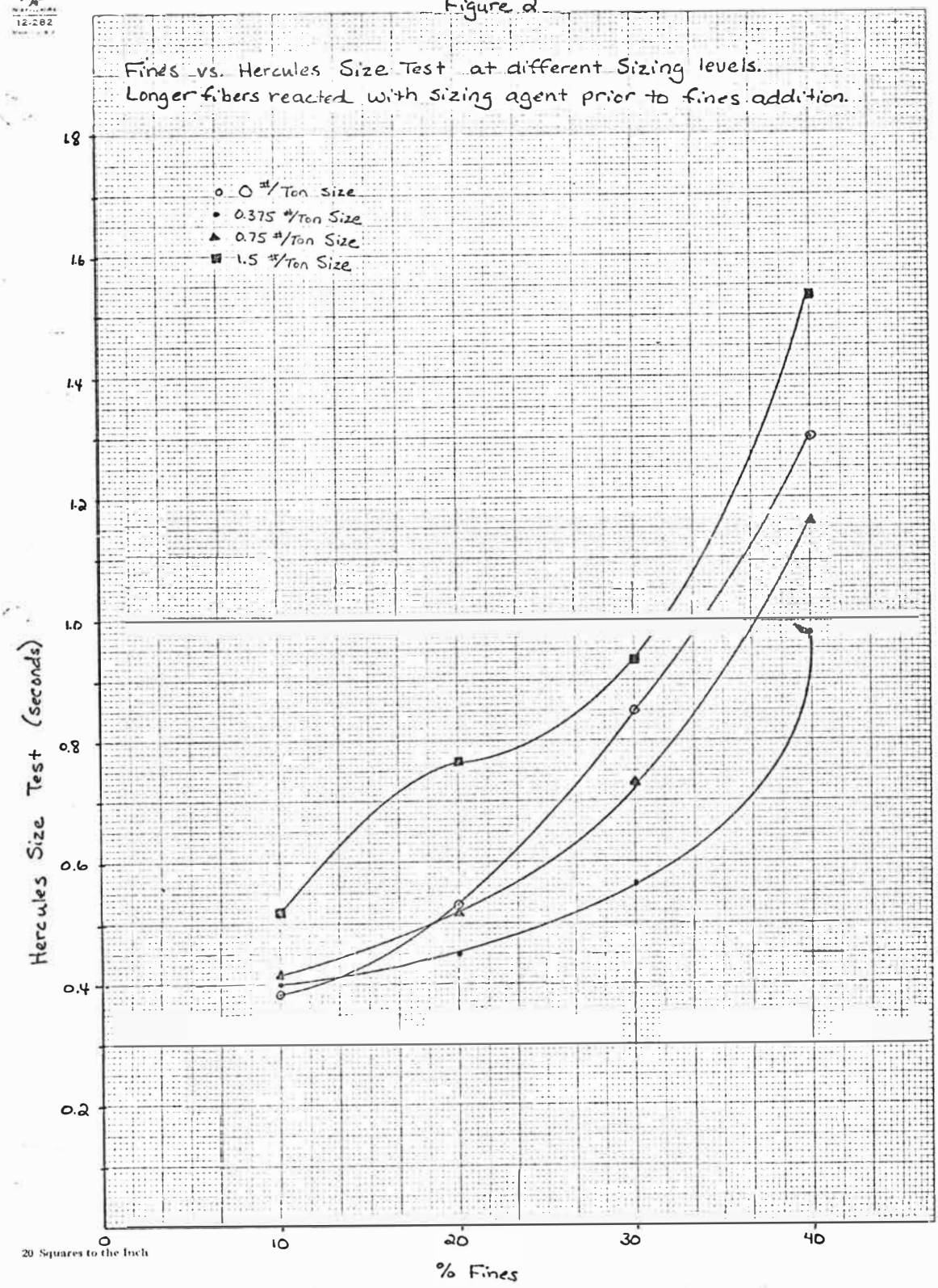

Fines vs. Hercules Size Test at different Sizing levels.
Longer fibers reacted with sizing agent prior to fines addition.
0 #/Ton Size
0.375 #/Ton Size
0.75 #/Ton Size
1.5 #/Ton Size
Hercules Size Test (seconds)
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
10
20
30
40
% Fines
20 Squares to the Inch

Figure 3 Fines vs. Cobb Size Test at different Sizing levels (25)
Fines reacted with Sizing agent prior to addition of longer fibers

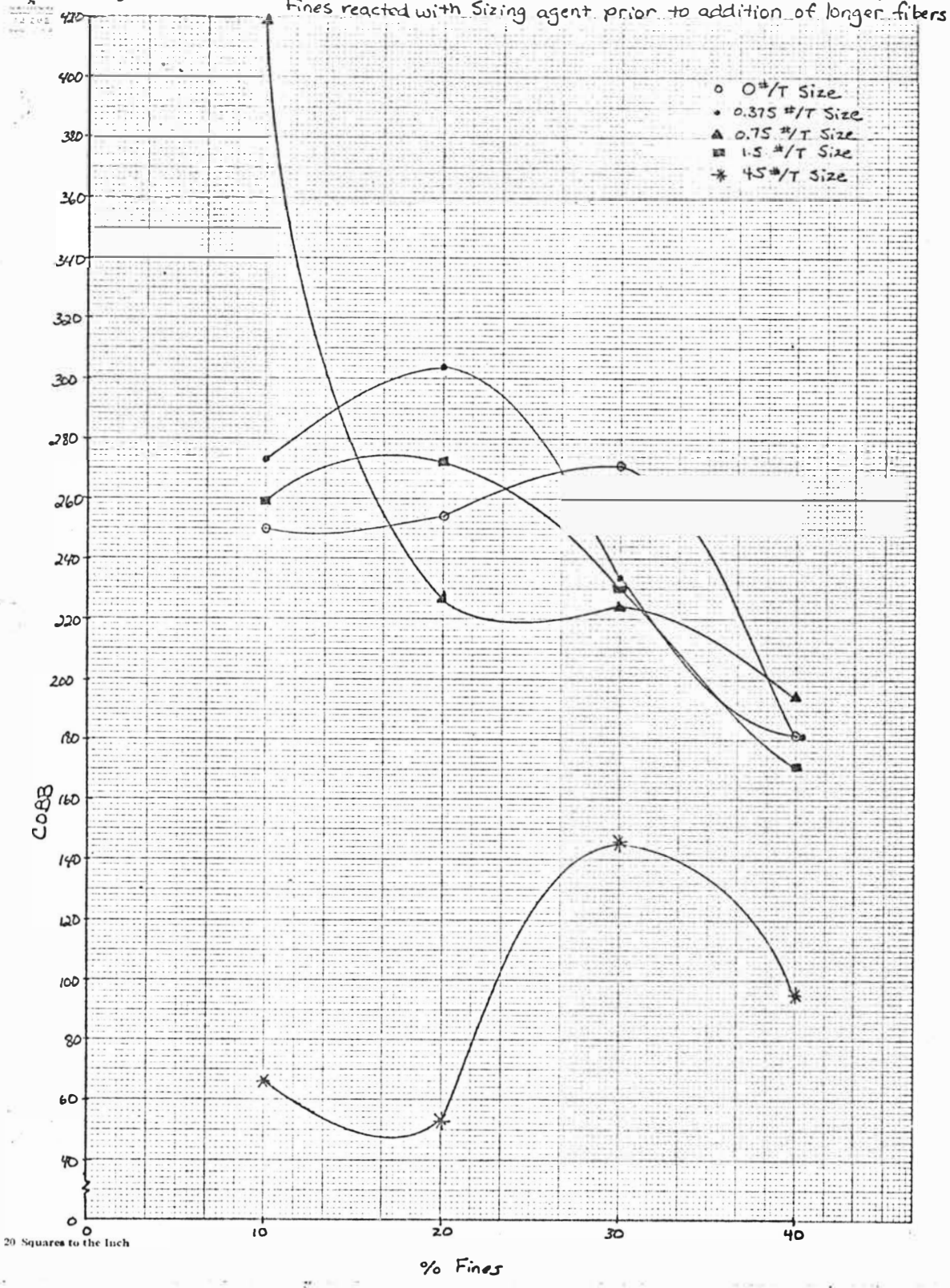


Figure 4

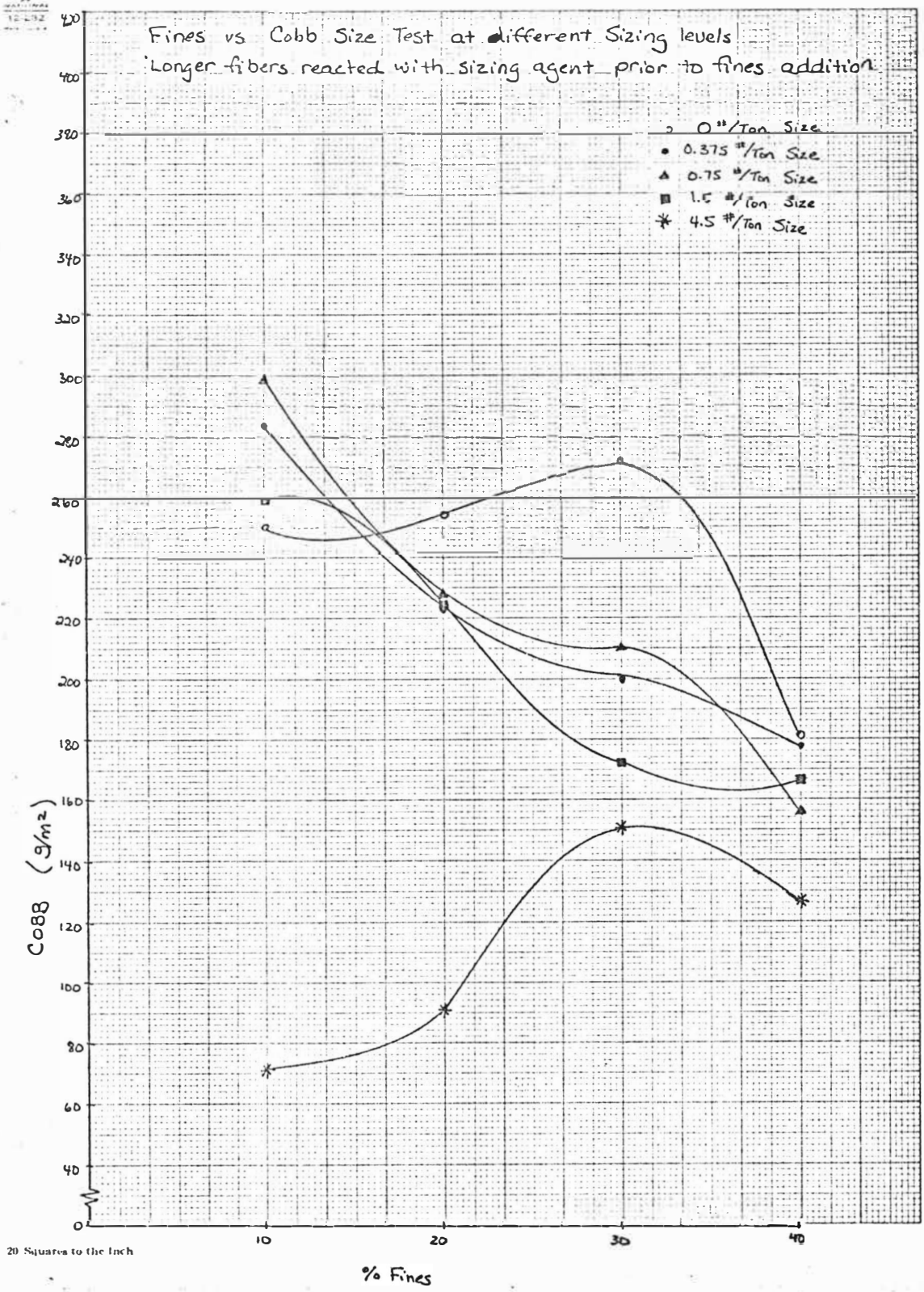

Fines vs Cobb Size Test at different Sizing levels
Longer fibers reacted with sizing agent prior to fines addition
0 #/Ton Size
0.375 #/Ton Size
0.75 #/Ton Size
1.5 #/Ton Size
4.5 #/Ton Size
Cobb (g/m2)
% Fines
20 Squares to the Inch

Figure 5

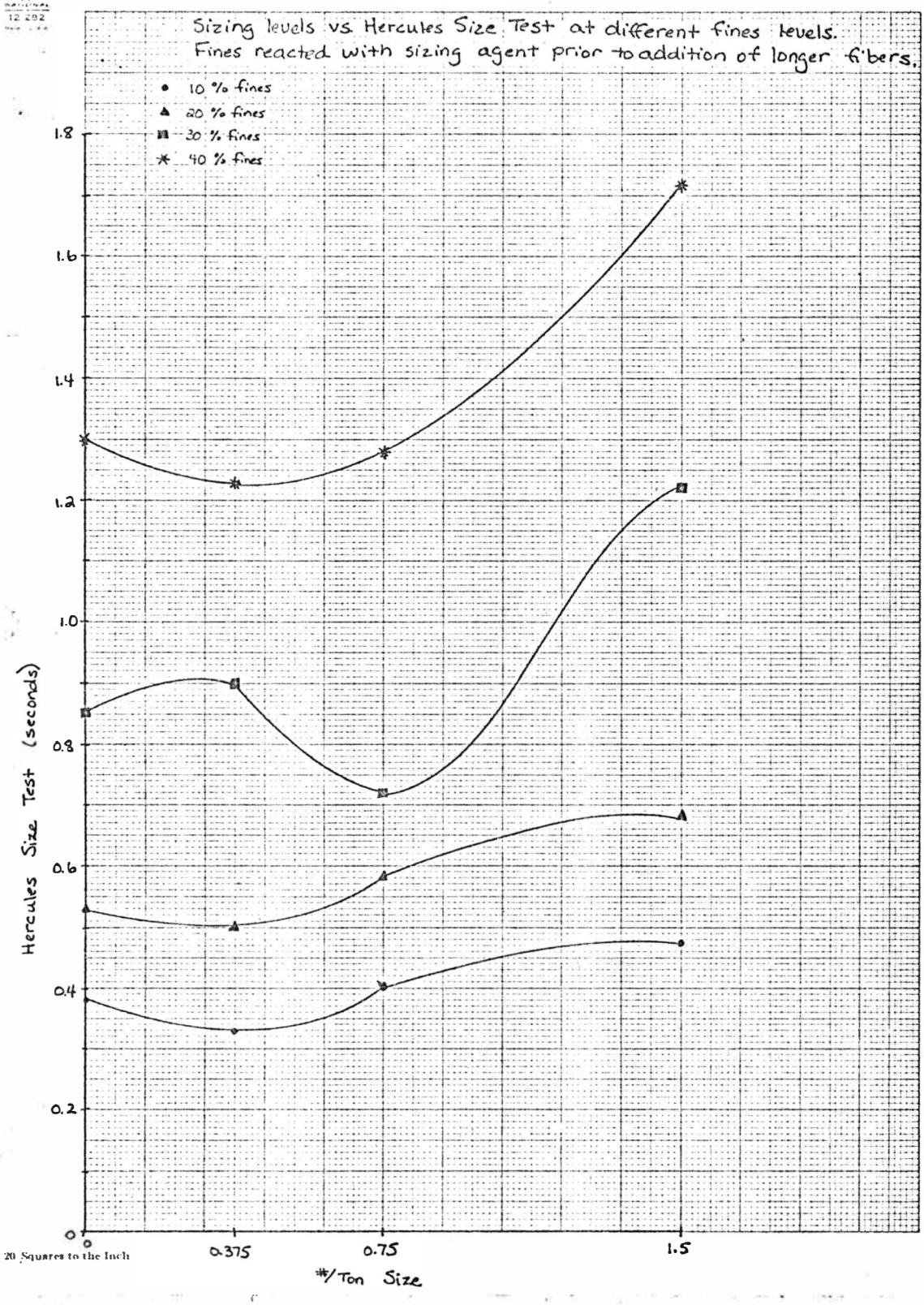

Sizing levels vs. Hercules Size Test at different fines levels.
Fines reacted with sizing agent prior to addition of longer fibers.
10 % fines
20 % fines
30 % fines
40 % fines
Hercules Size Test (seconds)
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
0
0.375
0.75
1.5
#/Ton Size
20 Squares to the Inch

Figure 6

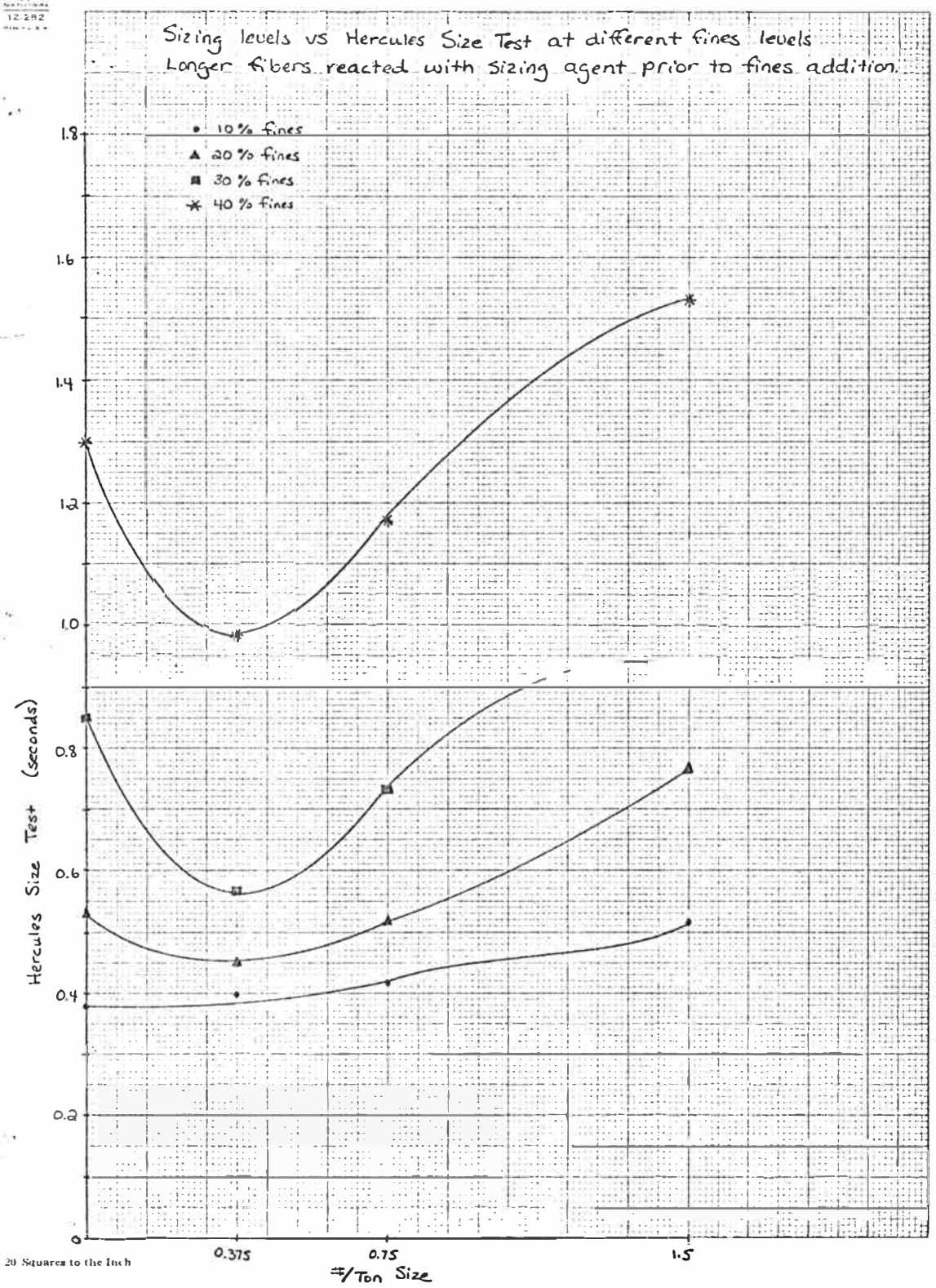

Sizing levels vs Hercules Size Test at different fines levels
Longer fibers reacted with sizing agent prior to fines addition.
10% fines
20% fines
30% fines
40% fines
Hercules Size Test (seconds)
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
0.375
0.75
1.5
#/Ton Size
20 Squares to the Inch

Figure 7

Sizing levels vs. Cobb size test at different levels of fines
Fines reacted with sizing agent prior to addition of longer fibers

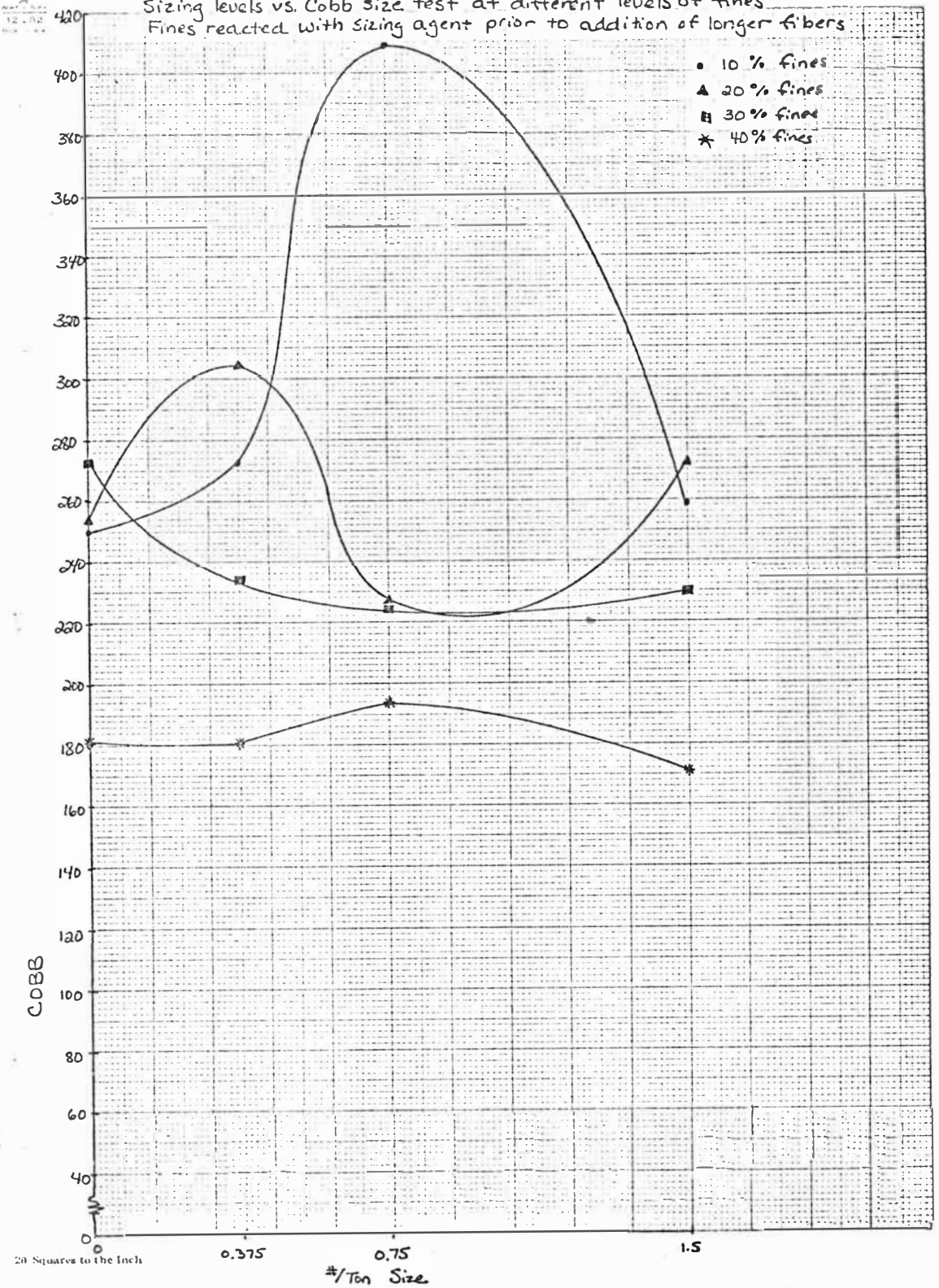


Figure 8

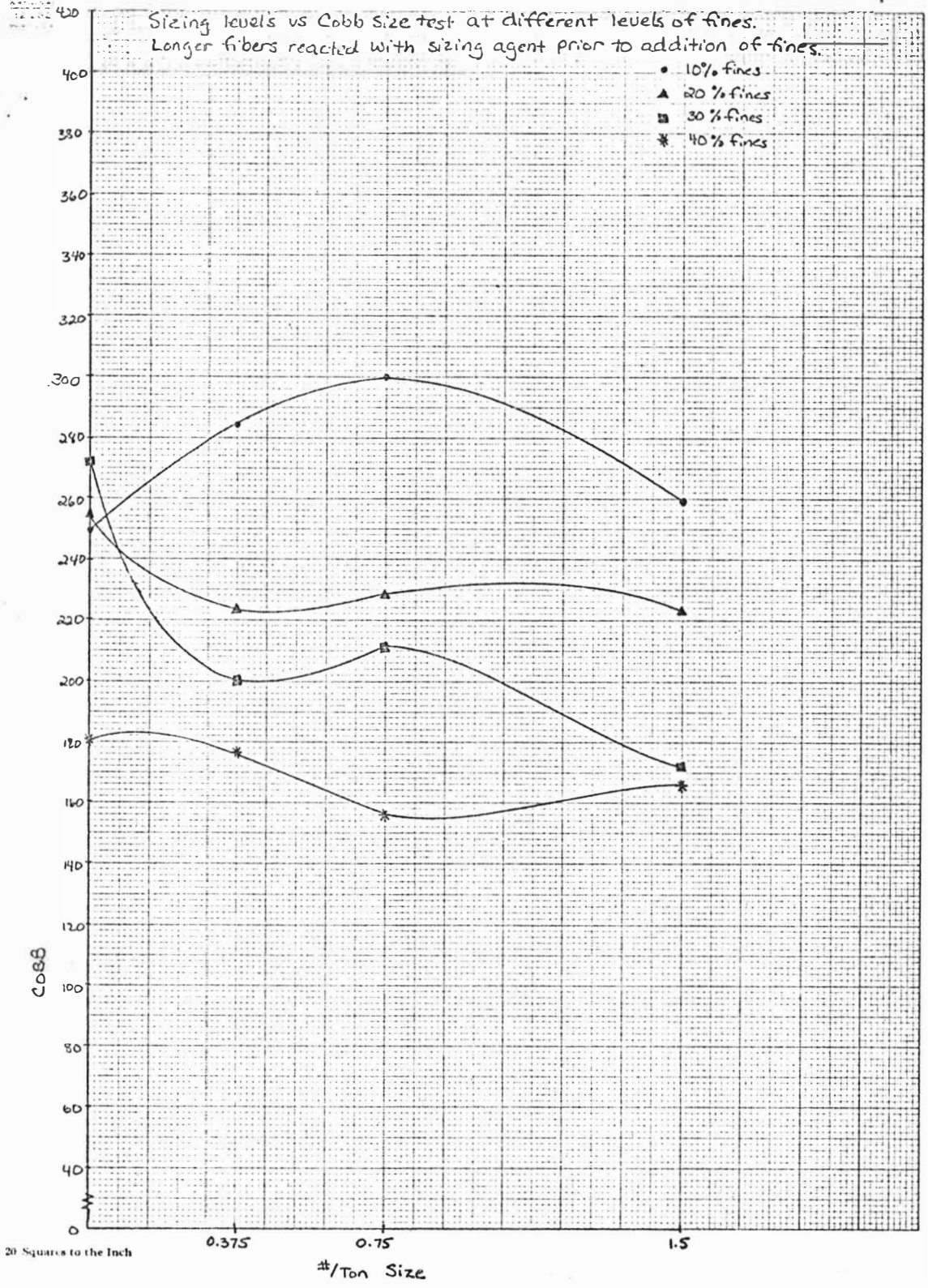

Sizing levels vs Cobb size test at different levels of fines.
Longer fibers reacted with sizing agent prior to addition of fines.
10% fines
20 % fines
30 % fines
40 % fines
COBB
420
400
380
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
0
0.375
0.75
1.5
#/Ton Size
20 Squares to the Inch

Figure 9

Hercules Size Test vs. % fines for 4.5#/ton O.D. pulp sheets.
Order of addition was varied.

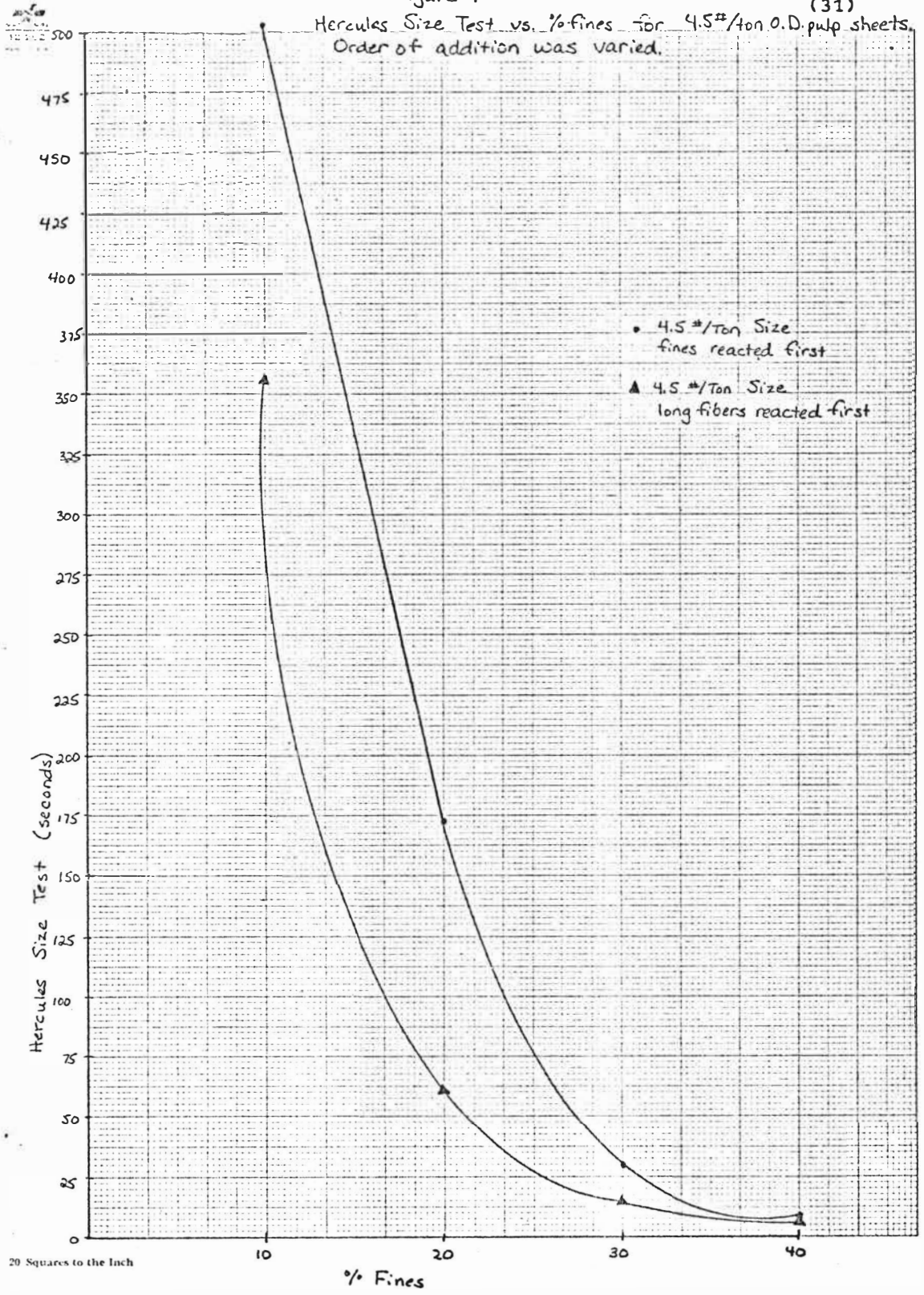
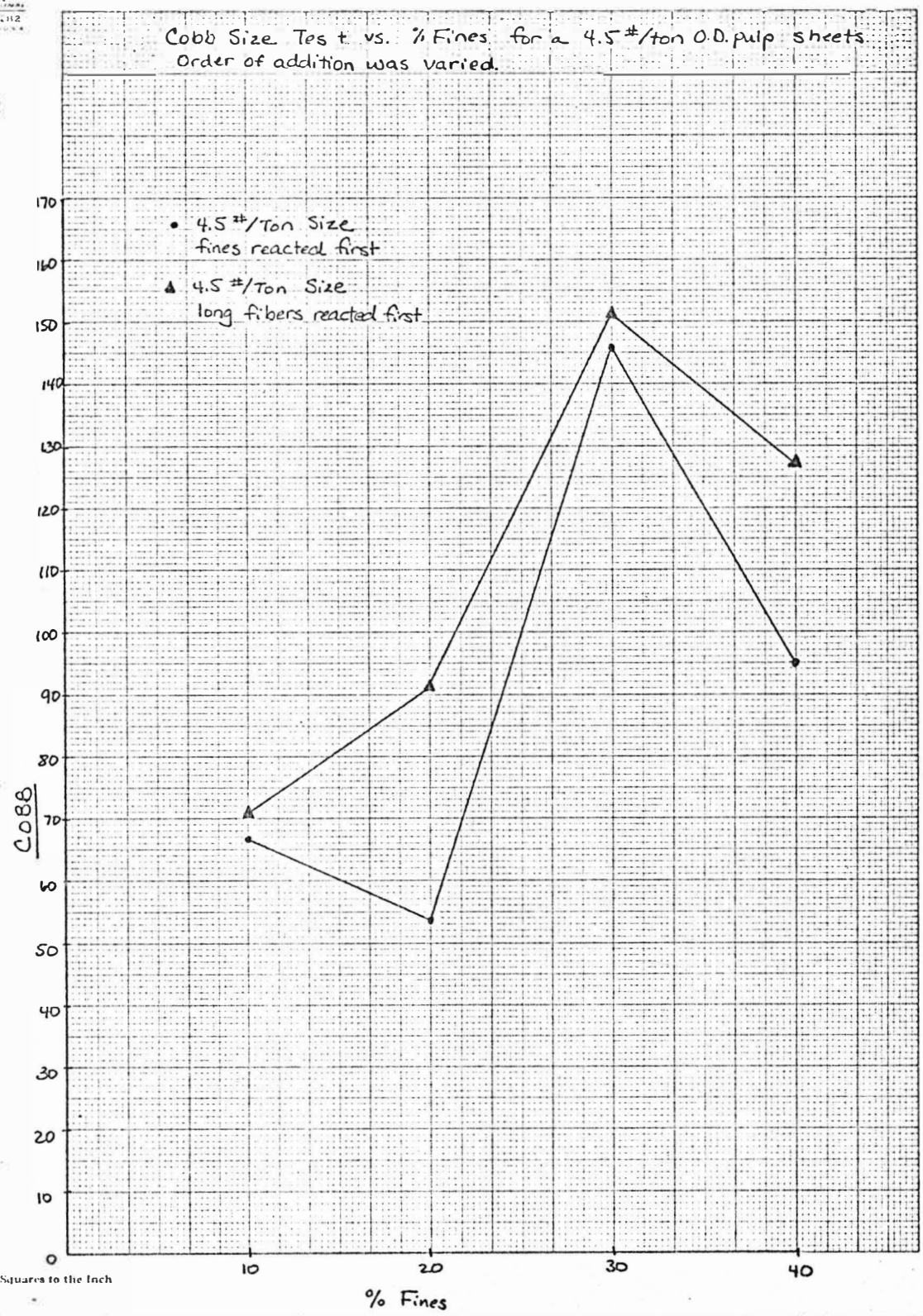


Figure 10


Cobb Size Test vs. % Fines for a 4.5 #/ton O.D. pulp sheets.
Order of addition was varied.
• 4.5 #/Ton Size fines reacted first
▲ 4.5 #/Ton Size long fibers reacted first
COBB
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
10
20
30
40
% Fines
20 Squares to the Inch

DISCUSSION OF RESULTS

During the experimentation, the levels of addition for the Hercon 40 were incorrectly calculated and as a result, the sheets contained only 15 percent of the sizing levels originally intended. The first three levels of addition of the sizing agent (0.375, 0.75, 1.50 lbs/ton O.D. pulp) gave virtually no sizing and threrfore only the role of fiber fines could be studied. For the final level of sizing agent (4.0 lbs/ton O.D. pulp) the sheet was sized lightly, thus the role of fines could be observed.

Effect of fines on sizing

The role of fines versus sizing is shown in Figures 1 thru 4. The Washburn equation predicts that the,

$$\text{rate of penetration} = \frac{\text{pore size} \times \text{surface tension} \times \text{cosine of the contact angle}}{\text{viscosity} \times \text{depth of penetration}}$$

For the first three levels of sizing agent the surface tension, contact angle, viscosity and depth of penetration were believed to be constant since the amount of sizing in the sheet was so small. It appears that the rate of penetration was dependent only on the pore size. Pore size was directly affected by the fines present. By increasing the amount of fines the pore size would decrease, hence, the rate of pnentration would decrease.

The Hercules Size Test (Figures 1,2) shows an increase

in sizing as fines were increased. The sheets containing a small amount of sizing agent were almost identical to the sheet containing no sizing agent. The Cobb Size Test (Figures 3,4) also showed an increase in sizing for the first three levels of sizing agent. These three levels did not follow the zero addition level of sizing as closely, however, the theory of increased sizing as fines are increased is still believed to be valid.

Figures 5-8 show the effect of a small amount of sizing on fines. Sizing in the sheets increased slightly as the amount of the sizing agent was increased. Again, as fines were increased, sizing also increased as predicted by the Washburn equation. The Hercules Size Test and the Cobb Size Test both showed an increase in sizing as fines were added.

Order of Addition

There was essentially no difference in order of addition of the sizing agent to the pulp due to the insufficiently sized sheets for the first three levels of sizing agent added.

For the sheets with the largest amount of sizing agent (4.50 lbs/ton O.D. pulp), the influence on order of addition was observed. Figures 9,10 show the effect of the order of addition of the sizing agent to the fines and the longer fibers. To define the difference in the order of addition, the following experimental procedures were used. Test A: The fines were allowed to react with the sizing agent for 5 minutes

and at the end of the time period the long fibers were added to the size/fines mixture and given an additional 5 minutes to react. Test B: the long fibers were allowed to react with the sizing agent and after the same length of time the fines were added to the mixture. The remaining procedures were identical.

The Hercules Size Test results show that test A initially had a high degree of sizing in the sheet and decreased rapidly as fines were increased. Test B also had a high degree of sizing which decreased as fines were added, however, the overall sizing in the sheet was lower for B than A. The reasoning for the lower amount of sizing in B is believed to be caused when the sheet was being formed. The fines had the capability to surround the sized fibers and "block off" the hydrophobic ends of the alkyl ketene dimer which was attached to the fiber. As a result the sizing efficiency was reduced and ease of water penetration was increased.

The Cobb test showed similar results since sizing in the sheet incresed as fines increased. Again, sizing was more pronounced for test A.

Effect of fines on sizing

By observing the trends in Figures 9 and 10, sizing efficiency decreased as fines increased. According to the Washburn equation, the smaller pores of the sheet should reduce the rate of fluid penetration. The results showed that penetration sizing tests, namely Cobb and Hercules Size Test, will generally show a lower degree of

sizing for this paper.

Since theoretically one-hundred percent of the fines and fibers were retained by the filter paper, none of the sized fibers or fines were lost in the filtrate. The decrease in sizing can be attributed to the following theory. As the amount of fines in the sheet are increased, there is more surface area avilable for the AKD reaction. Due to the increased available surface area, more sizing is required to obtain the same sizing efficiency in the sheet.

CONCLUSIONS

In a sheet containing an insignificant amount of synthetic sizing agent, fines tend to increase sizing in the sheet. The Washburn equation can be demonstrated where rate of penetration is proportional to pore size. By increasing the amount of fines the pore size was decreased and therefore, sizing increased.

A synthetic sized sheet decreased in sizing level as fines were added. Since there was more surface area available when fines were increased, more sizing agent was necessary in order to obtain the same level of sizing with a Hercules Size Test or the Cobb Size Test. Since the amount of sizing agent in the sheet was held constant, sizing decreased as a result of the addition of fines.

A sheet produced from long fibers reacting with the sizing agent prior to the addition of fines resulted in a lower degree of sizing than a sheet made from reacting the sizing agent with the fines first and then adding this to the long fibers. It is believed that the unsized fines blocked off the hydrophobic surfaces of the sized long fibers and therefore decreased sizing efficiency.

RECOMMENDATIONS

The study of the effect of fines on synthetic sizing agents is important and deserves further investigation. As more synthetic sizing agents are being used out in industry in closed white water systems, the fines have a significant impact on the sizing system as a whole.

For further experimentation I would recommend a study of the effect of fines on a synthetic sizing agent with a wide range of sizing levels to study the role of fines. When studying this, the effect of two-sidedness in the sheet should also be observed. The role of pH, temperature, contact time, and order of addition with the synthetic sizing agent may prove to be significant for sizing.

A study of a comparison of the different types of synthetic sizing agents on fines would be worthwhile. In doing so, the effectiveness, side effect, and cost benefits could be looked at. A paper machine trial could study the influency of sizing retention and the effect of sizing as a result of adding the sizing agent to the white water or to the thick stock.

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Hercules Size Test (seconds)

Test A: Fines reacted with Hercon 40 prior to long fiber addition

Chemical #/ton O.D. pulp	Percent Fines			
	10	20	30	40
0.0	0.38	0.53	0.85	1.30
0.375	0.33	0.50	0.90	1.23
0.75	0.40	0.58	0.72	1.28
1.50	0.48	0.68	1.22	1.72
4.50	509.2	173.5	30.3	9.03

Test B: Long fibers reacted with Hercon 40 prior to fines addition

Chemical #/ton O.D. pulp	Percent Fines			
	10	20	30	40
0.0	0.38	0.53	0.85	1.30
0.375	0.40	0.45	0.57	0.98
0.75	0.42	0.52	0.73	1.17
1.50	0.52	0.77	0.93	1.53
4.50	358.9	60.5	16.1	8.68

Cobb Size Test (g/m^2)

Test A: Fines reacted with Hercon 40 prior to long fiber addition

Chemical #/ton O.D. pulp	Percent Fines			
	10	20	30	40
0.0	249.5	254.5	271.7	181.1
0.375	272.8	304.3	233.8	181.4
0.75	409.5	227.1	224.3	194.1
1.50	259.2	272.0	230.0	171.1
4.50	66.9	53.7	145.8	95.2

Test B: Long fibers reacted with Hercon 40 prior to fines addition

Chemical #/ton O.D. pulp	Percent Fines			
	10	20	30	40
0.0	249.5	254.5	271.7	181.1
0.375	284.5	223.4	199.8	177.7
0.75	299.2	228.5	210.1	156.6
1.50	259.5	222.9	172.5	166.6
4.50	71.6	91.3	151.4	127.0