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Western Michigan University

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THE INFLUENCE OF FILLERS
ON
ALKALINE SIZING

by
Thomas K. Shannon

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

Western Michigan University
Kalamazoo, Michigan
April, 1982

ABSTRACT

The object of this study was to determine whether filler surface area or filler type has the greater effect on alkaline sizing efficiency. At a given surface area and sizing addition level, ground CaCO_3 consistently gave higher sizing efficiency than clay. As the filler surface area increases the sizing efficiency decreases. At higher filler loadings there is a dramatic decrease in sizing response.

This report shows the following conclusions: CaCO_3 gives higher sizing response than clay at a given surface area, both an increase in surface area and filler loading decreases sizing efficiency.

Many mills are going to or looking at alkaline sizing. It is recommended that these mills be aware that as they attempt to increase filler loading there will be a dramatic increase in sizing agent demand. Also, as the mills switch to ground CaCO_3 they should be aware that better sizing results will be obtained than with clay at equivalent surface areas, filler loadings, and sizing addition.

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INTRODUCTION

Since 1807 the rosin-alum system of sizing has been the backbone of the paper making industry. In that year, Morris Illig developed an engine sizing process by precipitating a rosin soap on the fibers during the paper making process (24). Rosin-alum was used for its ease of use and inexpensiveness. In recent years the cellulose reactive sizing agents (alkaline sizing) have come into more popularity for many claimed reasons; use of calcium carbonate as a filler, reduced energy consumption, better sheet strength, better sheet permanence, higher sizing values, reduced effluent loads, increased productivity (34, 20, 53, 26).

As more and more mills turn to alkaline papermaking and to higher degrees of white water closure there will be more emphasis on the effects of white water components on paper qualities, of which sizing is important. Also, as alkaline sizing is used, higher levels of filler will be used (one advantage of going alkaline), the effect of these higher levels of addition should be evaluated.

The objective of this thesis will be to see how fillers affect alkaline sizing efficiency. Synthetic sizes have a cellulose reactive side which bonds to the hydroxyl groups of the fiber, fine, or filler and a hydrophobic end. Fiber fines and fillers have a high surface area per unit weight and hence would consume a large amount of sizing

material (29, 27). Previous studies have indicated that this is true for fines with a rosin-alum system. Fillers have been tested using different fillers with various surface areas (clay has higher surface area than CuCO_3) but this does not indicate whether the filler's surface area affects the sizing or if it's the effect of the fillers themselves.

Several types of cellulose reactive sizing agents are on the market today including alkyl ketene **dimers**, stearic anhydrides, and alkenyl succinic anhydrides (20). This study will deal primarily with the alkyl ketene **dimer** (AKD) because of its popularity and ease of application. It comes pre-emulsified in a cationic starch solution ready for use.

THEORETICAL

SIZING

Sizing is defined as the addition of materials to a papermaking furnish or paper surface to provide resistance to wetting and liquid penetration in the paper (2) .

There are two pathways in which water may permeate through paper: (a) through paper via open spaces in the web structure (interfiber penetration), and (b) through the paper via fiber-to-fiber contact (intrafiber penetration), via capillary action, or by some other mechanism of sorption/desorption (23).

There are four basic properties of the paper that affect both the permeation of paper by water and also the pathway of penetration: the hydrophobicity of the fibers, the pores in the sheet structure, the surface of the paper, and the sheet structure itself (23).

By nature cellulose is very hydrophilic. So one way of increasing the sizing level is to increase the hydrophobicity of fibers, this will lower the rate of penetration of aqueous fluids through the sheet via intrafiber pathways (fiber-to-fiber contacts). One intrafiber penetration process is capillary action and the Washburn Equation describes this behavior for an ideal case (24, 20):

$$\text{rate of penetration} = \frac{dl}{dt} = \frac{1}{4} \left(\frac{\gamma}{\eta} \right) \left(\frac{r}{l} \right) \cos \theta$$

where r = capillary radius

l = distance of penetration of the liquid

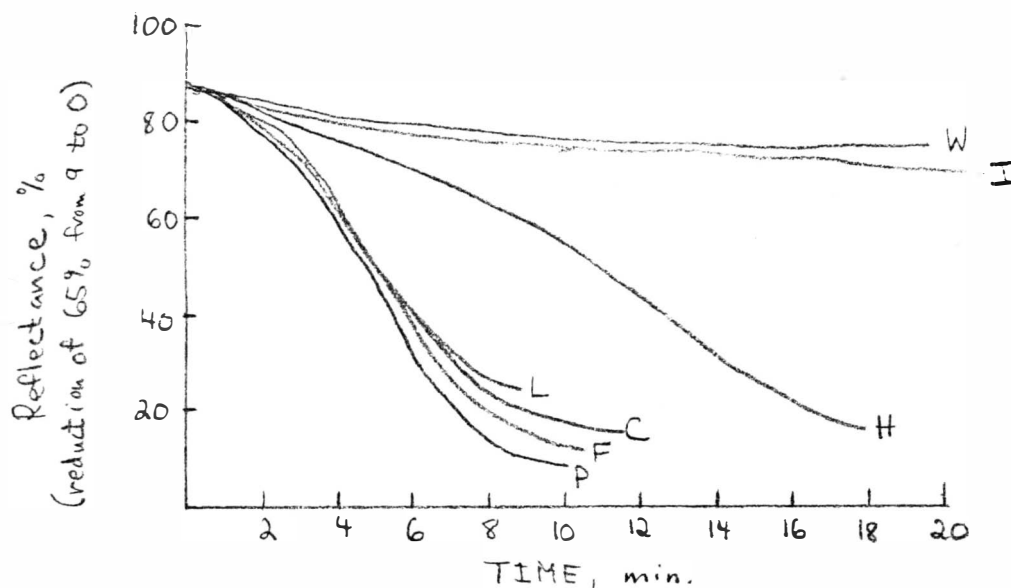
γ = surface tension of the penetrant

η = viscosity of the penetrant

$\cos \theta$ = Contact angle

This equation also suggests that the rate of penetration is a function of the surface tension of the penetrant. Many test fluids use a chemical to change the surface tension of the penetrant. This can cause a problem where the chemical may sorb onto the fibers, thus changing the surface tension of the penetrant with contact time. Figure 1 shows just such a case (23):

Figure 1 : HST curve of penetration of eight different ink mixtures through a given sheet of paper



W = distilled H₂O ink
H = sulfuric acid ink
I = isopropanol ink
F = 10% formic acid ink
P = phosphate ink
C = citric acid ink
L = lactic acid ink

Therefore, in this respect, the passage of water through paper is a function of the hydrophobicity of the fibers and surface tension and chemical nature of the penetrant.

A second penetration pathway is by the open spaces or

pores in a sheet of paper. Fluids can pass through the paper via the pores (interfiber penetration) and in theory can entirely bypass the fiber-fiber pathway. Any physical modification to the sheet which will reduce the radius of these interstitial pores will retard the rate of wetting and thus increase the penetration resistance (24). This physical blockage of the pores will decrease sheet porosity and increase the apparent density. Again, the penetrant's surface tension plays a factor.

The third consideration is the surface of the paper. This is mainly of importance with surface sizing. If the pores at the surface layer are small enough, then starch or other hydrocolloids will be able to physically bridge the pore and increase the penetration resistance.

The last consideration is the structure of the sheet itself. More specifically this is the way in which the fibers are laid down. A fiber mat that is formed with few interweaves, where the individual fibers tend to stay in the same place will promote lateral penetration of the fluid. This would be related to feathering. A much interwoven fiber mat will promote penetration through the mat.

CELLULOSE REACTIVE SIZES

There are four requirements of a sizing agent: hydrophobic (as mentioned earlier), retained, distributed, and anchored (20).

Regardless of the structure of the paper, a sizing agent should make the fiber surfaces hydrophobic. This requires that either the sizing material is totally hydrophobic or that the sizing material contains a hydrophobic end and a cellulose reactive end.

In rosin sizing, rosin itself is hydrophobic. The other three requirements of a sizing agent are met by the use of alum. Alum reacts with rosin to form a cationic entity, i.e. size precipitate, which is attracted to cellulose by electrostatic forces. The insoluble size precipitate coagulates to form 0.1 μ m particles that are retained on the fiber. The anchoring is probably provided by (1) coordination of aluminum in the size precipitate with hydroxyl or carboxyl groups on pulp fiber surfaces and (2) by weak van der Waals forces (20).

In alkaline sizing the requirements are met in a different way. The cellulose reactive alkaline sizes are nonionic hydrophobic organic chemicals which will not disperse easily in water (21). They must instead be emulsified by the use of dispersing agents and stabilizers. By using cationic stabilizers the particles are made cationic and thus self-retaining. In the case of the alkyl ketene dimer (AKD) made by Hercules Powder Company sold under the trade name Aquapel and Hercon the size is sold pre-emulsified in a solution of cationic starch (29). In this form they are water dispersible. Because of the use of cationic stabilizers, electrostatic forces are

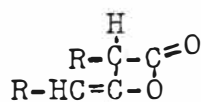
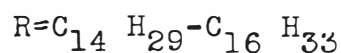
also responsible for the retention of reactive sizes, although this is probably not as useful as with rosin sizing. This is because the alkaline size emulsion particles are relatively large (0.2-1.0 μm) and the cationic stabilizer may not be very firmly attached to the particle surface (20).

Unlike the rosin-alum precipitate the cellulose reactive sizes spread over the fiber surface in a layer of molecular dimensions. This coverage is not necessary for high contact angles (9) but certainly will help and is one reason for the high efficiency of alkaline sizes. The anchoring step with alkaline sizes results from the formation of a covalent bond between the size and cellulose, this is not present in the rosin-alum system. This physical attachment of the sizing molecule to the fiber accounts for the ability of alkaline sizes to provide good resistance to a wide variety of penetrants. Again the rosin-alum system cannot make this claim.

There are now three different commercially available synthetic sizes as shown in Figure 2. All of these have two things in common: a hydrophobic group and a cellulose reactive functionality.

Figure 2 (20)
COMMERCIAL SYNTHETIC SIZES

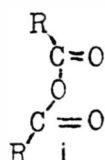
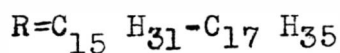
Alkyl Ketene Dimers



Cell-OH



Stearic Anhydride

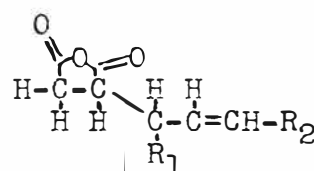


Cell-OH



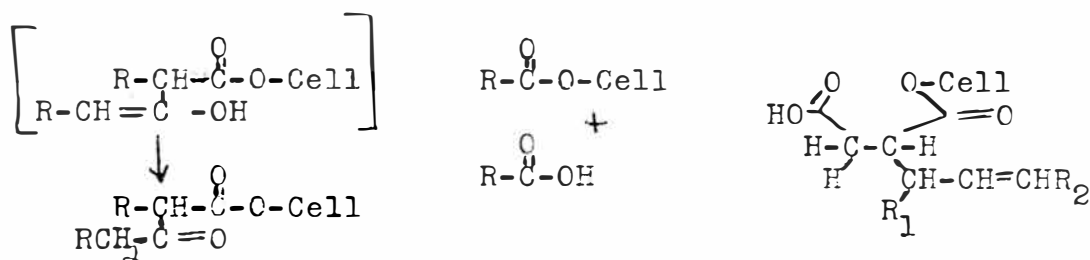
7.

Alkenyl Succinic Anhydrides
 $\text{R}_1=\text{CH}_3-\text{CH}_3 \quad \text{CH}_2-$
 $\text{R}_2=\text{C}_{12}\text{H}_{25}-\text{C}_{16}\text{H}_{33}$



Cell-OH

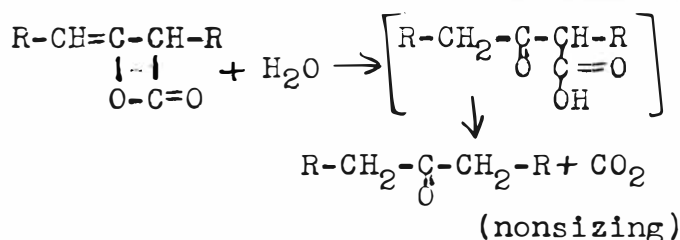




Of these cellulose reactive sizes the alkyl ketene dimer (AKD) is most common and easy to use. The AKD's are made from fatty acids such as myristic, palmitic, stearic, and oleic depending on the physical properties required of the resulting sizing agent (55).

AKD's are represented as the structure found in Figure 2 above. This Figure uses the stearic acid derivative as a model. Here the lactone ring of the ketene dimer can open to react with a cellulose hydroxyl to form the β -keto ester (29). AKD can react with any material which has an active hydrogen (28). As a result of this the AKD can react with water. The competing reaction in alkaline sizing, to form the unstable β -keto acid which decarboxylates to the ketone (see Figure 3).

Figure 3 (29)
AKD REACTION WITH WATER



This hydrolysis of the reactive size to a ketone leads to reduced sizing and must be avoided as much as possible. It can lead to press picking, which interferes with machine runnability. The press picking is partly due to the nonreactive,

unstabilized hydrolyzate which will not strongly bond to the fibers and, thus, picks out at the press roll. Formation of the hydrolyzate at the wet end is a function of the size's reactivity (20). Long contact with water at high temperature and high pH's encourages this competing reaction (17). This is one reason the AKD is added as close to the headbox as possible. Recently the emulsification in a cationic starch solution and increased stabilization have made the competing reaction less troublesome than before.

AKD imparts a high degree of resistance to penetration by aqueous penetrants when applied to paper in amounts ranging from 0.5 to 10 lb. per tons of paper. But like most chemical reactions, the reaction between AKD and fibers require certain favorable conditions. The reaction is not instantaneous but proceeds at a finite rate; heat and time are required for the development of sizing. In most cases heat and time sufficient to dry the sheet are also sufficient to bring about reaction or cure of the AKD (17). This is not always the case. One of the problems with AKD over that of some of the other alkaline sizing agents is its (AKD) slow curing time. Often the sizing does not develop early enough to provide proper control of size press pick-up (20). This can create problems in that more size is used at the size press and there is more difficulty in holding the size solution on the surface of the paper. In general the sizing resulting from the AKD continues to develop in the reel.

Fiber reactivity is also important and treatments which tend to decrease the reactivity of the cellulose surface make the paper more difficult to size with AKD. Previous drying of the fiber at low pH seems to reduce the reactivity and make it more difficult to size. Also the presence of rosin size and alum interferes; alum at low pH is particularly detrimental (17). Alum is still added at the wet end of many alkaline machines even though this decreases sizing. Broke containing rosin-alum is used in the manufacture of much of this paper and the addition of alum in the wet end seems to aid runnability.

FIBER FINES

There is a confusion as to the definition of fines. Jaycock considered all soluble or colloid dimensioned material in his furnish as fines. On the other end of the scale, Hinton and Quinn took the part of the furnish that passed through a 60-mesh wire as fines (35). In the present work, fines are defined as that part of the furnish passing through a 200-mesh or 75 μ m hole (8). But as seen above, the dividing line between fines and fiber is quite arbitrary. The present work definition of fines makes no distinction between cellulosic (pulp) fines and filler pigments. Since this paper is concerned with both the fiber fines and fillers separately, fines will be taken as only that portion which is of cellulosic character.

These fines are derived from a variety of sources. They may be small cells present in the original wood or other plant

material. They may be debris detached from fiber by chipping, cooking, and defibering in the pulp mill or from refining in the paper mill (8). Most papermaking furnishes contain a large amount of fines. Half of a typical fine-paper furnish may consist of fines (35). 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 the paper mill discharge contains fines, they are important also from both a fiber usage view and an environmental impact.

By virtue of their small particle size, fines have a much larger surface area than the coarse-fiber components. Pulp fines are rod-shaped, semicrystalline, fibrillar material with widths of 0.1-0.5 μm and lengths reaching several tens of micron. It is the structure and high surface area of fines that make them different-not any major differences in chemical composition. Most important, pulp fines swell considerably, retain 2-3 times as much water as the coarser fibers, and behave in many respects as a gel.(35).

FIBER FINES AND SIZING INTERACTIONS

Because of their large surface area, fines have much more potential area that may react with chemical additives than the coarse fibers. This higher surface area of the fines will adsorb more size than those of long fibers. For this reason a study of their effect on alkaline sizing is useful.

There has been much work done with measuring the amount of alum-rosin retained in a sheet (35). The aluminum concen-

tration in a fractionated bleached board furnish was found to be four times higher with the shorter fraction than the longer fraction. The adsorbed alum concentration on the fiber fraction was only around 0.5%. In this particular case, the fines fraction-amounting to about 13% of the furnish-carried almost 40% of the retained (adsorbed) alum. Marton went on to find in a similar experiment that the fines captured about 80% 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.

Further work by Marton showed similar results with a phthalocyanin (PC) blue pigment dye. His results are found in Figure 4. This would result in two-sidedness because the fines are retained more on the felt side as a result of filtration.

Figure 4
ADSORPTION OF PC PIGMENT DYE

<u>Alum added, % on pulp</u>	<u>% Dye Retention</u>
Whole pulp	
-	0
0.5	10
Fiber fraction	
-	1
0.5	2
Fines fraction	
0.5	43

FINES RETENTION

Concerning fines retention, there are three aspects to be considered: hydrodynamic, colloidal, and molecular (25).

The hydrodynamic aspect involves the motion of the particles, their collisions with one another, and their interception by fibers. Large particles of elongated shapes will behave similarly

to fibers which are retained by deposition at the sheet face. With intermediate sizes comparable to the pore sizes for the fiber sheet, the particles may be trapped in the pores. Small particles move with the fluid through the sheet unless they happen to be captured by the fibers. The collision of these particles with fibers is governed largely by Brownian motion or diffusion if the particles are very small (0.1μ) and the flow velocity is low. For somewhat larger particles (1μ), direct interception becomes effective, and inertial impaction soon takes over at higher velocities (25).

The colloidal aspect is more difficult to explain. In pure water, fibers and thus fines have very weak negative electrostatic charges. These charges are usually insufficient to keep them apart from other fines or fibers on collision. But certain ions tend to adsorb onto the surfaces of the hydrophobic particles. The adsorption of ions results in a so-called diffuse layer of opposite ions surrounding the charged particles by virtue of coulombic forces. These ions along with certain adsorbed molecules may create repulsive forces strong enough to keep the fines and fibers apart.

The third aspect is molecular. In the absence of repulsive forces, two particles in close proximity (10^{-6} cm) will attract each other due to van der Waals-London forces. Other types of forces exist in particular cases which may reinforce the attraction. These forces, being of molecular nature, are universally present.

Thus, the retention of fines is dependent on the net result of hydrodynamic, colloidal, and molecular forces at the site of collision. These are a function of the distance of separation.

FILLERS

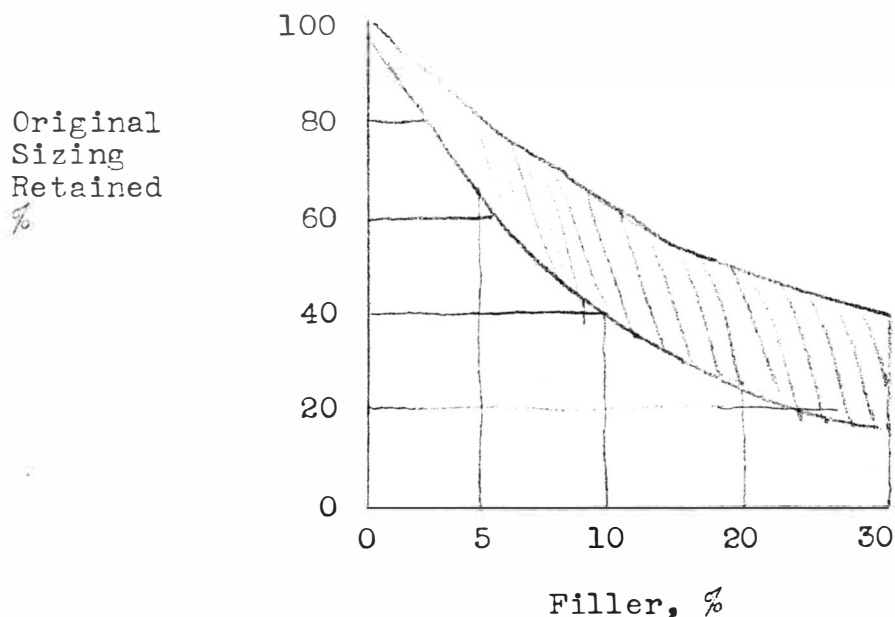
Filler is defined simply as a material, generally non-fibrous, added to the fiber furnish of paper (2). There is a long list of materials which are suitable for use as a filler, this list includes: barium sulphate, calcium carbonate, calcium silicate, calcium sulphate, calcium sulphite, clay, diatomaceous earth, luminescent pigments, talc, titanium dioxide, and zinc sulphite (56). Due to time limitations in this thesis, only the effect of clay and calcium carbonate will be evaluated as it effects alkaline sizing. When mills contemplate a switch from acid to alkaline papermaking the use of calcium carbonate as a replacement for clay is one of their prime considerations. Calcium carbonate is both cheap and brighter than clay and can usually aid in the reduction of titanium dioxide usage. CaCO_3 cannot be used in a low pH medium since it will effervesce at pHs much below 7.0. This makes CaCO_3 ideal for use in alkaline papermaking. Clay can be used in both acid or alkaline papermaking.

The definition of fines given earlier also denotes fillers as a part of the fines because they will pass a 75 μm screen. So, in many respects fillers will act similar to fiber fines.

As with fines, fillers have a very large surface area per unit weight. Fillers have an adverse effect on all types

of sizing. Although the effect of AKD sizing varies with the type of filler, the most commonly used fillers, such as clay, silica, and titanium dioxide reduce sizing as indicated by the shaded area in Figure 5. Highly adsorbent fillers, such as diatomaceous earth, have an adverse effect greater than that shown in the graph. On the other hand fillers such as calcium carbonate and hydrated alumina are much less detrimental to AKD sizing probably because of their buffering action on the system (29).

Figure 5 (29)
EFFECT OF FILLERS ON ALKYLKETENE DIMER SIZING



In addition to Kincannon and Watkins' study above, other studies have also indicated that better sizing is obtained by using CaCO_3 rather than clay. Beazley and Petereit (7) have concluded that sizing with AKD is a function of specific surface and that CaCO_3 requires less size than clay. In a series of

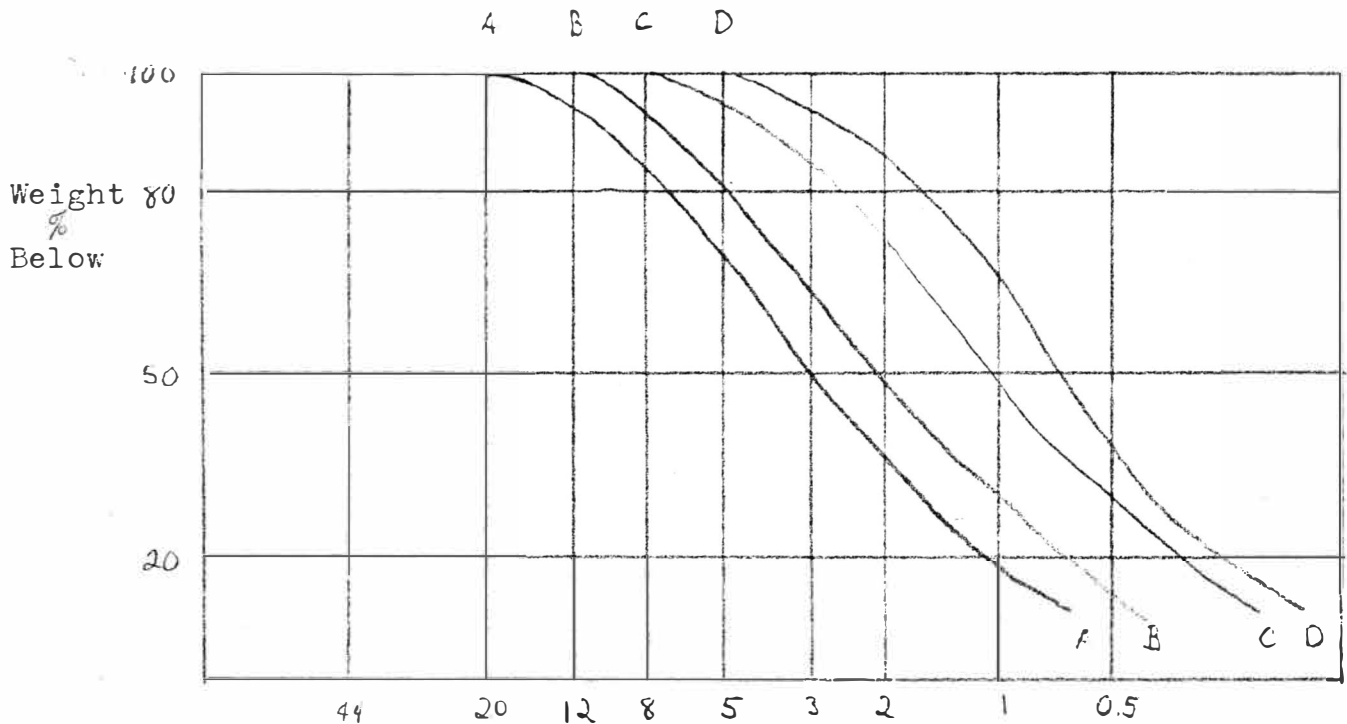
experiments reported by Perekal'shii and others (44, 45, 43, 46) found that sizing actually increased when small amounts of CaCO_3 were used as opposed to a decrease in sizing when clay was used. This is in direct contrast with the known detrimental effects of CaCO_3 on sizing.

There has been much work done concerning the comparison of clays to calcium carbonates with respect to effect on sizing. But it has not been made clear as to the true cause of the different effect on AKD sizing. Is it truly the difference between clay and an alkaline filler such as CaCO_3 or is it the effect of various surface areas? This is an interesting aspect which this paper intends to clarify.

CALCIUM CARBONATE

Calcium carbonate is available in two types: ground and precipitated types are both used in papermaking. In the precipitated calcium carbonates, two basic particle shapes are predominant, the rhombic, or cubic, and the acicular or needle shape. The natural ground CaCO_3 has little, if any, definite particle form (9). Recently there has been made available large quantities of fine ground natural CaCO_3 of high purity, low abrasivity and high brightness. Until recently, with but few exceptions, successful alkaline paper making in the U.S. employing CaCO_3 fillers involved the use of precipitated grades (15). CaCO_3 also is available in several particle sizes with corresponding different surface areas. Figure 6 indicates four different particle sizes with their distributions.

Figure 6 (32)
FINE GROUND LIMESTONE
PARTICLE SIZE DISTRIBUTION



Equivalent Spherical Diameter, microns

	A	B	C	D
Mean Diameter, μ	3.0	2-	1.0	0.7
Surface Area, m^2/g	2.8-3.2	5-6	7.2	12-14

(Braunauer, Emmet, and Teller)

Calcium Carbonate is attacked by alum and acids. If broke containing $CaCO_3$ is accidentally introduced to an acid back water severe foaming occurs from the effervescence given off when the $CaCO_3$ is broken down. For this reason $CaCO_3$ must be used at neutral or alkaline conditions.

CLAY

The term "clay" is subject to a wide variety of interpretations. In its broadest sense it is a generic term and may include almost any earthy material. As used in the paper

industry, the name ordinarily refers to kaolin, or china clay, which is a more exactly defined material (56).

Clay is used as a filler in paper because it is inexpensive, white in color, soft and nonabrasive, and increases the opacity of the sheet (9). This is by far the largest volume white pigment used by the paper industry. It is a hydrated aluminum silicate. The surface areas of clays range from 7 or 8 m²/g to 25 m²/g, depending on the particle size distribution (9).

FILLERS AND SIZING INTERACTIONS

The sizing interactions of CaCO₃ and clay will be similar to the fines interaction in several ways. The fillers represent a much larger surface area than the coarse fibers and as such would be expected to hinder sizing. The AKD will react with any material which has an active hydrogen (28) and hence should react with fillers because they have active hydrogens.

FILLER RETENTION

Again, the retention mechanisms for fillers are much the same as for fines. Hoslam and Steele suggested three different mechanisms of filler retention: (1) filtration, the process of removing particles larger than the pore openings during sheet formation, (2) entrapment, the physical collection of particles in the fiber lumens or in the fibril structure on the fiber surface, and (3) coflocculation, the interaction of the interfacial forces of the particles which control ordinary colloidal flocculation. This latter mechanism appears to be the most important in terms of filler retention (54). McKenzie

concluded that there are three factors which influence the coflocculation retention mechanism: the collision process, the aggregate formation, and the overall strength of the aggregate (54).

The fillers usually carry a negative charge due to the chemicals used in their manufacture.

pH AND ALKALINITY

Both of these variables have been found to play a role in AKD sizing development. The rate of reaction of AKD increases with increasing pH. High pH (10) in the stock is undesirable because the reaction would preferentially be with the water and because many cationic retention aids lose their effectiveness at high pH. A compromise pH of between 7-8 is usually accepted (29, 28).

Total alkalinity plays an even more important role on the rate of reaction. A higher total alkalinity gives quicker reaction rates. Best results are usually obtained in the range of 50-150 ppm (28). This level can be obtained by the addition of soda ash, preferably before refining.

TEMPERATURE

The reaction between AKD and fibers is seldom complete directly off of the paper machine. A good way to operate is to remove the water quickly and expose the paper to high temperatures before the size press so that the paper can be at least partially sized before the size press to control pick-up. Kincannon (29, 28) found that accelerated aging of the samples at elevated temperature is sufficient for control testing of

off-machine samples. Samples can be aged at 220^c F for 2 hours to obtain results similar to 2 weeks of natural aging (75^c F).

ALUM

The use of alum in an alkaline system has been thought of as a bad thing. But in actuality alum only reduces the rate of reaction, rather than the extent. Indeed most mills running alkaline are using alum to clean up the "anionic trash" in the system.

SUMMARY

Alkaline sizing agents react chemically with the cellulose fibers, unlike the rosin sizing. There are basically three available cellulose reactive sizing agents on the market today and of these three the alkylketene dimer is most popular. The fiber fines and fillers use more of the sizing agent than the longer fibers because of their much greater surface area. Fines and fillers are a major portion of the white water system and as such need to be studied.

Retention of the fines and fillers and thus the AKD is important as are these other variables: pH, alkalinity, temperature, and alum usage.

OBJECTIVES

The purpose of this thesis is to study the effect of fillers on an alkylketene dimer synthetic sizing agent. Previous studies have reported the role of fines in a rosin-alum system, however, synthetic sizing agents have not been studied till this time. The comparison between CaCO_3 and clay fillers with an AKD system has been made, but not from the point of view of finding out if the reason the clay gives poorer sizing is because of different surface areas or because of the fillers themselves.

It is believed that increasing the filler content with no sizing will increase the sizing level due to closure of sheet pores. Also as the filler level is increased with a given amount of AKD the sizing level should decrease. This decrease should occur because of the increased consumption of the AKD by the fillers. It is also believed that at a given surface area of filler, the sizing level with the CaCO_3 will be better than with clay.

STATEMENT OF THE PROBLEM

Many mills are now switching to or considering a change to alkaline sizing. One of the main reasons for doing so is that calcium carbonate can be used at higher filler loadings than with clay. These higher filler loadings should be evaluated as to their effect on sizing response. Also, as the switch is made from clay to CaCO_3 there will be some sizing response change due either to the different filler chemistry or to the simple fact that calcium carbonate has a lower surface area than clay. A lower surface area should retain less sizing agent and allow a higher sizing level in the final sheet.

The approach taken to the problem is to make buchner funnel handsheets with combinations of the following variables:

4 ADDITION LEVELS WITH AKD	X	4 PARTICLE SIZES CLAY	X	4 LEVELS FILLER ADDITION
		4 PARTICLE SIZES GROUND CaCO_3		

By taking this approach it is hoped that several things will be learned: (1) how clay and ground CaCO_3 influence sizing response, (2) how surface area of these fillers effect sizing efficiency, and (3) what influence filler loading level has on sizing.

EXPERIMENTAL PROCEDURE

The pulp used in this study was a mix of softwood and hardwood. This blend consisted of a 50% bleached softwood (Grand Prairie) and 50% bleached hardwood (Berlin) mix which was soaked in water for 3 hours and disintegrated for 15 minutes. The pulp was then refined to 350 CSF in a laboratory disc refiner at 2% consistency and preserved with 0.1% AMA 24 (based on solids) commercial biocide and by refrigeration at 38° F.

The fillers used were as follows: *

<u>CLAY</u>			<u>CaCO₃</u>		
	<u>BET Surface Area (m²/g)</u>	<u>Ave. Particle Size (μ)</u>		<u>BET Surface Area (m²/g)</u>	<u>Ave. Particle Size (μ)</u>
#1 Clay	17	0.5	Ground	9.4	0.7
#2 Clay	15	0.8	"	5.0	2.0
Water Washed Filler	12	1.4	"	3.8	2.5
Coarse Filler	7	3.8	"	1.5	5.0

The data concerning these fillers was obtained from the suppliers. These fillers were chosen with the intention that the results could be compared for various particle sizes and surface areas of the two types of fillers as they affect sizing.

*

#1 Clay = Spray Satin, Engelhard Minerals & Chemicals Corp.
 #2 Clay = HT Pulverized, " " " "
 Water Washed Filler = Klondyke, " " " "
 Coarse Filler = Hydrite Flat D, Georgia Kaolin Co.
 9.4 CaCO₃ = Micro-White 07, Sylacauga Calcium Products
 5.0 CaCO₃ = Micro-White 20, " " "
 3.8 CaCO₃ = Micro-White 25, " " "
 1.5 CaCO₃ = Micro-White 50, " " "

AKD = Hercon 48, Hercules Powder Company

Mill water from James River Corporation, Parchment, Michigan, was used during the course of the study and checked twice for chemical composition. The averages (little variance between the two tests) were as follows: 227 ppm hardness, 7.3 pH, 265 ppm alkalinity, and $< .06$ ppm iron. It is important to note that the hardness and alkalinity remained constant during the course of this study as both of these parameters affect alkaline sizing efficiency.

A buchner funnel using a water jet for vacuum with coarse filter paper was used to produce the necessary handsheets. The buchner funnel was used for several reasons: to keep the stock consistency high (0.5%) to avoid formation of the hydrolysis product of the AKD, to control vacuum, and to encourage filler retention (approximately 90% was retained).

The fiber, water, and filler (5%, 10%, 20%, and 40% addition was used) was combined to a final consistency of 0.5%. This combination was adjusted to a pH range of 8.2 - 8.3 by using dilute NaOH and then kept under agitation. From this large batch a quantity was removed and the AKD (at 2, 3, 4, and 5 pounds per ton) was added and allowed to react with the furnish for 5 minutes under constant agitation.

At the end of the prescribed time the suspension was poured into a 15 cm diameter buchner funnel and a low vacuum was applied for 30 seconds. The vacuum was then increased to maximum until the sheet was drained. The vacuum was controlled in the hope of creating a fiber mass at low vacuum

which would tend to filter and capture the filler.

The pad was then pressed between two blotter papers and a press felt on the Noble & Wood handsheet press (constant pressure maintained). The pad was then dried on the Noble & Wood cylinder drier with the filter and blotter paper intact and the filter paper toward the drier can. Handsheet formation was good and uniform. A basis weight of 70#/3000 ft² was obtained.

Prior to the testing all sheets were cured in an oven at 107°C for 2 hours.

The sheets were tested on the non filter paper side via the Hercules Size Test (HST) using the Hercules Test Solution #2 at a 55% reflectance. This reflectance was chosen because of the wide spread of values observed (from 1 to 3000 seconds). If this reflectance had been increased, the lower test values would have been even lower and become insignificant. Ash tests at 550°C for 12 hours (to eliminate filler conversion) were run on all 128 variables. The Percentage Voids (water) as described by Cobb was also determined on all of the pigments tested. (58).

There were four sheets of every variable made. Out of these four, three were used for HST testing (2 tests each sheet) and one sheet retained for ash testing. This produced six HST tests for all 128 variables.

DATA AND RESULTS

The data is shown in exact figures in the Appendix (including averages and standard deviations of each of six HST tests, and ash values) and graphically on the following pages in Figures 1 - 3. The data presented in these Figures was derived from the actual data listed in the Appendix. This was accomplished by plotting the HST vs. surface area for every AKD addition level with increasing filler loading. A normalized curve was drawn through these points and the data presented in the Figures was extracted from this curve at 5, 15, and 35% filler addition. Hence Figure 1 is at 5% loading, Figure 2 at 15% loading, and Figure 3 at 35% loading.

Figures 1, 2, and 3 show eight curves each. There are four curves marked "Ca" which indicate these were loaded with the indicated amount (5, 15, or 35%) of ground Calcium carbonate at one particular AKD addition level (2, 3, 4, or 5 lbs/ton) which is also marked on the curve. The other four curves marked "C" were loaded with clay again at four levels of AKD sizing agent. All of the clay curves are marked in red.

Now referring to Figure 1: 5% loading, several things can be noticed. With but one exception the CaCO_3 gives higher sizing responses at a given addition level and surface area over that achieved with clay. The one exception is at the 5#/ton AKD level which shows the clay to be better than the CaCO_3 . This could indicate that at low filler addition levels (5%) the clay gives better sizing response

than CaCO_3 . But since this occurred only once, this author is not prepared to make such a conclusion. Another thing to be noticed is that as the surface area of either the clay or CaCO_3 increases, the sizing takes a dramatic drop at a given AKD level.

Figure 2: 15% loading indicates much the same ideas as Figure 1 but the clay gives an even larger difference from the sizing obtained with CaCO_3 .

Figure 3 again shows the same trends. The clays here are so low in sizing that they are all drawn as one line. It should be noted that if the graph was expanded the clays would show some difference within themselves. These differences follow the same types of trends established earlier. The sizing also decreases with increasing surface area and decreasing sizing addition.

If the Figures are looked at as a series of increasing percentage filler loadings, it is noticed that as the filler loading increases the sizing curves decrease with respect to HST at any given surface area and AKD level.

Figure 4 is the average of two percent voids (water) determinations as outlined by Cobb. (58). While the difference in percent voids within the clays or CaCO_3 's is insignificant, it is noted that the clays had a higher percent voids than the CaCO_3 's. This fact goes along with the earlier indications that clay demands more sizing agent to give equal sizing performance.

All of these fillers were also evaluated on the basis of particle size. Particle sizes showed an even greater difference in sizing response between clays and carbonates. It was felt that the sizing response would be more a function of surface area than particle size so surface area was used as the basis for this investigation.

The ash values listed in the Appendix show some interesting trends. As stated earlier the ash was retained at approximately 90%. But some variations were seen. The larger particle sizes of fillers retained slightly better as did higher AKD addition levels.

FIGURE 1 : 5% LOADING

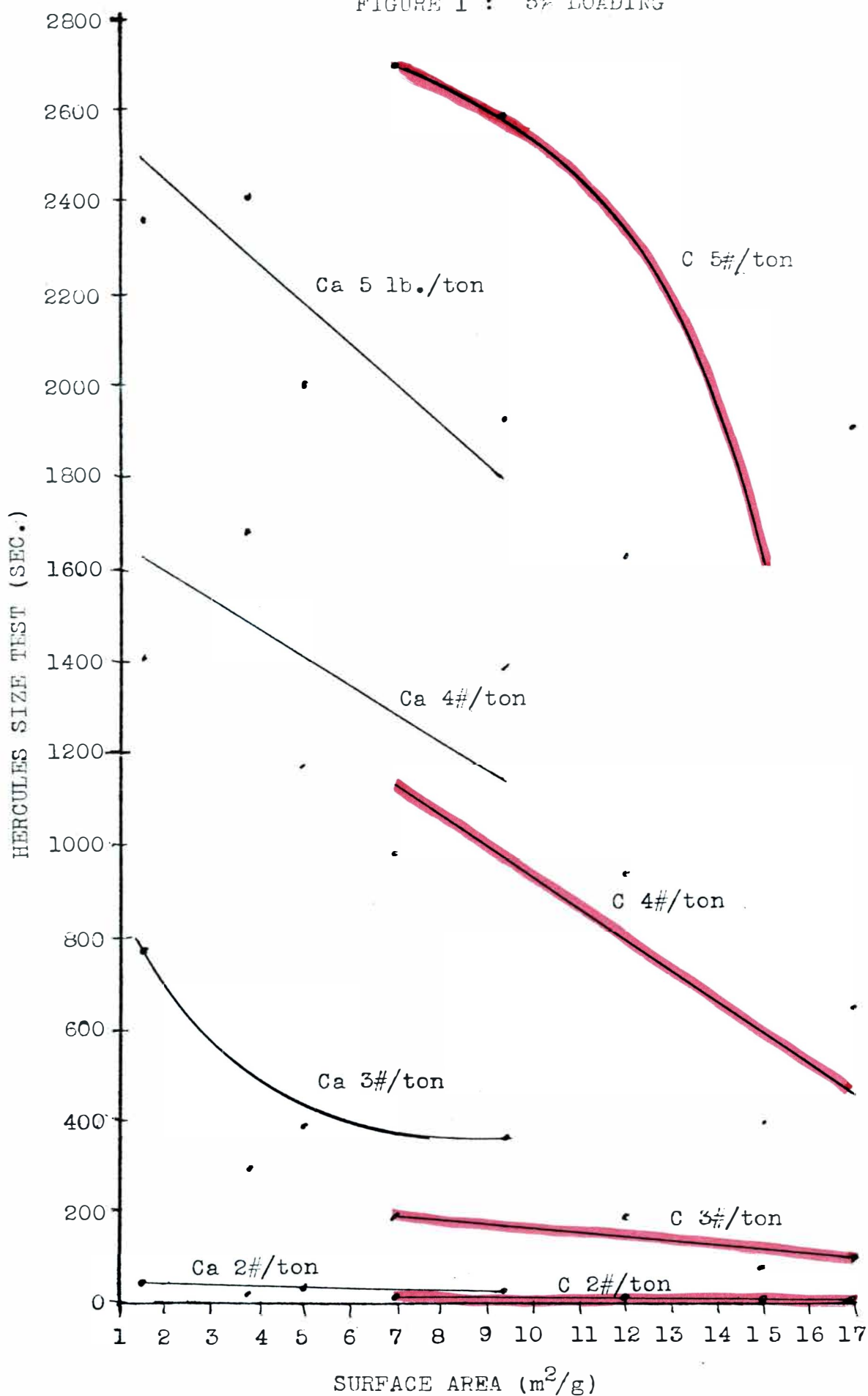


FIGURE 2 : 15% LOADING

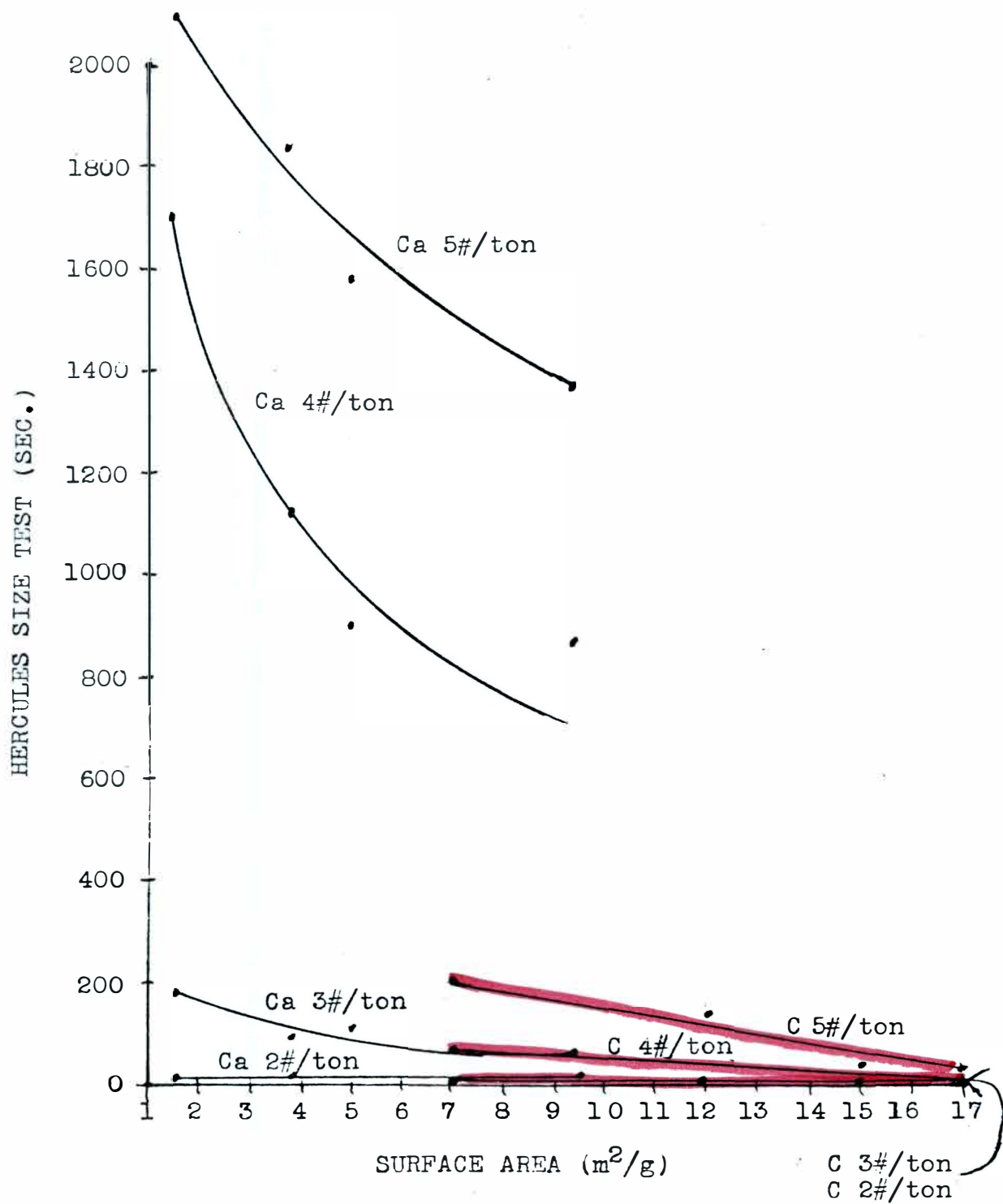


FIGURE 3 : 35% LOADING

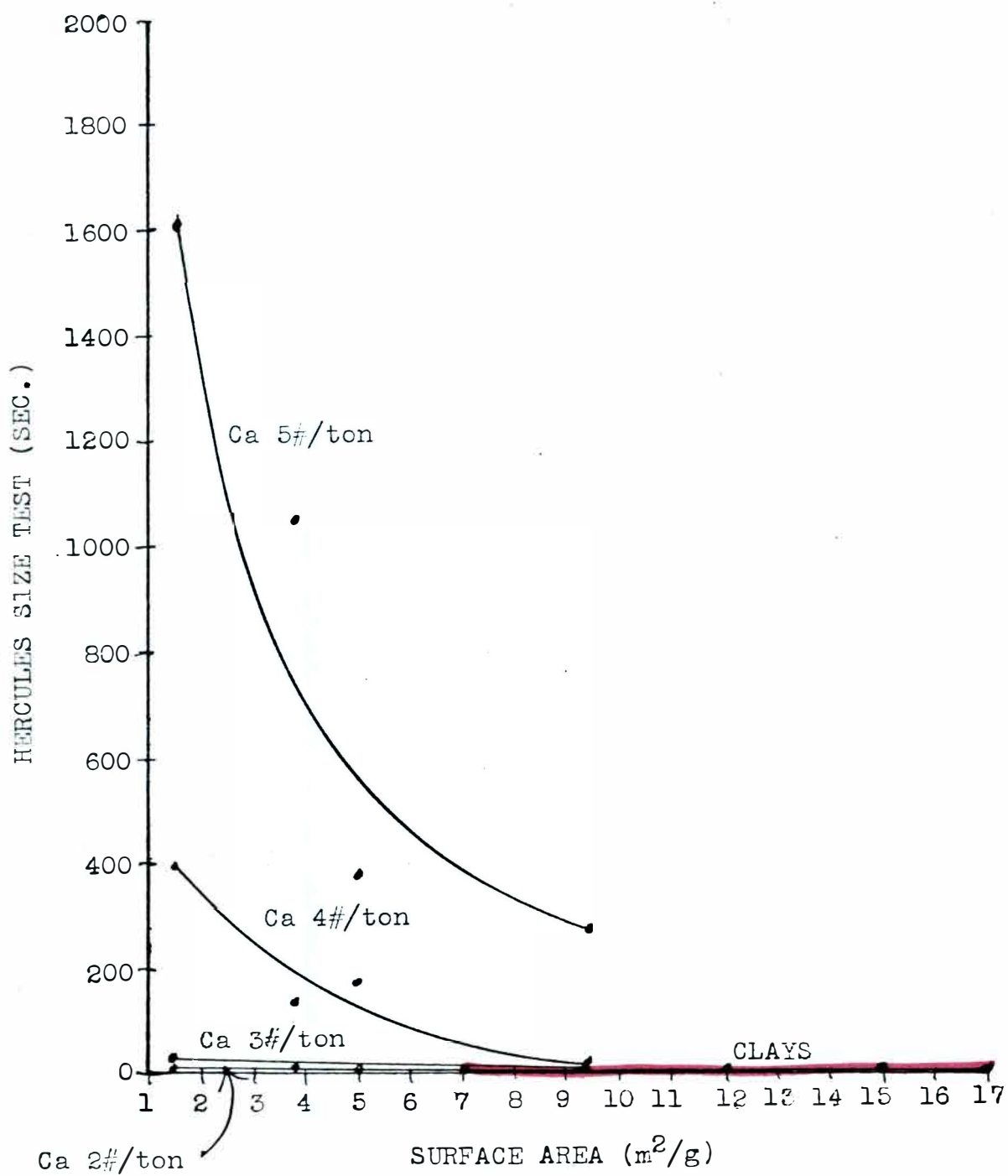


FIGURE 4
% VOIDS, WATER (58)

GROUND CaCO_3		CLAY	
<hr/>		<hr/>	
9.4 m^2/g	19.48% Voids	#1 Clay	26.50% Voids
5.0	17.66%	#2 Clay	24.72%
3.8	19.20%	Water Washed	28.16%
1.5	20.93%	Coarse Filler	28.00%

DISCUSSION OF RESULTS

The data tends to indicate that the ground Calcium Carbonate gives better sizing efficiency than the clay at a given surface area and AKD level. This was evidenced at every filler loading level. Clays generally have a much higher surface area than CaCO_3 because of the clay's platy structure. But the fillers used in this study were chosen so that there would be some overlap in surface area between CaCO_3 and clay. There is no indication as to why CaCO_3 will give better sizing than clay at a given surface area. Kincannon (28, 28) has suggested that the reason this occurs is because of the buffering capability of CaCO_3 . Kincannon has also shown how alkalinity and pH affect alkaline sizing response. He showed that as pH and alkalinity increase so does sizing efficiency. If the CaCO_3 buffers the sheet to a higher pH or alkalinity it is possible that the sizing efficiency would be higher.

Also shown in this study is the fact that as the surface area increases the sizing efficiency decreases. This confirmed our expectations. The AKD reacts with any component that has active hydrogens. The fillers have a high surface area and thus high areas of active hydrogens which are available for bonding to the AKD synthetic sizing agent. The fillers thus competed against the fibers for AKD. Since the fillers have a higher surface area than the fibers, the fillers pick up much sizing agent which is not available to provide hydrophobic properties to the hydrophilic fibers.

Thus as the particle size decreases (or surface area increases) the filler will tie up more and more sizing, making it unavailable to the fibers.

This thesis also showed that as filler loading level was increased the sizing efficiency decreased. Again this is explained as a part of the surface area phenomenon. As the filler level is increased the total filler surface in the sheet is increased which will adsorb some AKD and reduce overall sizing efficiency.

CONCLUSIONS

From the data presented here three conclusions were arrived at.

1. At a given filler surface area and AKD sizing level, calcium carbonate gives better sizing efficiency than clay.
2. For both clays and calcium carbonates an increase in surface area results in lower sizing efficiency.
3. As higher filler loadings are achieved more sizing agent will be needed to maintain an equal sizing level.

OTHER IMPLICATIONS

MILL SIGNIFICANCE

Of what importance is this thesis to actual mill production? As mentioned earlier many mills are looking at switching to alkaline sizing for the purpose of using CaCO_3 at high filler levels. As these mills go to very high filler levels (such as 34% ash) they will find a need to substantially increase their sizing use to maintain a desired level of sizing efficiency. Also the switch from CaCO_3 to clay is a favorable switch in terms of getting optimum sizing response from an alkyl ketene dimer synthetic sizing agent.

RECOMMENDATIONS

For further work it would be suggested to look at the other two commercially available alkaline sizing agents, namely, stearic anhydride and alkenyl succinic anhydride. It would be interesting to find out if the other alkaline sizing agents behave in the same manner as the AKD. Another approach would be to look at other types of fillers including precipitated calcium carbonate and titanium dioxide extenders as to their effect on alkaline sizing.

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APPENDIX

FILLER TYPE	SURFACE AREA (m ² /g)	MEAN PARTICLE SIZE (μ)	SIZING ADDITION (lbs./ton)	FILLER ADDITION (%)	MEAN HST (SEC.) (6 tests)	HST Std. Dev.	550°C Ash (%)
CaCO ₃	9.4	0.7	2	5	22.8	4.7	4.46
				10	9.2	2.4	8.51
				20	3.5	0.9	15.67
				40	0.9	0.2	32.55
			3	5	364.0	87.6	4.78
				10	149.5	31.8	8.66
				20	19.5	2.8	16.60
				40	2.1	0.2	34.41
			4	5	1388.4	190.3	4.87
				10	872.8	236.2	8.95
				20	124.6	22.1	16.96
				40	6.2	0.9	34.20
			5	5	1926.9	443.6	4.99
				10	2162.3	605.3	9.29
				20	290.8	59.8	17.68
				40	13.7	1.9	35.76

FILLER TYPE	SURFACE AREA (m ² /g)	MEAN PARTICLE SIZE (μ)	SIZING ADDITION (lbs./ton)	FILLER ADDITION (%)	MEAN HST (SEC.) (6 tests)	HST Std. Dev.	550°C Ash (%)
CaCO ₃	5	2.0	2	5	33.3	12.7	4.00
				10	16.7	3.9	8.16
				20	3.1	0.3	16.95
				40	0.7	0.0	31.11
			3	5	393.1	55.9	4.08
				10	238.2	28.7	8.25
				20	41.0	14.6	17.16
				40	2.4	0.6	37.51
			4	5	1177.2	450.7	4.27
				10	982.6	263.3	8.46
				20	793.8	259.7	16.59
				40	11.3	2.6	37.98
			5	5	1470.0	268.5	4.69
				10	1672.7	301.5	8.20
				20	1799.3	506.0	16.99
				40	77.1	14.3	38.21

FILLER TYPE	SURFACE AREA (m ² /g)	MEAN PARTICLE SIZE (μ)	SIZING ADDITION (lbs./ton)	FILLER ADDITION (%)	MEAN HST (SEC.) (6 tests)	HST Std. Dev.	550°C Ash (%)
CaCO ₃	3.8	2.5	2	5	14.3	4.6	4.41
				10	8.6	2.3	8.25
				20	5.2	2.5	16.77
				40	1.0	0.1	35.94
			3	5	297.0	86.5	4.46
				10	118.6	64.0	8.31
				20	93.3	33.4	16.98
				40	7.8	2.1	35.96
			4	5	1686.0	1137.0	4.59
				10	928.2	218.2	8.19
				20	770.7	221.5	17.31
				40	107.7	47.3	36.57
			5	5	2409.7	1629.6	4.62
				10	1725.2	479.6	8.42
				20	2115.5	658.6	16.64
				40	904.1	427.8	36.10

FILLER TYPE	SURFACE AREA (m ² /g)	MEAN PARTICLE SIZE (μ)	SIZING ADDITION (lbs./ton)	FILLER ADDITION (%)	MEAN HST (6 tests)	HST Std. Dev.	550°C Ash (%)
CaCO ₃	1.5	5.0	2	5	46.1	23.1	4.32
				10	11.2	2.9	8.40
				20	4.3	0.8	17.17
				40	1.0	0.2	37.67
			3	5	775.4	179.2	4.69
				10	339.0	75.1	8.65
				20	95.3	18.7	17.84
				40	13.5	2.9	38.06
			4	5	1409.3	145.6	4.76
				10	2467.2	874.4	9.06
				20	1072.5	297.8	17.98
				40	234.9	93.8	37.69
			5	5	1927.1	347.5	4.98
				10	2268.7	402.7	9.31
				20	2072.9	720.6	17.60
				40	1409.7	413.5	38.45

FILLER TYPE	SURFACE AREA (m ² /g)	MEAN PARTICLE SIZE(μ)	SUZZING ADDITION (lbs./ton)	FILLER ADDITION (%)	MEAN HST (SEC.) (6 tests)	HST Std Dev.	550°C Ash (%)
#1 Clay	17	0.5	2	5	8.5	2.1	3.64
				10	1.5	0.2	7.12
				20	0.82	0.17	15.04
				40	0.55	0.08	30.79
			3	5	99.1	16.4	3.94
				10	3.9	0.7	7.75
				20	1.15	0.18	15.40
				40	0.70	0.06	32.09
			4	5	650.8	232.5	4.03
				10	12.7	2.4	7.86
				20	1.66	0.28	15.71
				40	0.75	0.08	32.06
			5	5	1912.6	361.5	4.42
				10	61.0	10.5	8.06
				20	2.7	0.56	16.24
				40	0.82	0.10	32.69

FILLER TYPE	SURFACE AREA (m ² /g)	MEAN PARTICLE SIZE(μ)	SIZING ADDITION (lbs./ton)	FILLER ADDITION (%)	MEAN HST (SEC.) (6 tests)	HST Std. Dev.	550°C Ash (%)
#2 Clay	15	0.8	2	5	5.4	1.6	3.89
				10	1.7	0.2	7.51
				20	0.9	0.1	14.47
				40	0.63	0.12	30.48
			3	5	75.5	32.8	4.14
				10	4.4	1.0	7.73
				20	1.4	0.14	15.34
				40	0.68	0.12	30.90
			4	5	398.3	56.1	4.11
				10	14.5	3.6	7.81
				20	1.8	0.4	15.70
				40	0.85	0.05	31.97
			5	5	1632.5	997.5	4.33
				10	55.8	19.2	8.25
				20	2.8	0.4	15.84
				40	0.95	0.10	32.47

FILLER TYPE	SURFACE AREA (m ² /g)	MEAN PARTICLE SIZE (μ)	SIZING ADDITION (lbs./ton)	FILLER ADDITION (%)	MEAN HST (SEC.) (6 tests)	HST Std. Dev.	550°C Ash (%)
Water Washed Filler	12	1.4	2	5	10.8	1.3	3.89
				10	2.6	0.3	7.71
				20	0.8	0.2	15.43
				40	0.5	0.1	32.22
			3	5	190.9	55.1	4.26
				10	14.4	2.4	8.38
				20	1.3	0.15	17.14
				40	0.6	0.1	33.59
			4	5	940.0	348.4	4.47
				10	120.3	25.7	8.52
				20	2.3	0.4	17.89
				40	0.7	0.11	33.29
			5	5	2593.4	651.4	4.44
				10	435.9	136.5	8.92
				20	6.5	1.3	17.98
				40	0.83	0.05	33.77

FILLER TYPE	SURFACE AREA (m ² /g)	MEAN PARTICLE SIZE (μ)	SIZING ADDITION (lbs./ton)	FILLER ADDITION (%)	MEAN HST (SEC.) (6 tests)	HST Std. Dev.	550°C Ash (%)
Coarse Filler	7	3.8	2	5	11.7	2.6	3.93
				10	2.4	0.3	7.82
				20	0.8	0.1	15.79
				40	0.4	0.1	33.90
			3	5	191.8	36.0	4.18
				10	22.8	1.4	8.04
				20	1.9	0.2	16.10
				40	0.5	0.06	33.21
			4	5	983.7	248.1	4.42
				10	206.9	17.7	8.37
				20	11.3	3.8	16.16
				40	0.7	0.1	33.06
			5	5	2704.1	397.6	4.30
				10	533.7	182.9	8.53
				20	56.1	9.0	16.47
				40	1.0	0.1	32.49