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"THE APPLICATION OF ZETA POTENTIAL
FOR THE EFFECTIVE RETENTION OF
TITANIUM DIOXIDE IN CHEMICALLY
MODIFIED SYSTEMS"

by

John W. Clapp

A Thesis Submitted To The
Faculty of the Department of Paper Science and Engineering
In Partial Fulfillment
of the
Degree of Bachelor of Science

ABSTRACT

This study was done to determine how to obtain maximum effective filler retention in a fiber and titanium dioxide system. Retention of fillers in a fibrous system is greatly influenced through the use of high molecular weight polymers. It was found that by using cationic and anionic polymers in the same system, a synergistic effect results which yields a higher effective retention than if either polymers were used along. Furthermore, by precisely controlling the amounts of each polymer so as to obtain the isoelectric point in zeta potential; the peak effective retention is reached.

TABLE OF CONTENTS

	Page
HISTORICAL BACKGROUND & DEVELOPMENT	1
OF THE PROBLEM	
Zeta Potential	
Titanium Dioxide Retention	
Mechanisms of Retention.	
1. Mechanical.	
2. Physio-Chemical	
3. Briding	
Control of Zeta Potential.	
Efficiency of Titanium Dioxide Retention	
EXPERIMENTAL DESIGN	7
Preparation of Pulp.	
Control Runs	
Preparation of TiO_2 Slurry	
Determining Addition Sequence.	0
Application of Zeta Potential.	
Testing for Results.	
RESULTS	11
Table I, Control Runs	
Table II, Addition Sequence.	
Table III, Application of Zeta Potential	
DISCUSSION OF RESULTS	14
Figure 2, Relationship Between Zeta Potential and Effective Retention.	
CONCLUSIONS	18
BIBLIOGRAPHY.	19

electrophoretic mobility. This can be calculated into zeta potential utilizing the formula, $\zeta = \frac{4\pi\eta V}{HD}$ N is the viscosity of the suspension usually taken as the value of water, V is the velocity in milli-microns per second, H is the voltage gradient in volts per centimeter, and D is the dielectric constant of the media (2).

Other methods of measuring zeta potential include electro-osmosis and streaming current detection (2).

Certain forms of titanium dioxide will develop a positive charge when dispersed with aluminum chloride (3). However, the author indicates that the charge per unit weight is very small and the retention in paper is very poor. The positive-negative attraction between the titanium dioxide and the fibers would be ideal for retention. The use of larger titanium dioxide particles to get more surface area and thus more charge is not feasible since the optimum particle size for maximum opacity is about 0.2 microns.

There are three theories or mechanisms by which retention takes place. Although one particular mechanism usually predominates, it is usually a combination of all three that effects the actual amount retained.

The three theories are the mechanical, physio-chemical, and bridging theories (4).

The mechanical theory is simply the formation of a fibrous mat that entraps fines and conglomerates. This type of retention will always play an important role as conglomerate sizes become larger.

The second theory is the physio-chemical theory and is based on charge attraction. Here, the differences between the charges on the filler and fiber will cause an attraction provided that the charges are of opposite nature and are strong enough to bond.

With the discovery of high molecular weight polymers a third mechanism of retention has been developed. It is the mechanism of bridging and usually takes precedent in a system where high molecular weight polymers are employed. The following figures will help explain this mechanism:

Bridging Mechanism

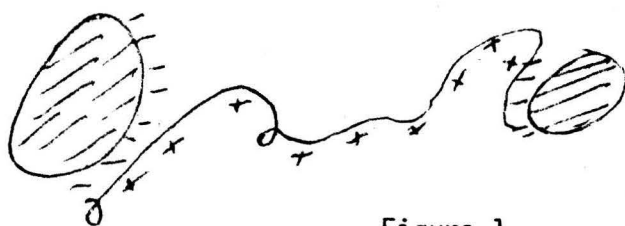


Figure 1

The curving line represents a long polymer chain of positive charge potential. The lined shapes are negatively dispersed particles in water. The high molecular weight polymer ionizes in water to form either an anionic or cationic long chain molecule. By the bridging

mechanism (5), portions of the polymer absorb onto a particle and other portions absorb onto other particles. This basic mechanism is dependent on several variables that will influence the resultant degree of flocculation. These variables are: 1) the strength of the initial absorption, 2) the degree of flocculation during absorption, and 3) the subsequent agitation that may break down the flocs. The strength of the absorption is important to its susceptibility to be broken up and is dependent on the charge in the system. The bond will be the strongest when the isoelectric point - no charge potential - is reached! The correct degree of flocculation is also important since too small a particle will pass through the wire and too large a particle will adversely affect the efficiency of the system.

In a comparison of the mechanisms of flocculation suggested previously, bridging of particles by high molecular weight polymers is shown to be the principle mechanism producing flocculation even though all three may be involved to a degree (6). Formation of the polymer bridges can occur even against appreciable electrostatic charge barriers. This type of mechanism is predominant when an anionic polyacrylamide is used for the retention of the anionic titanium dioxide onto the fibers. As a further note, once these bridges have been broken up by excessive agitation, the resultant particles are suspended in a very stable state and are held suspended by coulombic forces. These particles are very hard to reflocculate.

A further breakdown of the retention mechanism reveals that even though the bridging mechanism is predominant, the charges in the system will play an important role - sort of a fine tuning mechanism. A series of sizing experiments using cationic retention aids by Strazdins (6) shows that as the systems zeta potential moves towards the isoelectric point, that is, zero zeta potential, all measured properties approach their maximum values. Thus the peak efficiency is obtained at the isoelectric point. The reasoning behind this phenomenon is that in highly electronegative systems, there are several competitive forces which affect retention. The introduction of a strongly cationic material normalizes the condition. The result is a more permanent adhesion. Thus, that the hydrodynamic shear to the fiber-aggregates and the retention is greatest when the system possesses a high charge. This is because strong coulombic repulsion accelerates the disintegration process. Best retention is effected near the isoelectric point.

A further study into the literature reveals several methods by which the zeta potential of fibers can be controlled. The first of these is the pH. Raising the pH will enlarge the fiber surface area and increase the electronegative potential of the fibers (6). In studying various polymers for use in this study, the author found that the cationic polymers work well throughout the entire range of pH and is not affected by alum concentration (7). Thus, with cationic

polymers, a high pH is desirable. The anionic polymer grades give the highest efficiency at neutral to alkaline pH and again the higher pH is desired. Secondly, undesirable positive potentials can be alleviated by balancing the system with anionic polymers such as polyacrylamides (6). Thus, the synergistic effect of the cationic and anionic in precisely controlled amounts will have a superior efficiency in retention.

The Kubelka-Munk theory is the means by which the efficiency of a titanium dioxide retention study is measured. By a correlation of basis weight, percent TiO_2 retained, opacity, and brightness, the scattering power due to the titanium alone can be obtained. The scattering power is directly related to efficiency.

The experimental work done in this project is designed around the idea of the application of the zeta potential to obtain the maximum efficiency of titanium dioxide retention. From work done in a previous study by Richard Clapp (10), several cationic retention agents provided effective retention for fibrous-pigment systems. Anionic retention agents also give adequate retention due to the bridging mechanism (6).

The author suggests that by using the two together in the same system, the results could be superior. This is done by using the anionic polymer in such a way as to control the zeta potential provided by the cationic polymer. The polymers should however not adversely react chemically with each other.

EXPERIMENTAL DESIGN

Bleached softwood kraft pulp was selected for use in this study because of its abundance of usage today. The pulp was beaten to a freeness of five hundred Canadian Standard Freeness points by the Tappi Standard Method. The pulp was used immediately and not stored with preservative as to avoid any introduction of foreign chemicals in the system.

Next, control runs were made with the Noble and Wood sheet machine. The stock proportioner contained 22.5 grams of fiber to yield a 2.5 gram handsheet. pH controlling chemicals were not used in this study, as this was not the objective. The control samples consisted of a sheet of fibers only since a basis is needed to measure the scattering coefficient of TiO_2 , and sheets made with 5 g and 10 percent titanium dioxide based on the weight of the fibers. Samples with TiO_2 are also needed to measure the effectiveness of titanium dioxide when the polymers are added.

The titanium dioxide slurry was made by preparing a fifty percent solids dispersion of TiO_2 in water using a Cowles disperser. No dispersing agent was used as this would interfere with the retention agents being tested. The dispersion is then reduced to ten percent solids for further addition to the fiber slurries. An addition of 11.25 ml of the solution would give a five percent addition rate of TiO_2 .

The next phase of the experiment consists of varying the addition sequences of fibers, titanium dioxide, anionic polymers and cationic polymer. Sheets were prepared for testing and the zeta potential was also determined on the stock for comparison. The polymers used in the study were: 1) Percol 139, an anionic high molecular weight polyacrylamide, and 2) Percol H0, a cationic high molecular weight polyacrylamide. These are very compatible when mixed together, that is they will not violently react with each other. The solutions of these are prepared as follows, a one-half percent solution was prepared by wetting out one half gram of the polymer with three milliliters of methanol. The wet polymer is then diluted to one hundred milliliters immediately and shaken until dissolved. A final dilution to one liter is made yielding a five hundredths percent solution (.05%). An addition rate of fifteen thousandths percent (.015%) of the polymer based on the weight of the fiber is made by adding six and three fourths milliliters of the polymer solution to twenty two and one half grams of stock in the proportioner.

Samples were then made with the following polymer solutions in order to obtain the optimum addition sequence:

1. Fibers + 0.015% cationic polymer
+ 5% TiO_2
2. Fibers + 0.015% anionic polymer
+ 5% TiO_2

3. Fibers + 0.0075% cationic + 0.0075% anionic
+ 5% TiO_2
4. Fibers + 0.0075% anionic + 0.0075% cationic
+ 5% TiO_2
5. Fibers + 0.0075% cationic and 0.0075% anionic mixed prior
to addition
+ 5% TiO_2
6. Fibers + 5% TiO_2 + .0075% cationic
+ .0075% anionic
7. Fibers + 0.0075% cationic, added to a mixture of 5% TiO_2
and 0.0075 anionic polymers.

For each set of samples, a mixing time of five minutes was used between each addition. After the optimum addition sequence of materials was determined chemicals additions were varied to determine how to obtain optimum scattering coefficient. By varying the amounts of the chemicals used and calculating the electrophoretic mobility of each solution before handsheets are made, the effect of zeta potential on the optimum retention efficiency was obtained. The final part of the study was then conducted as follows. Starting with 0.015% of each polymer, the percentage of the anionic polymer was decreased and the zeta potential of each sample determined. This was done until the isoelectric point was reached. Next, the anionic addition rate was set at 0.0025% and the cationic addition rate was altered to find its effect.

The handsheets of all the trials were now tested and the scattering coefficient due to the titanium dioxide determined. This was done as

follows. The retention of TiO_2 was determined by ashing the sample. The brightness, opacity, and basis weight were also determined. Using the Kubelka-Monk theory (TAPPI Data Sheet # 65) graphical solution to the total scattering power is obtained. This can be broken down further to the scattering power of the titanium dioxide alone using the amount of TiO_2 in the sheet and the scattering power due to the fibers only as calculated from the control runs (see Table I).

DATA

TABLE I
CONTROL RUNS

<u>Additive</u>	<u>Basis Weight</u>	<u>Bright</u>	<u>Opacity</u>	<u>% Retention</u>	<u>S TiO₂</u>	<u>Zeta Potential</u>
Fibers	61.7g/m ²	71.8	70.8	-	1.5 ¹	-1.2(uV)
Fibers +5% TiO ₂	69.5	77.0	73.2	2.5	9.2	-1.4
Fibers +10% TiO ₂	62.0	73.0	74.2	2.4	5.4	-1.5
TiO ₂ (Slurry)	-	-	-	-	-	-0.9

Notes: 1 scattering coefficient for fibers.

TABLE II

Effect of Addition Procedure of Anionic and Cationic
Polymers to Fibers and TiO_2 Systems

<u>Additive</u>	<u>Basis Weight</u>	<u>Bright</u>	<u>Opacity</u>	<u>% Retention</u>	<u>S TiO_2</u>	<u>Zeta Potential</u>
Fibers +cationic polymer	58.6 g/m^2	75.4	77.5	33.4	1.96	+0.45
Fibers + anionic polymer + TiO_2	58.6	75.1	77.2	30.7	1.92	-1.95
Fibers +cationic polymer +anionic polymer + TiO_2	59.5	76.4	77.8	27.6	2.45	-0.35
Fibers +anionic polymer +cationic polymer + TiO_2	53.1	74.5	76.7	33.1	1.65	-0.58
Fibers +Anionic & cationic polymer + TiO_2	58.0	74.0	76.0	38.0	1.55	-1.85
Fibers + TiO_2 +polymers	60.5	75.0	76.5	41.0	1.42	-0.80
Fibers & Cationic + TiO_2 & Anionic	61.0	76.0	74.0	62.0	0.85	-0.75

TABLE III
Application of Zeta Potential
To The Retention of Titanium Dioxide

<u>% Additives</u>	<u>Basis Weight</u>	<u>Bright</u>	<u>Opacity</u>	<u>% Retention</u>	<u>S TiO₂</u>	<u>Zeta Potential</u>
.015 cationic +.015 anionic	62.0	77.5	74.1	62.2	0.85	-1.25
.010 cationic +.010 anionic	69.0	77.1	75.2	50.5	1.10	-0.95
.0075 cationic +.0075 anionic	61.0	76.5	77.8	27.0	2.45	-0.45
.0050 cationic +.0050 anionic	61.5	76.6	78.0	20.5	3.65	-0.25
.0025 cationic +.0025 anionic	63.4	76.9	77.7	21.0	3.55	-0.38
.0075 cationic +.0025 anionic	66.3	77.0	76.5	26.5	2.95	-0.50
.0050 cationic +.0040 anionic	59.2	77.3	75.9	30.0	2.85	-0.40
.0050 cationic +.0030 anionic	58.3	76.9	76.8	25.0	3.38	-0.15
.0050 cationic +.0020 anionic	60.8	76.8	76.8	24.0	3.25	-0.35

Notes: 1. In all cases fibers are present first with the addition of 5% TiO₂ last.
2. 5 minutes mixing between additives.

DISCUSSION OF RESULTS

The first section of experimentation included the control runs which were samples of fibers only, 5% addition of TiO_2 , 10% addition of TiO_2 , and a TiO_2 slurry. The results here give a reference point for the scattering power and zeta potential for comparison with further samples. The results are shown in Table I. The sample with only fibers have an opacity of 70.8 with a scattering power of 1.5. These figures represent the fibrous system and subsequent figures will be altered from this point with the addition of TiO_2 in the sheet. A comparison of five and ten percent additions of TiO_2 is interesting. At 5%, the opacity is 73.2 while the scattering power is up to 9.2 - being the scattering coefficient for the TiO_2 only. The 10% sample gave an opacity of 74.5 but a decrease in scattering coefficient - or efficiency. The result is a point rise in opacity with a decrease in efficiency. Here the TiO_2 particles are probably co-flocculating and being retained in larger bundles than the opacity efficiency calls for. The zeta potential results show an increase in zeta potential with the addition of TiO_2 . This is expected since the titanium dioxide is anionic in nature and would produce a more negative charge. This can be noted by the zeta potential of the TiO_2 slurry only.

The second phase of experimentation determined the optimum addition sequence of fibers, pigment, and polymers. This is an important step in the experiment as it is necessary to optimize the results to yield the best comparison.

The addition rate found to give the best results is that of adding the cationic polymer to the fiber slurry, followed by the addition of the anionic polymer and finally the TiO_2 slurry is added. Five minutes of mixing time between each addition is maintained. The results of the experiments in this phase can be seen in Table II. The optimum addition sequence taken from the point where the highest scattering coefficient occurs for a given amount of TiO_2 added. This sequence also gave the lowest zeta potential. A comparison of the addition of anionic and cationic polymers added alone to a system to that of mixed polymer additions was made in this series of tests. Either of the two polymers gave similar results in the efficient retention category and the effect on zeta potential is expected. However, it is seen that they are both inferior to the optimum sequence. A reversal of the order of addition of cationic and anionic polymers of the optimum sequence gives a lower retention efficiency than either of the polymers added separately and thus the importance of addition sequence is illustrated.

With the proper addition sequence selected, the final phase of the experiment involved varying the amounts of polymer - both cationic and anionic - to study the effects of the zeta potential of the system on the effective retention of the filler. As stated in the literature review earlier, the closer the system is to the isoelectric point,

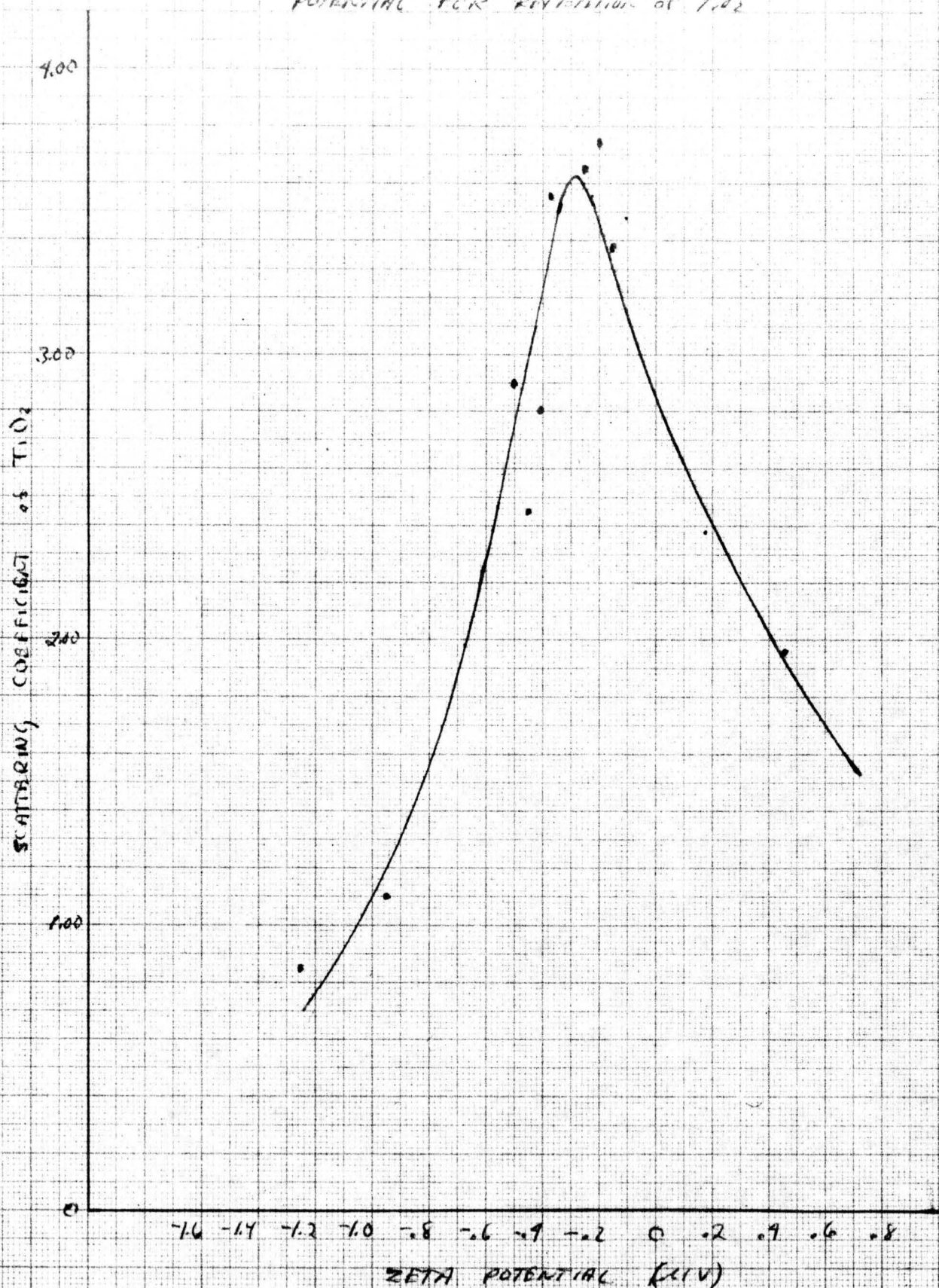
the more stable the system becomes and therefore, the best retention should be obtained. In Table III, this point is illustrated in the results of trials in which the addition rate of both anionic and cationic polymers were varied. The different trials are more or less random but follow a sequential pattern.

As both polymers are decreased by the same percentages yielding the same amount of each, the zeta potential decreases from the negative side approaching the isoelectric point. A point is reached however where the zeta potential is at its lowest and further decreases of polymer increase the zeta potential. This point is at 0.0025% cationic polymer plus 0.0025% anionic polymer. The reason the zeta potential starts to increase after this point is that the polymers become too weak and the charge inherent in the system without the polymers begin to take over. In this case the anionic nature of the titanium dioxide comes into play.

A low point in zeta potential results with the use of 0.0050% cationic and 0.0030% anionic polymers. This is within reason because the system is anionic in nature before polymers are added and thus a lower amount of anionic polymer would be expected to achieve the isoelectric point.

Figures II illustrates the relationship between the zeta potential of the system and its corresponding scattering coefficient. Within a very close margin, the peak scattering coefficient is at the lowest zeta potential value.

FIGURE 2.3 RELATIONSHIP BETWEEN
SCATTERING POWER AND ZETA
POTENTIAL FOR RETENTION OF TAO



CONCLUSIONS

This study in retention of TiO_2 shows that there is a definite relationship between zeta potential and effective retention of titanium dioxide. The effective retention of TiO_2 , along with other properties of a system that result from efficient formation seem to reach a high point as the zeta potential approaches the isoelectric point. The zeta potential of the system may very well be a chemical key to controlling and maximizing retention and other properties.

Anionic and cationic polymers were used to control the zero potential. It is very possible that this controlling mechanism can be applied in a mill situation to obtain maximum efficiency from retention of particles.

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