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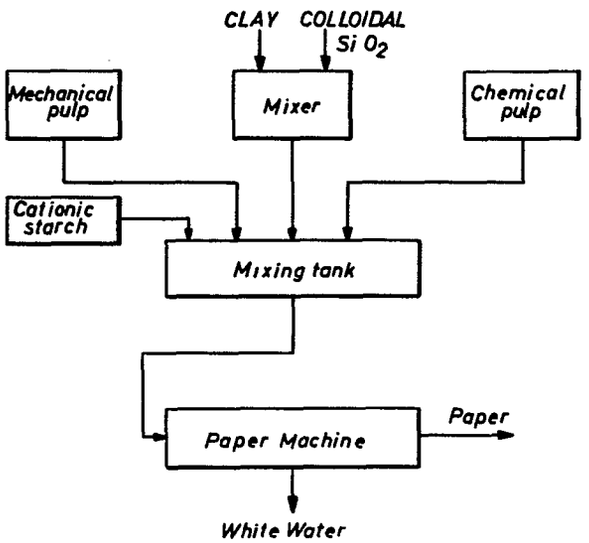
(54) Papermaking.

(57) In making paper from an aqueous papermaking stock, a binder comprising colloidal silicic acid and cationic starch is added to the stock for improving the paper or the retention of the stock components, or is added to the white water for reducing the pollution problems or recovering values from the white water.

The cationic starch of the binder has a degree of substitution of not less than 0.01, and the weight ratio of cationic starch to SiO_2 is between 1:1 and 25:1.



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PAPERMAKING

The present invention relates generally to papermaking processes and, more particularly, to the use of a binder in a papermaking process, the binder comprising a complex of cationic starch and colloidal silicic acid to produce a paper having increased strength and other characteristics. Such a binder, in addition, also effects highly improved levels of retention of added mineral materials as well as papermaking fines. Moreover, various features of the invention may be employed to effect clarification of the white water resulting from a papermaking process.

At the present time, the papermaking industry is plagued with a number of serious problems. First, the price of cellulosic pulp has escalated materially and high quality pulp is in relatively short supply. Second, various problems including the problems inherent in the disposal of papermaking wastes and the ecological requirements of various governmental bodies have markedly increased the cost of papermaking. Finally, the cost of the energy required to make paper has increased materially. As a result, the industry and its customers are faced with two choices: either pay the higher costs or materially decrease the amounts and/or quality of the cellulosic fibers with a consequential loss of quality in the finished paper product.

The industry has made various attempts to reduce the cost of the paper products. One approach that has been employed involves the addition of clay and other mineral fillers in the papermaking process to replace fiber but such additions have been found to reduce the strength and other characteristics of the resulting paper to a degree which is unsatisfactory. Also, the addition of such mineral filler results in poor retention of the filler material, e.g. they pass through

the wire to the extent that the level of filler materials builds up in the white water with the result that the clean-up of white water and the disposal of the material becomes a serious problem. Various binders have been employed in an attempt to alleviate the retention problem but their use has not been entirely satisfactory.

Attempts have also been made to use types of pulp which are less expensive and of lower quality, but this, of course, results in a reduction in the characteristics of the paper and often results in excessive fines which are not retained in the papermaking process with the consequent white water disposal problems.

Accordingly, the principal object of the invention is the provision of a binder system and method which produce improved properties in paper and which will permit the use of minimum amounts of fiber to attain strengths and other properties which are required. Another object of the invention is the provision of a binder system and a method of employing it which materially increases the strength and other characteristics of paper as compared to a similar paper made with known binders. An additional object of the invention is the provision of a binder and a method of employing it which maximizes retention of mineral filler and other materials in the paper sheet when used in the stock on the papermaking machine. A further object of the invention is the provision of a paper having high mineral concentration which has acceptable strength and other characteristics. A final object is the provision for a method of removing suspended solids from white water in a papermaking process.

Other objects and advantages of the invention will become known by reference to the following description and the appended drawings in which:

FIGURE 1 is a flow diagram of a papermaking process embodying various of the features of the invention:

FIGURE 2 and FIGURES 2A through 2S are charts

showing a test run on a papermaking machine in Example 1 and the properties of the paper resulting therefrom, the process employed embodying various of the features of the invention;

FIGURE 3 is a chart graphically portraying the results of Example II;

FIGURE 4 is a flow diagram of a papermaking process emboyding various features of the invention;

FIGURE 5 is a chart showing a test run on a papermaking machine, the process employed embodying various features of the invention;

FIGURE 6 is a chart showing the tensile index as a function of the added amount of cationic starch in an example of the papermaking process of the invention;

FIGURE 7 is a chart showing the settling rate of the solids in white water samples and showing various features of the inventions;

FIGURES 8A through 8G are charts graphically portraying results of Example XI.

We have discovered a binder and method of employing it which materially increases the strength and other characteristics of a paper product and which permits the use of substantial amounts of mineral fillers in a papermaking process while maximizing the retention of the filler and cellulosic fines in the sheet. This makes possible, for a given grade of paper, a reduction in the cellulosic fiber content of the sheet and/or the quality of the cellulosic fiber employed without undue reduction in the strength and other characteristics of the sheet. Also, by employing the principles of the invention the amount of mineral filler material may be increased without unduly reducing the strength and other characteristics of the resulting paper product. Thus, by a reduction in the amount of pulp employed to make a given sheet or the substitution of mineral filler for pulp, the reduction in fiber content permits a reduction in the energy required for pulping as well as a reduction in the energy required for drying the

sheet. In addition, it has been found that the retention of the mineral filler and fines is at a sufficiently high level that white water problems are minimized.

We have also discovered that the principles of this invention may be employed to remove suspended fibers and mineral materials in a white water system papermaking process.

In general, the system of the invention includes the use of a binder complex which involves two components, i.e. colloidal silicic acid and cationic starch. The weight ratio between the cationic starch and the SiO_2 in the colloidal silicic acid is greater than one and less than about 25. The two components are provided in the stock prior to formation of the paper product on the papermaking machine. It has been found that, after drying, the sheet has greatly enhanced strength characteristics. Also, it has been found that when mineral fillers such as clay, chalk and the like are employed in the stock, these mineral fillers are efficiently retained in the sheet and further do not have the degree of deleterious effect upon the strength of the sheet that will be observed when the binder system is not employed.

While the mechanism that occurs in the stock and during paper formation and drying in the presence of the binder is not entirely understood, it is believed that the cationic starch and the anionic colloidal silicic acid form a complex agglomerate which is bound together by the anionic colloidal silicic acid, and that the cationic starch becomes associated with the surface of the mineral filler material whose surface is either totally or partially anionic. The cationic starch also becomes associated with the cellulosic fiber and the fines, both of which are anionic. Upon drying, the association between the agglomerate and the cellulosic fibers provides extensive hydrogen bonding. This theory is supported in part by the fact that as the Zeta potential in the anionic stock moves towards

zero when employing the binder complex of the invention both the strength characteristics and the retention improve.

We have also discovered that when a binder of the type disclosed above is employed, the effect of the binder system may be enhanced by adding the colloidal silicic acid component in several increments, i.e. a portion of the colloidal silicic acid is admixed with the pulp and the mineral filler when present, then the cationic starch is added and thereafter when a complex agglomerate of pulp, filler (if any), silicic acid and starch is formed and before the stock is fed to the head box of the papermaking machine the remaining portion of the colloidal silicic acid is admixed with the stock containing the complex agglomerate. This procedure of supplying the colloidal silicic acid in two or more steps results in certain improvements in strength and other characteristics, but the most striking improvement is the increase in retention of filler and papermaking fines. The reason for these improvements is not entirely understood but it is believed that they result from the production of complex filler-fiber-binder agglomerates, which are more stable, i.e. that the later addition of the colloidal silicic acid causes the agglomerates initially formed to bond together to form even more stable agglomerates which are less sensitive to mechanical and other forces during the formation of the paper.

Based upon the work that has been done to date, the principles of this invention are believed applicable in the manufacture of all grades and types of paper products. For example, printing grades, including newsprint, tissue, paper board and the like.

It has been found that the greatest improvements are observed when the binder is employed with chemical pulps, e.g. sulfate and sulfite pulps from both hard and soft wood. Lesser but highly significant improvements

occur with thermo-mechanical and mechanical pulps. It has been noted that the presence of excessive amounts of lignin in ground wood pulps seems to interfere with the efficiency of the binder so that such pulps may require either a greater proportion of binder or the inclusion of a greater proportion of other pulp of low lignin content to achieve the desired result. (As used herein, the terms "cellulosic pulp" and "cellulosic fiber" refer to chemical, thermo-mechanical and mechanical or ground wood pulp and the fibers contained therein.)

The presence of cellulosic fibers is essential to obtain certain of the improved results in the invention which occur because of the interaction or association of agglomerate and the cellulosic fibers. Preferably, the finished paper should contain over 50% cellulosic fiber but paper containing lesser amounts of cellulosic fibers may be produced which have greatly improved properties as compared to paper made from similar stocks not employing the binder agglomerate described herein.

Mineral filler material which can be employed includes any of the common mineral fillers which have a surface which is at least partially anionic in character. Mineral fillers such as kaolin (china clay), bentonite, titanium dioxide, chalk, and talc all may be employed satisfactorily. (The term "mineral fillers" as used herein includes in addition to the foregoing materials, wollastonite and glass fibers and also low-density mineral fillers such as expanded perlite). When the binder complex disclosed herein is employed, the mineral fillers will be substantially retained in the finished product and the paper produced will not have its strength degraded to the degree observed when the binder is not employed.

The mineral filler is normally added in the form

of an aqueous slurry in the usual concentrations employed for such fillers.

As mentioned above, the mineral fillers in the paper may consist of or comprise a low-density or bulky filler. The possibility of adding such fillers to conventional paper stocks is limited by factors such as the retention of the fillers on the wire, the dewatering of the paper stock on the wire, the wet and dry strength of the paper product obtained. We have now discovered that the problems caused by the addition of such fillers can be obviated or substantially eliminated by using the binder complex of the present invention which also makes it possible to add higher than normal proportions of such fillers to obtain special properties in the paper product. Thus, using the binder complex of the invention it has become possible to produce a paper product of lower density and consequently higher stiffness at the same grammage and simultaneously to keep the strength properties of the paper product (such as the modulus of elasticity, the tensile index, the tensile energy absorption and the surface picking resistance) at the same level as or even at a better level than before.

As pointed out above, the binder comprises a combination of colloidal silicic acid and cationic starch. The colloidal silicic acid may take various forms, for example, it may be in the form of polysilicic acid or colloidal silicic acid sols although best results are obtained through the use of colloidal silica sols.

Polysilicic acid can be made by reacting water glass with sulfuric acid by known procedures to provide molecular weights (as SiO_2) up to about 100,000. However, the resulting polysilicic acid is unstable and difficult to use and presents a problem in that the presence of sodium sulfate causes corrosion and other problems in papermaking and white water disposal. The sodium

sulfate may be removed by ion exchange through the use of known methods but the resulting polysilicic acid is unstable and without stabilization will deteriorate on storage. Salt-free polysilicic acid may also be produced by direct ion exchange of diluted water glass.

While substantial improvements are observed in both strength and retention with a binder containing polysilicic acid and cationic starch, superior results are obtained through the use with the cationic starch of colloidal silicic acid in the form of a sol containing between about 2-60% by weight of SiO_2 and preferably about 4-30% SiO_2 by weight.

The colloidal silicic acid in the sol should desirably have a surface area of from about 50 to 1000 m^2/g and preferably a surface area from about 200 to 1000 m^2/g with best results being observed when the surface area is between about 300 to 700 m^2/g. The silicic acid sol is stabilized with an alkali having a molar ratio of SiO_2 to M_2O of from 10:1 to 300:1 and preferably a ratio of from 15:1 to 100:1 (M is an ion selected from the group consisting of Na, K, Li and NH_4). It has been determined that the size of the colloidal silicic acid particles should be under 20 nm and preferably should have an average size ranging from about 10 down to 1 nm. (A colloidal silicic acid particle having a surface area of about 500 m^2/g involves an average particle size of about 5.5 nm).

In essence, it is preferably sought to employ a silicic acid sol having colloidal silicic acid particles which have a maximum active surface and a well defined small size generally averaging 4-9 nm.

Silicic acid sols meeting the above specifications are commercially available from various sources including Nalco Chemical Company, Du Pont & de Nemours Corpo-

ration and the assignee of this invention.

The cationic starch which is employed in the binder may be made from starches derived from any of the common starch producing materials, e.g. corn starch, wheat starch, potato starch, rice starch, etc. As is well known, a starch is made cationic by ammonium group substitution by known procedures. Best results have been obtained when the degree of substitution (d.s.) is between about 0.01 and 0.05 and preferably between about 0.02 and 0.04, and most preferably over about 0.025 and less than about 0.04. While a wide variety of ammonium compounds, preferably quaternary, are employed in making cationized starches for use in our binder, we prefer to employ a cationized starch which was prepared by treating the base starch with either 3-chloro-2-hydroxypropyl-trimethyl ammonium chloride or 2,3-epoxypropyl-trimethyl ammonium chloride to obtain a cationized starch having 0.02-0.04 d.s.

In the papermaking process the binder is added to the papermaking stock prior to the time that the paper product is formed on the papermaking machine. The two ingredients, the colloidal silicic acid component and the cationic starch, may be mixed together to form an aqueous slurry of the silica-cationic starch binder complex which then can be added to and thoroughly mixed with the papermaking stock. However, this procedure does not provide maximized results. It is preferable that the silica-cationic starch complex is formed <u>in situ</u> in the papermaking stock. This can be accomplished by adding the colloidal silicic acid component in the form of an aqueous sol and the cationic starch in the form of an aqueous solution separately to the stock in a mixing tank or at a point in the system where there is adequate agitation so that the two com-

ponents are dispersed with the papermaking components so that they interact with each other, and with the papermaking components at the same time.

Even better results are obtained if the colloidal silicic acid component is added to a portion of the stock and thoroughly mixed therewith after which the make-up of the stock is completed and the cationic starch component is added and thoroughly mixed with the stock prior to the formation of the paper product.

In the event that a mineral filler is to be added to the stock it has been found preferable to slurry the mineral filler in water with the colloidal silicic acid, or in the event of incremental additions of the colloidal silicic acid component, the initial portion of the colloidal silicic acid component and then to introduce the filler-colloidal silicic acid component slurry into a mixing device where it is incorporated into the stock along with the pulp and cationic starch.

Thereafter, when using incremental additions of the colloidal silicic acid component, the final portion or portions of the colloidal silicic acid component are thoroughly mixed with the stock after the initial agglomerate is formed and prior to or at the time the stock is conducted into the head box. The initial addition of the colloidal silicic acid should comprise about 20 to about 90 percent of the total amount to be added and then, after the initial agglomerate is formed, the remainder should be added before the sheet is formed. Preferably, the initial addition should comprise from about 30 to about 80% of the colloidal silicic acid component.

It has been found that in a papermaking process employing the binder complex described herein, the pH of the stock is not unduly critical and may range

from a pH of from 4 to 9. However, pH ranges higher than 9 and lower than 4 are undesirable. Also, other paper chemicals such as sizing agents, alum, and the like may be employed but care should be taken that the level of these agents is not great enough to interfere with the formation of the silicic acid cationic starch agglomerate and that the level of the agent in recirculating white water does not become excessive so as to interfere with the formation of the binder agglomerate. Therefore, it is usually preferred to add the agent at a point in the system after the agglomerate is formed.

According to the invention, the ratio of cationic starch to the total colloidal silicic acid component should be between 1:1 and 25:1 by weight. Preferably, the ratio is between 1.5:1 and 10:1 and most preferably between 1.5:1 and 4.5:1.

The amount of binder to be employed varies with the effect desired and the characteristics of the particular components which are selected in making up the binder. For example, if the binder includes polysilicic acid as the colloidal silicic acid component, more binder will be required than if the colloidal silicic acid component is colloidal silicic acid sol having a surface area of 300 to 700 m^2/g. Similarly, if the cationic starch, for example, has a d.s. of 0.025 as compared to a d.s. of 0.030, more binder will be required assuming the colloidal silicic acid component is unchanged.

In general, when the stock does not contain a mineral filler the level of binder may range from 0.1 to 15% by weight and preferably from 1 to 15% by weight based upon the weight of the cellulosic fiber. As pointed out above, the effectiveness of the binder is greater with chemical pulps so that less binder will be required

with these pulps to obtain a given effect than other types. In the event that a mineral filler is employed the amount of binder may be based on the weight of the filler material and may range from 0.5 to 25% by weight and usually between 2.5 to 15% by weight of the filler.

As has been pointed out, the binder may be added to the white water of a papermaking machine in a system in which the binder system is not being used. The binder effectively forms an agglomerate with the papermaking fines and the suspended mineral material which makes possible the efficient settling or concentration of the suspended solids to provide a relatively clear fraction of water which can be returned to the papermaking system, and a fraction in which the suspended solids are concentrated and from which they can be removed by filtration or other means. The amount of the binder system or complex required, with the cationic starch to SiO_2 ratios as set forth above, can be relatively small and in most instances is less than about 10% by weight based upon the dry weight of solids in the white water and the dry weight of the binder system. A useful broad range of the amount of the binder system or complex is from about 1 to about 20% by weight, preferably from about 2 to about 10% by weight.

The following specific examples show the effects of the binder employed in a papermaking process upon the retention of mineral filler and upon the strength characteristics of the paper produced and upon white water.

EXAMPLE I

A trial was run making a base stock for wallpaper, the paper stock having a high clay content. The run was made on a Fourdrinier machine having an estimated capacity of about 6000 kg/h. The machine speed was approximately 250 m/min. and the target grammage was 90 g/m^2. FIGURE 1 is a flow diagram indicating the sequence of operations.

The fiber in the stock comprised a mixture of a mechanical pulp and a chemical pulp. The mechanical pulp was unbleached and was refined to a Canadian Standard Freeness (CSF) of 100. The chemical pulp employed was a bleached sulfate hardwood pulp which was refined to 400 CSF. During the refining process, suitable amounts of water were, of course, added to the pulp to provide the desired consistency.

Papermakers' china clay and a colloidal silicic acid sol were dispersed in water to provide a slurry containing 5 percent clay by weight. The china clay had a particle size distribution in the range of from about 0.5 to 10 μm. The colloidal silicic acid was in the form of a 15% sol which was stabilized with alkali with a molar ratio of SiO_2:Na_2O of 45:1. The silicic acid had a particle size in the range of from about 5-7 nm and a surface area of approximately 500 m^2/g. The colloidal silicic acid was added to provide 2.86% SiO_2 based upon the weight of the clay. The pH of the clay-SiO_2 slurry was about 8.

FIGURE 2 shows the level of feed to the papermaking machine during the test run, in kg/min. at the various times during the run. The consistency of the stock flowing to the paper machine ranged from about 6 to about 15 g/l, as shown in FIGURE 2A, the time in FIGURE 2A being correlated to the times shown in FIGURE 2.

As illustrated in FIGURE 2, the run was begun at 1410 hours by mixing the chemical pulp and mechanical pulp in the proportions shown. At 1440 hours the stock valve was opened and stock flowed to the papermaking machine. The dotted line in FIGURE 2 shows the adjustment of the stock valve during the process.

Initially, the stock feed to the machine was constituted entirely of a mixture of chemical and mechanical pulp. However, at 1450 hours the china clay-colloidal

silica mixture was introduced into the mixing tank and the papermaking machine was run with the fiber-clay stock until the ash content of the stock and the white water came to equilibrium. At approximately 1535 hours, a slurry of cationic starch was added to and thoroughly mixed with the pulp, clay and colloidal silicic acid in the mixing tank to provide the stock containing the complete binder. The level of cationic starch added at 1535 hours was 7.14 percent by weight of starch based upon the weight of clay, the ratio of cationic starch to colloidal silicic acid being 2.49. (This level of starch in this example and in the drawings is sometimes referred to as "LEVEL 1"). At 1625 hours, the level of cationic starch was raised to 8.57 percent based upon the weight of clay, the ratio of cationic starch to colloidal silicic acid then being raised to 2.99. (This level of starch in this example and in the drawings is sometimes referred to as "LEVEL 2"). At 1702 hours, the level of cationic starch was raised to 11.43 percent based upon the weight of clay, the ratio of cationic starch to colloidal silicic acid then being 3.99. (This level of starch in this example and in the drawings is sometimes referred to as "LEVEL 3"). At all times during the run, the pH of the stock on the machine was approximately 8.

The cationic starch was prepared by treating potato starch with 3-chloro-2-hydroxypropyl-trimethylammonium chloride to provide a degree of substitution (d.s.) in the starch of 0.03. It was dispersed in cold water at a concentration of about 4% by weight, heated for 30 min. at about 90°C, diluted with cold water to a concentration of about 2% by weight and then added to the mixing tank as indicated in FIGURE 1.

For reference purposes, it was determined that after an addition or change was made in the mixing tank (the time of addition being indicated by the vertical arrows in FIGURE 2), it required approximately 15 minutes for the change to stabilize on the papermaking machine (indi-

cated by the horizontal arrows in FIGURE 2).

After the addition of the cationic starch to Level 1, i.e. to a ratio of 2.49 to the silicic acid, the grammage of the paper rose rapidly as the mineral content in the paper was increased because of the retention of the mineral content with the papermaking fibers on the wire of the machine. The stock valve was then adjusted to reduce the grammage to the 90 g/m^2 level and, by adjustment of the stock valve, the grammage was maintained relatively constant as the ash content rose slowly. During this period of time, the solids in the white water were reduced by approximately 50 percent as more and more of the solid materials were retained.

When the level of cationic starch was increased to Level 2, i.e. a ratio of 2.99 to the silicic acid, the grammage and ash content of the paper again increased and the solids in the white water were further reduced as the level of retention again increased.

After the addition of the cationic starch to the system and the increased retention of clay was observed, it was found that the driers overdried the paper. The steam consumption in the drier was lowered and several of the drying cylinders were shut off because of more rapid drying. In spite of the reduction in heat to the driers, the paper was periodically overdried. The decrease in steam consumption resulted from the fact that the fiber content of the paper was markedly reduced as the retention increased, thus facilitating drying.

Even though the mineral content (measured as ash content) of the paper was greatly increased, the papermaking machine was run at the same speed and without changes in dewatering conditions throughout the trial.

The conditions and results of the run are graphically illustrated in FIGURES 2A-2S.

In FIGURE 2A the concentration of solids in the stock is shown correlated to the time of the run. It will be noted that the total concentration of solids slightly exceeds the total of fiber and ash. This is because the

ash determination drives out the water of hydration and other water associated with the clay.

FIGURE 2B shows the level of solids in the white water. Again, the total concentration of solids exceeds the sum of fiber and ash for the reason given above. In connection with FIGURE 2B it should be noted that the level of ash (in this case non-retained minerals) rises rapidly until the cationic starch at Level 1, has been added and has had a chance to reach equilibrium in the system. When the level of cationic starch is increased to Level 2 another dramatic decrease occurs.

The combination of the colloidal silicic acid and the cationic starch as a binder also increases the filtering speed of the white water through the wire as shown in FIGURE 2C. The drainage time per unit volume increased until the combination binder was present at Level 1 and thereafter rapidly decreased. With the addition of the cationic starch at Level 2 the decrease in time per unit volume was even greater.

FIGURE 2D shows the Zeta potential in the stock which is adjusted towards 0 by the addition of the cationic starch component. As will be noted, the adjustment corresponds to increased retention and improved characteristics.

FIGURE 2E graphically illustrates the grammage of the paper during the run. There were two occasions when the web broke on the machine as indicated.

FIGURE 2F is a chart showing the tensile index of the paper produced in this example. It should be noted that, because of the moisture driven from the ash, the amount of china clay in the paper is approximately 120 percent of the amount of ash shown. As will be observed, the tensile index is greatly improved and the clay acts in the presence of the colloidal silica-cationic starch complex binder to increase the tensile index.

FIGURE 2G is a chart similar to FIGURE 2F, except that the tensile index is correlated to the level of chemical pulp.

FIGURE 2H shows the improved Z strengths in the resulting paper despite the fact that the paper contains substantial amounts of clay.

FIGURE 2I through 2S are charts showing the properties of the paper made by the process of this example which demonstrate the effectiveness of the complex silica-cationic starch bond. It should be noted that in the case of FIGURE 2M having to do with the roughness of the sheet, the paper was somewhat overdried at times so the conclusions as to this property which can be drawn from the chart may not be entirely valid.

As will be apparent from the results of the run and the properties of the papers produced thereby, the employment of the binder complex causes a mutual flocculation of the mineral matter, the cellulosic materials and the binder to produce highly improved retention and paper properties. Thus, the binder permits the incorporation of substantial amounts of mineral filler with a cellulosic pulp to obtain the same or better properties than can be obtained in a sheet having a greater proportion of cellulosic fibers and a lesser amount of mineral filler when the binder of the invention is not employed.

EXAMPLE II

Hand sheets were made up in a laboratory hand sheet former from various stocks made from bleached soft wood sulfate pulp with and without wollastonite as a filler, the stock including the cationic starch colloidal silicic acid complex binder to enhance the properties of the resultant paper. The wollastonite used was in the form of acicular crystals between about 1 and 20 μm in diameter and having a length of about 15 times the diameter.

The colloidal silicic acid which was used was a silicic acid sol containing 15 percent of colloidal silicic acid having a surface area of approximately 500 m^2/g. The sol was alkali stabilized with a molar ratio of $SiO_2:Na_2O$ of 40:1.

The cationic starch (C.S.) employed was the same

starch employed in Example I having a degree of substitution of 0.03. The cationic starch was added in the form of a 4 percent (by weight) aqueous solution.

In the procedure, the colloidal silicic acid sol was added to the stock before the cationic starch. In the examples containing wollastonite, the sol and cationic starch were added with the mineral to form a mineral-binder slurry which was then added to the cellulose. The usual amount of water was added to make up a papermaking stock of the desired consistency of about 1% by weight solids. After the hand sheets were made they were pressed and dried under substantially identical conditions.

In the following table the composition of the solids in each stock is set forth and the Z-strength (Scott Bond) was measured to provide an indication of the properties of the resulting sheet after pressing and drying.

Sample No.	Pulp g	Wollastonite g	4% C.S. g	15% Sol g	Z-strength (Scott Bond)
1	2.1	0	0	0	204
2	2.1	0.9	0	0	154
3	2.1	0	1.69	0	313
4	2.1	0.9	1.69	0	209
5	2.1	0	1.69	0.450	388
6	2.1	0	1.69	0.225	622
7	2.1	0	1.69	0.150	586
8	2.1	0	1.69	0.113	568
9	2.1	0.9	1.69	0.450	266
10	2.1	0.9	1.69	0.225	291
11	2.1	0.9	1.69	0.150	380
12	2.1	0.9	1.69	0.133	410

The results are plotted in FIGURE 3 which illustrates the enhanced strength which results from the silicic acid-cationic starch complex binder. As will be seen from the chart, the Z-strength of a sheet made from a stock containing 30% wollastonite in the solids as compared with a sheet containing only the fibrous cellulosic portion when the binder is employed, is higher. Also, the use of the binder with

a sheet containing only cellulosic fiber, dramatically increases the Z-strength.

EXAMPLE III

Hand sheets were made up in a laboratory hand sheet former from various stocks made of 2.0 g of bleached soft wood sulfate pulp and 2.0 g of English china clay Grade C. The china clay was dispersed in an alkali stabilized colloidal silicic acid sol diluted from 15% to 1.5% total solids by weight and the dispersion was added to the pulp in 500 ml of water in a laboratory disintegrator. A 2% solution of cationic starch (d.s. = 0.03) was added and the resulting stock was transferred to a sheet mold. The hand sheets which were made were pressed and dried under substantially identical conditions.

During the runs different silicic acid sols were used, the sols having differing surface areas per unit weight and stabilized with different molar ratios of alkali.

Sheets of the following compositions were made, all of which included in addition to the 2 g of pulp and 2 g of clay the amounts and type of sol and the amounts of cationic starch indicated. The properties of hand sheets produced are also set forth.

	1.5% sol g	Surface Area of SiO_2 m^2/g	SiO_2 Na_2O (molar ratio)	20 2% CS g	Grammage g/m^2	Density kg/m^3	Tensile Index (Scan P16:76)	Elongation %	Ash %
1	2.3	900	20	8.5	153	780	21.5	3.5	37
2	3.3	900	40	7.5	170	780	19.7	4.0	40
3	1.7	900	40	8.7	151	760	22.8	5.0	36
4	2.3	650	40	8.5	190	830	17.7	4.5	47
5	3.8	550	20	7.1	196	810	18.0	5.0	48
6	3.0	550	20	7.8	176	800	17.4	4.5	45
7	3.8	500	45	7.1	199	800	16.0	4.5	45
8	3.0	500	45	7.8	182	790	18.0	5.0	43
9	3.3	350	45[x]	7.5	185	840	15.7	6.0	46
10	3.3	200	100	7.5	170	730	16.5	6.0	33
11	5.0	200	100	7.5	165	730	16.5	5.5	37
12	0	-	-	10.0	141	700	19.4	6.0	28
13	No SiO_2, no cationic starch only 2.0 pulp + 6g china clay.				200	800	5.5	2.5	41

[x]Stabilized with ammonia instead of NaOH Molar Ratio = $\frac{SiO_2}{NH_3}$

From this example, it is apparent that the silicic acid sol cationic starch complex greatly aids in the retention of clay, in many instances resulting in almost complete retention. Also, the above results show that maximum retention of the clay occurs when the collodial silicic acid particles have a size range such that the surface area is between about 300 and 700 m^2/g.

EXAMPLE IV

Hand sheets were made in a laboratory hand sheet former from a stock including a binder which includes as the colloidal silicic acid component a polysilicic acid 100 ml of water glass (R = SiO_2:Na_2O = 3.3 and SiO_2 = 26.5% by weight) were diluted with 160 ml of water and slowly fed into 130 ml of 10% sulfuric acid under vigorous agitation. When all of the water glass had been added the pH was 2.7 and the SiO_2 content was 8% by weight. This

acid sol was diluted to 2% SiO_2 by weight and added to English china clay Grade C followed by the addition of a 2% cationic starch (CS) solution (d.s. 0.03). The following suspensions were made.

	Clay g	2% sol g	2% CS g
1	2.0	5.2	9.0
2	2.0	4.4	7.4
3	2.0	4.4	7.4
4	2.0	2.9	7.1
5	2.0	2.9	7.1

Each of suspensions 1, 2 and 4 was fed into a laboratory disintegrator containing 2.0 g of bleached softwood sulfate pulp in 500 ml of water and thoroughly agitated. Suspensions 3 and 5 were stored for 5 hours before mixing as above. Immediately after mixing, hand sheets were made, pressed and dried. The sheets had the following characteristics.

	Grammage g/m^2	Tensile Index (Scan P16:76)	Elongation %	Ash Content %
1	139	28.8	7.5	26
2	151	25.3	6.5	30
3	148	23.6	7.0	32
4	157	22.4	6.5	28
5	154	21.2	7.0	31

As compared with the samples produced in Example III, while the tensile index is improved, the retention of the mineral filler is not as great as in that Example.

EXAMPLE V

Hand sheets were made in a laboratory hand sheet former from various stocks as follows:

1. 2.0 g chalk having a particle size ranging from about 2 to 20 μm with the major portion being about 5 μm, 2.0 g of water and 3.8 g colloidal silicic acid (1.5% total solids and surface area of 500 m^2/g) are added to a stock consisting of 2.0 g fully bleached soft wood sulfate pulp

and 500 ml of water in a laboratory disintegrator. To the chalk-silicic-acid pulp stock 7.1 g cationic starch solution (2.0% total solids, d.s. = 0.03) is added. A sheet is made from the sample in a laboratory sheet mold and the sheet is pressed and dried.

2. A sheet as in stock 1 above was made, except that the amount of colloidal silicic acid sol was 5.7 g and the amount of cationic starch solution was 9.7 g.

3. A sheet as in stock 1 above was made, except that the amount of colloidal silicic acid sol was 5.0 g and the amount of cationic starch solution was 10.3 g.

4. The same procedure was followed to make a reference sheet without chalk where 3.8 g of the colloidal silicic acid sol were added to 2.0 g of the pulp in 500 ml of water and then 7.1 g of the cationic starch solution are added.

5. The same procedure was followed to make a reference sheet containing no binder. 10 g of chalk were added to 2.0 g of pulp in 500 ml of water, but no binder was added. The amount of chalk added was large so that, even with the poor retention observed, the mineral content in the final sheet would approximate that observed when the binder was employed.

6. Another sheet was made from a stock consistency of 2.0 g of the pulp in 500 ml of water with no additive.

The resulting paper had the following characteristics:

Sample No	1	2	3	4	5	6
Grammage g/m^2	192	201	200	110	174	100
Density kg/m^3	740	800	760	635	820	605
Tensile Index SCAN P16:76 Nm/g	16.0	20.0	17.3	50.7	10.5	31.4
Elongation %	7.5	5.5	4.0	5.5	6.0	7.5
Ash Content %	50	47	48	4	45	1

The foregoing demonstrates the increase in strength that results from the use of the binder of the invention both with and without mineral fillers and also demonstrates the increased retention which results from the use of the binder. From the amounts of binder employed relative to pulp it can be seen that substantially all of the mineral filler was retained in samples 1-3.

EXAMPLE VI

A slurry made of 2.0 g of Norwegian talc Grade IT Extra having a particle size ranging from about 1 to 5 µm, 8.0 g of water and 3.8 g of colloidal silicic acid (1.5% total solids, specific surface area 480 m^2/g) was added to a stock consisting of 2.0 g of fully bleached soft wood sulfate pulp and 500 g of water in a laboratory disintegrator. To the resulting stock 5.9 g of cationic starch (2.4% total solids, d.s. = 0.033) were added. A sheet was made in a laboratory hand mold and was pressed and dried.

A reference sample was made where 4.0 g of the talc were added to 2.0 g of the pulp in 500 g of water, but no binder was added. (The amount of talc is larger to compensate for the poor retention so that the finished sheet will have approximately the same mineral content as the sheet made above with the binder).

	With binder	Without binder
Grammage, g/m^2	198	214
Density, kg/m^3	825	715
Tensile Index SCAN P16:76, Nm/g	16.5	3.1
Elongation, %	6.5	3.0
Ash content, %	48	51

It will be noted again, as in Example V, that the strength characteristics are markedly better as is the retention when the binder is employed with a talc mineral filler.

EXAMPLE VII

In this Example, the binder system of the present invention was added to different papermaking stocks to

show that the invention is useful even in stocks containing considerable amounts of non-cellulosic fibers.

As cellulosic fibers fully bleached soft sulfate pulp was used, and as non-cellulosic fibers glass fibers having a diameter of about 5 µm and having been phenolic resin treated were used. The colloidal silicic acid sol contained silica particles with a specific surface area of about 400 m^2/g, and the silicic acid content of the sol was originally 15% by weight, but the sol was diluted with water to a silicic acid content of 1.5% by weight before it was used in the binder system. The cationic starch used had a degree of substitution of 0.02 and was used as a 2% by weight solution.

The following stocks were made, the stocks 1 to 3, inclusive, being comparative stocks:

Stock	Cellulosic fibers g	Glass fibers g	Silicic acid sol g	Cationic starch g	Ratio starch/sol
1	1.6	-	-	-	-
2	1.6	0.3	-	-	-
3	1.6	0.3	-	1.12	∞
4	1.6	0.3	0.187	1.12	8
5	1.6	0.3	0.372	1.12	4
6	1.6	0.3	0.496	1.12	3
7	1.6	0.3	0.744	1.12	2

From the seven stocks, hand sheets were made in a laboratory hand sheet former, the resulting papers having the following characteristics:

Paper from stock	Grammage g/m^2	Density kg/m^3	Tensile index Nm/g	Z-strength (Scott Bond)	Elongation %
1	68	650	55	135	9
2	91	530	33	84	11
3	88	520	40	120	10
4	90	520	44	132	10
5	85	520	44	138	11
6	94	540	48	152	12
7	93	550	47	149	11

As appears from the above, the Z-strength decreased when glass fibers were added (compare stocks 1 and 2) and then increased to about the initial value (compare stocks 1 and 4) when silicic acid sol and cationic starch both were added. The sheets made from stocks 5, 6 and 7 had higher Z-strength values than the sheets made from stock 1 containing no glass fibers.

EXAMPLE VIII

A commercial trial run was made making a coated, off-set, supercalendered printing paper having a grammage of 85 g/m^2. The machine employed was a twin wire Beloit "Bel-Baie" machine having a capacity of about 10,000 kg/hour at a speed of about 600 m/min. The coating was accomplished "on-line" with 10 g/m^2 of calcium carbonate applied to each side of the sheet. The cellulosic fiber comprised 70% sulfate hardwood and 30% sulfate softwood pulp both of which were fully bleached. The pH of the white water was about 8.5.

In the operation of the machine which was employed, the quality requirements for the paper produced by it were very rigid. As a result, in normal operation, a high proportion of the finished coated paper, about 25%, is classified as "broke". Broke, is unsatisfactory paper which is recycled into the stock and is reformed into a paper web. As a result, the stock to the machine head box contains a large proportion of filler in the form of reslurried coating from the broke. The proportion of the broke is often as high as 50% of the solids in the total stock.

The presence of the additional filler from the broke constitutes a serious problem in normal operation of the machine since its retention on the papermaking wire is extremely poor and most of it finds its way into the white water and eventually into the sewer. Also, since the amount of broke always varies, the filler content in the base sheet varies causing uneven sheet properties with the result that there are numerous

breaks in the paper web during production with attendant loss of production.

Fig. 4 is a flow diagram indicating the general operation which was employed in the run of this example employing incremental additions of the colloidal silicic acid in the process of the invention.

In Mixing Tank No. 1, the two types of bleached pulp which were typically used in the plant, i.e. the 70% sulfate hardwood and 30% sulfate softwood pulp, both fully bleached, were mixed together with the slurried broke. In order to compensate for varying amounts of filler in the stock caused by differing amounts of broke, arrangements were made to add a desired amount of extra filler (calcium carbonate). At this point, the amount of extra filler added was dependent upon the ash content which was measured continuously on line in the base sheet and enough calcium carbonate filler was added to maintain the level of ash in the finished paper base sheet at 15% by weight of dry paper.

In addition, in Mixing Tank No. 1, there was added in the form of an aqueous solution of colloidal silicic acid containing 15% by weight SiO_2, in an amount equivalent to 1.7 kg of SiO_2 per metric ton of dry base sheet (prior to coating). The colloidal silicic acid sol was stabilized with alkali with a molar ratio of SiO_2:Na_2O of 45:1. The silicic acid had a particle size in the range of from about 5-7 nm and a surface area of approximately 500 m^2/g.

The materials were thoroughly mixed and were conducted to Mixing Tank No. 2 where cationic starch was added to the stock, in an amount equal to 10.2 kg of cationic starch per metric ton of dry base sheet. The cationic starch was prepared by treating potato starch with 3-chloro-2-hydroxypropyl-trimethyl-ammonium chloride to provide a degree of substitution (d.s.) in the starch of 0.03. It was dispersed in cold water at a concentration of about 4% by weight, heated for 30 minutes

at about 90°C, diluted with cold water to a concentration of about 2% by weight and then added to Mixing Tank No. 2.

After the cationic starch was thoroughly intermixed the stock was conducted to Mixing Tank No. 3 wherein a second increment of colloidal silicic acid sol, of the type described above, was added to the stock in an amount equal to 2.1 kg SiO_2 per metric ton of dry base sheet.

From Mixing Tank No. 3 the stock was fed into the head box of the paper machine which was operated at normal speeds to form the base sheet which was subsequently dried, coated with a coating slip containing calcium carbonate and calendered in the same manner as before.

Fig. 5 graphically illustrates the effect of the addition of the colloidal silicic acid and cationic starch, as set forth above. The left hand side of the chart shows the condition of the stock and the white water in the commercial run prior to the addition of the colloidal silicic acid and the cationic starch as outlined above. As will be noted, the total solids in the stock at the former or head box is approximately 15.5 g/l, of which approximately 8.5 g/l is fiber and 7 g/l is ash. The base sheet produced from this stock contained approximately 3 percent ash.

As appears from Fig. 5, the white water in the commercial run before the addition of the colloidal silicic acid and cationic starch, contained approximately 10.5 g/l of solids, 6.0 g/l ash, and 4.5 g/l fiber.

The dramatic effect of the addition of the colloidal silicic acid and cationic starch as outlined above, is shown on the right hand side of FIGURE 5 where the total solids in the head box decreased to approximately 6 g/l; slightly less than 5 g/l fiber; and about 1.5 g/l ash. The total solids in the white water dropped to about 1 g/l; about 0.5 g/l fiber; and about 0.5 g/l

ash. The base sheet contained approximately 15 percent ash and, the machine breaks during operation were substantially less than in the commercial operation where the sheet contained only 3 percent ash.

Test results showed that even though the finished base sheet made, as outlined above, had an increased amount of filler, i.e. from about 3 percent to about 15 percent which normally degrades the properties of the sheet, the additional filler did not materially decrease the strength properties or printing properties of the paper. To the contrary, certain properties were increased markedly. For example, Z-strength or internal bond strength measured by the Scott-Bond method increased by 85 percent at the 15 percent filler level as compared to the 3 percent filler level in the commercial runs. The IGT (Instituut Voor Grafische Techniek, Amsterdam) surface picking resistance increased by 40 percent and the bursting strength increased by 40 percent.

During the trial, which extended over a several week period, it was found that it was possible to add much more broke to the stock than before. At one period extending for about 16 hours, the entire stock was broke. Further, with the addition of additional filler material it was found that it was possible to maintain 15 percent filler in the base sheet over a two-week period and that the resulting even level of ash permitted an increase in the productivity of the paper machine due to fewer breaks and a saving of fiber.

It was also found that the coupling of increased retention and decreased head box consistency resulted in a marked improvement in the drainage rate of the stock on the wire. This, of course, means that an increase in the machine speed is made possible, which will even further enhance the productivity.

The retention of fibers and fines on the wire in the papermaking machine was also greatly improved.

Retention percentage is determined by dividing the difference between the concentration of total solids in the head box and the concentration of total solids in the white water by the concentration of total solids in the head box and multiplying by 100. Thus, on the commercial run preceding the addition of the silicic acid sol and cationic starch as outlined above, the percentage of retention was $\frac{15.5-10.5}{15.5} \times 100$ or 32%. As a result of the use of our process the percentage of retention increased to about 83%$\left(\frac{6.0-1.0}{6.0} \times 100\right)$. This high level of retention simplified white water clean-up and disposal.

EXAMPLE IX

To further demonstrate the advantages of the two-step operation, extended runs were made under various conditions on the commercial machine described in Example VIII. The results of these runs are set forth in tabular form in the table below.

	RUN 1	RUN 2	RUN 3
Grammage g/m^2	85	85	85
Ash content %	17	28	24
Tensile index machine direction Nm/g	66.2	64.2	64.5
cross direction Nm/g	21.7	22.5	26.8
Burst Strength kPa	214	294	310
Surface picking resistance IGT			
top side	73.4	92	112
wire side	68.7	83	112
Internal bond strength Scott Bond J/m^2	225	506	525
Concentration at head box g/l solids	15.5	10.1	6.3
White water concentration g/l solids	10.5	5.2	1.2
Retention %	32.3	48.5	81.0

Run 1 reflects the average operation of the machine of Example VIII in making coated, supercalendered printing paper over an extended period of time. The cellulosic fiber comprised 70% sulfate hardwood and 30% sulfate softwood, both fully bleached. Normal amounts of broke were recycled. The base sheet was coated with 10 g/m^2 of calcium carbonate per side.

Run 2 reflects the average operation of the machine of Example VIII over an extended period in making coated, supercalendered printing paper in which the same fiber was employed and normal amounts of broke were recycled in which the colloidal silicic acid employed was a 15% aqueous sol having the specifications set forth in Example VIII. It was added to Mixing Tank No. 1 at a level of 3.8 kg of SiO_2 per metric ton of dry base sheet. Cationic starch was added in Mixing Tank No. 2 at a level of 11.8 kg of cationic starch per metric ton of dry base sheet, the cationic starch having the specification as set forth in Example VIII and the method of addition was as set forth in Example VIII. No additions were made in Mixing Tank No. 3. The base sheet after drying was coated on each side with 10 g/m^2 of calcium carbonate.

Run 3 followed the procedure of Run 2 except that the addition of the silicic acid sol was added in two increments. There was added in Mixing Tank No. 1, 2.9 kg of SiO_2 per metric ton of dry base sheet. In Mixing Tank No. 2 the cationic starch was added at a level of 13.7 kg of cationic starch per metric ton of dry base sheet. In Mixing Tank No. 3 a second addition of the silicic acid sol was added at a level of 1.5 kg of SiO_2 per metric ton of dry base sheet.

EXAMPLE X

To further demonstrate the invention and the effect of various degrees of substitution of the cationic starch component of the binder, two series of hand sheets were made in a laboratory hand former using

stocks which all contained the same type and amount of colloidal silicic acid sol but which contained cationic starches of various degrees of substitution (d.s).

The cationic starches used in this example were prepared from two different base material starches (A and B) to obtain the degrees of substitution mentioned in the table below.

All stocks for making the hand sheets were prepared by mixing 1.09 g china clay (English China Clay Grade C) with 2.72 g of a colloidal silicic acid sol (1.5% total solids and surface area 530 m^2/g) and adding this slurry to a laboratory disintegrator containing 1.63 g of fully bleached softwood sulfate pulp in 500 ml water. After mixing the components in the disintegrator during 30 seconds, the relevant cationic starch was added. The mixing was then continued for about 15 seconds and then the stock was poured into the hand sheet former.

The degrees of substitution of the various starches and the amounts of addition thereof to the stocks as well as the properties of the hand sheets made are shown in the table below.

The tensile index of the different sheets is graphically shown as a function of the amount of starch added (calculated as a weight percentage of the sum of the filler and fiber contents) in FIGURE 6 which clearly shows that a lower degree of substitution (d.s.) necessitates a larger amount of starch to bring about the maximum strength (tensile index). Thus starch A having 0.033 d.s. gives the maximum strength at about 3.5% addition, while starch A having 0.020 d.s. gives the maximum strength at about 4.3% addition. The same tendency is true for starch B which at 0.047 d.s. gives the best strength at about 4.2% addition and at 0.026 d.s. gives the best strength at about 4.8%.

Sheet No.	Starch				Ratio starch/SiO_2	Grammage g/m^2	Density kg/m^3	Tensile index Scan P16:76 Nm/g	Elongation %	Ash content %
	label	d.s.	addition g	addition %						
A1	A	0.020	49.0	3.6	2.4	91.6	619	22.0	7	30
A2	A	0.020	57.1	4.2	2.8	91.6	621	24.4	7	32
A3	A	0.020	65.3	4.8	3.2	94.3	624	23.8	7.5	33
A4	A	0.033	40.8	3.0	2.0	78.9	556	25.0	8.5	24
A5	A	0.033	49.0	3.6	2.4	80.7	564	25.4	8	27
A6	A	0.033	57.1	4.2	2.8	82.8	587	23.7	8	27
A7	A	0.033	65.3	4.8	3.2	85.3	575	21.6	8	29
B1	B	0.026	49.0	3.6	2.4	95.9	586	17.7	6	34
B2	B	0.026	57.1	4.2	2.8	91.1	562	19.8	6	31
B3	B	0.026	65.3	4.8	3.2	87.0	572	20.4	6.5	25
B4	B	0.047	49.0	3.6	2.4	75.4	546	19.5	6	30
B5	B	0.047	57.1	4.2	2.8	81.0	542	20.5	6.5	25
B6	B	0.047	65.3	4.8	3.2	76.1	575	18.4	6	22

EXAMPLE XI

This Example concerns the applicability of the invention in producing light-weight fine paper.

A series of trials were run on an experimental paper machine to produce a light-weight fine paper having a grammage of 75 g/m^2. The paper stock fed to the headbox of the machine consisted of 50% by weight of fully bleached hardwood and 20% by weight of fully bleached softwood sulfate pulp and 30% by weight of filler. Two types of filler were used, a conventional filler consisting of paper making chalk ($CaCO_3$) and a low-density filler consisting of expanded perlite having a density of about 0.2 g/cm^3 and a particle size of 99% below 10 µm. In a reference run (run A) 0.2% by weight of a polyacrylamide retention aid was added to a stock containing $CaCO_3$ as the sole mineral filler. In runs B through E the mineral filler was changed successively from solely chalk via mixtures of chalk and expanded perlite to solely expanded perlite. In all the runs of this example the amount of binder added was the same, viz. 0.5% by weight of silicic acid sol (specific surface about 500 m^2/g) and 1.5% by weight of cationic starch (having a degree of substitution of 0.03) calculated as solids in the binder and based on the weight of the stock as a whole.

The results of the trial runs will appear from the table below and from FIGURES 8A through 8G graphically showing some of the results given in the table.

		Reference	According to invention			
		A	B	C	D	E
$CaCO_3$	%wt	30	30	25	15	-
Perlite	%wt	-	-	5	15	30
Density	kg/m^3	630	645	610	570	500
Stiffness (SCAN P29:69)						
machine direction	mN	4.7	4.2	4.6	5.4	6.9
cross direction	mN	2.8	2.5	3.2	3.0	4.4
Tensile index (SCAN P16:76)						
machine direction		28	38	33	30	29
cross direction		15	22	20	19	20
Tensile energy absorption						
machine direction	J/m^2	27	48	41	35	32
cross direction	J/m^2	18	37	30	25	23
Surface picking resistance (Dennison wax pick)						
top side		9	16	12	12	10
wire side		12	18	12	13	12

As will be seen from the table of this example and from the graphs of Fig. 8A through 8G the binder complex of the invention makes it possible to add substantial amounts of expanded perlite and still obtain the same or even better properties of the paper product.

Figure 8A shows that the binder of the present invention substantially improved the modulus of elasticity compared to the known additive (run A) both in the machine direction (curve M.D.) and in the cross direction (curve C.D.). In fact, the modulus of elasticity in runs C and D where the expanded perlite had been added was higher than in reference run A and was still at about the same level in run E as in run A in spite of the complete replacement of the chalk filler with the expanded perlite filler.

Figures 8B, 8C, 8E and 8F show that the same good trend is obtained with regard to the tensile index, the tensile energy absorption, the stiffness and the surface picking resistance (expressed as Dennison wax pick).

Figure 8D shows the decrease of density obtained by the replacement of the chalk mineral with the expanded perlite mineral.

Figure 8G shows the Bendtsen roughness number (SCAN P-21) at different density levels of paper products. The curves for the reference paper (run A) and for run B (chalk as the sole mineral using the binder complex of the invention) were so close to each other that they had to be drawn as a single curve in the chart. As appears from the chart, the inventive binder complex and the expanded perlite filler in high proportions made it possible to obtain smooth papers (low Bendtsen numbers) at low densities.

EXAMPLE XII

This Example shows that the invention is useful for producing special papers from stocks which contain both cellulosic and non-cellulosic fibers and which are extended with mineral fillers, specially good results being obtained when using low-density mineral fillers as extenders.

Three different stocks were used. All the stocks contained 50% by weight of fully bleached softwood sulfate pulp, 20% by weight of mineral fibers (mineral wool fibers), 1.43% by weight of colloidal silicic acid sol (specific surface area about 500 m^2/g) and 3.57% by weight of a cationic starch (degree of substitution 0.03). The remaining 25% by weight of the stock consisted of either chalk or expanded perlite or a mixture thereof. All the percentages are calculated as dry solids and are based on the stock as a whole.

When preparing the stocks to be formed on a laboratory hand sheet former the silicic acid sol was used as a 1.5% solution and the cationic starch as a 1% solution. In preparing the stocks for samples A and C the mineral filler (solely chalk and solely expanded perlite, respectively) was initially slurried in the silicic acid sol solution. In preparing the stock for

sample B the mineral fillers (15% chalk and 10% expanded perlite) were initially mixed and then slurried in the silicic acid sol solution. In all three cases the mineral-sol-slurry was added to the premixed mineral fiber-sulfate pulp in 500 ml water in a laboratory disintegrator. After 30 s mixing time in the disintegrator the different sheets were formed on the hand sheet former and pressed at a pressure of 5 kg/cm^2. The properties of the dried papers will appear from the table of this example.

Sample		A	B	C
cellulosic fiber	%wt	50	50	50
mineral fiber	%wt	20	20	20
chalk	%wt	25	15	0
expanded perlite	%wt	0	10	25
binder				
silicic acid sol	%wt	1.43	1.43	1.43
cationic starch	%wt	3.57	3.57	3.57
grammage	g/m^2	315	325	320
thickness	mm	0.62	0.72	0.77
density	kg/m^3	510	450	415
tensile index	Nm/g	12.6	12.9	11.7
elongation	%	6	6	6
stiffness	N	0.275	0.328	0.284
ash content	%	45.1	46.8	45.1
retention, based on ash content	%	97.0	100	97.0

The samples A, B and C show that it is possible to replace some or all of the chalk filler with an expanded perlite filler to lower the density, still keeping the other properties at about the same level as with chalk as the sole mineral extender or filler. It is to be noted that the retention calculated on the ash content was almost 100% in all samples, which is high considering that the retention of the expanded perlite filler is low when the binder complex of the present invention is not used.

EXAMPLE XIII

This Example concerns the clarification of white water from a twin wire papermaking machine making wood-free coated paper. White water samples were taken from the normal production run of the papermaking machine and were analyzed for solids content and kinds of solids. The solids content was 7 grams/liter, and about 60% by weight of the solids consisted of china clay and chalk.

To the samples of white water different amounts of cationic starch and silicic acid sol were added. The cationic starch having a degree of substitution of 0.033 was used as a solution containing 4% by weight of the starch. The colloidal silicic acid sol had a particle size of about 6 nm, a specific surface area of about 500 m^2/g and a silicic acid concentration of 15% by weight.

In each test in the Table below, 500 ml of the white water were poured in a beaker and the indicated additions of silicic acid sol and cationic starch were made. The contents of the beaker were vigorously agitated and the agitation then stopped. After the time lapse indicated, 20 ml turbidity test samples were taken by means of a pipette 5 mm below the surface of the contents in each beaker. The turbidity testing was performed according to Swedish Standard SIS in a turbidity tester (Hach model 2100A) giving the result in Formazin Turbidity Units (FTU). The lower the units, the better was the clarification obtained.

The additions to the white water samples and the test result appear from the Table below.

Test	White water ml	4% starch solution g	15% silicic acid sol g	Weight ratio R	Addition** (dry weight) %	Turbidity FTU after 15 s	1 min	5 min
1	500	-	-		-	*	*	900
2	500	1.75	-	∞	2	*	*	550
3	500	1.17	0.15	2	2	*	580	270
4	500	2.93	0.39	2	5	*	100	91
5	500	5.85	0.78	2	10	23	18	17

* = not measurable, more than 1000 FTU

** = the addition is calculated, on the one hand, on the dry weight of added cationic starch and added silicic acid sol and, on the other hand, on the 3.5 grams of solids appearing in the 500 ml sample of white water.

R = weight ratio of cationic starch to silicic acid sol

The results presented in the Table of this Example demonstrate that the addition of the binder according to the present invention to white water results in a higher settling rate of the solids in the white water and thus in a decrease of turbidity. The results also show that an almost clear white water was obtained in test 5 which is a substantial improvement over the untreated white water in test 1.

EXAMPLE XIV

This Example concerns the clarification of white water from a combined board and printing paper mill. White water samples were taken from the mixed white waters from the mill and were analyzed for solids content and types of solids. The solids content was 1.1 g/l and about 25% of the solids was pigment (mainly china clay). A number of tests were made to determine the settling rates and the turbidity of the white water when treated with PERCOL® 1697 (a typical example of agents for white water treatment) and with a binder according to the present invention comprising a silicic acid sol and a cationic starch.

The settling rates were determined by using a graded conical funnel having a diameter of 110 mm at the wide top end and a height of 400 mm and being graded. To 1200 ml samples of the white water there were added a silicic acid sol and a cationic starch under vigorous agitation. The samples were then poured into the graded funnel and left standing while the interface between an almost clear upper phase and a lower turbid phase gradually sank. The time for this interface to pass every 50 or 100 ml mark on the funnel was noted, and the settling rates calculated were plotted in FIGURE 7.

The almost clear upper phase was nearly free from flocks but was opalescent due to various amounts of fines and pigment particles. For this reason, the turbidity was measured, using a sample taken from the top of the funnel well above the interface 15 minutes after pouring the sample into the funnel. Samples from the funnel were also taken for determining the solids content of the white water after this settling time.

The turbidity was measured according to Swedish Standard SIS in a turbidity tester (Hach model 2100 A) giving the result in Formazin Turbidity Units (FTU). The lower the FTU figures, the better is the clarification. The test results are tabulated below together with the solids content of the clear phase and the settling rates. The settling rates given in the table were calculated from the straight lines between the levels 200 ml and 600 ml in FIGURE 7.

A reference test using no additive was made and the settling time determined and plotted (Sample A) shown in FIGURE 7.

A comparative test series was made using PERCOL® 1697 as an additive (0.5% solution). To 1200 ml white water additions of 2 ml, 1 ml, 0.8 ml, 0.6 ml and 0.4 ml, respectively, of the 0.5% solution of PERCOL® 1697 were added, and then the settling times were determined. With this additive the 0.6 ml addition gave the best result (Sample B shown in FIGURE 7).

Then tests using the binder according to the present invention were performed. The additions of silicic acid sol and cationic starch were varied in this test series and so was the weight ratio (R) between the starch and the silicic acid sol. Two of the best results were obtained with the addition of 3.7 g of a 2% solution of cationic starch with a degree of substitution of 0.047 and 3.3 g of a 1.5% solution of silicic acid sol (sample C) and with the addition of 2.5 g of a 2% solution of cationic starch with a degree of substitution of 0.047 and 1.65 g silicic acid sol (sample D). The weight ratio (R) of starch:SiO_2 was 1.5:1 for sample C and 2.0:1 for sample D, and in both cases the silicic acid sol used was an alkali stabilized silicic acid sol having a specific surface area of about 500 m^2/g and the original concentration of 15%, although diluted to 1.5% concentration before use.

The results for samples A-D appear from the following table:

Sample	Turbidity after 15 min FTU	Solids content mg/l	Settling rate ml/min	Degree of clarification*
A	80	580	340	52
B	38	320	400	73
C	23	280	-	77
D	20	270	690	78

*solids content in the "clear phase" divided by the initial concentration 1100 ml/g

As will appear from the table, the best results are obtained when using the invention, i.e. samples C and D, especially the latter.

As will be seen from the foregoing, the use of a colloidal silicic acid-cationic starch binder complex, especially a complex in which the colloidal silicic

acid component is added incrementally, a portion being added after the initial agglomerate is formed, makes possible substantial economics in the papermaking process as well as a unique paper product. By using the binder system in connection with pulp stocks alone, the strength characteristics can be improved to the point that mechanical pulps can be substituted in substantial proportions for chemical pulps, while still maintaining the strength and other properties desired. On the other hand, if specific strength characteristics are required, the grammage of the sheet may be reduced while maintaining the desired properties.

Similarly, a mineral filler may be employed in much larger proportions than heretofore used while maintaining or even improving the characteristics and properties of the sheet. Or in the alternative the properties of a sheet containing filler may be enhanced.

In addition, the use of the binder system results in increased retention of both minerals and fines so that white water problems are minimized. As indicated, the system disclosed herein can also be used to advantage to agglomerate solids in white water to facilitate its disposal or reuse.

Further, because of the ability to reduce the grammage of a sheet or to increase the mineral content, it is possible to reduce the energy required to dry the paper and to pulp the wood fibers since less fibers can be employed. Also, the increased rate of drainage and the higher retention on the wire make possible higher machine speeds.

In addition, the binder complex makes it possible to reduce the solids content of the white water and thus to reduce the environmental problems also in papermills not using the binder complex of this invention as an additive to the stock per se. The binder system thus

improves the recovery of solids in the white water and improves the economy of the entire papermaking process.

While a preferred embodiment has been shown and described, it will be understood that there is no intent to limit the invention by such disclosure, but rather, it is intended to cover all modifications and alternate constructions falling within the spirit and scope of the invention as defined in the appended claims.

CLAIMS

1. A papermaking process in which an aqueous papermaking stock containing a cellulosic pulp is formed and dried, characterized by incorporating into the stock prior to the formation of the sheet a binder comprising colloidal silicic acid, and cationic starch having a degree of substitution of not less than 0.01, preferably from about 0.01 to about 0.05 and most preferably from about 0.02 to about 0.04, the weight ratio of cationic starch to SiO_2 being between 1:1 and 25:1, preferably between 1.5:1 and 10:1, and most preferably between 1.5:1 and 4.5:1.

2. The process of claim 1, characterized in that the colloidal silicic acid is provided as a colloidal silicic acid sol having silica particles with a surface area of about 50 to about 1000 m^2/g, preferably from about 300 to about 700 m^2/g.

3. The process of claim 1 or 2, characterized in that the pH of the stock is maintained between about 4 and about 9.

4. The process of claim 1, 2 or 3, characterized in that the solids in the binder amount to 0.1-15%, preferably 1.0-15% of the weight of pulp.

5. The process of any one of claims 1-4, characterized in that the aqueous papermaking stock contains a cellulosic pulp and a mineral filler material.

6. The process of claim 5, characterized in that the amount of cellulosic pulp in the stock is adjusted to give a finished paper containing at least 50% by weight of cellulosic fibers.

7. The process of claim 5 or 6, characterized in that the solids in the binder amount to from about 0.5 to 25%, preferably from about 2.5 to 15% by weight based upon the weight of the mineral filler.

8. The process of claim 5, 6 or 7, characterized in that the colloidal silicic acid is added to and mixed with the mineral filler prior to incorporating the mineral filler into the stock and the cationic starch is mixed with the pulp and filler colloidal silicic acid mixture.

9. The process of any of claims 1 to 7, characterized in intermixing in the stock a portion of the colloidal silicic acid, thereafter intermixing the cationic starch in the stock containing the initial portion of colloidal silicic acid, and, after an agglomerate has formed, adding and intermixing the remainder of the colloidal silicic acid in the stock prior to the formation of the sheet.

10. The process of claim 9 wherein between about 20 and about 90 percent, preferably between about 30 and about 80 percent of the colloidal silicic acid is added to the stock to form an agglomerate and the remaining portion of the colloidal silicic acid is added after the formation of the agglomerate.

11. An improved paper product containing cellulosic fibers, preferably in a content of at least 50% by weight of the paper product and characterized by enhanced strength characteristics, wherein the bond between the cellulosic fibers is enhanced by a binder comprising a complex of a colloidal silicic acid and cationic starch having a degree of substitution of not less than 0.01, preferably from about 0.01 to about 0.05 and most preferably from about 0.02 to about 0.04, and wherein the ratio of cationic starch to SiO_2 is between 1:1 and 25:1, preferably between 1.5:1 and 10:1, and most preferably between 1.5:1 and 4.5:1.

12. A papermaking process in which an aqueous papermaking stock containing cellulosic pulp is formed and dried, characterized in that the white water from the papermaking process is treated with a binder comprising colloidal silicic acid, and cationic starch having a degree of substitution of not less than 0.01, preferably from about 0.01 to about 0.05, and most preferably from about 0.02

to about 0.04, the weight ratio of cationic starch to SiO_2 being between 1:1 and 25:1, preferably between 1.5:1 and 10:1, and most preferably between 1.5:1 and 4.5:1 and the amount of said binder added to the white water for treating same being from about 1 to about 20% by weight, preferably from about 2 to about 10% by weight, based upon the dry weight of solids in the white water and the dry weight of said binder.

13. A papermaking process in which an aqueous papermaking stock containing a cellulosic pulp is formed and dried, to be performed substantially as hereinbefore described and claimed with particular reference to the accompanying drawings.

14. An improved paper product containing cellulosic fibers, substantially as hereinbefore described and claimed with particular reference to the accompanying drawings.

FIG. 1

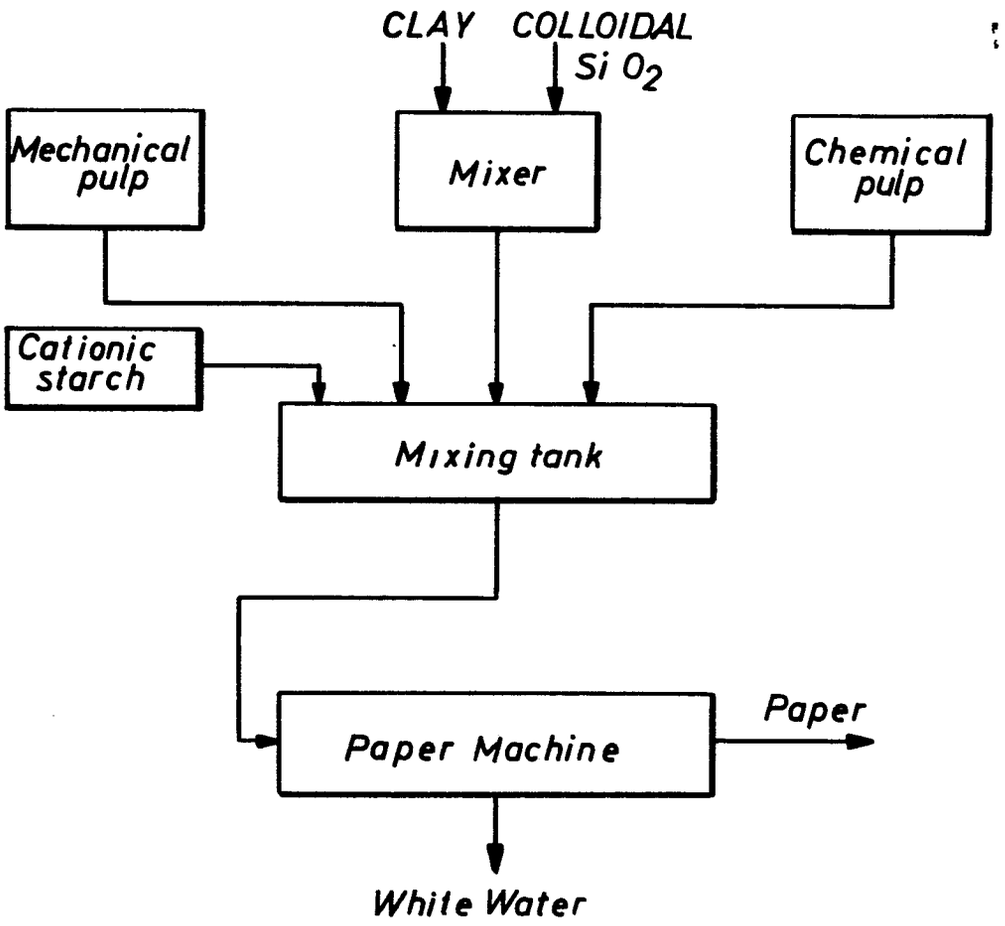
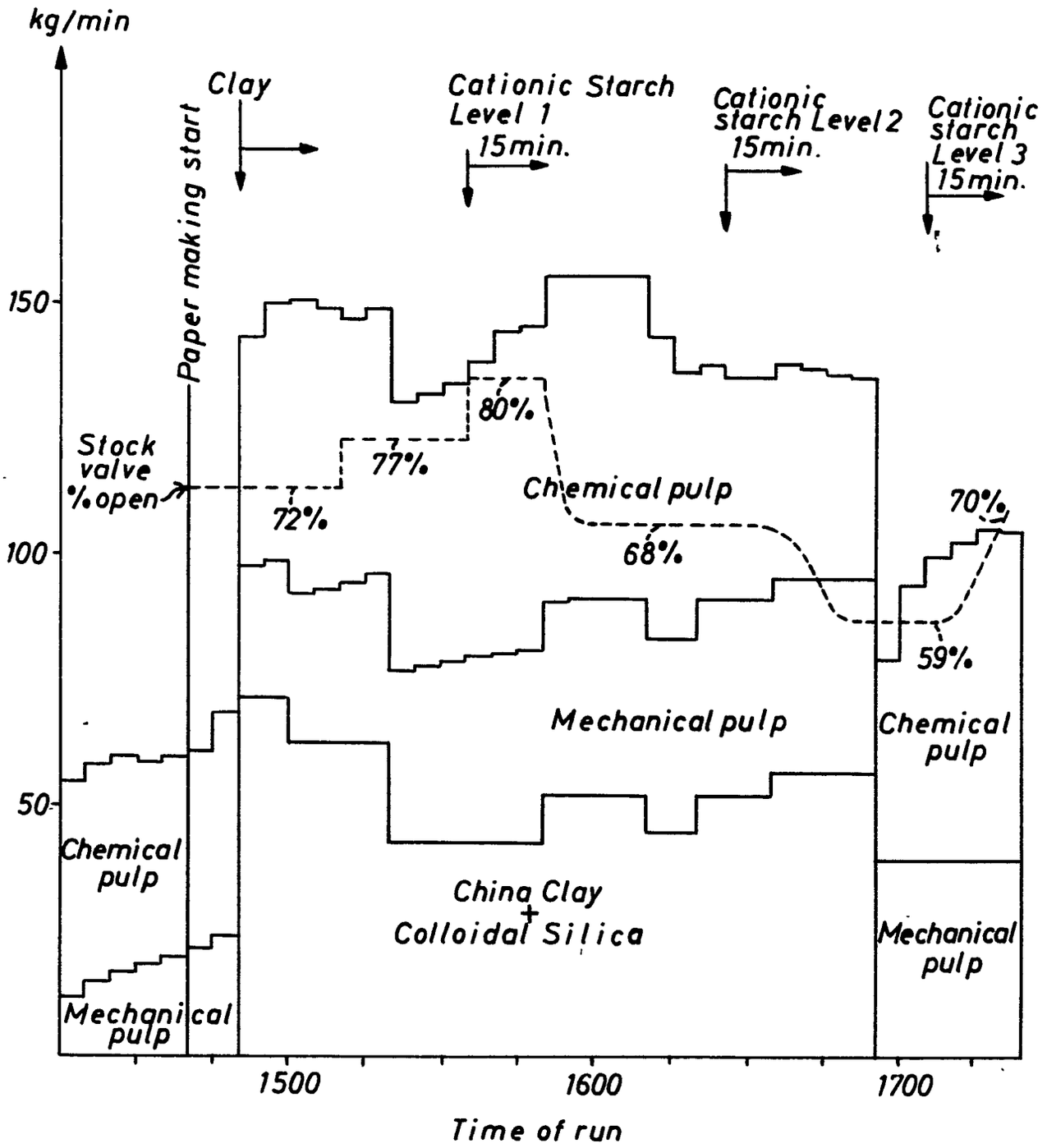

CLAY
COLLOIDAL Si O_2
Mechanical pulp
Mixer
Chemical pulp
Cationic starch
Mixing tank
Paper Machine
Paper
White Water

FIG. 2


kg/min
Clay
Cationic Starch Level 1 15min.
Cationic starch Level 2 15min.
Cationic starch Level 3 15min.
Paper making start
150
100
50
Stock valve % open
72%
77%
80%
Chemical pulp
68%
70%
59%
Mechanical pulp
Chemical pulp
Chemical pulp
China Clay + Colloidal Silica
Mechanical pulp
Mechanical pulp
1500
1600
1700
Time of run

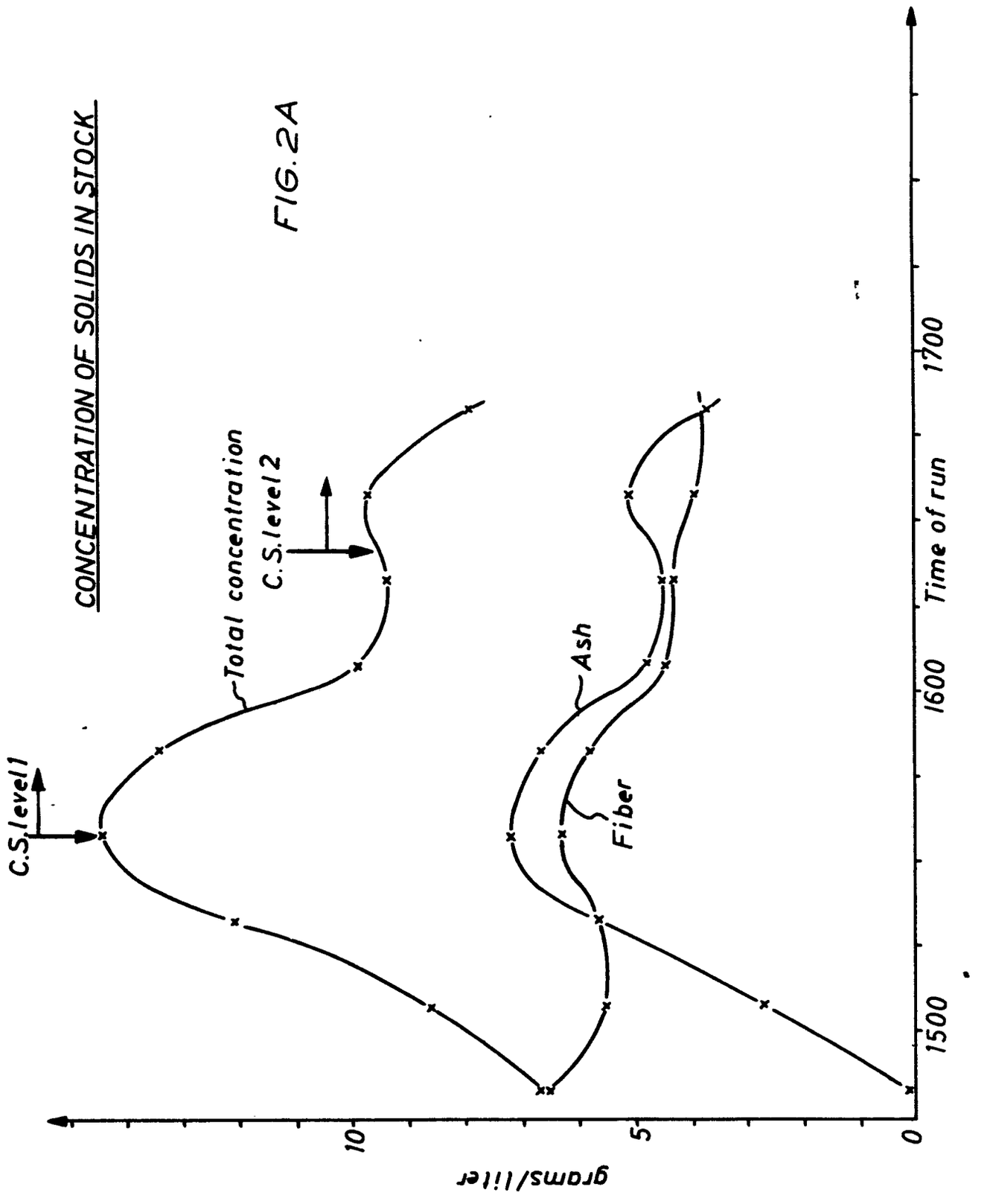

CONCENTRATION OF SOLIDS IN STOCK
C.S. level 1
Total concentration
C.S. level 2
Ash
Fiber
grams/liter
0
5
10
1500
1600
1700
Time of run

FIG. 2A

FIG. 2B

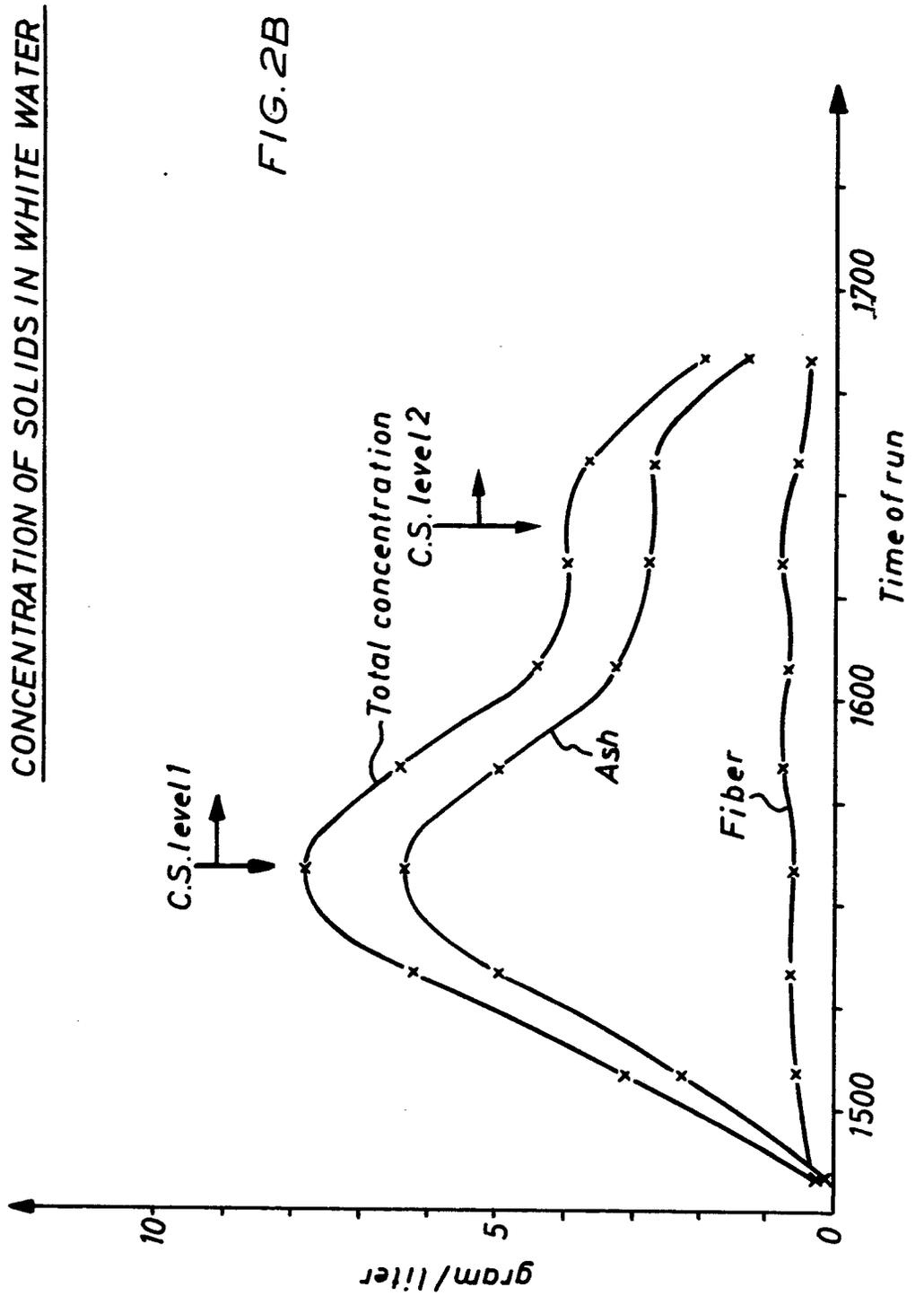
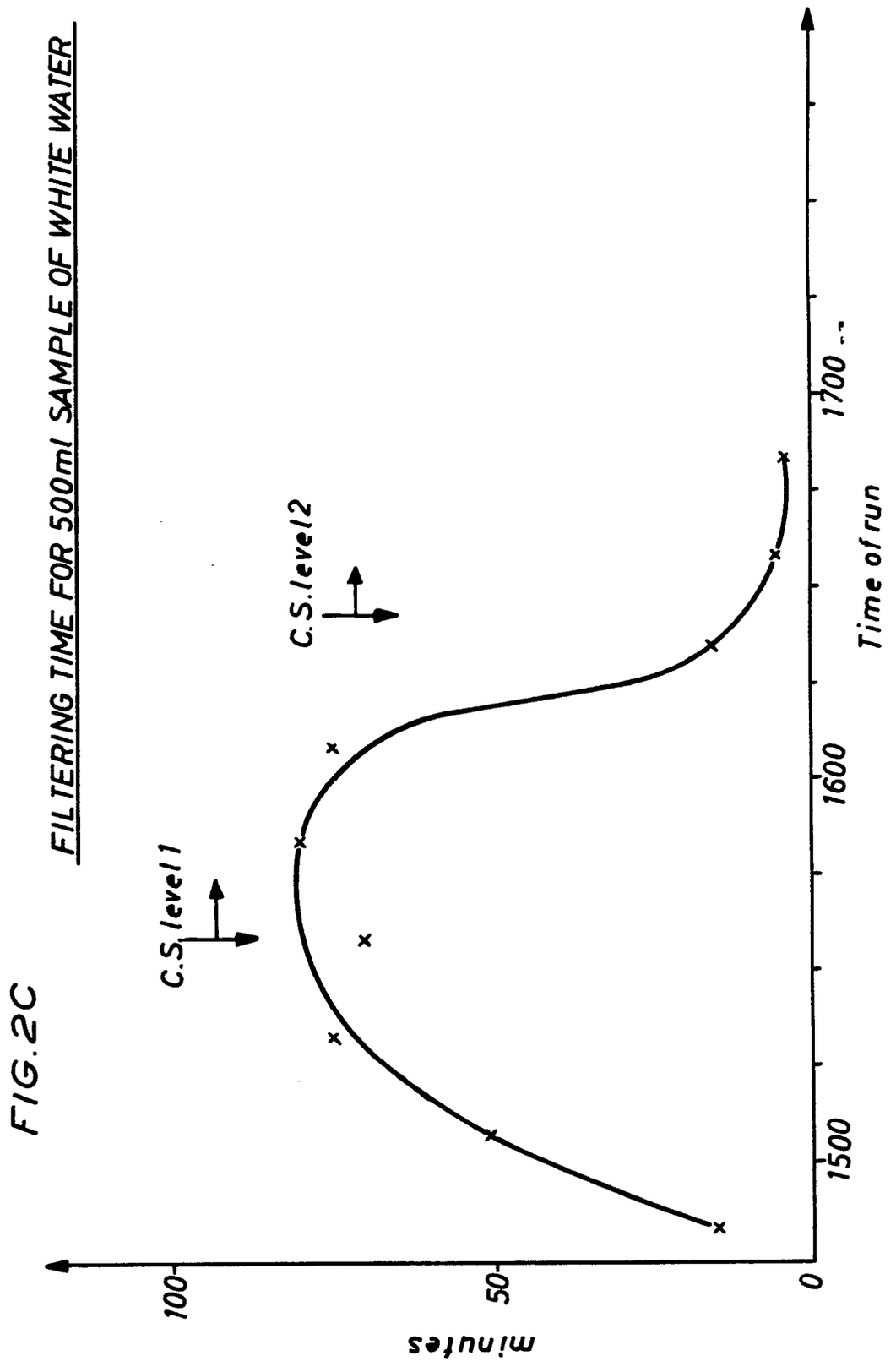

CONCENTRATION OF SOLIDS IN WHITE WATER
C.S. level 1
C.S. level 2
Total concentration
Ash
Fiber
gram / liter
0
5
10
1500
1600
1700
Time of run

FIG.2C


FILTERING TIME FOR 500ml SAMPLE OF WHITE WATER
C.S. level 1
C.S. level 2
minutes
100
50
0
1500
1600
1700
Time of run

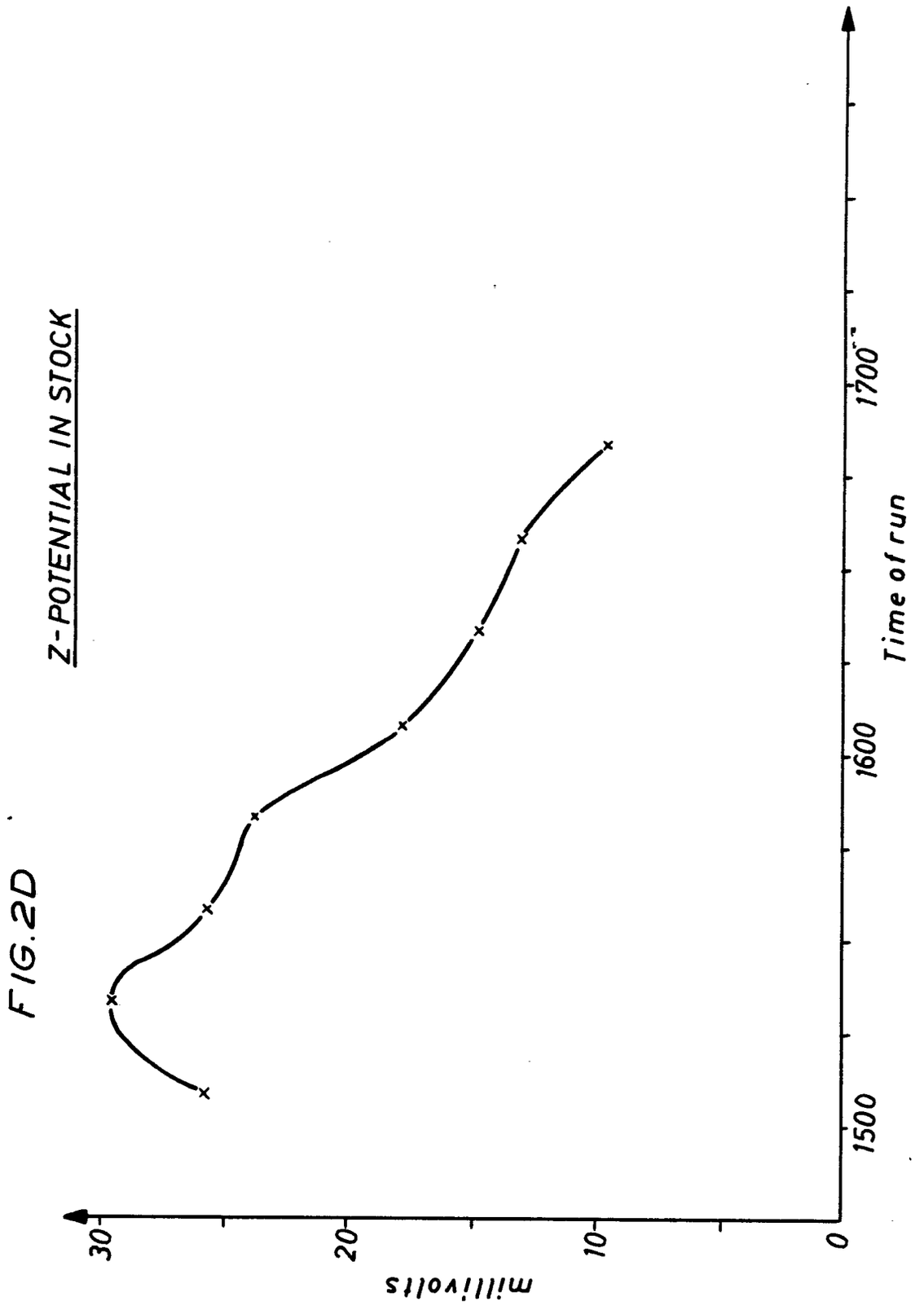
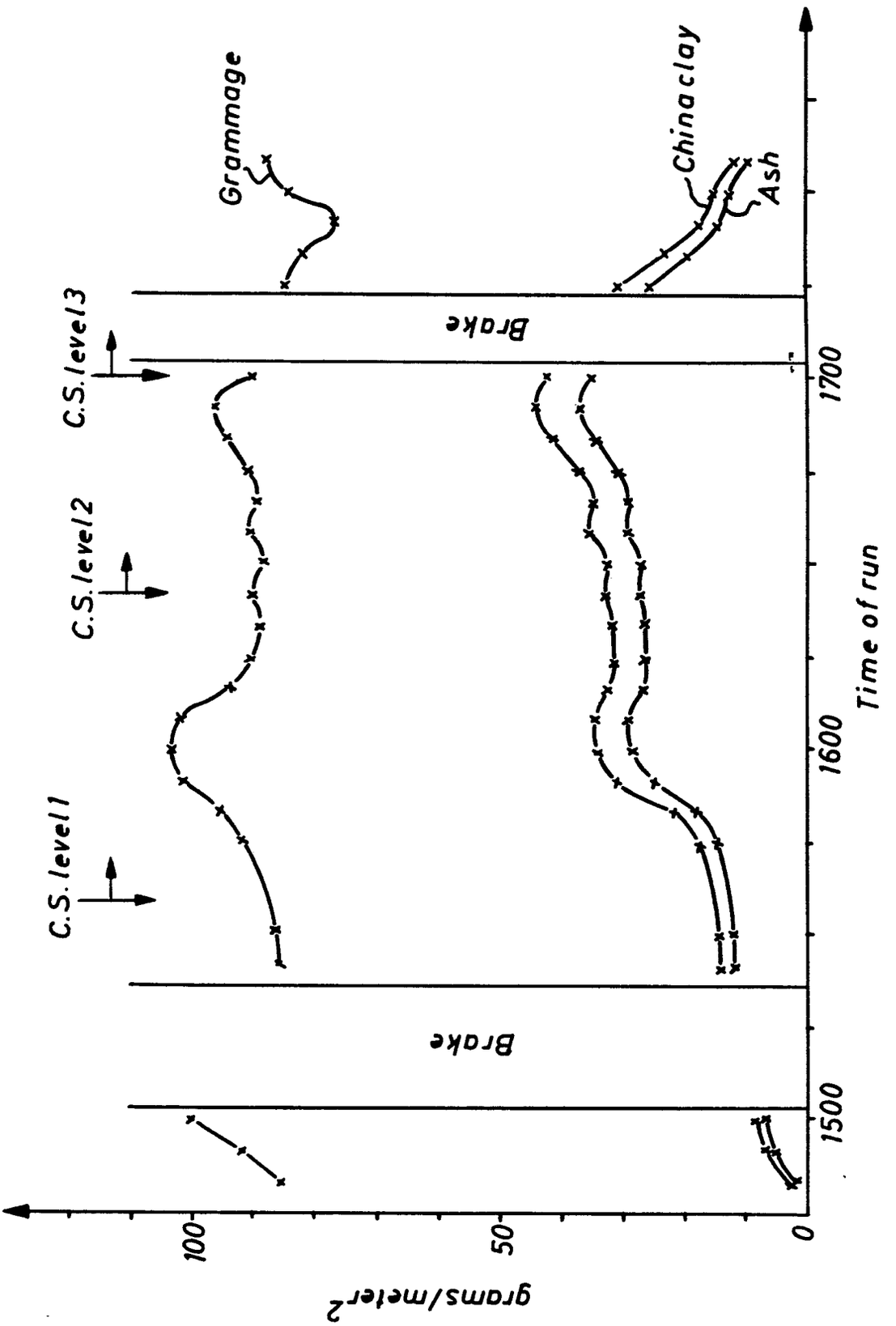

Z-POTENTIAL IN STOCK
millivolts
30
20
10
0
1500
1600
1700
Time of run

FIG.2D

FIG. 2E PAPER, GRAMMAGE-ASH-CHINA CLAY



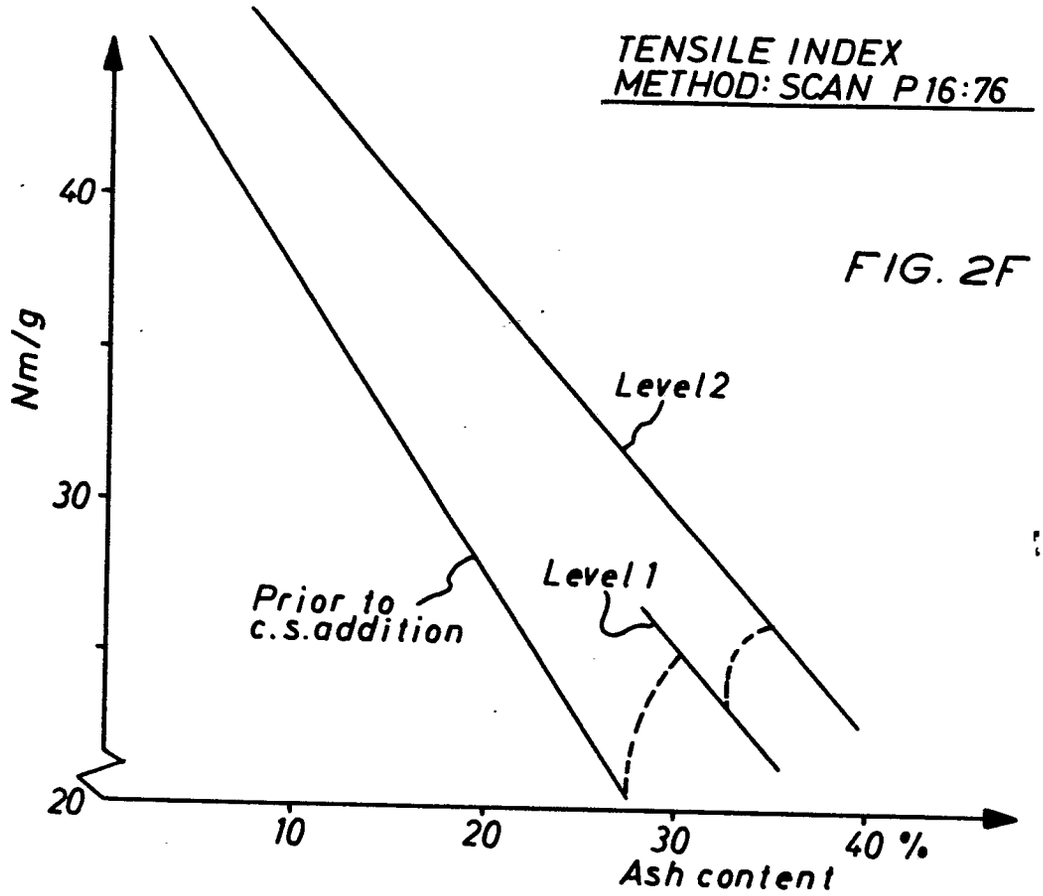

TENSILE INDEX
METHOD: SCAN P16:76
Nm/g
40
30
20
Level2
Level 1
Prior to
c.s.addition
10
20
30
40 %
Ash content

FIG. 2F

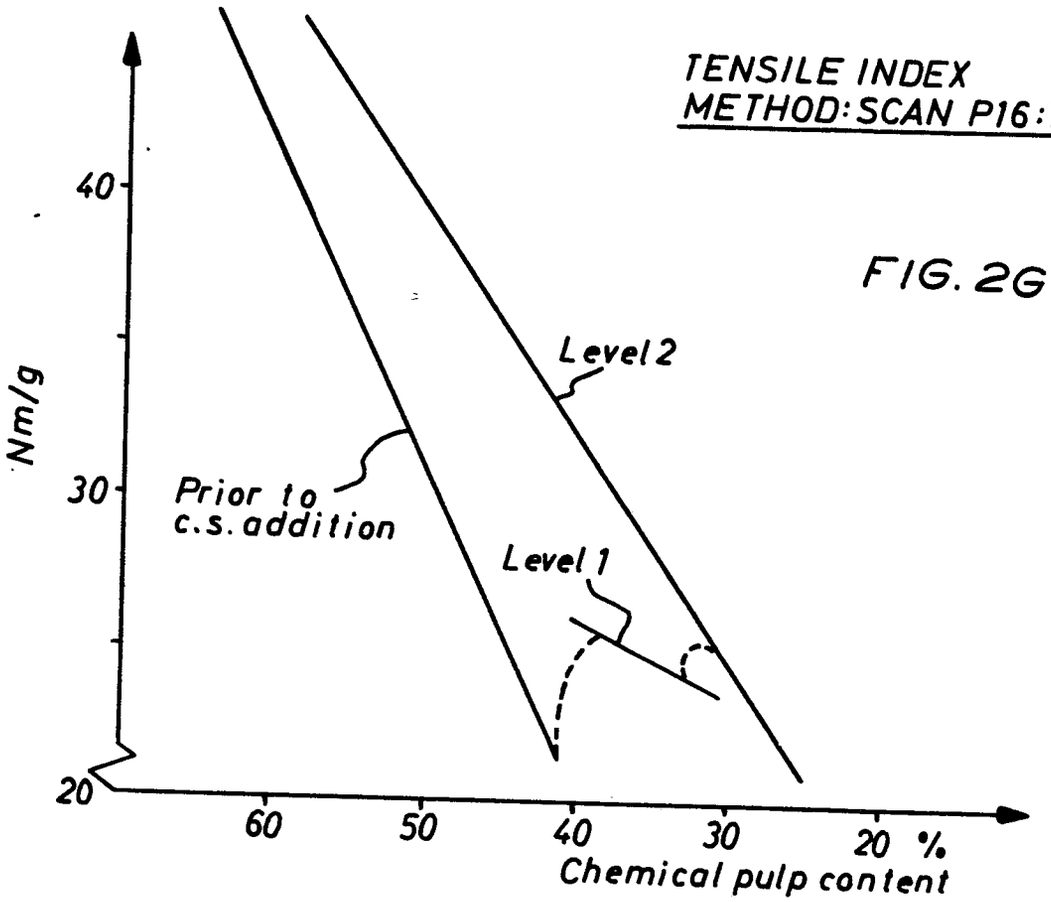
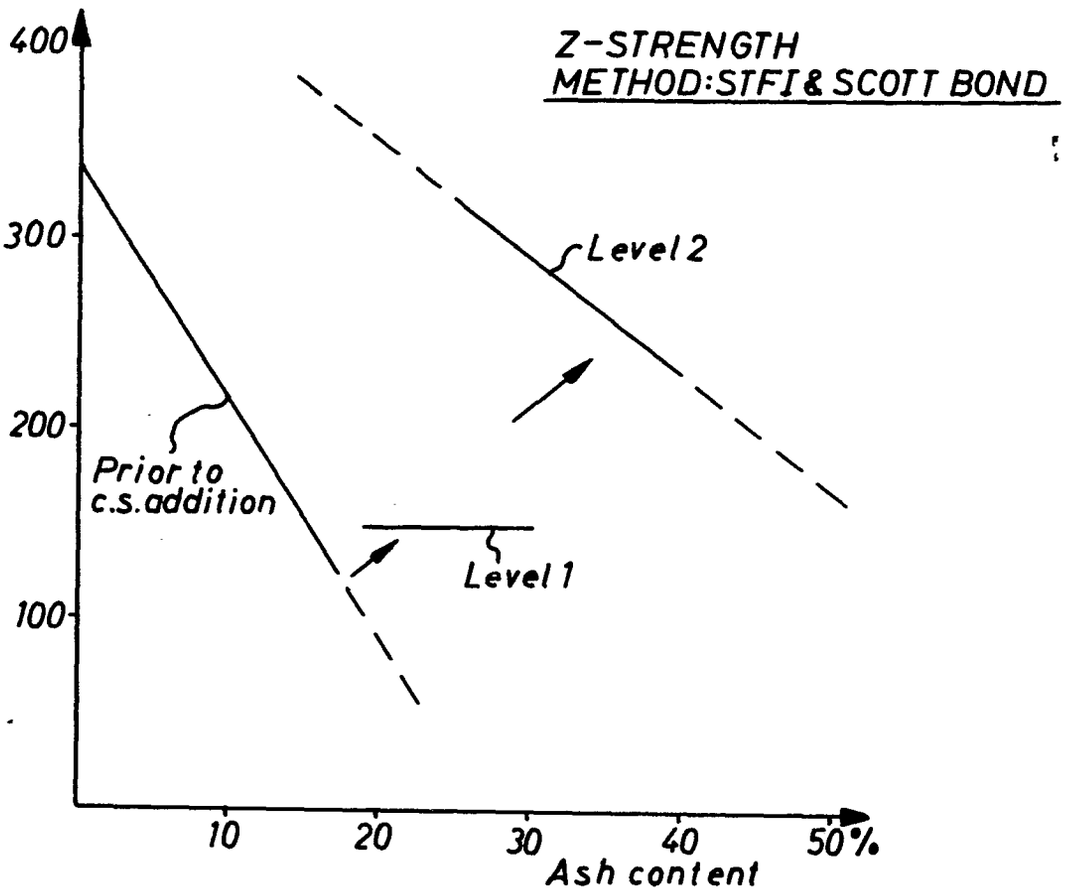

TENSILE INDEX
METHOD:SCAN P16:76
Nm/g
40
30
20
Level2
Prior to
c.s.addition
Level 1
60
50
40
30
20 %
Chemical pulp content

FIG. 2G

FIG. 2H


Z-STRENGTH
METHOD: STFI & SCOTT BOND
400
300
200
100
Level 2
Prior to
c.s. addition
Level 1
10
20
30
40
50%
Ash content

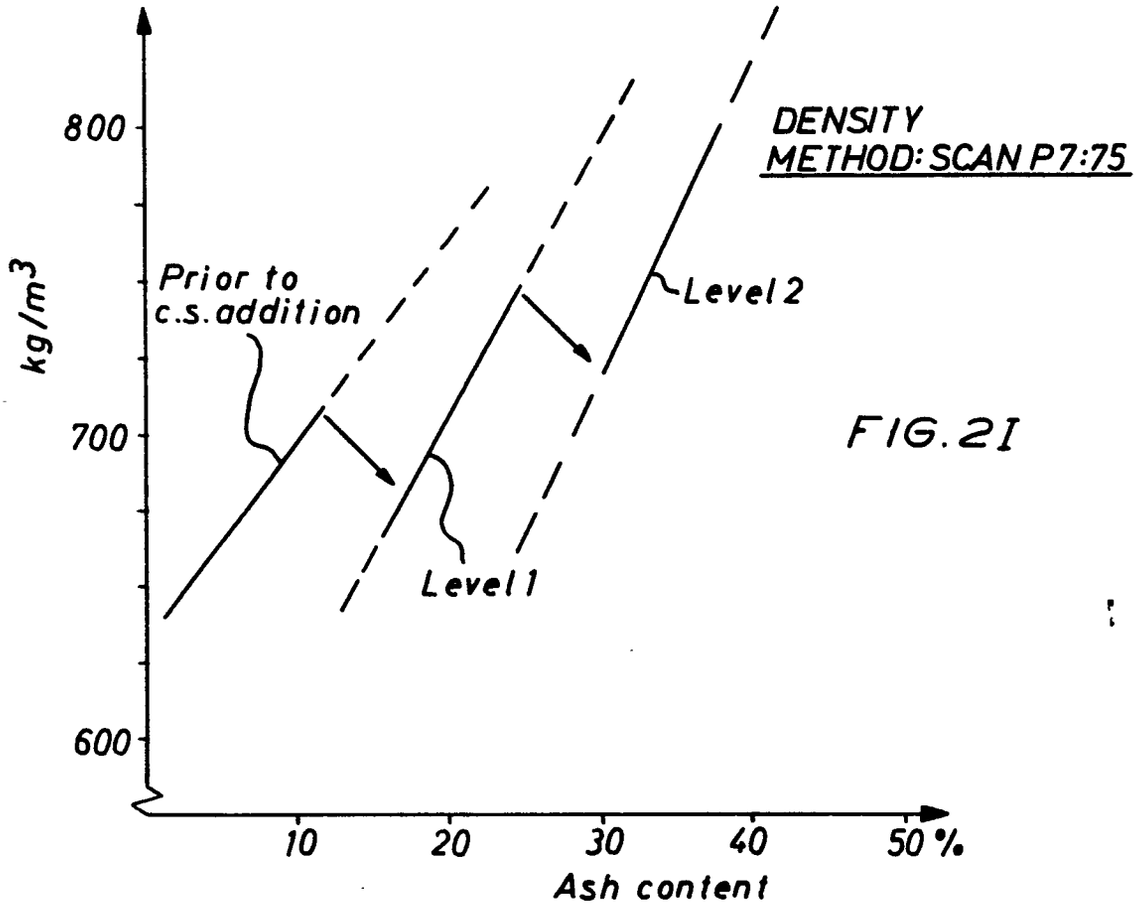

DENSITY
METHOD: SCAN P7:75
800
700
600
kg/m3
Prior to
c.s. addition
Level 2
Level 1
10
20
30
40
50 %
Ash content

FIG. 2I

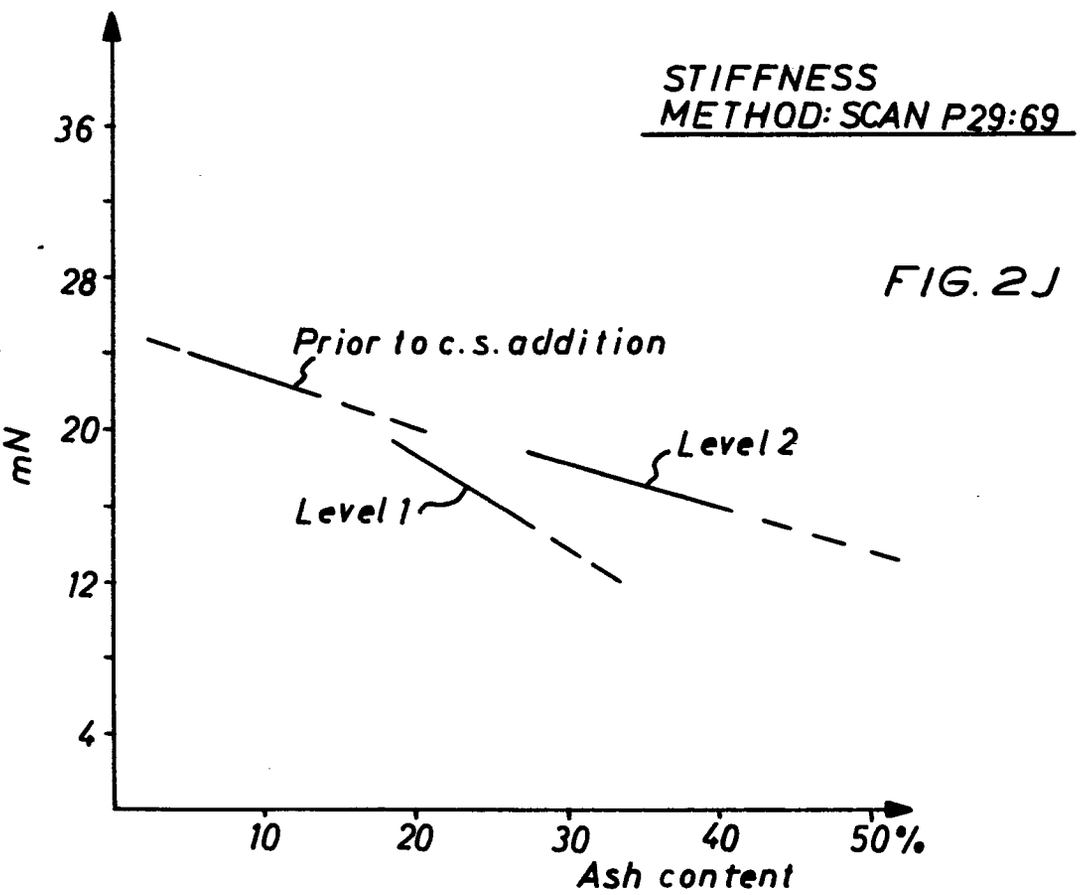

STIFFNESS
METHOD: SCAN P29:69
36
28
20
12
4
mN
Prior to c.s. addition
Level 2
Level 1
10
20
30
40
50 %
Ash content

FIG. 2J

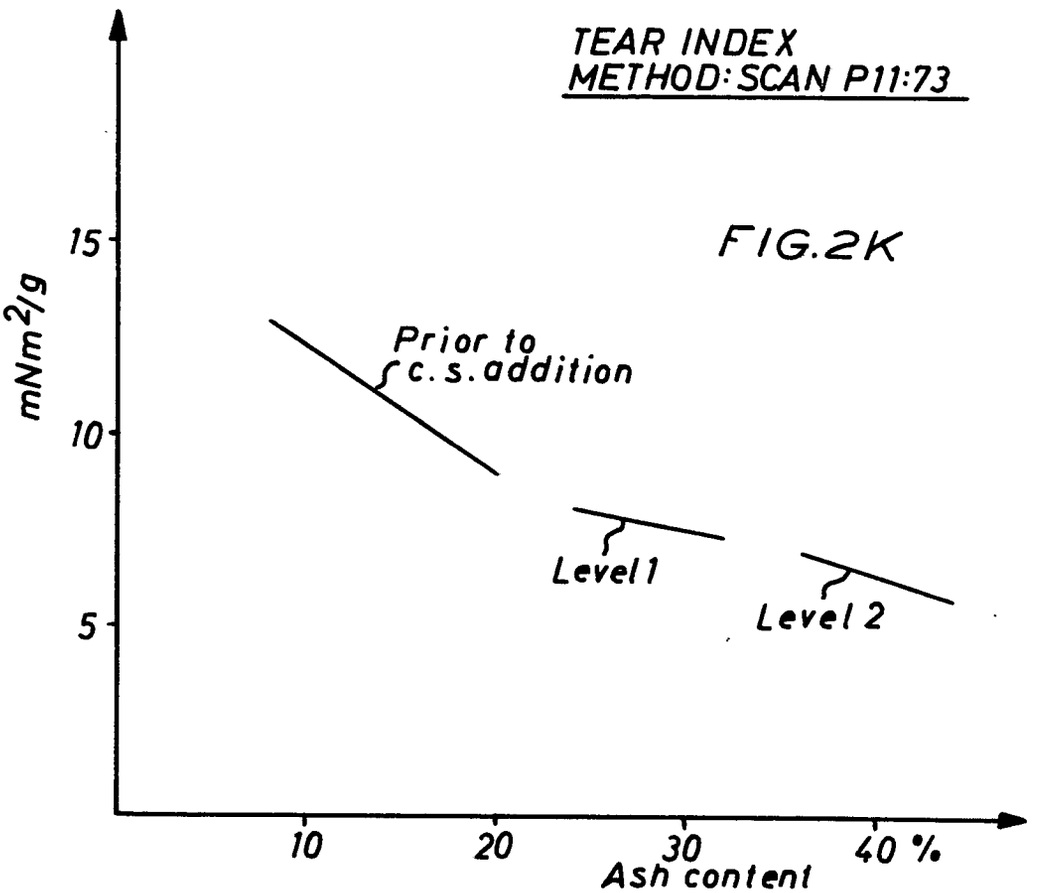

TEAR INDEX
METHOD: SCAN P11:73
15
10
5
mNm²/g
Prior to c.s. addition
Level 1
Level 2
10
20
30
40 %
Ash content

FIG. 2K

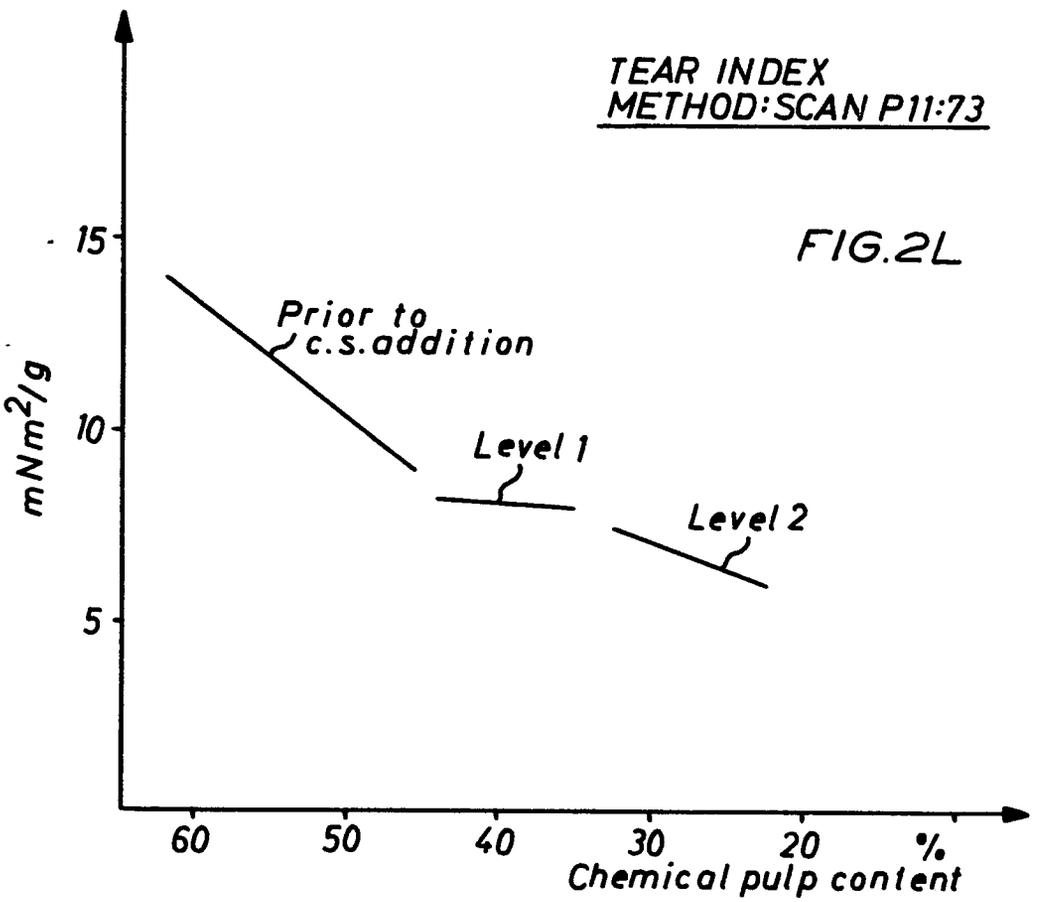

TEAR INDEX
METHOD: SCAN P11:73
15
10
5
mNm²/g
Prior to c.s. addition
Level 1
Level 2
60
50
40
30
20
%
Chemical pulp content

FIG. 2L

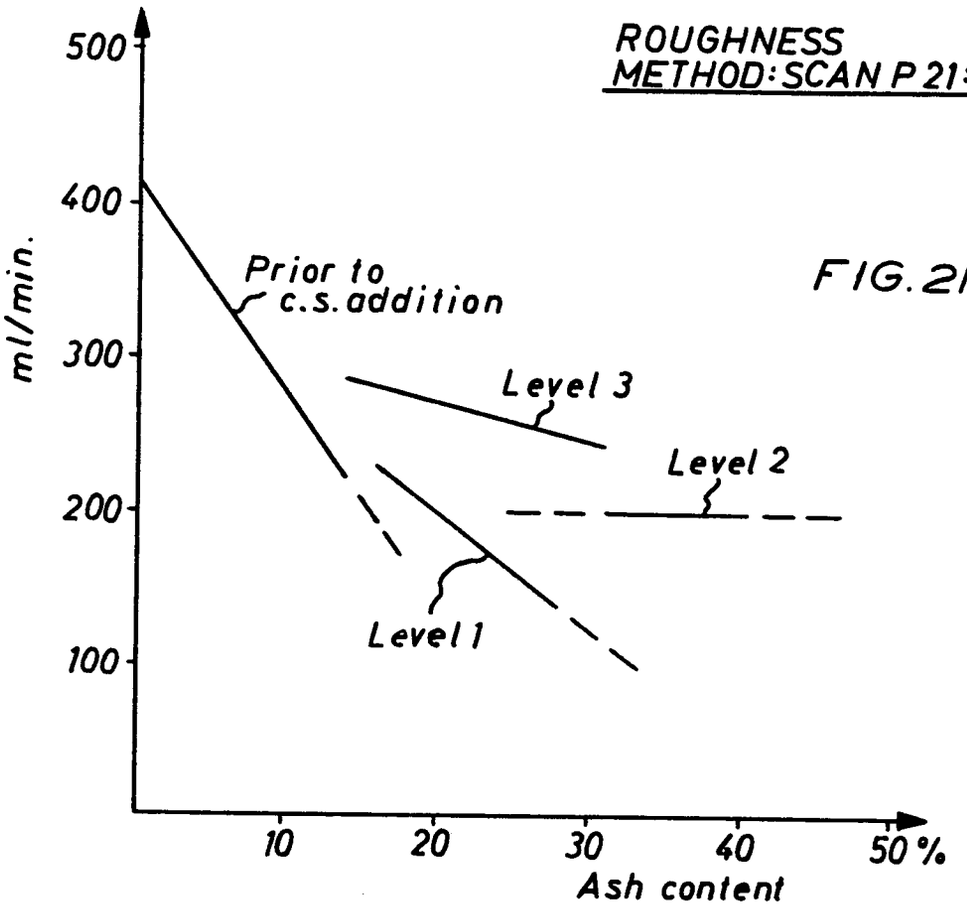

ROUGHNESS
METHOD: SCAN P 21:67
500
400
300
200
100
ml/min.
Prior to
c.s. addition
Level 3
Level 2
Level 1
10
20
30
40
50 %
Ash content

FIG. 2M

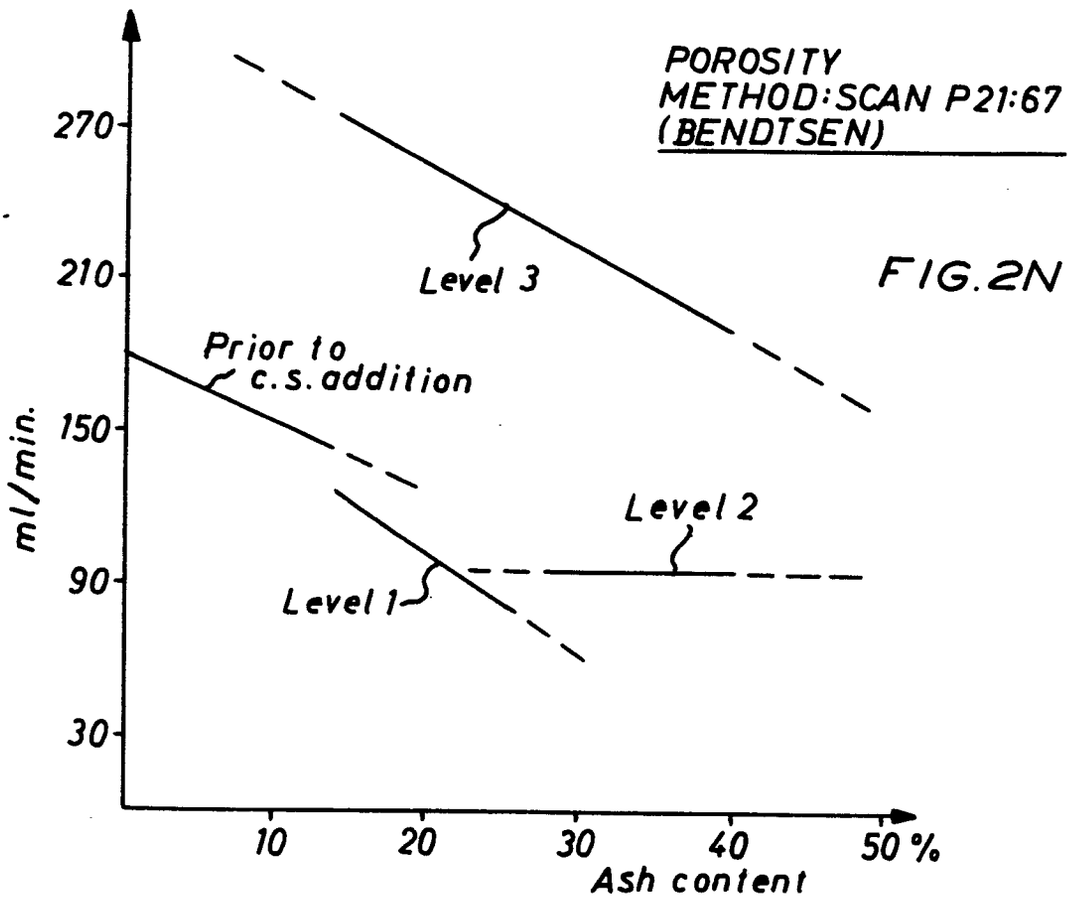

POROSITY
METHOD: SCAN P21:67
(BENDTSEN)
270
210
150
90
30
ml/min.
Level 3
Prior to
c.s. addition
Level 2
Level 1
10
20
30
40
50 %
Ash content

FIG. 2N

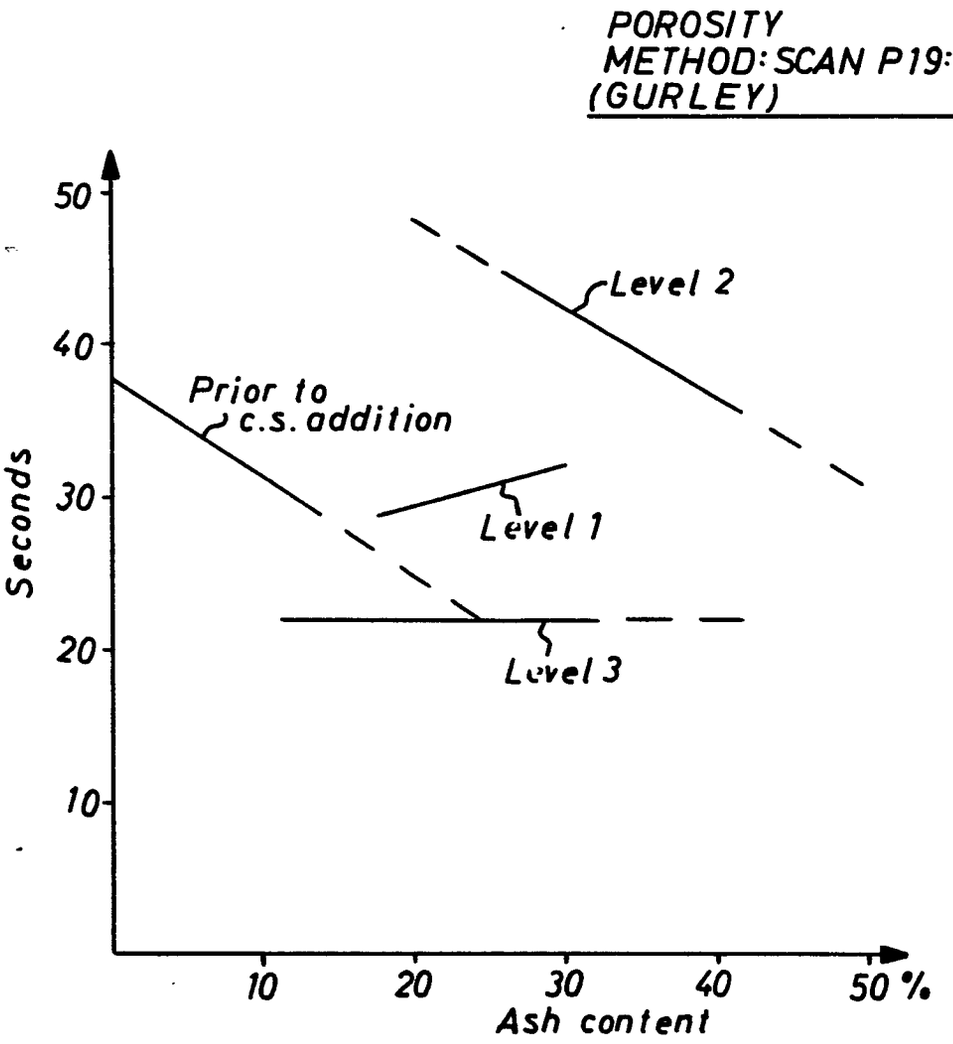

POROSITY
METHOD: SCAN P19:66
(GURLEY)
50
40
30
20
10
Seconds
Level 2
Prior to
c.s. addition
Level 1
Level 3
10
20
30
40
50 %
Ash content

FIG. 2.0

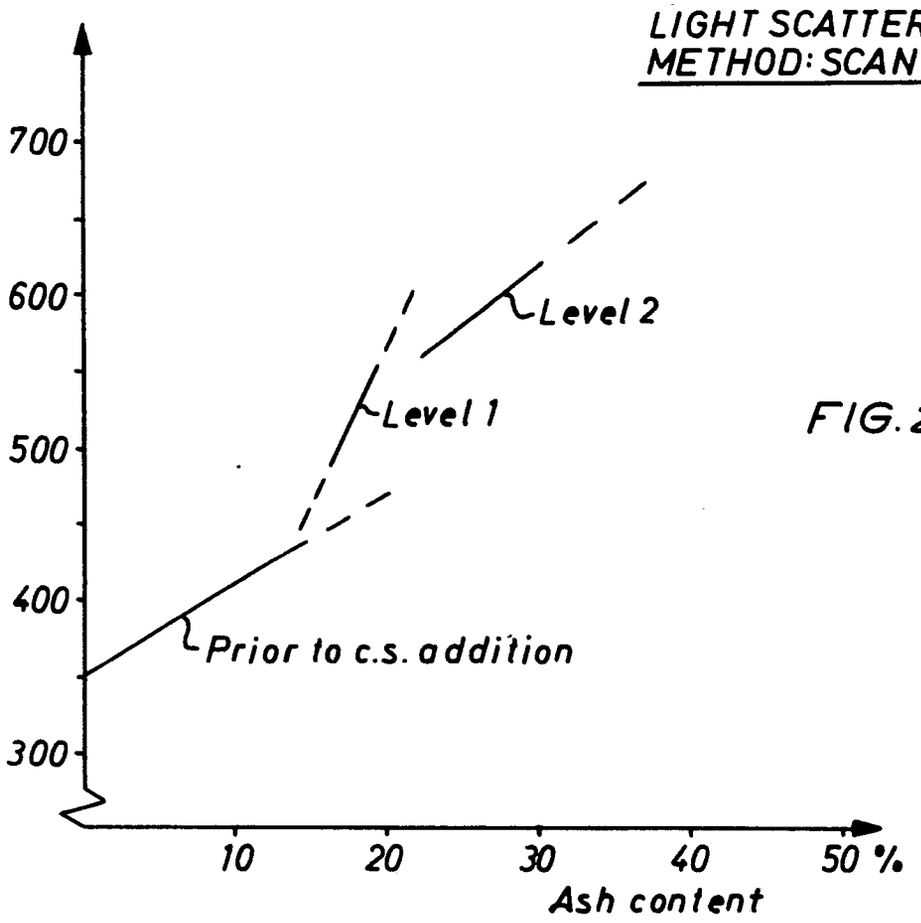

LIGHT SCATTERING
METHOD: SCAN P8:75
700
600
500
400
300
Level 2
Level 1
Prior to c.s. addition
10
20
30
40
50 %
Ash content

FIG. 2R

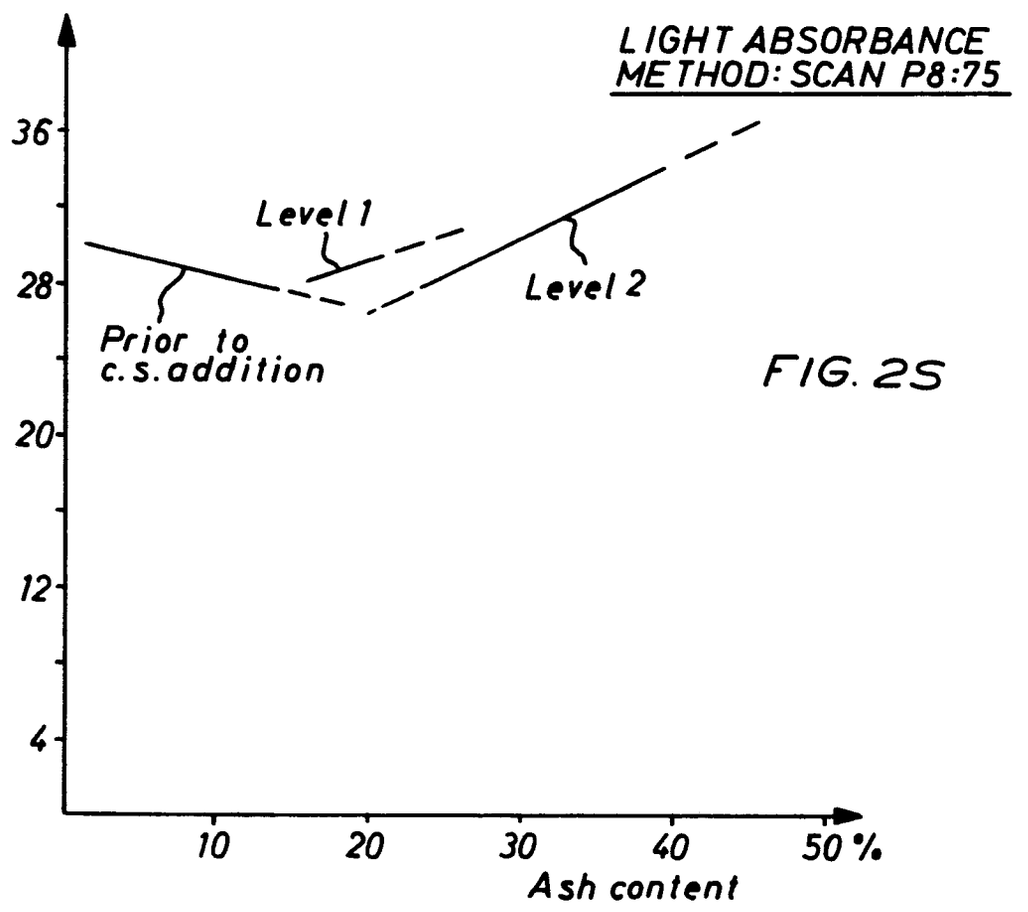

LIGHT ABSORBANCE
METHOD: SCAN P8:75
36
28
20
12
4
Level 1
Level 2
Prior to
c.s. addition
10
20
30
40
50 %
Ash content

FIG. 2S

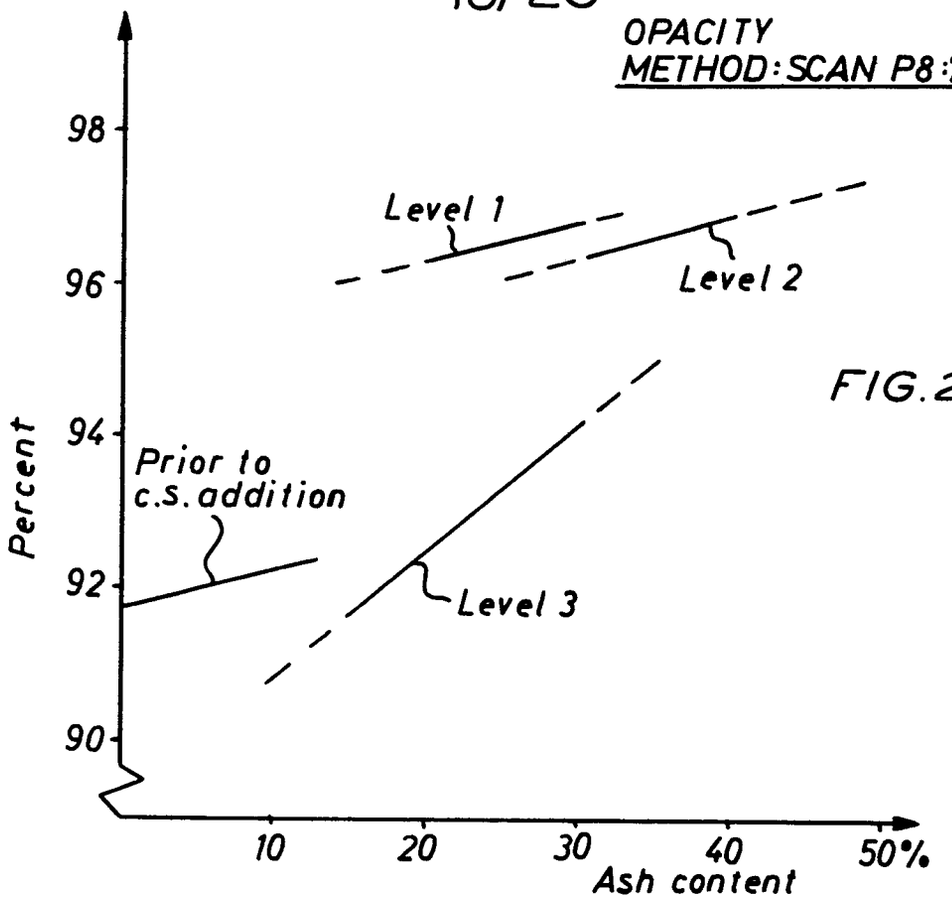

OPACITY
METHOD: SCAN P8:75
98
96
94
92
90
Percent
Level 1
Level 2
Prior to
c.s. addition
Level 3
10
20
30
40
50%
Ash content

FIG. 2P

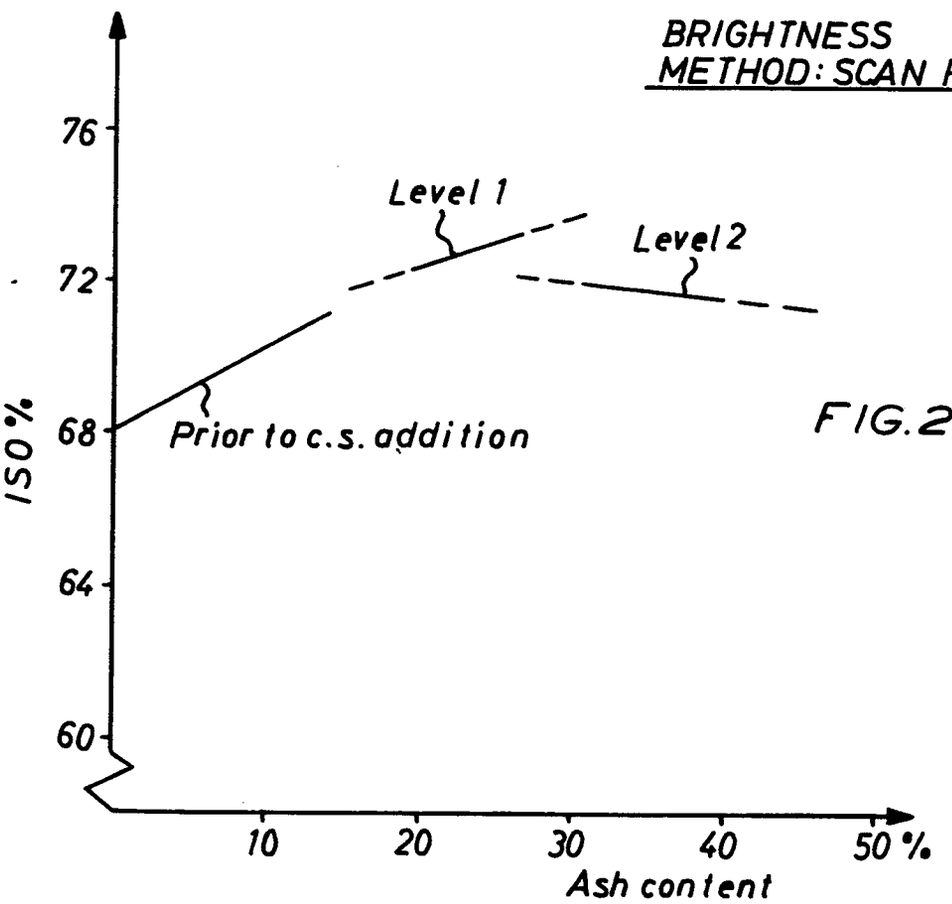

BRIGHTNESS
METHOD: SCAN P3:75
76
72
68
64
60
ISO %
Level 1
Level 2
Prior to c.s. addition
10
20
30
40
50 %
Ash content

FIG. 2Q

FIG. 3

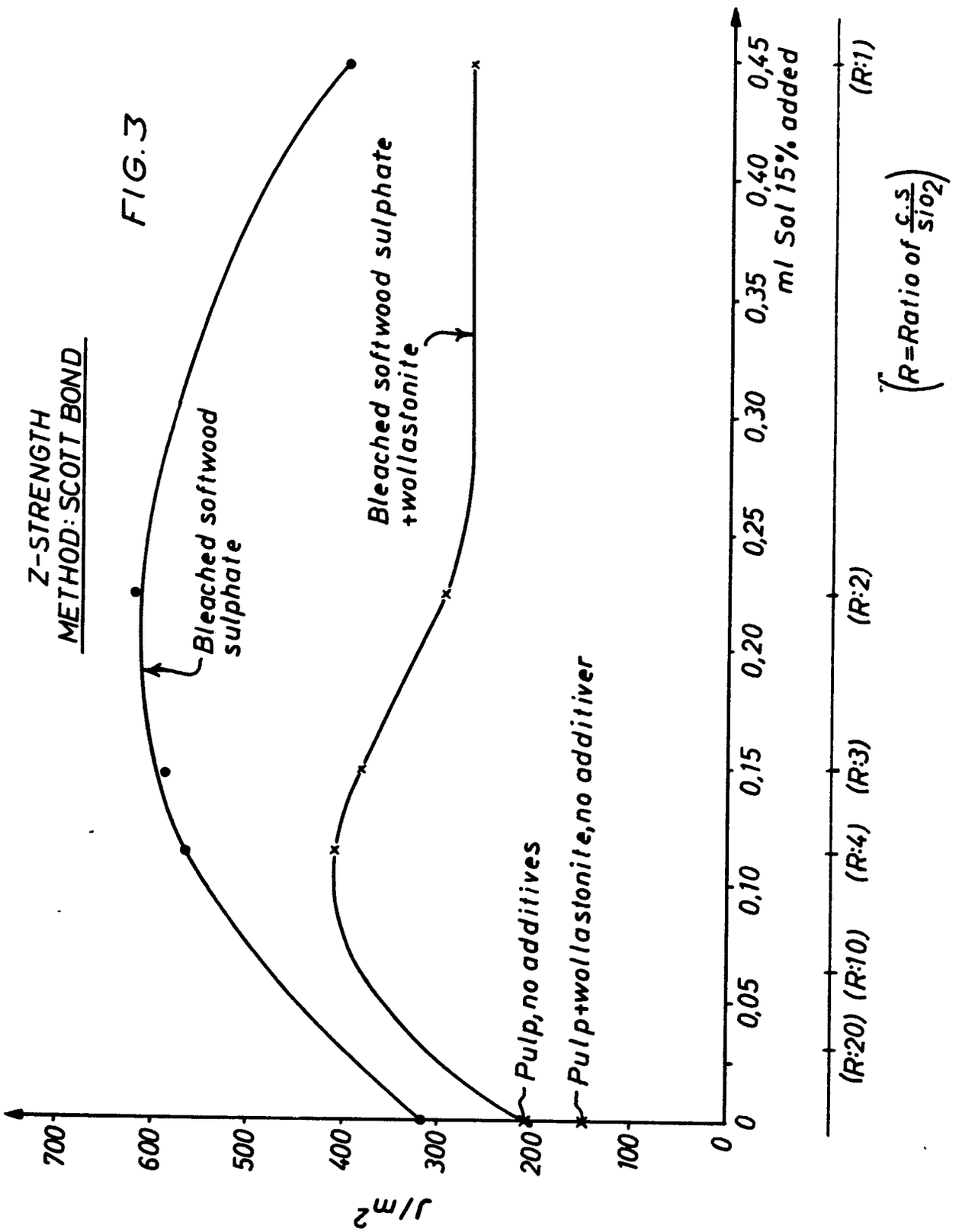

Z-STRENGTH
METHOD: SCOTT BOND
Bleached softwood sulphate
Bleached softwood sulphate +wollastonite
Pulp, no additives
Pulp+wollastonite, no additiver
J/m²
700
600
500
400
300
200
100
0
0,05
0,10
0,15
0,20
0,25
0,30
0,35
0,40
0,45
ml Sol 15% added
(R:20)
(R:10)
(R:4)
(R:3)
(R:2)
(R:1)
(R=Ratio of C.S / SiO2)

FIG. 4

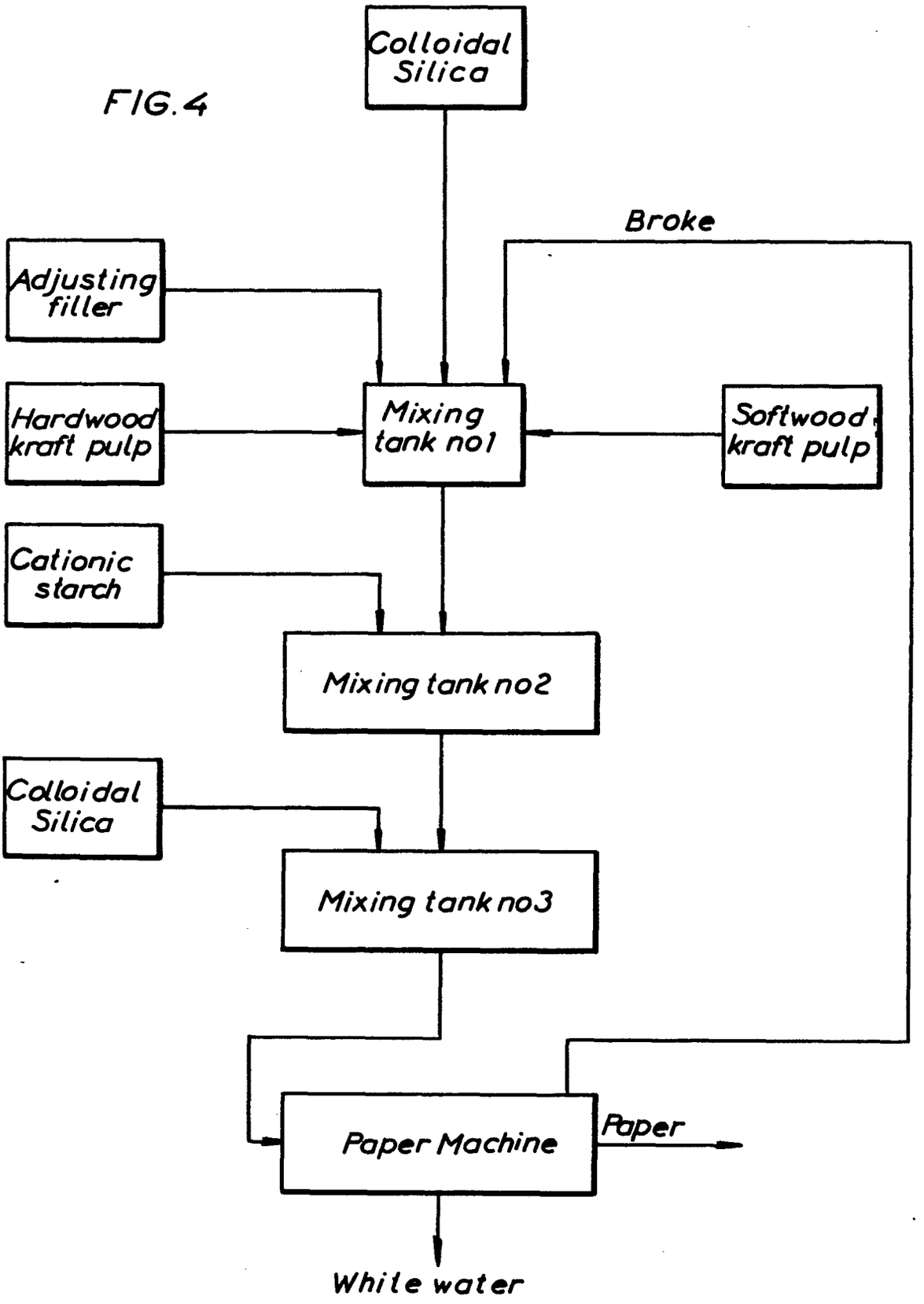

Colloidal Silica
Broke
Adjusting filler
Hardwood kraft pulp
Mixing tank no1
Softwood kraft pulp
Cationic starch
Mixing tank no2
Colloidal Silica
Mixing tank no3
Paper Machine
Paper
White water

FIG.5

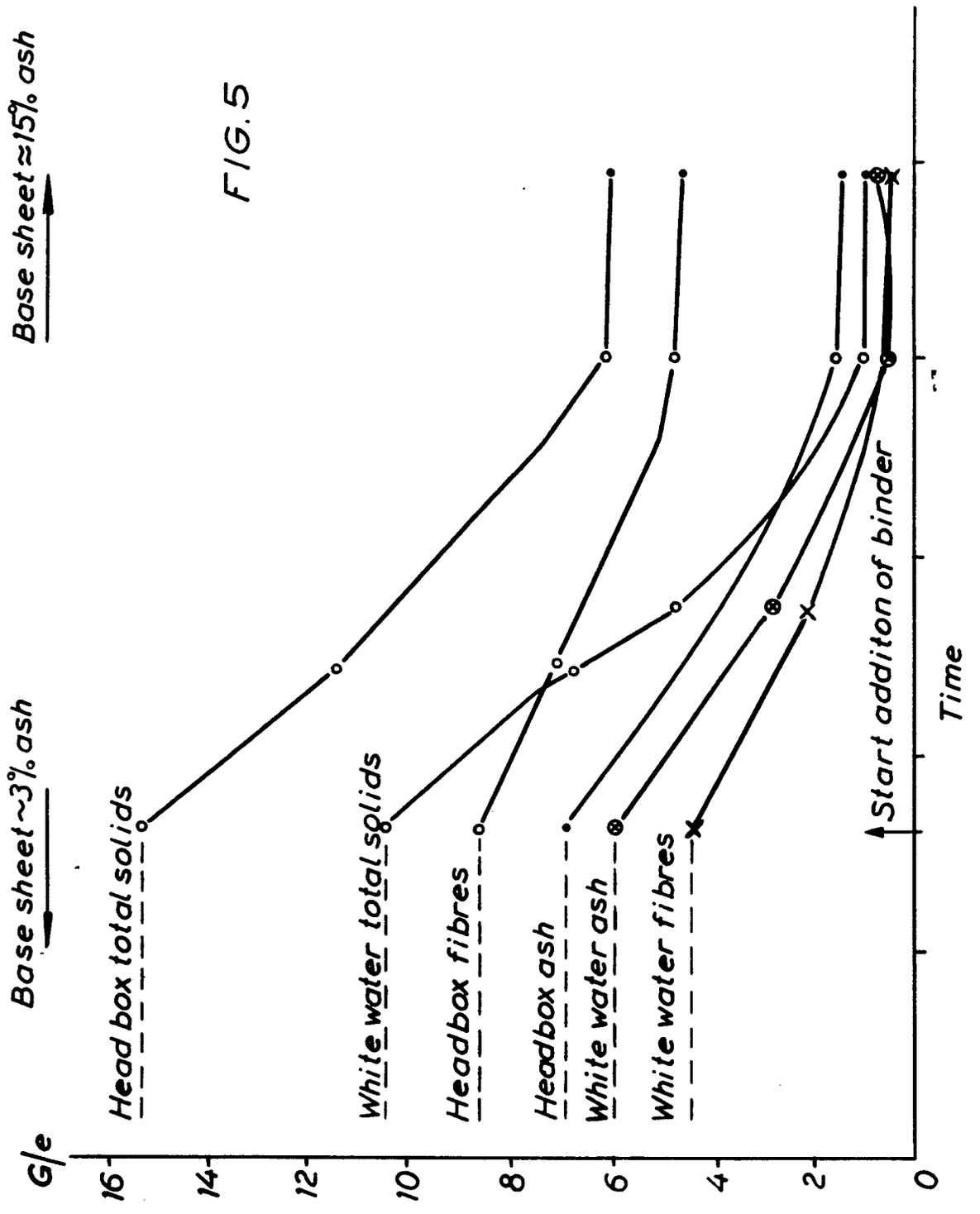
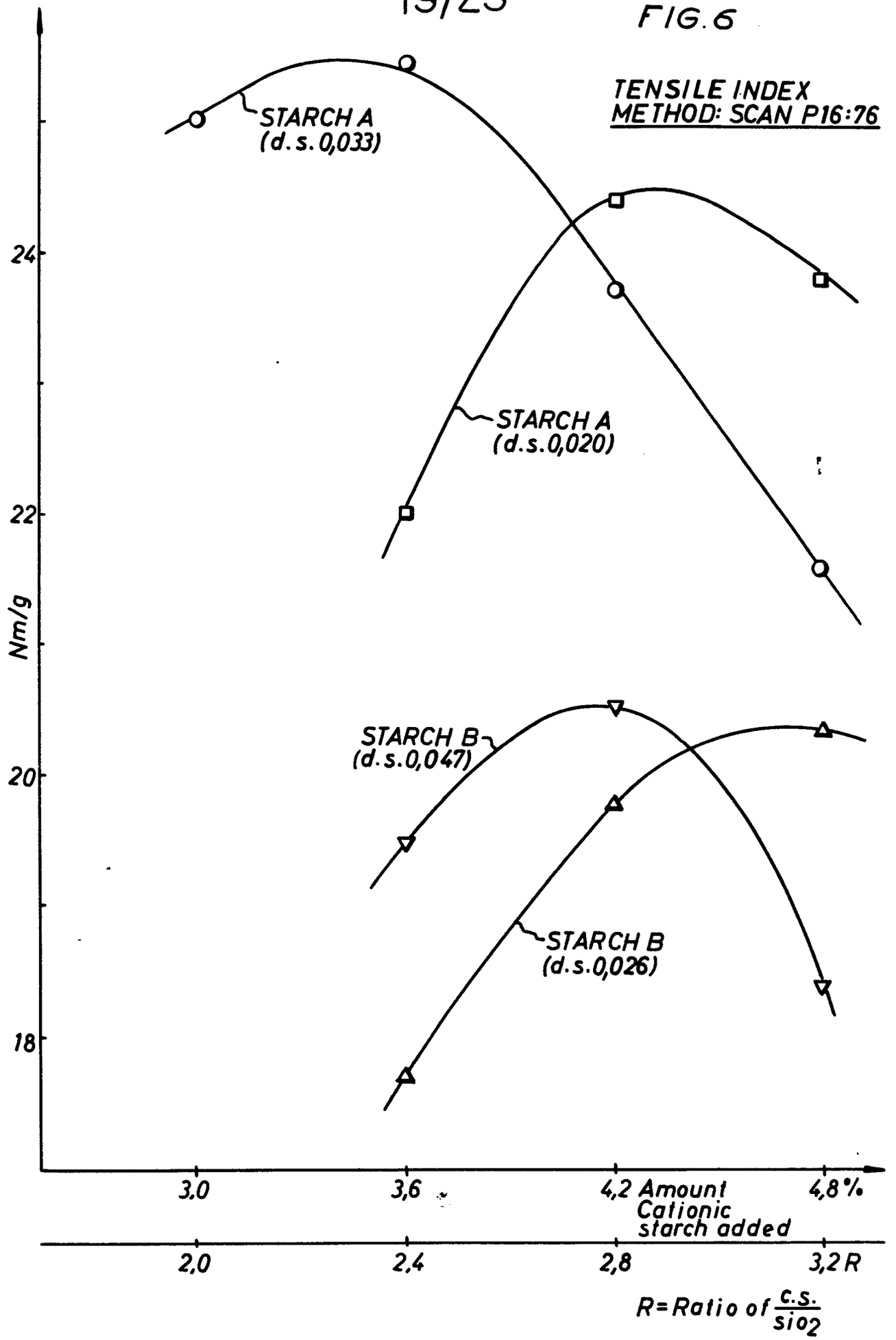

G/e
Base sheet ~3% ash
Base sheet ≈15% ash
Head box total solids
White water total solids
Headbox fibres
Headbox ash
White water ash
White water fibres
Start addition of binder
Time
16
14
12
10
8
6
4
2
0

FIG. 6


TENSILE INDEX
METHOD: SCAN P16:76
STARCH A
(d.s.0,033)
STARCH A
(d.s.0,020)
STARCH B
(d.s.0,047)
STARCH B
(d.s.0,026)
24
22
20
18
Nm/g
3,0
3,6
4,2
4,8 %
Amount
Cationic
starch added
2,0
2,4
2,8
3,2 R
R=Ratio of c.s./sio2

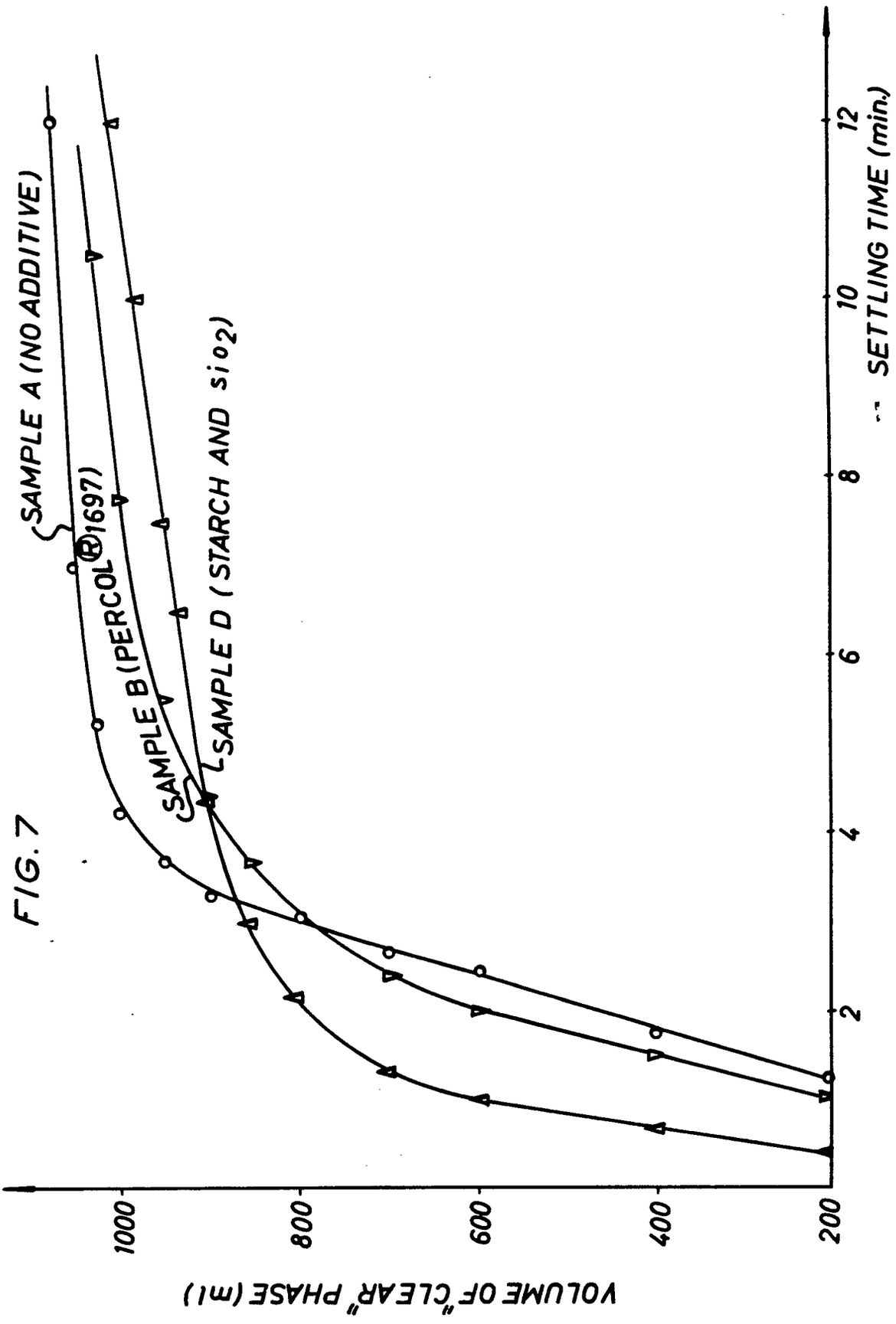

SAMPLE A (NO ADDITIVE)
SAMPLE B (PERCOL® 1697)
SAMPLE D (STARCH AND SiO_2)
VOLUME OF "CLEAR" PHASE (ml)
1000
800
600
400
200
2
4
6
8
10
12
SETTLING TIME (min.)

FIG. 7

FIG. 8A

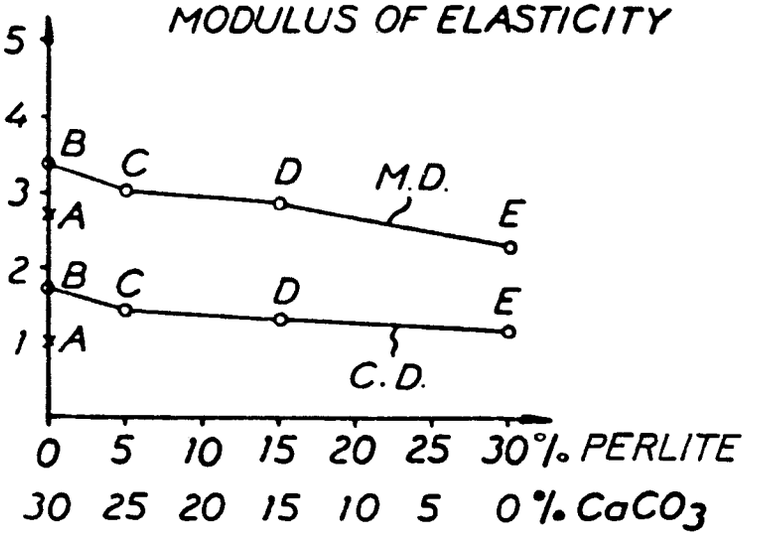


FIG. 8B

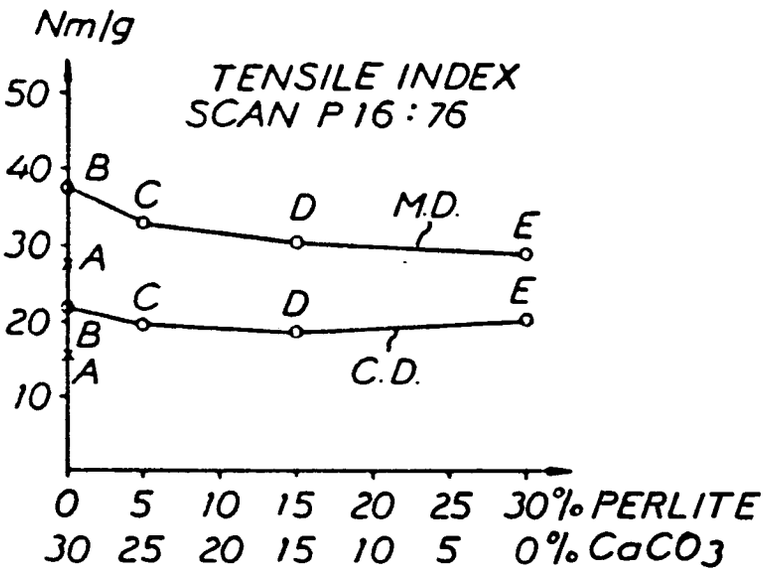


FIG. 8C

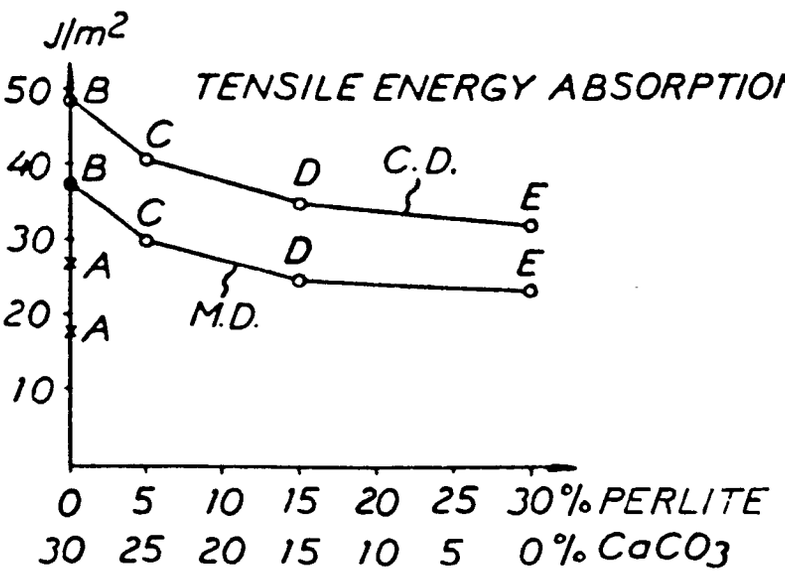


FIG.8D

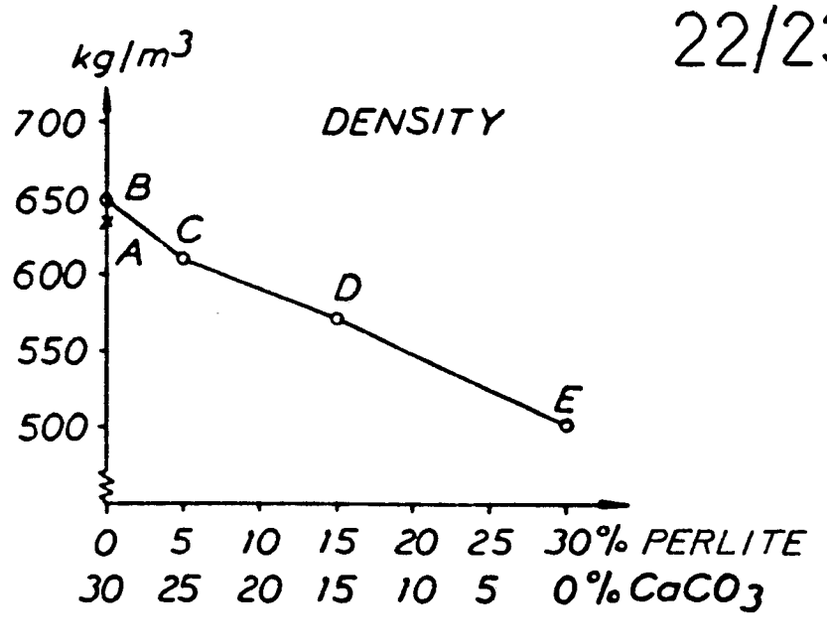


FIG.8E

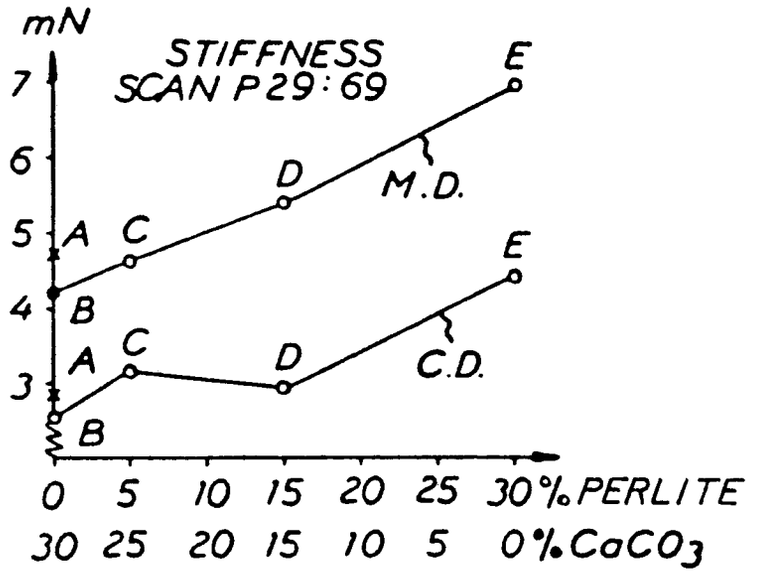


FIG.8F

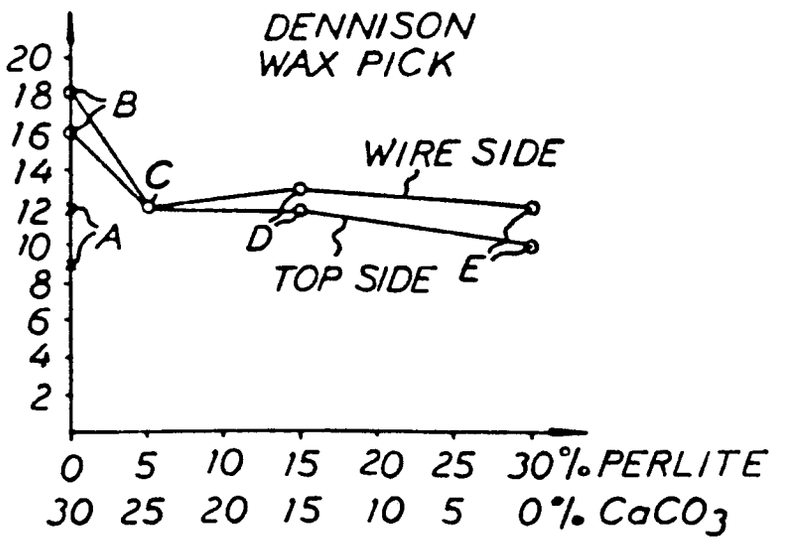
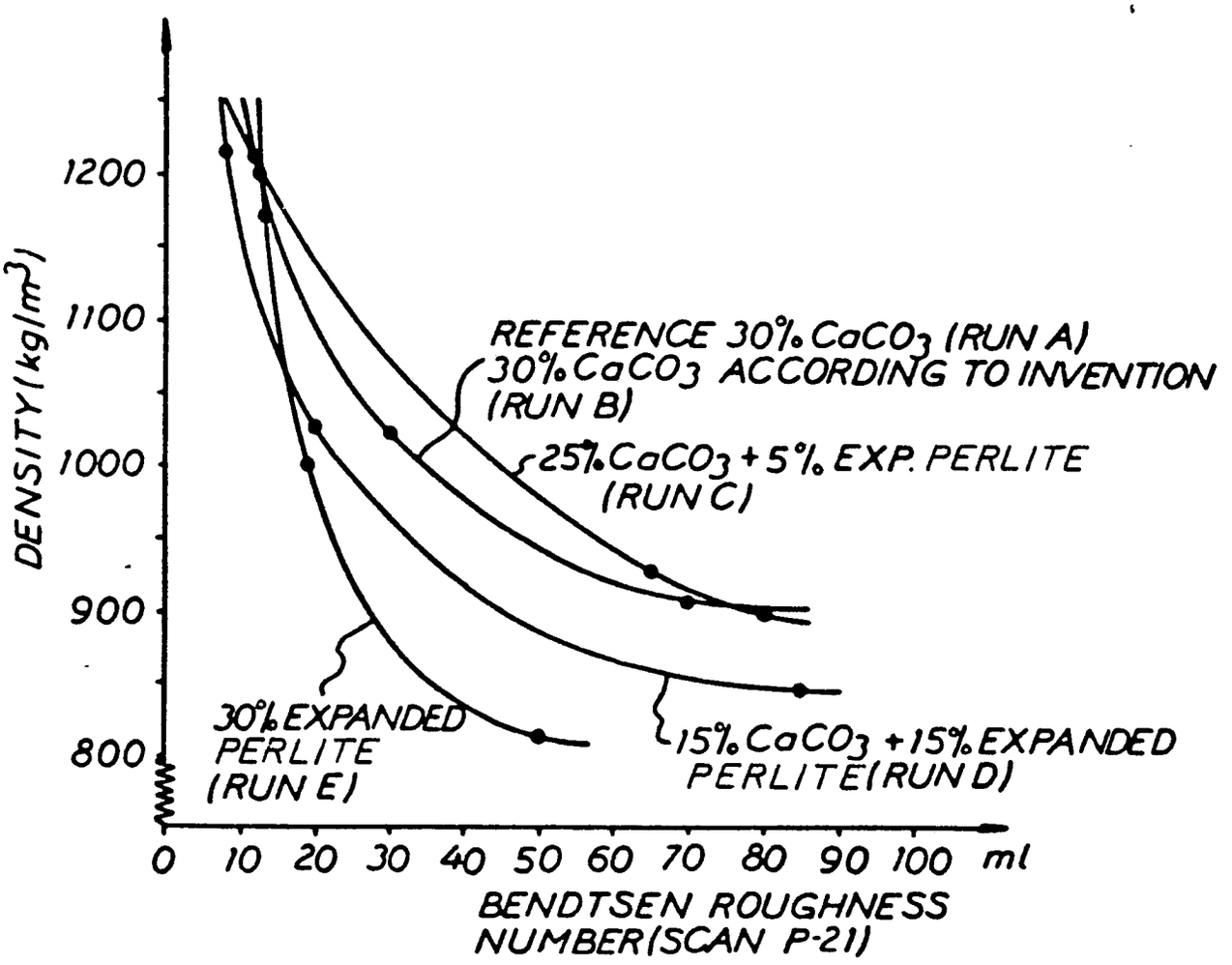


FIG.8G


DENSITY (kg/m³)
1200
1100
1000
900
800
0
10
20
30
40
50
60
70
80
90
100
ml
BENDTSEN ROUGHNESS NUMBER (SCAN P-21)
REFERENCE 30% CaCO3 (RUN A)
30% CaCO3 ACCORDING TO INVENTION (RUN B)
25% CaCO3 + 5% EXP. PERLITE (RUN C)
15% CaCO3 + 15% EXPANDED PERLITE (RUN D)
30% EXPANDED PERLITE (RUN E)

European Patent Office

EUROPEAN SEARCH REPORT

0041056

Application number
EP 81 85 0084

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
X	US - A - 3 253 978 (W.J. BODENDORF et al.) * the whole document * --	1,3,4, 8,13
	TAPPI, Journal of the Technical Association of the Pulp and Paper Industry, vol.63, no.4, April 1980 ATLANTA GA (US) J. MARTON:"The role of surface chemistry in fines-cationic starch interactions" pages 87-91 * the whole article * --	1,3,5, 6
	EP - A - 0 006 390 (ARJOMARI-PRIOUX) * claim 1; page 9, lines 5-14 * --	9
	GB - A - 1 387 744 (TATABANYAI SZENBANYAK) * the whole document * --	12
	DE - A - 1 636 335 (ZSCHIMMER & SCHWARZ) * claims I,II; page 2 * -----	12

CLASSIFICATION OF THE APPLICATION (Int. Cl.³)

D 21 D 3/00
D 21 F 1/82

TECHNICAL FIELDS SEARCHED (Int. Cl.³)

D 21 D 3/00
D 21 F 1/82
D 21 H 3/28
D 21 H 3/78

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
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T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	27-08-1981	NESTBY

EPO Form 1503.1 06.78