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An agency of Industry Canada

CA 2607332 C 2016/02/16

(11)(21) **2 607 332**

(12) **BREVET CANADIEN**
CANADIAN PATENT

(13) **C**

(86) **Date de dépôt PCT/PCT Filing Date:** 2006/05/11
(87) **Date publication PCT/PCT Publication Date:** 2006/11/16
(45) **Date de délivrance/Issue Date:** 2016/02/16
(85) **Entrée phase nationale/National Entry:** 2007/11/01
(86) **N° demande PCT/PCT Application No.:** EP 2006/062255
(87) **N° publication PCT/PCT Publication No.:** 2006/120235
(30) **Priorité/Priority:** 2005/05/11 (US60/679,734)

(51) **Cl.Int./Int.Cl.** ***D21H 17/00*** (2006.01)

(72) **Inventeurs/Inventors:**
LEGNERFAELT, BJOERN, SE;
DOLFF, ELISABETH, SE;
OLAUSSON, JAN, SE

(73) **Propriétaire/Owner:**
STORA ENSO AB, SE

(74) **Agent:** FETHERSTONHAUGH & CO.

(54) **Titre : PROCEDE DE FABRICATION D'UN PAPIER ET PAPIER FABRIQUE SELON CE PROCEDE**
(54) **Title: PAPER PRODUCTION PROCESS FEATURING ALTERNATING CATIONIC AND ANIONIC POLYMER ADDITIONS**

(57) **Abrégé/Abstract:**
The present application relates to a process for the production of a paper product, which process comprises: providing a furnish comprising fillers and fibers; subjecting said furnish to polymer treatment, in which an excess of polymers is added to the furnish by alternating cationic and anionic polymer additions in at least three steps; dewatering the furnish on a wire to form a fiber web; pressing said fiber web; drying the fiber web to form said paper product, said furnish containing fillers in such an amount that the paper product obtained by the process contains at least 15% by weight of fillers.

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ABSTRACT

The present application relates to a process for the production of a paper product, which process comprises: providing a furnish comprising fillers and fibers; subjecting said furnish to polymer treatment, in which an excess of polymers is added to the furnish by alternating cationic and anionic polymer additions in at least three steps; dewatering the furnish on a wire to form a fiber web; pressing said fiber web; drying the fiber web to form said paper product, said furnish containing fillers in such an amount that the paper product obtained by the process contains at least 15% by weight of fillers.

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PAPER PRODUCTION PROCESS FEATURING ALTERNATING CATIONIC AND ANIONIC POLYMER ADDITIONS

The present invention relates to a process for the production of a paper product with high filler content wherein the furnish used is treated with polymers in steps.

Background of the invention

In papermaking processes there is an ongoing concern to find ways to produce paper at reduced costs. Since fillers are cheaper than fibers, one way is to increase the filler content of the paper and thus be able to reduce the amount of fibers in the paper. Besides being economically beneficial, fillers also improve the opacity and printability properties of the paper. However, large amount of fillers in the paper decreases the strength of the paper. Thus, there is a balance between the possible amount of fillers added and the required strength of the paper produced. Current levels of fillers in paper vary depending on paper grade, for example the filler content of newsprint may be up to about 12-14%. The maximum filler content today, considering available publication paper grades and fine paper grades, is about 35%, as it is in uncoated magazine paper.

One way to compensate for the decrease in strength caused when filler is added is to improve the fiber bonding properties between the fibers in the paper, thereby maintaining the strength of the paper. With increased strength of the paper it is possible to increase the filler content. The predominant treatment for improving paper strength, particularly dry strength, of paper has so far been to add a strength agent, preferably cationic starch, to the pulp fiber slurry prior to the sheet forming operation. Cationic starch molecules added to the pulp slurries can adhere to the naturally anionic pulp fibers by electrostatic attraction and thus be retained in the wet fiber mat and remain in the final paper or board. It is however difficult to adsorb large amounts of cationic starch to the fibers.

When adding large amounts of cationic starch to a papermaking furnish, in order to achieve high resulting paper strength, two major problems arise. The first is that the cationic starch molecules tend to saturate the anionic charge on the cellulose fibers, thus setting a limit to the amount of cationic starch which can be added to the slurry. If an excess of cationic starch is added, only a portion of the starch added will be retained in the sheet, and the rest will circulate in the paper or board machine white water system. A second problem is that fibers which are made cationic by excessive cationic starch addition, will not be able to adsorb other cationic additives which are commonly added to the pulp slurry, such as sizing agents and retention aids.

Another method to enhance the strength properties of paper is to treat the fibers with polymers in consecutive steps. The international application WO 2006041401 describes such method where a part of a furnish is treated with polymers in consecutive steps, whereby a paper or board with improved strength and with reduced amount of polymers is obtained.

Yet another method to enhance the strength properties of paper is described in WO 0032702, in which particles (such as fibers or fillers) are provided with a multilayer coating of interacting polymers.

It is however still a need for a process by which paper products having a maintained or improved strength could be produced at a lower cost.

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Summary of the invention

The invention relates to a process by which a paper product having a high strength can be produced at low cost.

It has now surprisingly been found that by subjecting both fillers and fibers of a furnish to polymer treatment as defined herein the strength of the resulting paper product is significantly improved even though the filler content is high.

In one embodiment, the present invention concerns a process for the production of a paper product, which process comprises providing a furnish comprising fillers and fibers; subjecting the furnish to polymer treatment, in which polymers are added to the furnish in at least three steps; dewatering the furnish on a wire to form a fiber web, pressing said fiber web and drying the fiber web to form said paper product; said furnish containing fillers in such an amount that the paper product obtained by the process contains at least 15% by weight of fillers. By treating the furnish, which contains fibers and a high amount of fillers, with polymers, a paper product with high strength is obtained.

The paper product produced preferably contains 15-70% fillers by weight of the total paper weight.

The polymer used in each of the consecutive polymer treatment steps is preferably interacting with the polymer used in the subsequent step. The polymer treatment preferably includes one step in which cationic polymer is added, and at least one step in which anionic polymer is added. By alternating cationic and anionic polymer additions it is believed that interacting polymer layers are obtained. The cationic polymer is preferably cationic starch and the anionic polymer is preferably CMC. The polymer treatment preferably comprises three to seven consecutive steps.

The invention also relates to a paper product produced according to the process of the present invention.

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Brief description of the drawings

Figure 1 shows the results of the z-strength measurement of the paper sheets 1-10.

Figure 2 shows the results of the tensile index of the paper sheets 1-10.

Figure 3 shows the tensile index compared to the amount of starch in the paper sheets 1-10.

Detailed description of the invention

The invention relates to a process for the production of a paper product from a furnish comprising fillers and fibers, wherein the furnish is treated with polymers in at least three steps and of which said furnish contains fillers in such an amount that the paper product produced contains at least 15% by weight of fillers. The invention also relates to a paper product produced according to the process of the present invention.

It is possible to produce a paper or board with high amounts of cationic starch and consequently receive a strong product. This is shown in both WO 0032702 and in WO 2006041401.

It has now been found that by treating a furnish containing both fillers and fibers with polymers in three or more polymer treatments steps, the amount of fillers in the produced paper product can be increased and the strength of the paper is very good in spite of the high filler content of the paper. Surprisingly, the filler content can be increased even more when the furnish treated contains both fillers and fibers as compared to only treating the fibers or the fillers of the furnish with polymers in consecutive steps. One theory behind this is that when a furnish containing both fillers and fibers is treated with polymers according to the invention, the filler particles bind stronger to other filler particles or to the fibers, and the filler content can consequently be increased without affecting the strength of the paper negatively. By treating the entire furnish with polymers in consecutive steps and not only one part of the furnish as done in WO 2006041401, it has even more

surprisingly been seen that the strength of the paper is maintained or even increased, even though the filler content of the paper is increased.

The present process for producing a paper or board product comprises, providing a furnish comprising fillers and fibers; subjecting the furnish to polymer treatment, in which polymers are added to the furnish in at least three steps; dewatering the furnish on a wire to form a fiber web; pressing said fiber web and drying the fiber web to form said paper product; said furnish containing fillers in such an amount that the paper product obtained by the process contains at least 15% by weight of fillers. By treating the entire furnish, which comprises both fillers and fibers, the filler content of resulting paper product, can be increased and the strength of the resulting paper is still surprisingly significantly good.

The filler content of the paper product is at least 15% by weight of the total paper sheet weight, preferably 15-70% and even more preferably 20-70% or 20-50% by weight, since it has been seen that the strength of the paper still is high, even if the filler content is increased, and it thus makes it possible to produce a paper product at lower cost. The filler content is even more preferably between 30-50% by weight since the strength of the paper is good even at this high filler content, this can bee seen in table 1. The filler content is adjusted in order to achieve the desired strength of the paper product. It is desirable to have as high filler content as possible without decreasing the strength to unacceptable levels. The appropriate amount of fillers depends on the properties of the furnish and on the quality demands of the paper product. The amount of fillers added to the furnish, in order to receive a paper product with a desired filler content, depends on the filler retention of the fiber web, i.e. how much of the added fillers that are retained in the resulting paper product. The filler retention varies a lot and there are many factors that affect it, some examples are: the grammage of the paper, the formation unit of the paper machine, the fiber components of the furnish and the use and amount of added retention agents. Consequently, there is a wide range of what the filler retention can be, normally the filler retention is about 20-70%, i.e. 20-70% of the added fillers are

retained in the paper product. To treat the furnish with polymers according to the invention might also affect the filler retention, however it is believed that the polymer treatment affects the filler retention in a positively way. This is due to the fact that both filler particles and fibers form complexes and that these complexes might improve the fillers ability to bind to the fibers in the paper and thus improve the fillers ability to remain in the paper.

The polymer used in each of the consecutive polymer treatment steps is preferably interacting with the polymer used in the subsequent step, thereby enabling a larger amount of polymers to be attached to the fillers and fibers and thus result in increased strength of the final paper product. The polymer treatment preferably includes one step in which anionic polymer is added, and at least one step in which cationic polymer is added. By alternating anionic and cationic polymer coatings interacting polymer layers may be obtained.

The anionic polymer used may be one or more chosen from the group consisting of: carboxy methyl cellulose (CMC), polyvinyl sulphate, anionic galactoglucomannan, anionic starch, polyphosphoric acid, alginate and polymethacrylic acid. The anionic polymer is preferably CMC, since it has high charge density, which reduces the amount of CMC needed in each addition, and which is therefore economically beneficial. CMC also interacts very well with cationic polymers, and especially cationic starch. Thus, the use of CMC is very economically beneficial both due to its low price as well as the reduced amount needed. The cationic polymer used may be one or more chosen from the group consisting of: cationic starch, polyvinyl amine, chitosan, primary and secondary amines, polyethylene imines, polyvinyl pyrrolidone and modified polyacryl amides. The cationic polymer is preferably cationic starch, which is advantageous because it results in a paper having enhanced strength properties and it is economically beneficial, due to its low price and easy availability. It is preferable to use cationic starch in combination with CMC since these two polymers have been found to interact well with each other, resulting in paper with good strength at a low cost.

The polymer treatment preferably comprises three to seven consecutive steps. The optimal number of steps depends on what properties of the paper that are desired and on the properties of the furnish being treated. The more steps the treatment consists of, the larger amount of polymers are added and thus retained in the paper. Often it is a balance between the cost and the desired properties, for example strength of the paper. There is usually a limit when it is no longer cost effective to add more polymers with respect to the improvement of the desired properties, for example increase of strength or filler content of the paper manufactured. It is preferred to add cationic polymer in a first step of the polymer treatment and to add anionic polymer in a subsequent and to continue with alternating additions of cationic and anionic polymers, until the desired amount of polymers has been added in the desired number of steps.

The furnish need not be washed between each polymer treatment steps. Any unabsorbed excess of polymer added in the preceding step can remain in the furnish and need not be rinsed away. Washing between the polymer treatment steps has not been shown to enhance the properties of the resulting product. It is thus advantageous to subject the furnish to each of the polymer treatment steps without any intermediate washing. Thereby, washing between the polymer treatment steps is unnecessary and may be excluded, thus a faster process is achieved which, in addition, has lower water consumption.

After each polymer treatment step there should be sufficient time and mixing for the polymer to be absorbed to the fillers and fibers of the furnish. A time period of at least 5 seconds between each polymer treatment step is suitable. The optimal time period depends on the capacity of the mixing of the equipment.

The polymer of each polymer treatment step can be added to the furnish in a pulp vessel, such as a pulp chest, or in-line in a furnish transport pipe, or a combination thereof. The point of addition of the polymer depends on the equipment available

and where it is practically possible to make the addition. When carrying out three or more polymer treatment steps by in-line addition of polymer it needs to be ensured that the pipe is long enough to allow both thorough blending of polymer, filler and fibers, and to allow enough time between each addition step for absorption of the polymer. Alternatively an in-line mixer can be used to ensure good mixing in the pipe.

The amount of polymer to be added varies depending of the properties of the furnish. When cationic starch and CMC are used for the polymer treatment the amount of cationic starch added in each step is typically between 5-30 kg/ton and the amount of CMC added in each step is typically between 0.25-3 kg/ton. The amount of polymers added to the furnish may be decided by measuring the charge of the pulp or the process water. Even if an excess amount of added polymer is not detrimental to the final result, it may be advantageous to add an amount of polymer that is close to what can be absorbed by the pulp, both for economical and environmental reasons. However, for some paper products it has been seen that an excess of polymers added to the furnish results in an improved paper product, i.e. a stronger product or a product with higher filler content with remained strength. This might be explained by that the polymers form polyelectrolyte complexes that could have favorable affects on the properties of the paper product.

The furnish typically contains a mixture of different kinds of pulp, for example chemical pulp (hardwood pulp, softwood pulp, sulphate pulp or sulfite pulp) or mechanical pulp (CTMP or TMP).

Examples of fillers used in the furnish are; kaolin, calcium carbonate, precipitated calcium carbonate, talcum, gypsum and synthetic fillers.

The paper product produced can be of any paper grade at any grammage, for example fine paper, magazine paper or newsprint.

If necessary, additional generally known paper process steps, such as coating and calendering, can be used in order to produce the paper product according to claim 1.

Example

Ten different furnish samples 1-10 were used to evaluate the process. The furnish used was a mixture of groundwood and kraft pulp in the ratio 2.5:1. In six of the samples only the fiber part of the furnish was treated with polymers and in the remaining four samples the entire furnish was treated with polymers. Clay was used as filler and the filler content of the paper product was either 30% or 50%. For comparison, some samples were treated with cationic starch in one step and the other samples were treated with cationic starch and CMC in consecutive steps according to the invention.

The three sequential steps of the polymer treatment were:

I. addition of cationic starch to the furnish sample;

II. addition of CMC to the furnish sample; and

III. addition of cationic starch to the furnish sample.

The charge of the furnish was measured after each addition, and the amount of polymer added in each subsequent step was decided based on these measurements. The polymers were added in excess as compared to the amount determined on basis of the charge measurement.

In samples 1-6 only the fiber part was subjected to polymer treatment and thereafter fillers were added, and the fibers and fillers were mixed into a furnish. Samples 7-10 were subjected as a whole to the polymer treatment, i.e. the entire furnish comprising both fibers and fillers were subjected to the polymer treatment.

Sheets were then prepared by dewatering the furnish, pressing and drying the fiber web and the density (ISO 5270), tensile index (ISO 5270) and z-strength (SCAN P

80) were determined for all sheets. Prior to testing the sheets were conditioned at 23°C/50% RH. The results are shown in Table 1.

Table 1

Paper sheets	Treatment	Filler content (%)	Starch-CMC-Starch (kg/ton)	Density (kg/m3)	Tensile index (Nm/g)	z-strength (kPa)	Starch analyzed in paper (%)
1	Fiber part	30	10-0-0	513	24,7	436	0,79
2	Fiber part	30	20-0-0	497	22,4	433	1,3
3	Fiber part	30	25-0-0	486	23,1	427	1,3
4	Fiber part	30	25-2-20	502	22,4	485	2,6
5	Fiber part	50	25-0-0	512	11,5	334	0,97
6	Fiber part	50	25-2-20	512	11,7	373	2,1
7	Entire furnish	30	22-0-0	544	35,7	540	1,8
8	Entire furnish	30	22-2-22	554	41,3	720	3,1
9	Entire furnish	50	20-0-0	582	20,9	454	1,6
10	Entire furnish	50	20-2-20	620	25,6	634	3,2

Table 1 shows an increase in z-strength and tensile index for the resulting paper product when the entire furnish is subjected to polymer treatment, as compared to if only the fiber part of the furnish were treated. It can also be seen that treatment with polymers in consecutive steps improves both the z-strength and the tensile index.

The density was also measured and it can be seen that in many cases there is an increase of density as the amount of starch in the sheet increases. However, the density increase is not large enough to explain the increase of tensile index.

In order to get a better view of the results, they are also shown in Figure 1, Figure 2 and Figure 3. The abbreviation st, as can be seen in the Figures stands for addition of cationic starch in kg/ton.

Figure 1 shows that the z-strength of the paper sheets increases when the entire furnish is treated with polymers. The highest z-strength can be found when the furnish is treated with polymers in consecutive steps according to the invention. Surprisingly, the z-strength of the paper sheets with a filler content of 50% is very high.

Figure 2 shows that the tensile index of the paper sheets increases when the entire furnish is treated with polymers. The highest value of the tensile index can be found when the furnish is treated with polymers in consecutive steps according to the invention.

Figure 3 shows that the tensile index of the sheets is best for those sheets for which the entire furnish was treated with polymers, even if the amount of starch in the sheets is not so high. The tensile index of sheets with a filler content of 50% where the entire furnish has been treated, is comparable to the sheets with a filler content of 30% where only the fiber part of the furnish has been treated with polymers.

Consequently, these tests presented in table 1, and Figures 1, 2 and 3 show that it is advantageous to treat the entire furnish since it results in a paper having high strength at the same time as the filler content can be increased.

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CLAIMS:

1. A process for the production of a paper product, which process comprises:

providing a furnish comprising fillers and fibers;

subjecting said furnish to polymer treatment, in which an excess of polymers is added to the furnish by alternating cationic and anionic polymer additions in at least three steps;

dewatering the furnish on a wire to form a fiber web;

pressing said fiber web;

drying the fiber web to form said paper product,

said furnish containing fillers in such an amount that the paper product obtained by the process contains at least 15% by weight of fillers.

2. The process as claimed in claim 1, wherein the paper product contains 15-70% by weight of fillers.

3. The process as claimed in any one of claims 1 to 2, wherein the anionic polymer is carboxy methyl cellulose.

4. The process as claimed in any one of claims 1 to 3, wherein the cationic polymer is cationic starch.

5. The process as claimed in any one of claims 1 to 4, wherein the polymer treatment comprises three to seven steps.

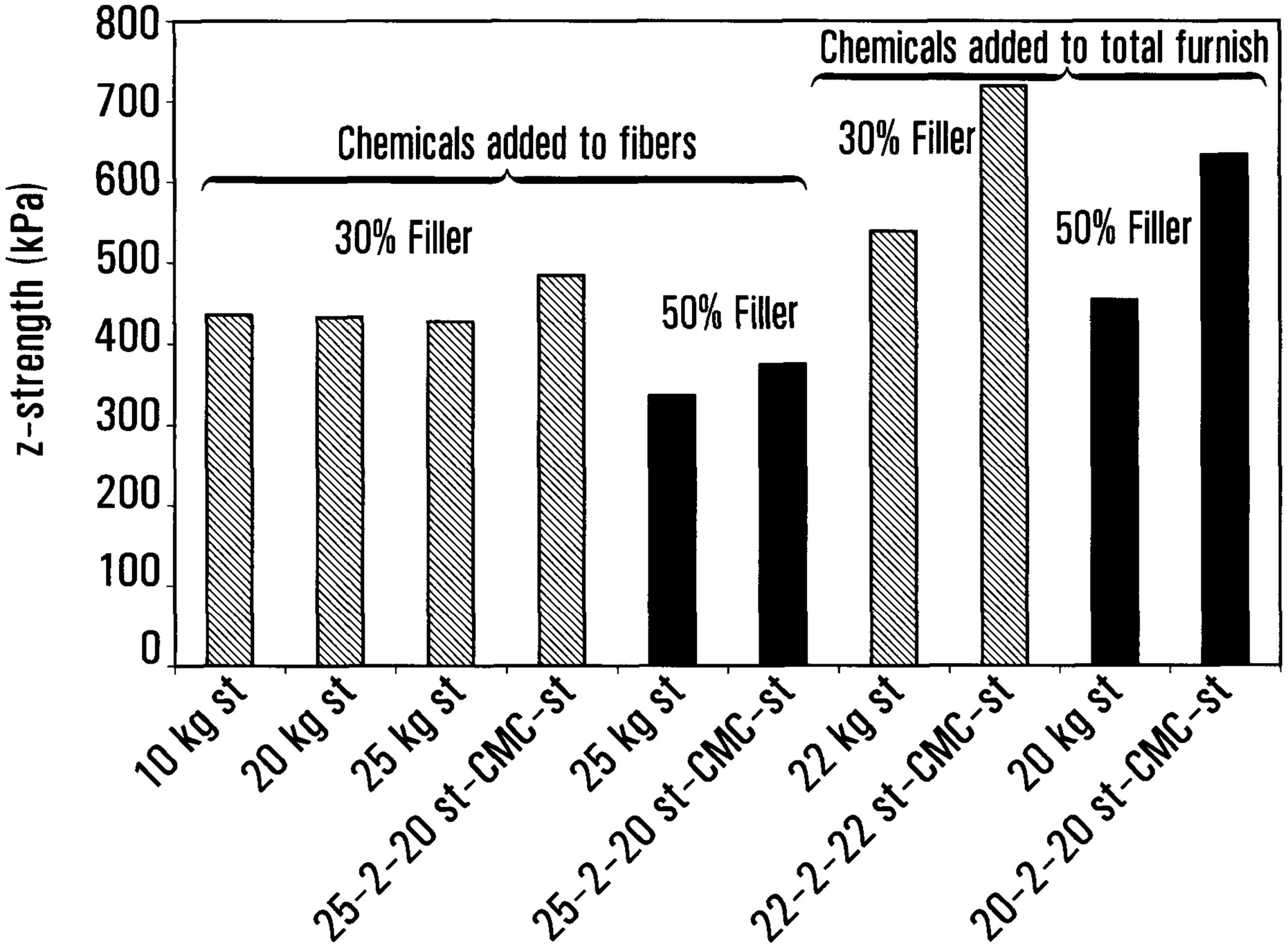
z-strength of the paper sheets 1-10
z-strength (kPa)
800
700
600
500
400
300
200
100
0
Chemicals added to fibers
30% Filler
50% Filler
Chemicals added to total furnish
30% Filler
50% Filler
10 kg st
20 kg st
25 kg st
25-2-20 st-CMC-st
25 kg st
25-2-20 st-CMC-st
22 kg st
22-2-22 st-CMC-st
20 kg st
20-2-20 st-CMC-st

FIG. 1

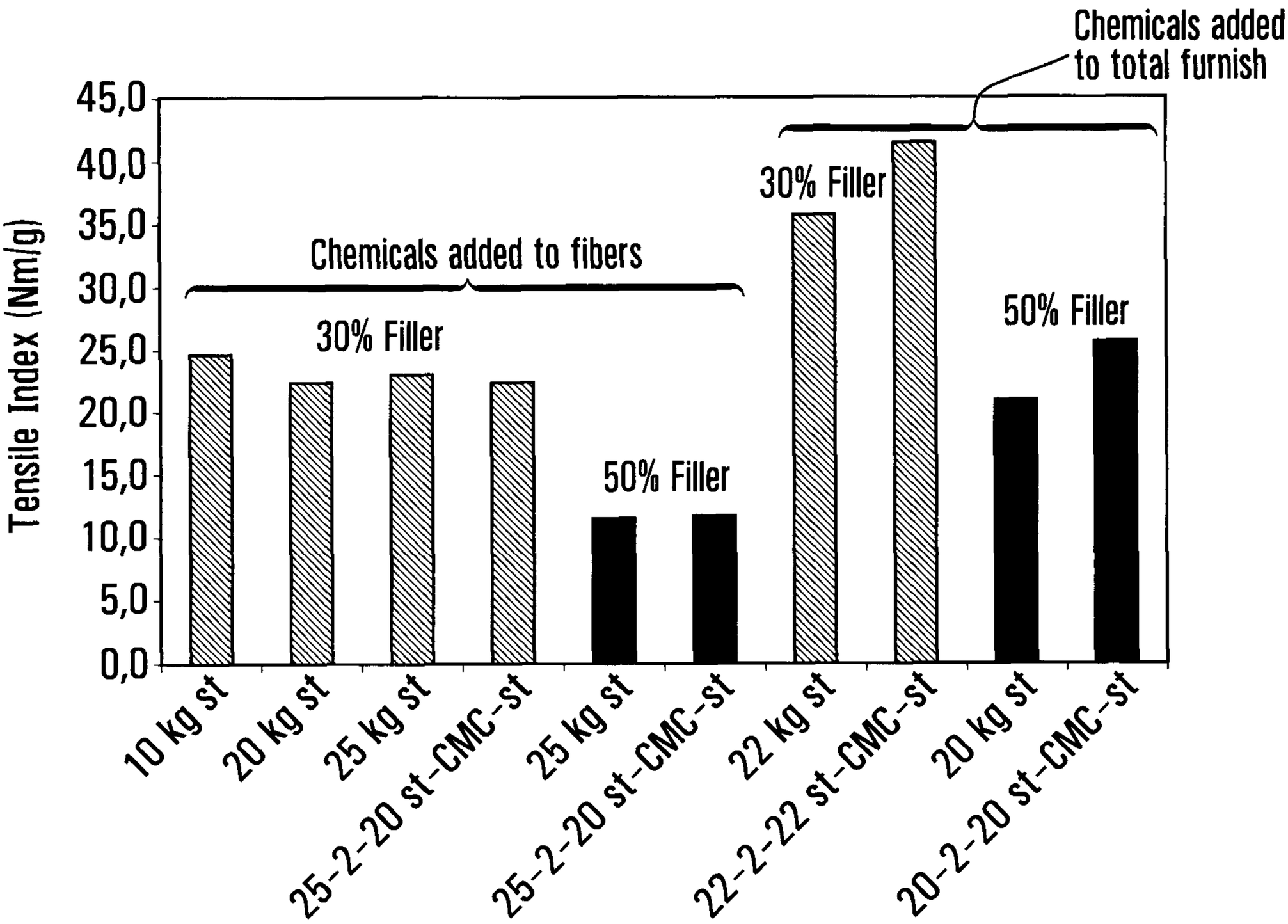
Tensile index of the paper sheets 1-10
Chemicals added to total furnish
Chemicals added to fibers
30% Filler
50% Filler
30% Filler
50% Filler
Tensile Index (Nm/g)
45,0
40,0
35,0
30,0
25,0
20,0
15,0
10,0
5,0
0,0
10 kg st
20 kg st
25 kg st
25-2-20 st-CMC-st
25 kg st
25-2-20 st-CMC-st
22 kg st
22-2-22 st-CMC-st
20 kg st
20-2-20 st-CMC-st

FIG. 2

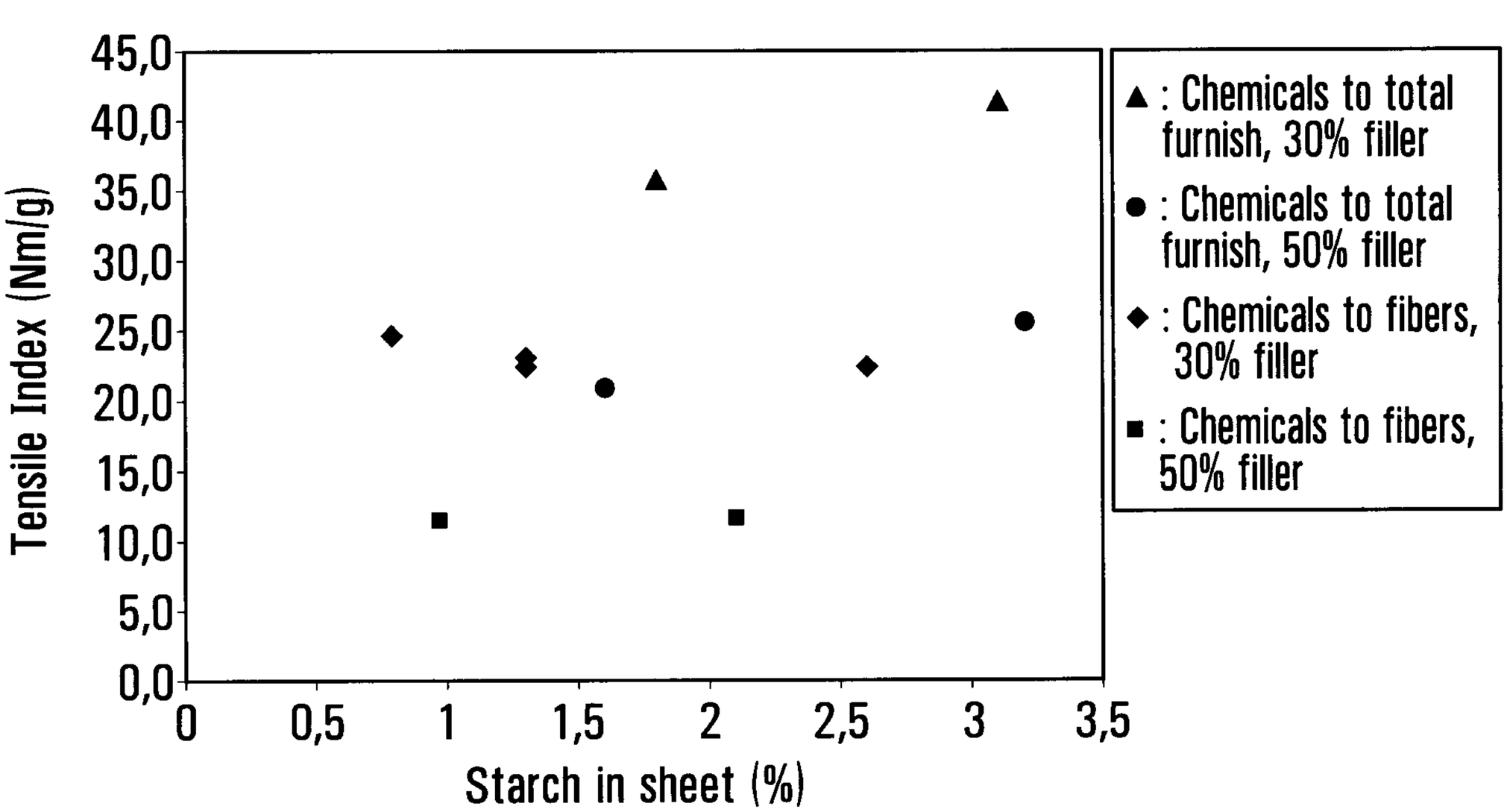
Tensile index compared to the amount of starch in the paper sheets 1-10
Tensile Index (Nm/g)
45,0
40,0
35,0
30,0
25,0
20,0
15,0
10,0
5,0
0,0
0
0,5
1
1,5
2
2,5
3
3,5
Starch in sheet (%)
▲ : Chemicals to total furnish, 30% filler
● : Chemicals to total furnish, 50% filler
◆ : Chemicals to fibers, 30% filler
■ : Chemicals to fibers, 50% filler

FIG. 3