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(54) Title: PAPER SUBSTRATES CONTAINING A SILICON-CONTAINING COMPOUND

(57) Abstract: This invention relates to a paper substrate containing a silicon-containing compound, as well as methods of making and using the composition.



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PAPER SUBSTRATES CONTAINING A SILICON-CONTAINING COMPOUND

This application claims the benefit of US provisional application serial number 60/812,123, filed June 8, 2006, entitled "PAPER SUBSTRATES CONTAINING A SILICON-CONTAINING COMPOUND", which is hereby incorporated, in its entirety, herein by reference.

Field of the Invention

This invention relates to a paper substrate containing a silicon-containing compound, as well as methods of making and using the composition.

Background of the Invention

The brightness of paper substrates is increase traditionally by using large amounts of optical brightening agents in and/or on the paper during papermaking. However, dumping large amounts of optical brightening agents into a paper substrate during its production can be very costly.

In addition, the opacity of paper substrates is increased traditionally by using large amounts of dye, usually black dye, in and/or on the paper during papermaking. However, again, dumping large amounts of dye onto and/or into a paper substrate can also be costly.

Accordingly, there is still a need for a low cost and efficient solution to increase the brightness and the opacity of a paper substrate, while reducing print loss .

Detailed Description

The present inventors have now discovered a low cost and efficient solution to increase the brightness and the opacity of a paper substrate.

The paper substrate contains a web of cellulose fibers. The paper substrate of the present invention may contain recycled fibers and/or virgin fibers. Recycled fibers differ from virgin fibers in that the fibers have gone through the drying process several times.

The paper substrate of the present invention may contain from 1 to 99 wt%, preferably from 5 to 95 wt% of cellulose fibers based upon the total weight of the substrate, including 1, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95 and 99 wt%, and including any and all ranges and subranges therein.

Preferably, the sources of the cellulose fibers are from softwood and/or hardwood species. Other fibers, including non-woody herbaceous plants including, but not limited to, kenaf, hemp, jute, flax, sisal, or abaca although legal restrictions and other considerations may make the utilization of hemp and other fiber sources impractical or impossible.

The paper substrate of the present invention may contain from 1 to 100 wt% cellulose fibers originating from softwood species based upon the total amount of cellulose fibers in the paper substrate. This range includes 1, 2, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, and 100wt%, including any and all ranges and subranges therein, based upon the total amount of cellulose fibers in the paper substrate.

The paper substrate may alternatively or overlappingly contain from 0.01 to 100 wt% fibers from softwood species most preferably from 10 to 60wt% based upon the total weight of the paper substrate. The paper substrate contains not

more than 0.01, 0.05, 0.1, 0.2, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95 and 100wt% softwood based upon the total weight of the paper substrate, including any and all ranges and subranges therein.

The paper substrate may contain softwood fibers from softwood species that have a Canadian Standard Freeness (csf) of from 300 to 750, more preferably from 450 to 750. This range includes 300, 310, 320, 330, 340, 350, 360, 370, 380, 390, 400, 410, 420, 430, 440, 450, 460, 470, 480, 490, 500, 510, 520, 530, 540, 550, 560, 570, 580, 590, 600, 610, 620, 630, 640, 650, 660, 670, 680, 690, 700, 710, 720, 730, 740, and 750 csf, including any and all ranges and subranges therein. Canadian Standard Freeness is as measured by TAPPI T-227 standard test.

The paper substrate of the present invention may contain from 1 to 100 wt% cellulose fibers originating from hardwood species based upon the total amount of cellulose fibers in the paper substrate. This range includes 1, 2, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, and 100wt%, including any and all ranges and subranges therein, based upon the total amount of cellulose fibers in the paper substrate.

The paper substrate may alternatively or overlappingly contain from 0.01 to 100 wt% fibers from hardwood species, preferably from 60 to 90wt% based upon the total weight of the paper substrate. The paper substrate contains not more than 0.01, 0.05, 0.1, 0.2, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 99 and 100wt% fines based upon the total weight of the paper substrate, including any and all ranges and subranges therein.

The paper substrate may contain fibers from hardwood species that have a Canadian Standard Freeness (csf) of from 300 to 750, more preferably from 450 to

750 csf. This range includes 300, 310, 320, 330, 340, 350, 360, 370, 380, 390, 400, 410, 420, 430, 440, 450, 460, 470, 480, 490, 500, 510, 520, 530, 540, 550, 560, 570, 580, 590, 600, 610, 620, 630, 640, 650, 660, 670, 680, 690, 700, 710, 720, 730, 740, and 750 csf, including any and all ranges and subranges therein. Canadian Standard Freeness is as measured by TAPPI T-227 standard test.

When the paper substrate contains both hardwood and softwood fibers, it is preferable that the hardwood/softwood ratio be from 0.001 to 1000, preferably from 90/10 to 30/60. This range may include 0.001, 0.002, 0.005, 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1, 2, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 200, 300, 400, 500, 600, 700, 800, 900, and 1000 including any and all ranges and subranges therein and well as any ranges and subranges therein the inverse of such ratios.

Further, the softwood and/or hardwood fibers contained by the paper substrate of the present invention may be modified by physical and/or chemical means. Examples of physical means include, but is not limited to, electromagnetic and mechanical means. Means for electrical modification include, but are not limited to, means involving contacting the fibers with an electromagnetic energy source such as light and/or electrical current. Means for mechanical modification include, but are not limited to, means involving contacting an inanimate object with the fibers. Examples of such inanimate objects include those with sharp and/or dull edges. Such means also involve, for example, cutting, kneading, pounding, impaling, etc means.

Examples of chemical means include, but is not limited to, conventional chemical fiber modification means including crosslinking and precipitation of complexes thereon. Examples of such modification of fibers may be, but is not

limited to, those found in the following patents 6,592,717, 6,592,712, 6,582,557, 6,579,415, 6,579,414, 6,506,282, 6,471,824, 6,361,651, 6,146,494, H1,704, 5,731,080, 5,698,688, 5,698,074, 5,667,637, 5,662,773, 5,531,728, 5,443,899, 5,360,420, 5,266,250, 5,209,953, 5,160,789, 5,049,235, 4,986,882, 4,496,427, 4,431,481, 4,174,417, 4,166,894, 4,075,136, and 4,022,965, which are hereby incorporated, in their entirety, herein by reference. Further modification of fibers is found in United States Patent Applications having Application Numbers 11/358,543 filed February 21, 2006; 11/445,809, filed June 2, 2006, and 11/810,117 filed June 2, 2007, which may include the addition of optical brighteners (i.e. OBAs), as discussed therein and which are hereby incorporated, in their entirety, herein by reference.

The paper substate may contain a combination of hardwood fibers, softwood fibers and “fines” fibers. Sources of “Fines” may be found in SaveAll fibers, recirculated streams, reject streams, waste fiber streams. The amount of “fines” present in the paper substrate can be modified by tailoring the rate at which such streams are added to the paper making process.

The paper substrate contains from 0.01 to 100 wt% fines, preferably from 0.01 to 50wt%, most preferably from 0.01 to 15wt% based upon the total weight of the substrate. The paper substrate contains not more than 0.01, 0.05, 0.1, 0.2, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95 and 100wt% fines based upon the total weight of the paper, including any and all ranges and subranges therein.

The paper substrate may alternatively or overlappingly contain from 0.01 to 100 wt% fines, preferably from 0.01 to 50wt%, most preferably from 0.01 to 15wt% based upon the total weight of the fibers contained by the paper substrate. The paper substrate contains not more than 0.01, 0.05, 0.1, 0.2, 0.5, 1, 2, 3, 4, 5, 6,

7, 8, 9, 10, 12, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95 and 100wt% fines based upon the total weight of the fibers contained by the paper substrate, including any and all ranges and subranges therein.

The paper substrate contains at least one silicon-containing compound. Examples of silicon containing compounds are silicate-containing compounds. Examples of silicate-containing compounds are silicas (such as colloids and/or sols), borosilicates, and aluminosilicates (aluminum silicates). The aluminum silicate may be in salt form. An example of an aluminum silicate-containing compound and/or salt is sodium aluminum silicate. Other such salts include those formed with alkali metals, alkaline metals, transition metals and/or heavy metal salts, more specifically such salts with the aluminum silicate.

The silicon containing compound may be in any form. The silicon containing compound may be in the form of a colloid, gel, sol, and/or a zeolite. Preferably the silicon-containing compound is a silicate containing compound in the form of a colloid, gel, sol, and/or a zeolite. More preferably, the silicon-containing compound is an aluminum silicate containing compound and/or salt in the form of a colloid, gel, sol, and/or a zeolite. Most preferably, the silicon-containing compound is a sodium aluminum silicate in the form of a colloid, gel, sol, and/or a zeolite.

The silicon containing compound may be any particle size. In one embodiment, the silicon containing compound may be greater than a micron. In another embodiment, the silicon containing compound may be less than a micron. Accordingly, particle size of the silicon containing compound may be more than 10, 9, 8, 7, 6, 5, 4, 3, 2, and 1 microns, including any and all ranges and subranges therein. Also, the particle size of the silicon containing compound may be less

than 1, 2, 3, 4, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 150, 200, 300, 400, 500, 600, 700, 800, 900, and 1000 nanometers, including any and all ranges therein.

The paper substrate of the present invention may contain the silicon containing compound at any amount. Preferably, the paper substrate contains not more than 25wt%, more preferably not more than 10wt%, most preferably not more than 5wt% of the silicon-containing compound based upon the total weight of the substrate. This amount of the silicon-containing compound contained in the substrate may include not more than 25, 24, 23, 22, 21, 20, 19, 18, 17, 16, 15, 14, 13, 12, 11, 10, 9, 8, 7, 6, 5, 4, 3, 2, and 1wt% based upon the total weight of the substrate, including any and all ranges and subranges therein.

The paper substrate of the present invention may contain a filler. Examples of fillers include, but are not limited to; clay, calcium carbonate, calcium sulfate hemihydrate, and calcium sulfate dehydrate. A preferable filler, when used, is calcium carbonate. Calcium carbonate may be ground calcium carbonate and/or precipitated calcium carbonate (PCC). Commercial sources of such a filler include those available under the Albacar name, such as Albacar HO, Albacar PO, and Albacar LO, all available from Specialty Minerals Inc.

In one embodiment of the present invention, the filler, preferably calcium carbonate is contained therein the paper substrate of the present invention at an amount that is not more than 50wt%, more preferably not more than 45wt%, most preferably not more than 25wt% upon the total weight of the substrate. This amount of the filler contained in the substrate may include not more than 50, 45, 40, 35, 30, 25, 24, 23, 22, 21, 20, 19, 18, 17, 16, 15, 14, 13, 12, 11, 10, 9, 8, 7, 6, 5, 4, 3, 2, and 1wt% based upon the total weight of the substrate, including any and all ranges and subranges therein.

In another embodiment of the present invention, the substrate contains the filler and the silicon-containing compound. The paper substrate preferably contains the filler and silicon containing compound at a filler:silicon-containing compound weight ratio that is not more than 50:1, preferably not more than 25:1, more preferably not more than 20:1, most preferably not more than 10:1. The filler:silicon-containing compound weight ratio may be not more than 50:1, 40:1, 35:1, 30:1, 25:1, 20:1, 19:1, 18:1, 17:1, 16:1, 15:1, 14:1, 13:1, 12:1, 11:1, 10:1, 9:1, 8:1, 7:1, 6:1, 5:1, 4:1, 3:1, 2:1, 1:1, 1:2, 1:4, 1:5, and 1:10, including any and all ranges and subranges therein.

The paper substrate may contain at least one sizing agent. A sizing agent is the substance added to a paper to make it moisture or water-resistant in varying degrees. Examples of sizing agents can be found in the "Handbook for pulp and paper technologists" by G.A. Smook (1992), Angus Wilde Publications, which is hereby incorporated, in its entirety, by reference. Preferably, the sizing agent is a surface sizing agent. Preferable examples of sizing agents are starch and polyvinyl alcohol (PVOH), as well as polyvinylamine, alginate, carboxymethyl cellulose, etc. A preferable example of a method of making paper containing a sizing agent is found in United States Patent Application having Application number 11/665,004 filed January 17, 2007, as well as those methods described in United States Published Patent Applications having Publication numbers 2004-0065423 and 20 05-0056391, which are all also hereby incorporated, in their entirety, herein by reference.

The paper substrate preferably has any opacity, but preferably opacity of from 85 to 100%, more preferably from 90 to 97%. This range includes 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, and 100%, including any and all ranges and subranges therein. The opacity is measured by test TAPPI t-425.

The paper substrate of the present invention may have any CIE whiteness, but preferably has a CIE whiteness of greater than 70, more preferably greater than 80, most preferably greater than 90. The CIE whiteness range may be greater than or equal to 70, 80, 90, 100, 110, 120, 125, 130, 135, 140, 145, 150, 155, 160, 65, 170, 175, 180, 185, 190, 195, and 200 CIE whiteness points, including any and all ranges and subranges therein. Examples of measuring CIE whiteness and obtaining such whiteness in a papermaking fiber and paper made therefrom can be found, for example, in United States Patent 6,893,473, which is hereby incorporated, in its entirety, herein by reference. Further examples of measuring CIE whiteness and obtaining such whiteness in a papermaking fiber and paper made therefrom can be found, for example, in United States Patent Applications having Application Numbers 11/358,543 filed February 21, 2006; 11/445,809, filed June 2, 2006, and 11/810,117 filed June 2, 2007, which may include the addition of optical brighteners (i.e. OBAs), as discussed therein and which are hereby incorporated, in their entirety, herein by reference.

The paper substrate of the present invention may have any ISO brightness, but preferably greater than 80, more preferably greater than 92, most preferably greater than 95 ISO brightness points. The ISO brightness may be preferably from 80 to 100, more preferably from 90 to 100, most preferably from 95 to 100 ISO brightness points. This range include greater than or equal to 80, 85, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, and 100 ISO brightness points, including any and all ranges and subranges therein. Examples of measuring ISO brightness and obtaining such brightness in a papermaking fiber and paper made therefrom can be found, for example, in United States Patent 6,893,473, which is hereby incorporated, in its entirety, herein by reference. Further examples of measuring CIE whiteness and obtaining such whiteness in a papermaking fiber and paper made therefrom can be found, for example, in United States Patent Applications having Application Numbers 11/358,543 filed February 21, 2006; 11/445,809,

filed June 2, 2006, and 11/810,117 filed June 2, 2007, which may include the addition of optical brighteners (i.e. OBAs), as discussed therein and which are hereby incorporated, in their entirety, herein by reference.

The substrate of the present invention may have any bulk, but preferably the bulk is at least 1, more preferably at least 1.3, most preferably at least 1.5 cm^3/g . The bulk may be at least 1, 1.1, 1.15, 1.2, 1.25, 1.3, 1.35, 1.4, 1.45, 1.5, 1.55, and 1.6 cm^3/g , including any and all ranges and subranges therebetween.

The substrate of the present invention may have any Gurley porosity, but preferably the Gurley Porosity is less than 20 Gurley seconds, more preferably less than 15 Gurley seconds. The Gurley Porosity may be not more than 20, 19, 18, 17, 16, 15, 14, 13, 12, 11, 10, 9, 8, 7, 6, and 5 Gurley seconds, including any and all ranges and subranges therebetween. The Gurley Porosity may be measured according to TAPPI T460.

The substrate of the present invention may have any Internal Bond. The Internal Bond of the substrate may be from 10 to 350 $\text{ft-lbs} \times 10^{-3}/\text{in}^2$. This range includes 10, 11, 12, 13, 14, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 105, 110, 115, 120, 125, 130, 135, 140, 145, 150, 160, 165, 170, 175, 180, 185, 190, 195, 200, 210, 220, 230, 240, 250, 260, 270, 280, 290, 300, 310, 320, 330, 340, and 350 $\text{ft-lbs} \times 10^{-3}/\text{in}^2$, including any and all ranges and subranges therein. The internal bond is Scott Bond as measured by test TAPPI t-569.

Both of the above-mentioned CD and MD internal bond as measured by Scott Bond test TAPPI t-569 may also be measured in J/m^2 . The conversion factor to convert $\text{ft-lbs} \times 10^{-3}/\text{in}^2$ to J/m^2 is 2. Therefore, to convert an internal bond of 100 $\text{ft-lbs} \times 10^{-3}/\text{in}^2$ to J/m^2 , simply multiply by 2 (i.e. $100 \text{ ft-lbs} \times 10^{-3}/\text{in}^2 \times 2 \text{ J}/\text{m}^2 / 1 \text{ ft-lbs} \times 10^{-3}/\text{in}^2 = 200 \text{ J}/\text{m}^2$). All of the above-mentioned ranges in $\text{ft-lbs} \times$

$10^{-3}/\text{in}^2$, therefore, may then include the corresponding ranges for internal bonds in J/m^2 as follows.

The paper substrate of the present invention may have any GM Gurley Stiffness. The GM Gurley Stiffness may be at least 30. The GM Gurley Stiffness may less than 120. The GM Gurley Stiffness may be 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95 and 100. A suitable technique for determining the Gurley stiffness is set forth in TAPPI T 543. For the purposes of the present invention, the stiffness values are measured and expressed in terms of Standard Gurley Units (SGU) (traditionally reported as milligrams of force).

Young's Modulus is defined as the change in specimen stress per unit change in strain expressed in pounds per square inch. The stress-strain relationship is expressed as the slope of the initial linear portion of the curve where stress is the y-axis and strain is the x-axis. The substrate of the present invention may have any Young's Modulus. The substrate may have a Young's Modulus of at least 100 pounds per square inch. Further, the substrate may have a Young's Modulus of not more than 400 pounds per square inch. The Young's Modulus of the substrate may be 100, 125, 150, 175, 200, 225, 250, 275, 300, 325, 350, 375, and 400 pounds per square inch, including any and all ranges and subranges therein.

The paper substrate according to the present invention may have any Sheffield Smoothness, preferably less than 400 Sheffield Units (SU). However, the preferred Sheffield Smoothness will be driven by the end product paper substrate's intended use. Preferably, the paper substrate according to the present invention may have a Sheffield Smoothness of less than 350 SU, more preferably less than 250 SU, most preferably less than 200 SU, as measured by TAPPI test method T 538 om-1, including any and all ranges and subranges therein. The paper substrate may have a Sheffield Smoothness that is 400, 350, 300, 275, 250,

225, 200, 190, 180, 170, 160, 150, 140, 130, 120, 110, 100, 90, 80, 70, 60, 50, 40, 30, 20, and 10, including any and all ranges and subranges therein.

The substrate of the present invention may have any GM Tensile. The GM tensile of the substrate may be less than 50, more preferably less than 45, most preferably less than 35 w pounds per inch. The GM tensile of the substrate may be at least 3, more preferably at least 5, most preferably at least about 10 w pounds per inch. The GM Tensile of the substrate may be 5, 6, 7, 8, 9, 10, 12, 15, 17, 20, 25, 30, 35, 40, 45, and 50 w pounds per inch, including any and all ranges and subranges therein. Examples of measuring GM tensile can be found in US Patent 6919111, which are hereby incorporated, in their entirety, herein by reference.

The paper substrate of the present invention preferably has an improved print performance and improved runnability (e.g. print press performance). Print performance may be measured by determining improved ink density, dot gain, trapping, print contrast, and/or print hue, to name a few. Colors traditionally used in such performance tests include black, cyan, magenta and yellow, but are by no means limited thereto. Press performance may be determined by print contamination determinations through visual inspection of press systems, blankets, plates, ink system, etc. Contamination usually consists of fiber contamination, coating or sizing contamination, filler or binder contamination, piling, etc. The paper substrate of the present invention has an improved print performance and/or runnability as determined by each or any one or combination of the above attributes.

Another measurement of print performance is a print-through performance characteristic which is fully explained, including methodology and test procedures, in the Examples below. The present inventive paper substrate has a print through performance that is preferably less than 0.02, more preferably less

than 0.015, most preferably less or equal to 0.01. This print through performance includes less than 0.02, 0.019, 0.018, 0.017, 0.016, 0.015, 0.014, 0.013, 0.012, 0.011, 0.01, 0.008, 0.006, 0.004, 0.002, 0.001, 0.0008, 0.0005, and 0.0001, including any and all ranges and subranges therein.

The paper substrate according to the present invention may be made off of the paper machine having either a high or low basis weight, including basis weights of at least 10 lbs/3000 square foot, preferably from at least 20 to 500 lbs/3000 square foot, more preferably from at least 40 to 325 lbs/3000 square foot. The range includes 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, 200, 210, 220, 230, 240, 250, 260, 270, 280, 290, 300, 310, 320, 330, 340, 350, 360, 370, 380, 390, 400, 410, 420, 430, 440, 450, 460, 470, 480, 490, and 500 lbs/3000 square foot, including any and all ranges and subranges therein.

The paper substrate according to the present invention may have an apparent density of from 1 to 20, preferably 4 to 14, most preferably from 5 to 10 lb/3000sq. ft.per 0.001 inch thickness. The range includes 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, and 20 lb/3000sq. ft.per 0.001 inch thickness, including any and all ranges and subranges therein.

The paper substrate of the present invention, when containing an optional bulking agent (discussed in much more detail below), preferably has an increase in bulk that is at least 3%, as compared to that of a paper substrate not containing a bulking agent. Preferably the increase in bulk is from 3 to 20%. This range includes 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, and 20%, including any and all ranges and subranges therein.

The paper substrate according to the present invention may have a caliper of from 2 to 35 mil, preferably from 5 to 30mil, more preferably from 10 to 28 mil, most preferably from 12 to 24 mil. The range includes 2, 3, 4, 5, 6, 7, 8, 9, 01, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, and 35 mil, including any and all ranges and subranges therein.

The paper substate preferably has an I-beam structure. This I-beam structure is produced as a result of the selective placement of the sizing agent within and/or on the paper. Such effect is described in United States Patent Application having Application number 11/665,004 filed January 17, 2007, as well as those methods described in United States Published Patent Applications having Publication numbers 2004-0065423 and 2005-0056391, which are all also hereby incorporated, in their entirety, herein by reference.

The paper substrate of the present invention may also include optional substances including retention aids, binders, fillers, thickeners, and preservatives. Examples of binders include, but are not limited to, Amres (a Kymene type), Bayer Parex, polychloride emulsion, polyacrylamide, modified polyacrylamide, polyol, polyol carbonyl adduct, ethanedial/polyol condensate, polyamide, epichlorohydrin, glyoxal, glyoxal urea, titanium dioxide, ethanedial, aliphatic polyisocyanate, isocyanate, 1,6 hexamethylene diisocyanate, diisocyanate, polyisocyanate, polyester, polyester resin, polyacrylate, polyacrylate resin, acrylate, and methacrylate.

The paper substrate of the present invention may contain retention aids selected from the group consisting of coagulation agents, flocculation agents, and entrapment agents dispersed within the bulk and porosity enhancing additives cellulosic fibers.

The paper substrate of the present invention may contain any amount of the optional substances. The substrate may contain from 0.001 to 20 wt% of the optional substances based on the total weight of the substrate, preferably from 0.01 to 10 wt %, most preferably 0.1 to 5.0wt%, of each of at least one of the optional substances. This range includes 0.001, 0.002, 0.005, 0.006, 0.008, 0.01, 0.02, 0.03, 0.04, 0.05, 0.1, 0.2, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 2, 4, 5, 6, 8, 10, 12, 14, 15, 16, 18, and 20wt% based on the total weight of the substrate, including any and all ranges and subranges therein.

The paper substrate may be made by contacting the silicon containing compound with the cellulose fibers. Still further, the contacting may occur at acceptable concentration levels that provide the paper substrate of the present invention to contain any of the above-mentioned amounts of cellulose and silicon containing compound.

The paper substrate of the present application may be made by contacting the substrate with the silicon containing compound. The contacting may occur anytime in the papermaking process including, but not limited to the wet end, head box, size press, water box, and/or coater. Further addition points include machine chest, stuff box, and suction of the fan pump. The cellulose fibers, silicon containing compound, and/or optional components may be contacted serially, consecutively, and/or simultaneously in any combination with each other.

Preferably, the paper substrate is made by having at least one silicon containing compound contacted with the fibers at the wet end of the papermaking process. A representative wet-end of papermaking is described in the examples below. In one embodiment, filler and silicon containing compound are added to the cellulosic fibers at the wet end, consecutively and/or simultaneously, so long as the above-mentioned amounts of filler and silicon containing compound are

obtained in the substrate. In an additional embodiment, OBA and/or black dye is added to the fibers at the wet end and/or before the wet end. Further, OBA and/or black dye may be added at the size press and/or coated thereon. Any manner of applying the OBA and/or black dye is acceptable so long as the above mentioned brightness, opacity and/or CIE whiteness attributes are bestowed on the substrate. It is preferably that the above mentioned brightness, opacity and/or CIE whiteness attributes are bestowed on the substrate using less OBA and/or black dye than conventionally used and contained in conventional paper substrates. In one embodiment, there is at least a 2% decrease in the OBA and/or black dye contained in the substrate of the present invention as compared to conventional substrates that do not contain the silicon-containing compound described herein at the above-mentioned amounts. This decrease is preferably at least 5%, more preferably at least 10%, most preferably at least 15%. In one embodiment the above-mentioned reductions in OBA and/or black dye contained in the substrate occurs at the same time as the above-mentioned targeted opacity, brightness, and/or CIE Whiteness is achieved by the paper substrate of the present invention.

The paper substrate may be pressed in a press section containing one or more nips. However, any pressing means commonly known in the art of papermaking may be utilized. The nips may be, but is not limited to, single felted, double felted, roll, and extended nip in the presses. However, any nip commonly known in the art of papermaking may be utilized.

The paper substrate may be dried in a drying section. Any drying means commonly known in the art of papermaking may be utilized. The drying section may include and contain a drying can, cylinder drying, Condebelt drying, IR, or other drying means and mechanisms known in the art. The paper substrate may be dried so as to contain any selected amount of water. Preferably, the substrate is dried to contain less than or equal to 10% water.

The paper substrate may be passed through a size press, where any sizing means commonly known in the art of papermaking is acceptable. The size press, for example, may be a puddle mode size press (e.g. inclined, vertical, horizontal) or metered size press (e.g. blade metered, rod metered). At the size press, sizing agents such as binders may be contacted with the substrate. Optionally these same sizing agents may be added at the wet end of the papermaking process as needed. After sizing, the paper substrate may or may not be dried again according to the above-mentioned exemplified means and other commonly known drying means in the art of papermaking. The paper substrate may be dried so as to contain any selected amount of water. Preferably, the substrate is dried to contain less than or equal to 10% water.

The paper substrate may be calendered by any commonly known calendaring means in the art of papermaking. More specifically, one could utilize, for example, wet stack calendering, dry stack calendering, steel nip calendaring, hot soft calendaring or extended nip calendering, etc.

The paper substrate may be microfinished according to any microfinishing means commonly known in the art of papermaking. Microfinishing is a means involving frictional processes to finish surfaces of the paper substrate. The paper substrate may be microfinished with or without a calendaring means applied thereto consecutively and/or simultaneously. Examples of microfinishing means can be found in United States Published Patent Application 20040123966 and references cited therein, which are all hereby, in their entirety, herein incorporated by reference.

The paper board and/or substrate of the present invention may also contain at least one coating layer, including two coating layers and a plurality thereof. The

coating layer may be applied to at least one surface of the paper board and/or substrate, including two surfaces. Further, the coating layer may penetrate the paper board and/or substrate. The coating layer may contain a binder. Further the coating layer may also optionally contain a pigment. Other optional ingredients of the coating layer are surfactants, dispersion aids, and other conventional additives for printing compositions.

The substrate and coating layer are contacted with each other by any conventional coating layer application means, including impregnation means. A preferred method of applying the coating layer is with an in-line coating process with one or more stations. The coating stations may be any of known coating means commonly known in the art of papermaking including, for example, brush, rod, air knife, spray, curtain, blade, transfer roll, reverse roll, and/or cast coating means, as well as any combination of the same.

The coated substrate may be dried in a drying section. Any drying means commonly known in the art of papermaking and/or coatings may be utilized. The drying section may include and contain IR, air impingement dryers and/or steam heated drying cans, or other drying means and mechanisms known in the coating art.

The coated substrate may be finished according to any finishing means commonly known in the art of papermaking. Examples of such finishing means, including one or more finishing stations, include gloss calendar, soft nip calendar, and/or extended nip calendar.

In one embodiment of the present invention, the substrate may include bulking agents such as those described in United States Published Patent Application Numbers 2005-0056391 and 2007-0044929; as well as United States

Patent Application Number 60/926,214 filed April 25, 2007, entitled “EXPANDABLE MICROSPHERES AND METHODS OF MAKING AND USING THE SAME”, which are all hereby incorporated, in their entirety, herein by reference.

As used throughout, ranges are used as a short hand for describing each and every value that is within the range, including all subranges therein.

Numerous modifications and variations on the present invention are possible in light of the above teachings. It is, therefore, to be understood that within the scope of the accompanying claims, the invention may be practiced otherwise than as specifically described herein.

All of the references, as well as their cited references, cited herein are hereby incorporated by reference with respect to relative portions related to the subject matter of the present invention and all of its embodiments

The present invention is explained in more detail with the aid of the following embodiment example which is not intended to limit the scope of the present invention in any manner.

Examples

Example 1

Paper substrates were made under standard dynamic sheet formation conditions to simulate the addition of various amounts (0 to 30wt% based on the weight of the substrate) of calcium carbonate (Albacar), aluminum silicate (Alusil), or mixtures thereof (i.e. Blend at from 20 to 55% aluminum silicate based upon the total weight of the filler (i.e. aluminum silicate and calcium carbonate and optionally titanium dioxide). Then, the substrates were optionally calendared. The Bulk, Smoothness, Gurley Porosity, Brightness, CIE Whiteness, Internal Bond, GM Tensile, Young's Modulus, and GM Gurley Stiffness of each substrate was measured. Results of these studies are found in Figures 1-35.

Example 2.

50lbs/ton of an aluminum silicate (i.e. Alusil) was added to the Blend Chest and 450 lbs/ton of a calcium carbonate (90/10 blend of Albacar HO/Albacar PO) was added to the Stuff Box to produce a paper substrate according to the present invention under standard papermaking conditions. As a control, the same process was used to make a control substrate except that no aluminum silicate was added and only calcium carbonate was added in its place at similar quantities, i.e. the total calcium carbonate was 500lbs/ton. Accordingly, these conditions represent when a silicon containing compound is added at the wet end of a papermaking process. The print performance of the resultant papers were measured according to the following methods and definitions. Further, Printhrough and Strikethrough calculations are found in Table 1 and represented performance enhancements are shown in Figure 36. The blanket used was Blankets Day 3000 and the ink used was Ink Sun Heatset Offset.

Table 1: Printhrough and strikethrough performances.

Reel	Blank Area	Black Density	Showthrough	Covered black	Showthrough Total	Strikethrough due to opacity	Printhrough due to Ink Penetration
control	0.05	1.2825	0.1025	0.0825	0.0525	0.0325	0.02
invention	0.05	1.2875	0.0925	0.0825	0.0425	0.0325	0.01

Inkjet Print-Through Test methodology For the Paper substrate of the present invention

1.0 Definitions

- 1.1 *Print-Through* – The combination of show-through and strike-through. This happens when you print something on one side of a sheet of paper and a ghost image appears on the other side. The measurement combines the wet ink traveling through the pores and gaps in the paper, and the dark ink showing through low opacity areas of the sheet.
- 1.2 *Show-Through* – Print-through due to lack of opacity.
- 1.3 *Strike-Through* – Print-through due to ink penetration.
- 1.4 *Blank area* – A section of the sheet that has not been printed
- 1.5 *Back of Print* – The area directly behind the printed area on the back side of the sheet. (This is where print-through may be visible)
- 1.6 *Covered Print* – the area of the printed area covered by a single sheet of unprinted paper of the same type.
- 1.7 *Show-Through Ratio* – The ratio of Print-through density to the printed density. This is used to quantify the ability of a paper to be duplexed.

2.0 Test Method

2.1 Papers tested:

HP Advanced (20#)
 HP Multipurpose ColorLok™ (20#)
 HP Multipurpose previous generation (20#)
 Office Depot Premium Multipurpose (20#)
 Xerox Multipurpose (20#)
 Hammermill Ultra Multipurpose P (20#)
 MaxBrite Multipurpose (20#)
 Staples Multipurpose Bright White (20#)

2.2 Equipment - Densitometer (X-rite 518)

2.3 Procedure

- 2.3.1 Print a black box that is 150mm by 450mm using the hp deskjet 6122 printer. Prints are made using the plain paper mode and varying the print quality settings (draft, fast normal, normal, best).
- 2.3.2 Using the densitometer, measure density of the printed area, back of print, blank area, and covered print. Measure 3 times per area per sheet.
- 2.3.3 Additional HST, TAPPI Opacity, and Gurley Porosity tests were done to determine if they have an affect on print-through.

2.4 Equations

(Eq. 1) *"Print-Through Density" = Back of Print Density (-) Blank Area density*

(Eq. 2) *"Show-Through Density" = Covered Print Density (-) Blank Area density*

(Eq. 3) *"Strike-Through Density" = Back of Print Density (-) Covered Print Density*

(Eq. 4) *"Print-Through Ratio" = $\frac{\text{Back of Print Density (-) Blank Area Density}}{\text{Printed Area Density (-) Blank Area Density}}$*

Exemplified Modifications of the above test method

Definition and Description of Print Through Measurement

Definitions

- 2.5 *Print-Through* – The combination of show-through and strike-through. This happens when you print something on one side of a sheet of paper and a ghost image appears on the other side. The measurement combines the wet ink traveling through the pores and gaps in the paper, and the dark ink showing through low opacity areas of the sheet.
- 2.6 *Show-Through* – Print-through due to lack of opacity.
- 2.7 *Strike-Through* – Print-through due to ink penetration.
- 2.8 *Unprinted area* – A “infinitely opaque” (usually 6 sheets) pad of plain paper identical to the printed sample.
- 2.9 *Back of Print* – The area directly behind the printed area on the back side of the sheet. (This is where print-through may be visible)
- 2.10 *Covered Print* – the area of the printed area covered by a single sheet of unprinted paper of the same type.
- 2.11 *Show-Through Ratio* – The ratio of Print-through density to the printed density.

Test Method

The generic test method for print through measurement can be employed on virtually any light weight paper and ink system. All that is required is a solid print area of consistent ink density, 6 unprinted sheets of the printed material and a calibrated densitometer.

Equipment - Densitometer (X-rite 518)

Using the densitometer, measure density of the printed area, the unprinted blank area of the sheet, back of print, blank area, and covered print. Measure 3 times per area per test area and average the

Note: All density measurements to be made on single thickness sheets backed by the infinitely opaque sample pad.

Equations

(Eq. 1) *"Print-Through Density" = Back of Print Density (-) Plain Sheet density*

(Eq. 2) *"Show-Through Density" = Covered Print Density (-) Plain sheet density*

(Eq. 3) *"Strike-Through Density" = Back of Print Density (-) Covered Print Density*

(Eq. 4) *"Print-Through Ratio" = $\frac{\text{Back of Print Density (-) Blank Area Density}}{\text{Printed Area Density (-) Blank Area Density}}$*

Web offset procedure 1

1. A blue-black solid consisting of 100% black and 100% cyan solids is printed near the center of web. Target ink densities are 1.2 and 1.1 for Black and Cyan ink films respectively.
2. 3 consecutive sheets are sampled and measured. 3 readings per sheet are averaged. The 9 readings for each measurement are averaged to calculate print through, show through, strike through, and print-through ratio as described above.

Prufbau procedure 2

1. 2.5-3 g of Huber cyan proofing and mottling ink (400 0083) is applied to the ink distribution system and distributed for 1 minute
2. A blanket covered print is brought into contact with the ink distribution system and inked for an additional 30 second.
3. The inked print form is transferred to the first printing station.
4. A paper sample (mounted on the appropriate sample carrier) is inserted into the sample track
5. The sample is printed at 23 deg C 1200N pressure and 2 m/sec. Cyan density should be 1.1 +/- 0.1
6. Subsequent samples can be run by re-inking the print form. A small amount of replenishment ink (0.1-0.2 gm) is added to the distribution system and the print form is reinked without cleaning from subsequent print.
7. Samples should be left to dry overnight before density measurements are made.
8. 3 density readings per sample are made and averaged to calculate the results.

What is claimed is:

1. A paper substrate, comprising
a silicon containing compound; and a plurality of cellulosic fibers.
2. The paper substrate according to Claim 1, wherein the silicon-containing compound is a silicate containing compound.
3. The paper substrate according to Claim 1, wherein the wherein the silicon-containing compound is an aluminum silicate-containing compound.
4. The paper substrate according to Claim 1, wherein the wherein the silicon-containing compound is a sodium aluminum silicate.
5. The paper substrate according to Claim 1, wherein the particle size of the silicon containing compound is at least one micron.
6. The paper substrate according to Claim 1, wherein the particle size of the silicon containing compound is at most 1 micron.

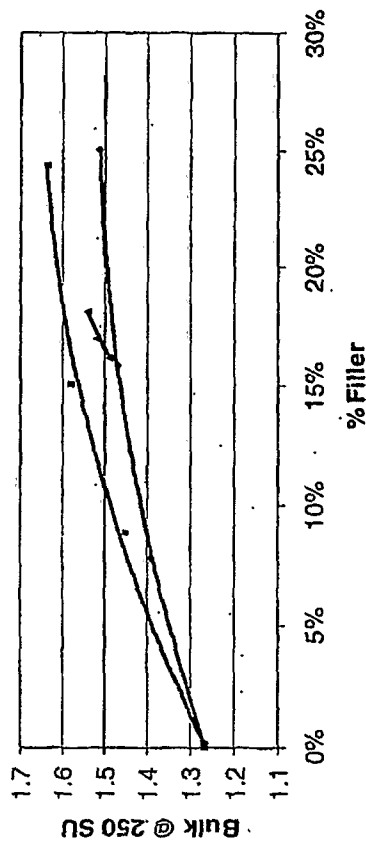
7. The paper substrate according to Claim 1, wherein the weight ratio of the silicon-containing compound is an aluminum silicate-compound and the filler is calcium carbonate.
8. The paper substrate according to Claim 7, wherein the filler is precipitated calcium carbonate.
9. The paper substrate according to Claim 8, wherein the weight ratio of the precipitated calcium carbonate to aluminum silicate-compound is at most 10:1.
10. The paper substrate according to Claim 9, wherein the substrate has an ISO Brightness of at least 90 and a CIE whiteness of at least 1.
11. The paper substrate according to Claim 9, wherein the substrate has a printthrough performance of less than 0.02.

12. The paper substrate according to Claim 11, wherein the substrate has a print through performance of at most 0.01.
13. The paper substrate according to Claim 12, further comprising titanium dioxide.
14. A method of making the paper substrate according to Claim 12, comprising contacting aluminum silicate containing compound and precipitated calcium chloride with at least one cellulosic fiber.
15. The method according to Claim 14, further comprising premixing the aluminum silicate containing compound with the precipitated calcium chloride.
16. The method according to Claim 14, wherein the contacting occurs at a headbox.
17. The method according to Claim 14, wherein the contacting occurs at a size press.

18. The method according to Claim 14, wherein the contactin~~er~~
coater.
19. The method according to Claim 14, further comprising c~~a~~
substrate to Sheffield Smoothness that is not more than 3
20. The method according to Claim 14, comprising contactin~~er~~
silicate containing compound and precipitated calcium c~~o~~
least one cellulosic fiber such that the weight ration of p~~r~~
calcium chloride to aluminum silicate containing compo~~u~~
than 10:1.

Bulk

Wet End Filler Comparison
Albacar LO vs Alusil

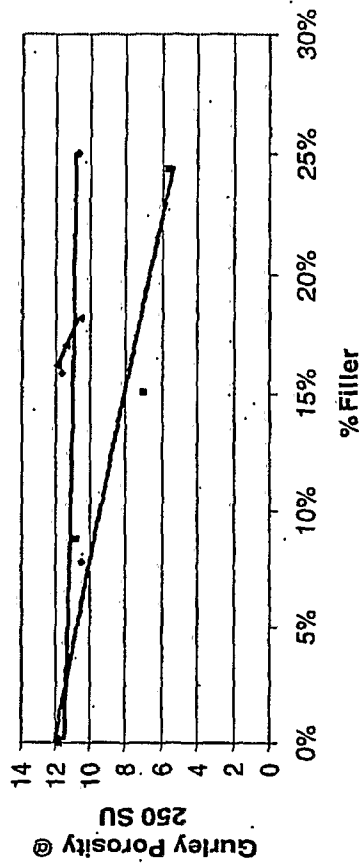


• Albacar LO • Alusil • Blend

@ const.
smoothness

Porosity

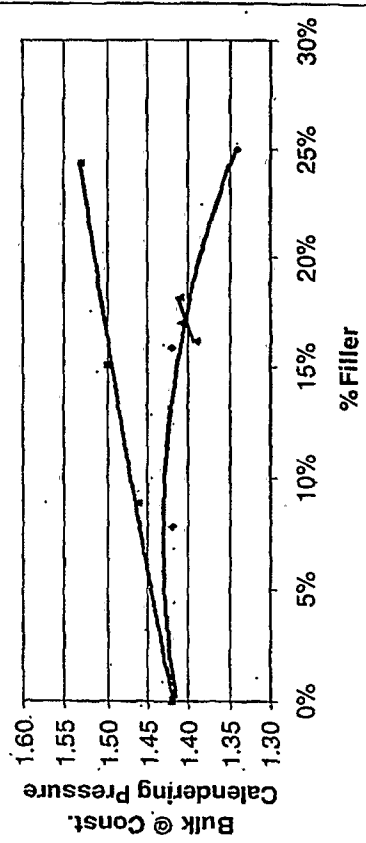
Wet End Filler Comparison
Albacar LO vs Alusil



• Albacar LO • Alusil • Blend

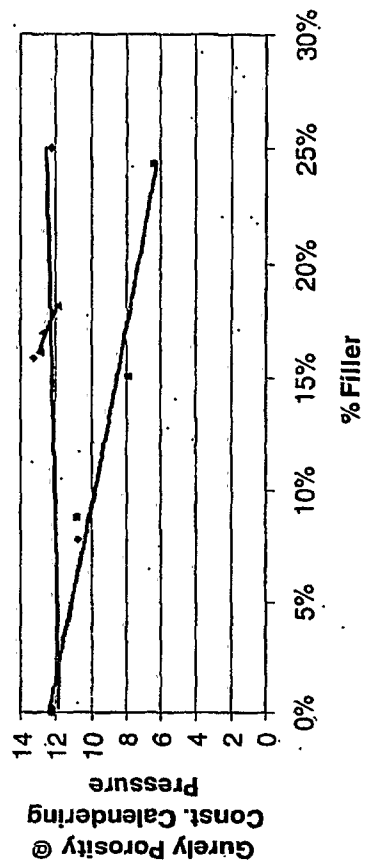
@ const.
calendering

Wet End Filler Comparison
Albacar LO vs Alusil



• Albacar LO • Alusil • Blend

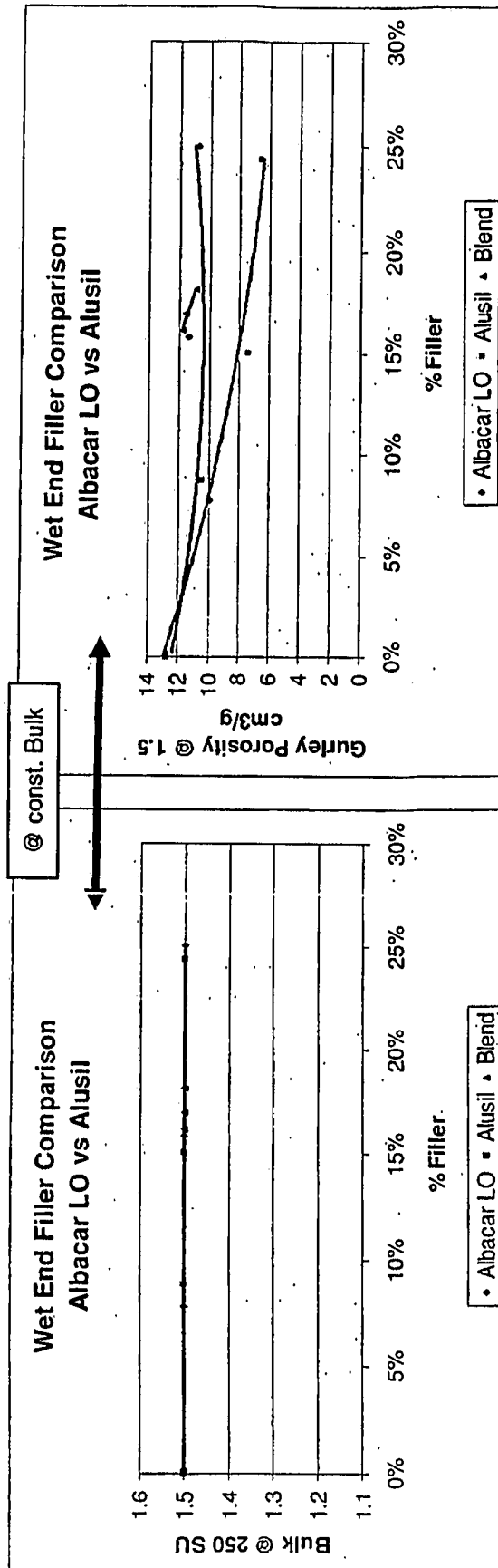
Wet End Filler Comparison
Albacar LO vs Alusil



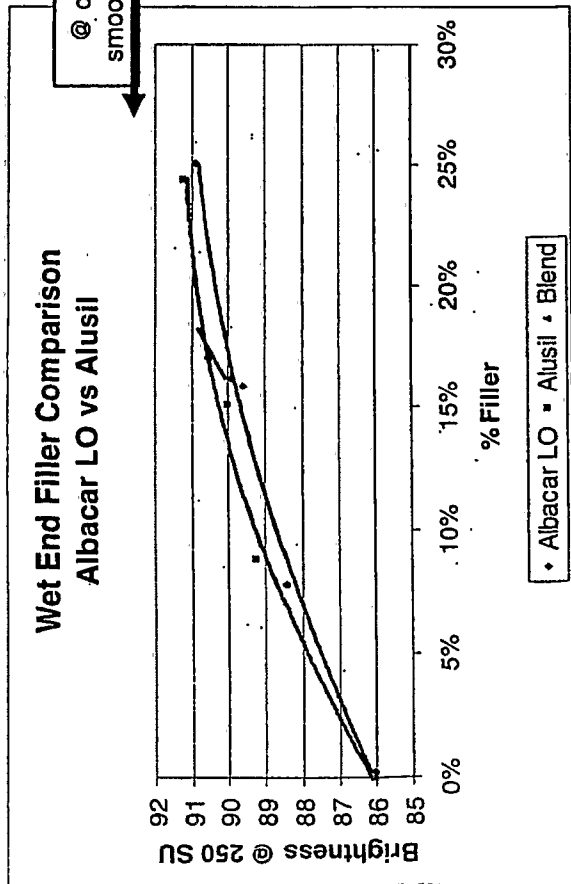
• Albacar LO • Alusil • Blend

Bulk

Porosity

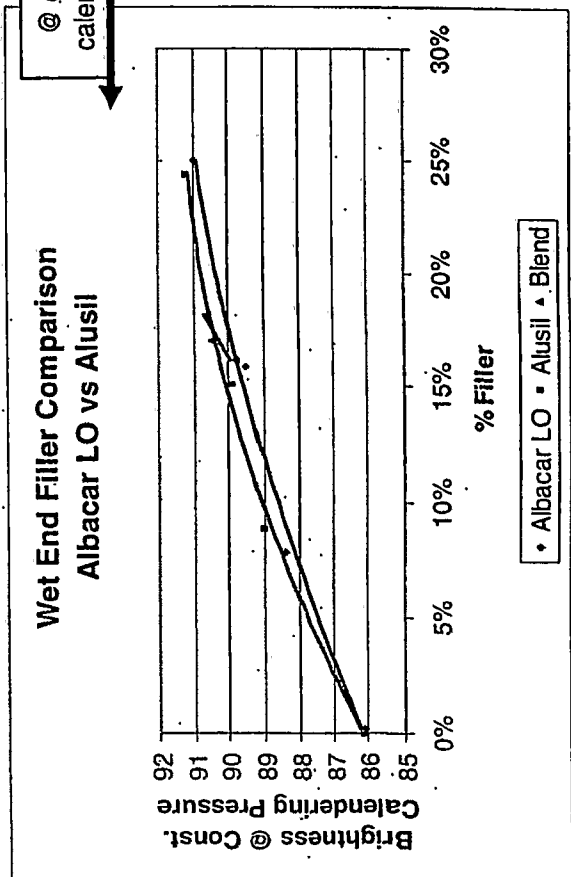
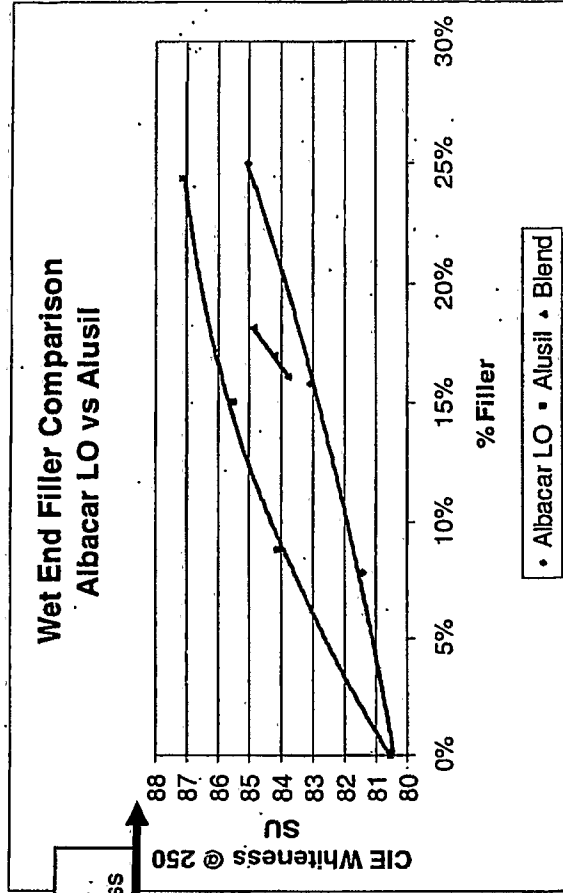


Brightness

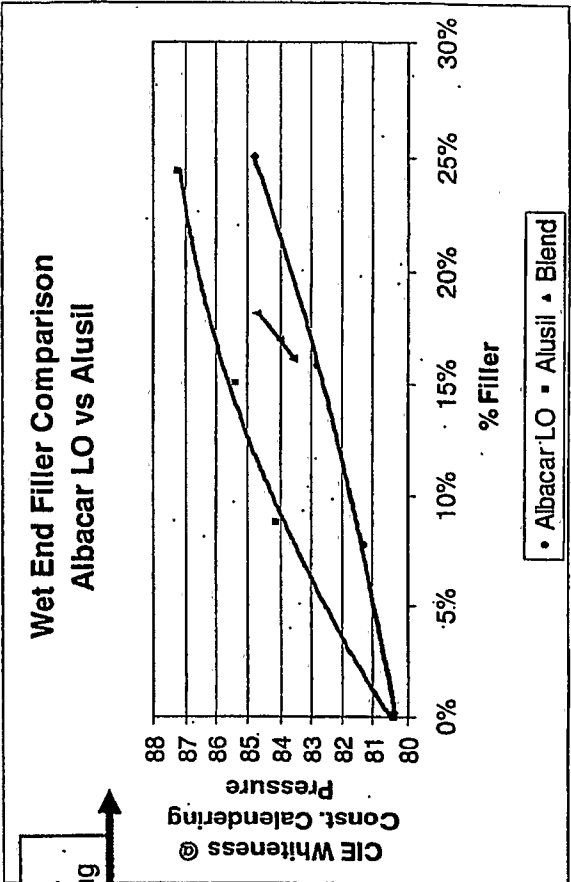


@ const. smoothness

Whiteness

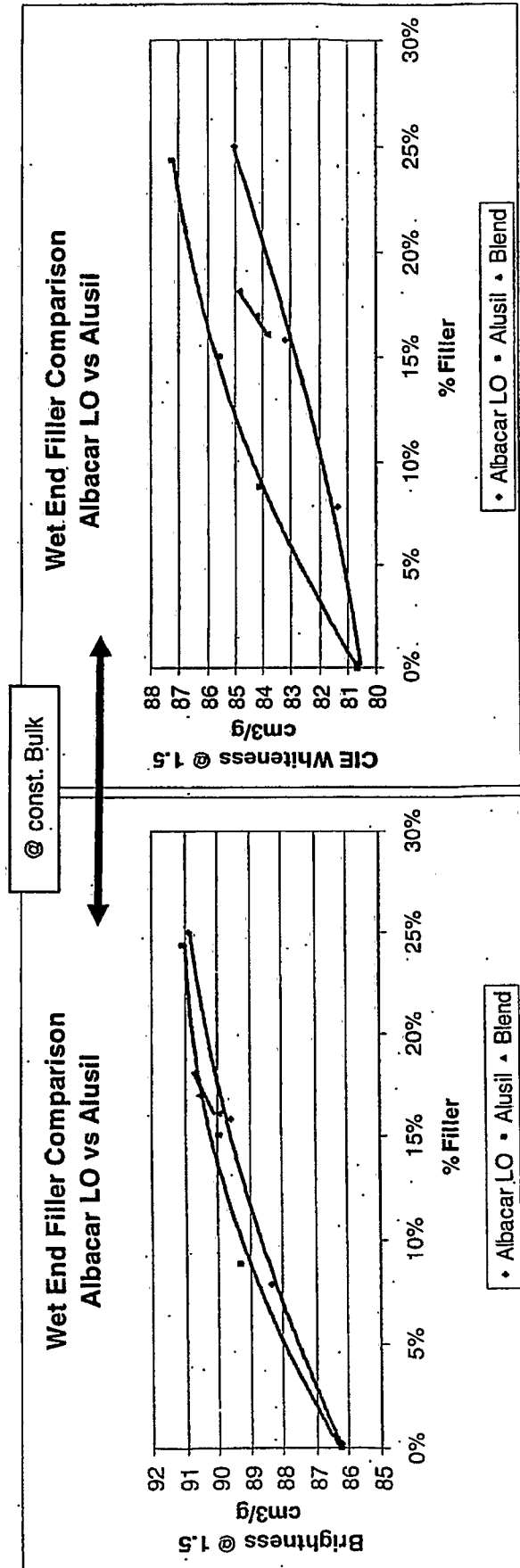


@ const. calendaring



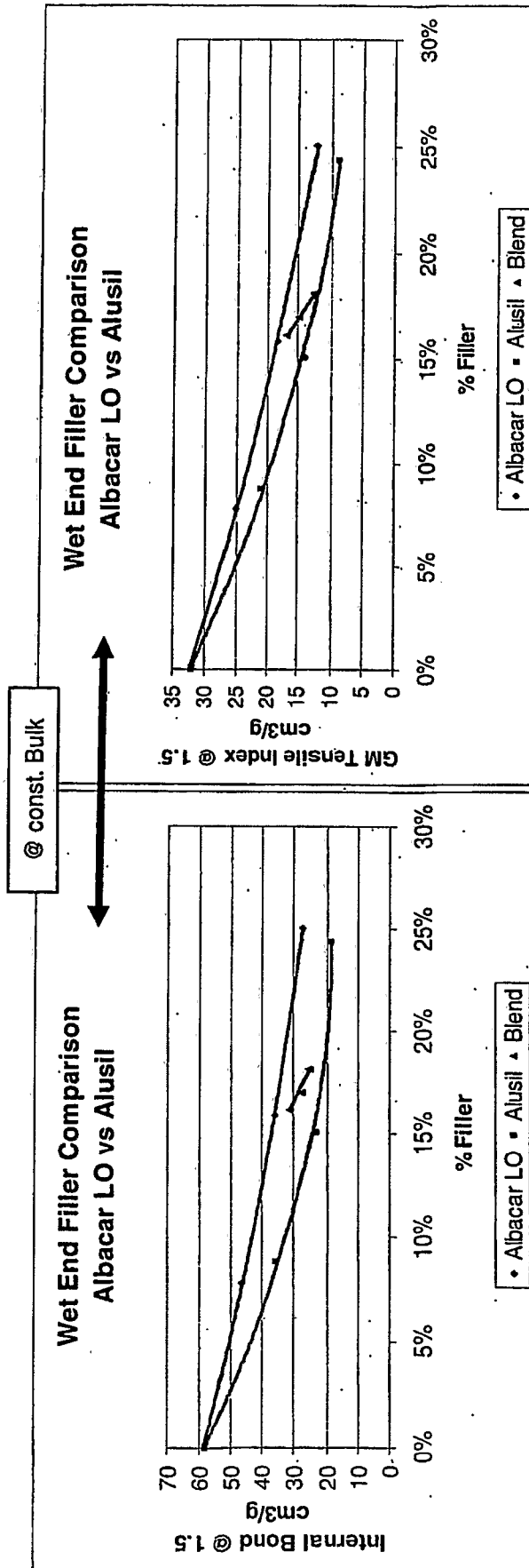
Brightness

Whiteness



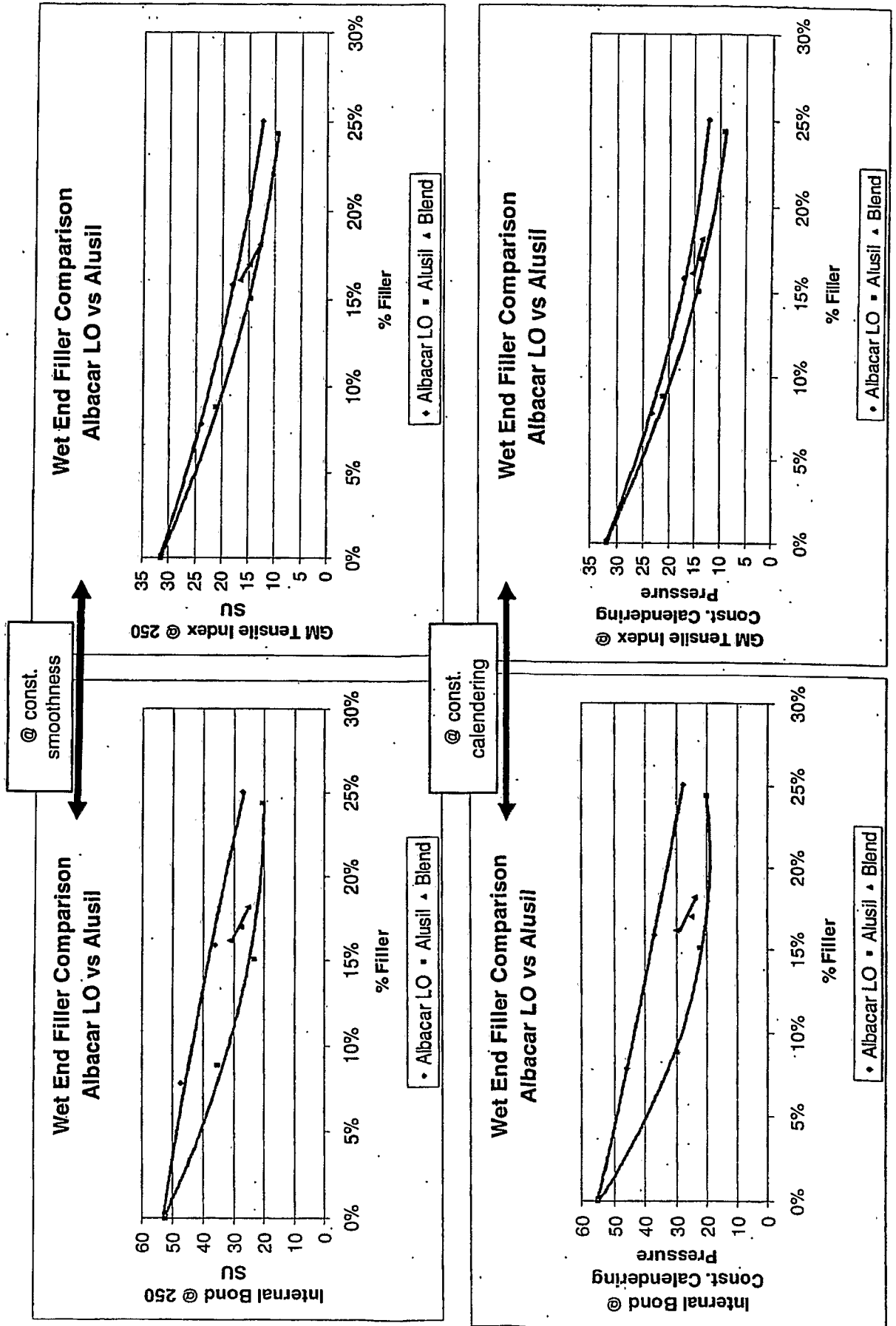
Internal Bond

Tensile Index



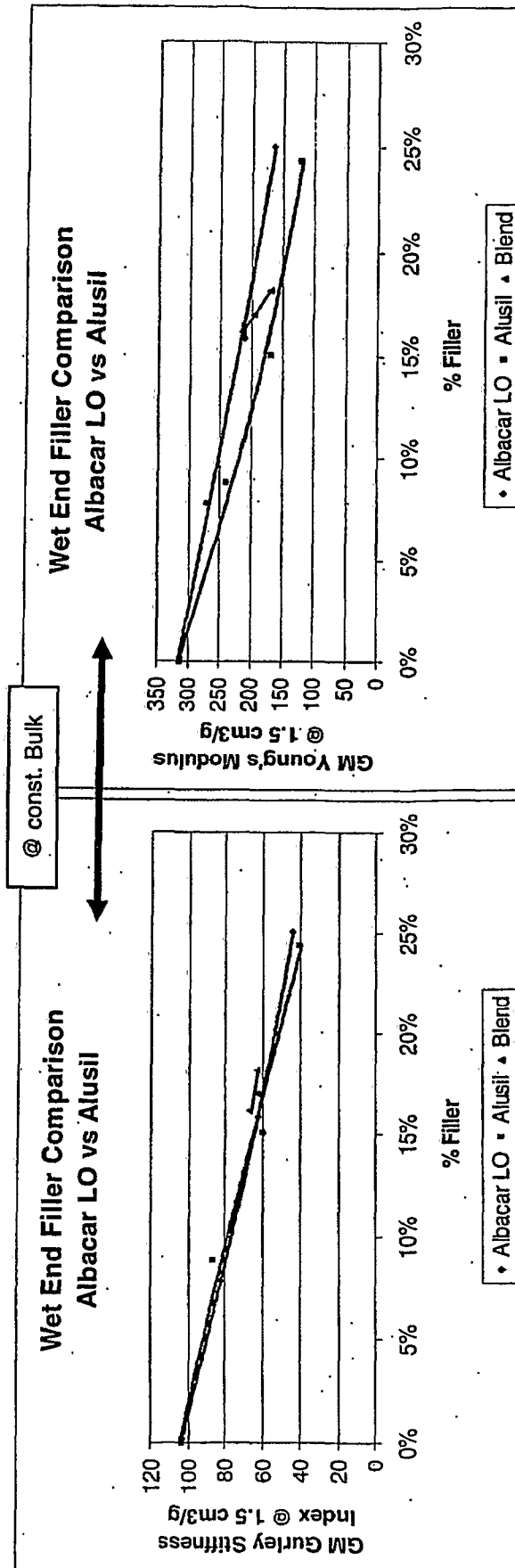
Internal Bond

Tensile Index



Stiffness

Modulus

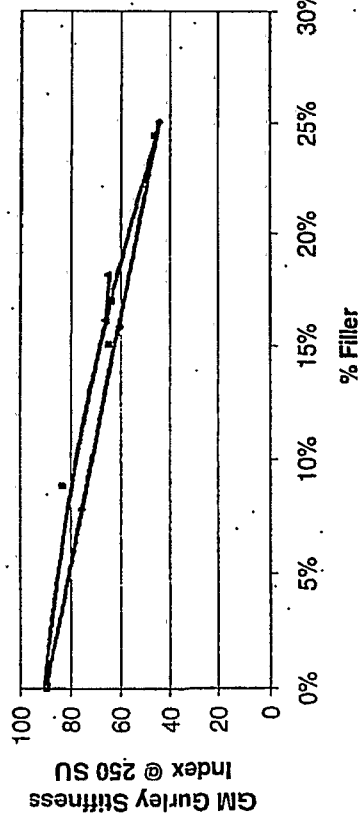


Stiffness

Modulus

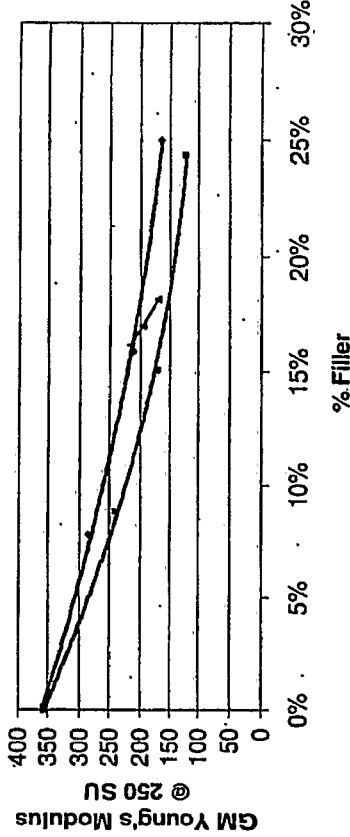
@ const. smoothness

Wet End Filler Comparison
Albacar LO vs Alusil



• Albacar LO • Alusil • Blend

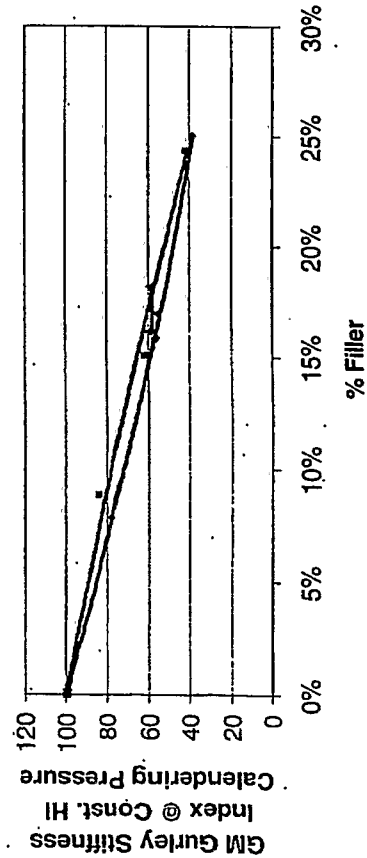
Wet End Filler Comparison
Albacar LO vs Alusil



• Albacar LO • Alusil • Blend

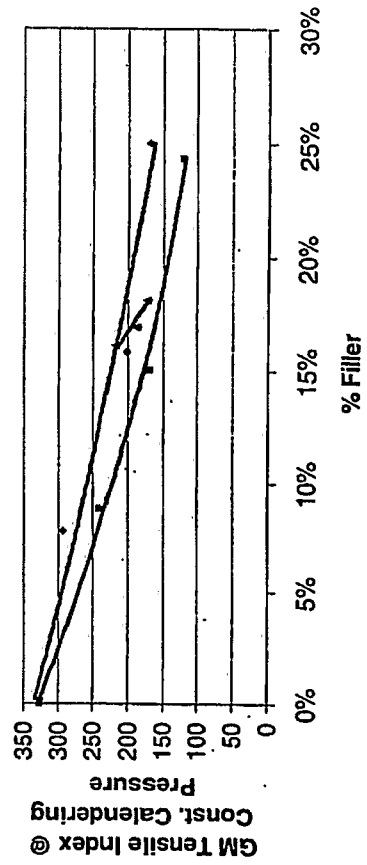
@ const. calendaring

Wet End Filler Comparison
Albacar LO vs Alusil



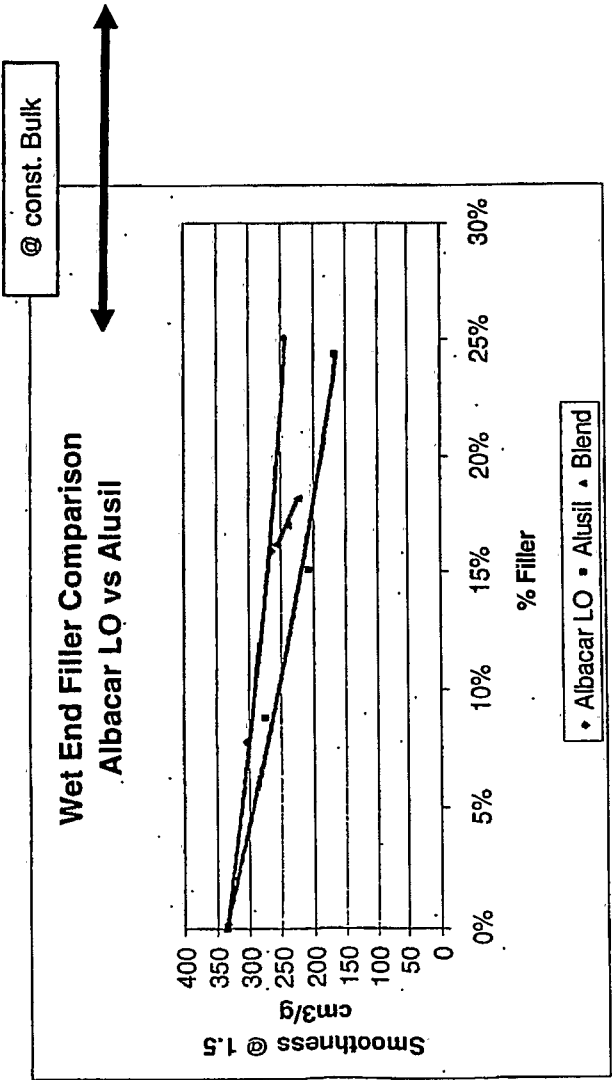
• Albacar LO • Alusil • Blend

Wet End Filler Comparison
Albacar LO vs Alusil

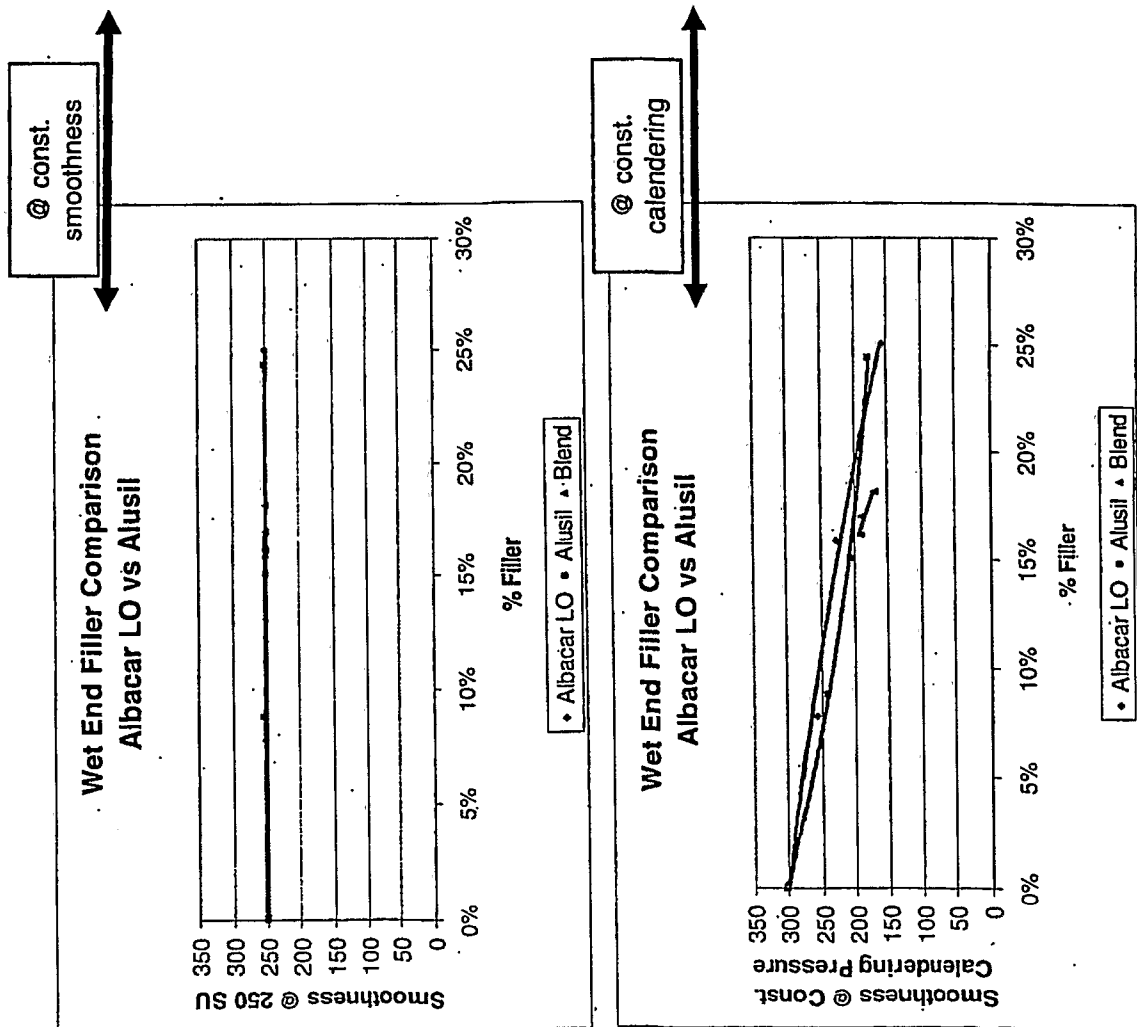


• Albacar LO • Alusil • Blend

Smoothness

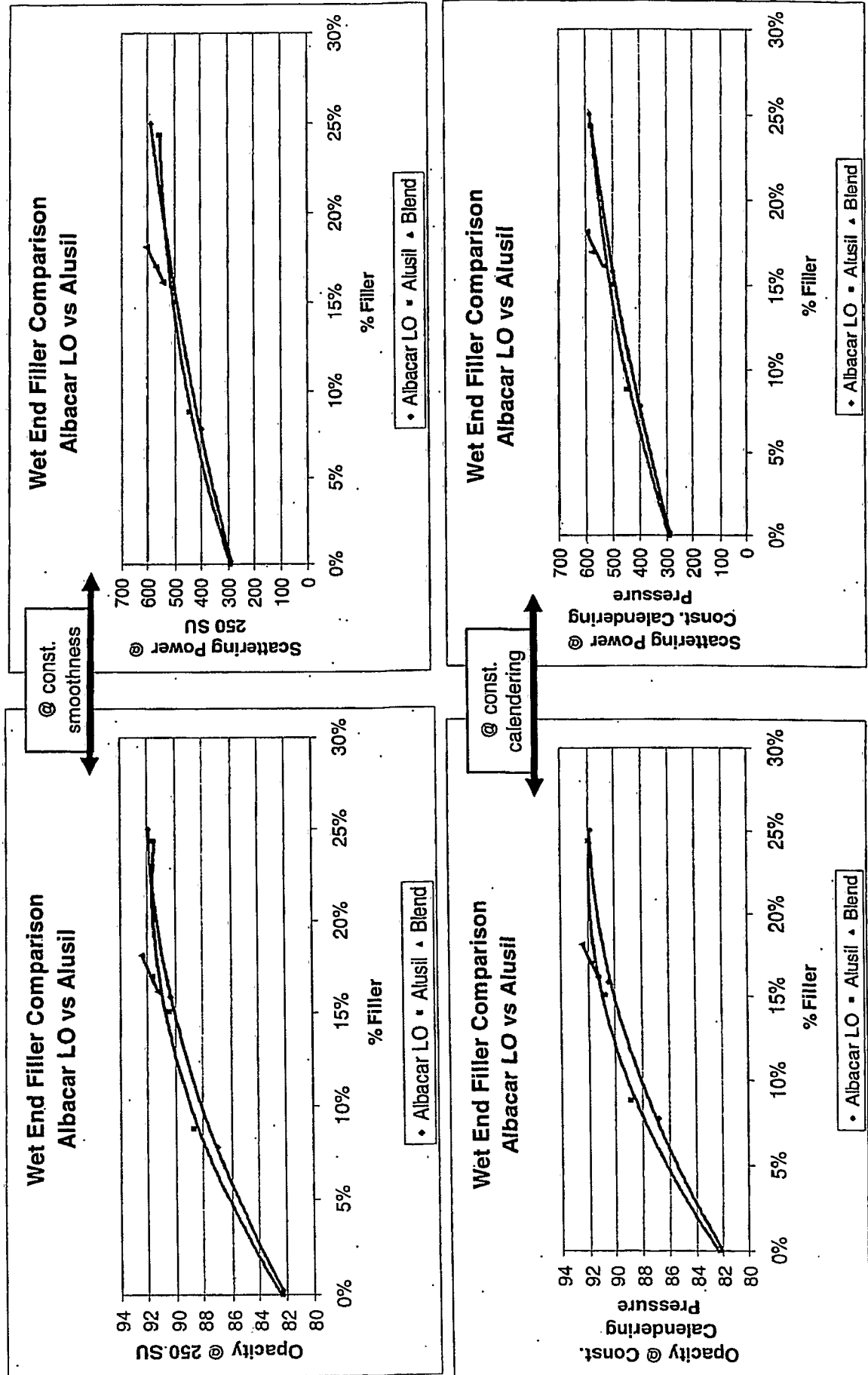


Smoothness



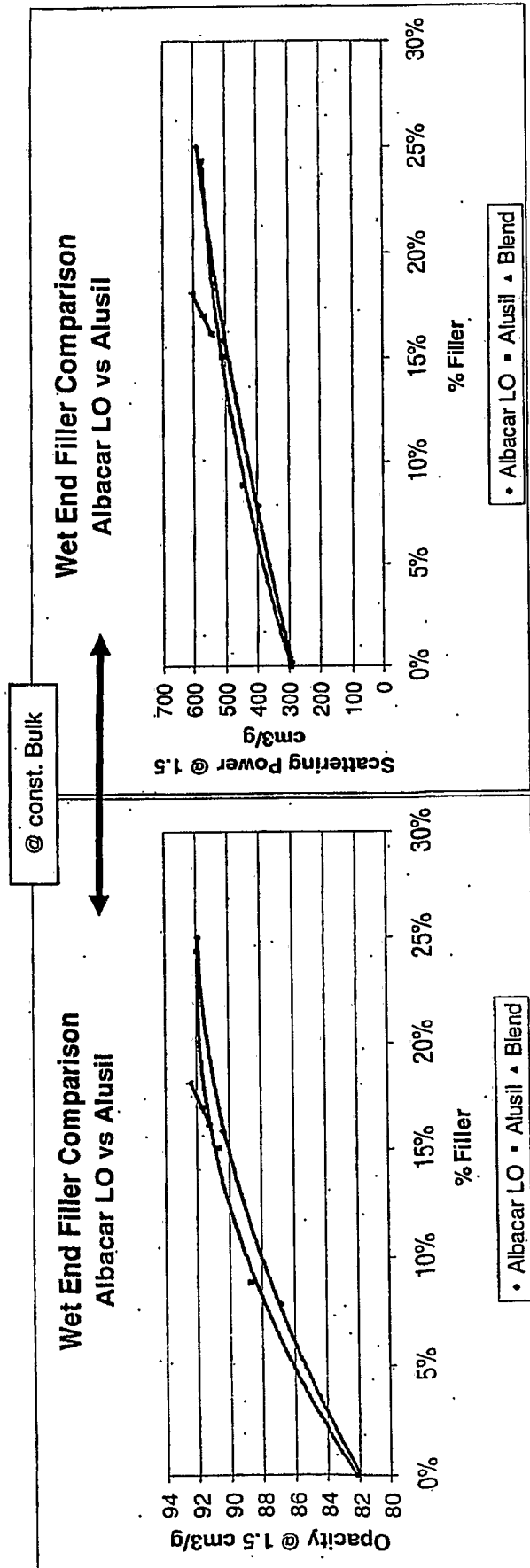
Opacity

Scattering

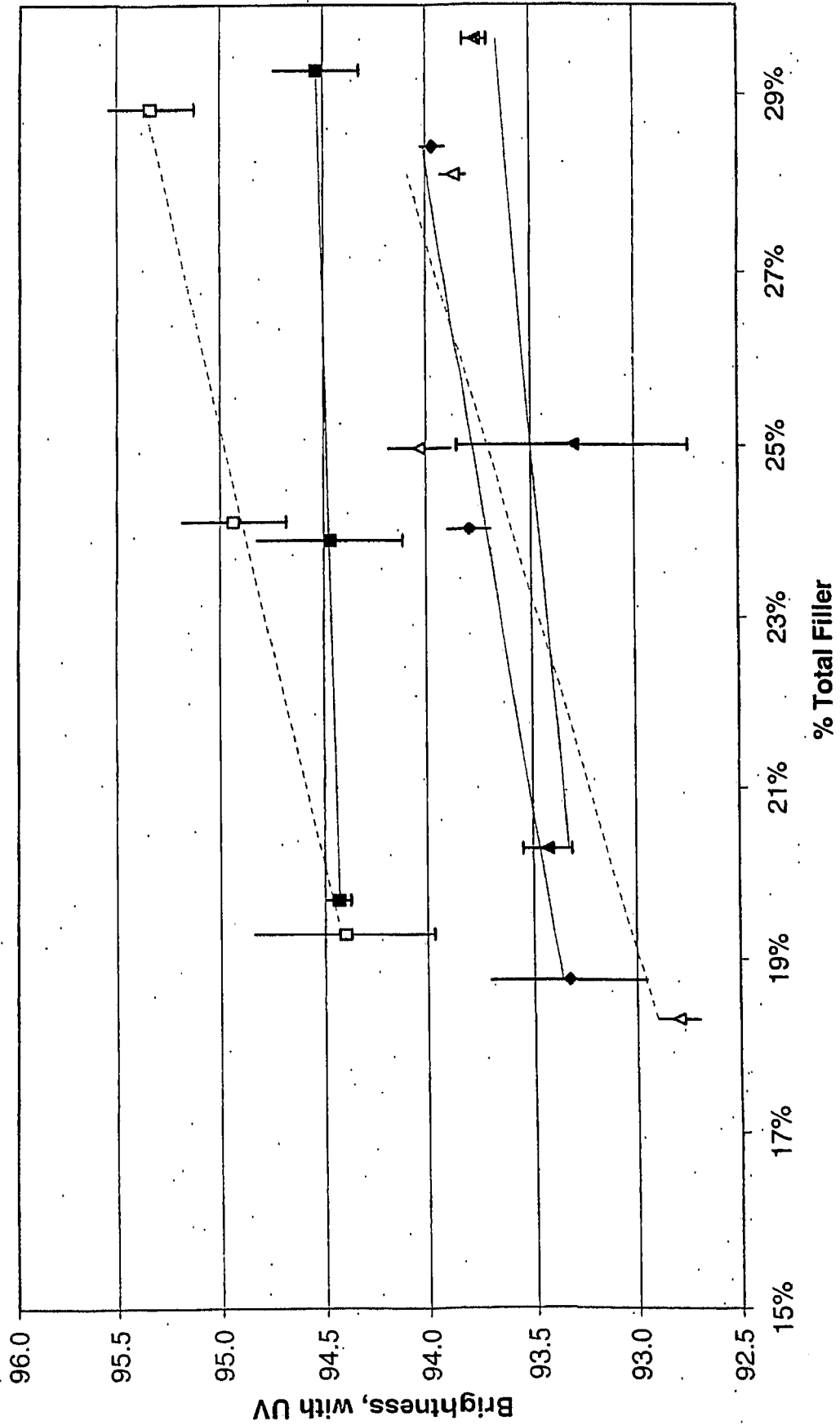


Opacity

Scattering

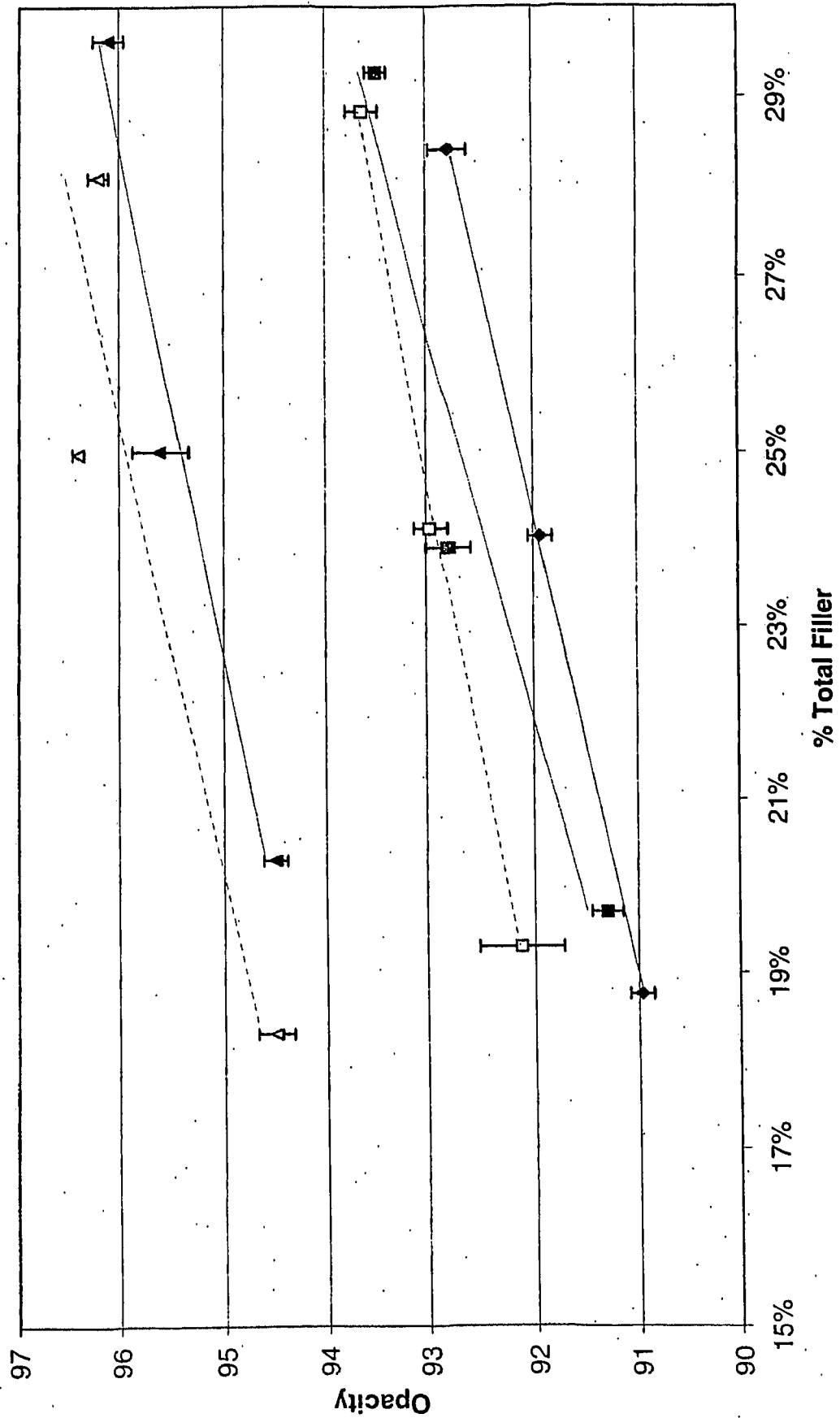


Ticonderoga DSF Study with Alusil



♦ Albacar HO/PO Blend ■ 20% Alusil □ 40% Alusil ▲ 20% TiO2 ▼ 40% TiO2

Ticonderoga DSF Study with Alusil



◆ Albacar HO/PO Blend ■ 20% Alusil □ 40% Alusil ▲ 20% TiO2 ▼ 40% TiO2

