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(54) Title: KAOLIN PRODUCTS AND THEIR USE

(57) Abstract: A particulate kaolin suitable for use as a filler material in compositions for making uncoated paper, the kaolin having a mean particle size of between 0.7 µm and 3 µm and a shape factor of at least 60.

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KAOLIN PRODUCTS AND THEIR USE

The present invention relates to kaolin products and blends or compositions containing them. In 5 particular, it relates to particulate kaolin products and blends containing them for use as fillers in making uncoated, e.g. supercalendered (SC) papers and their production.

Mineral fillers are used in the production of 10 most papers for printing or writing applications. The incorporation of such fillers together with cellulose fibres in a paper making composition reduces the overall cost of the raw materials and can improve optical and printing properties of the paper. 15 However, adding fillers causes reduction in the strength of the paper, so there is a practical limit to the amount of fillers normally used in the paper making composition.

Highly filled uncoated papers can compete with 20 some coated paper grades.

Suitable smoothness, gloss, density per unit area and printing ink porosity can be achieved by multiple calendering of the filled paper sheets. The well known process of calendering involves passing 25 the sheets of paper between rollers to compress the sheets.

Highly filled uncoated, calendered papers having properties approaching those of coated papers are generally known as supercalendered (SC) papers. 30 Such papers can be used for various applications,

particularly involving printing upon the paper by rotogravure or offset processes.

Kaolin materials have been widely used in the prior art as fillers for making papers, especially SC 5 papers. One purpose of the present invention is to provide hydrous kaolin materials suitable for use as improved fillers in the production of uncoated writing and printing grade papers, especially SC papers.

10 According to the present invention in a first aspect there is provided a particulate kaolin suitable for use as a filler material in compositions for making uncoated paper, the kaolin having a mean particle size of between 0.7 μ m and 3 μ m and a shape 15 factor of at least 60.

In this specification, mean particle size and all other particle size properties are as determined for a fully dispensed dilute aqueous suspension of the particulate material in question by sedimentation 20 using a SEDIGRAPHTM 5100 machine, (supplied by the Micromeritics Corporation) in a well-known manner.

The mean particle size of the kaolin product may be from 0.9 μ m to 2.5 μ m, especially from 0.9 μ m to 1.2 μ m, or from 1.2 μ m to 1.7 μ m.

25 The powder brightness of the particulate kaolin according to the first aspect may be at least 80 ISO units, preferably at least 83 ISO units measured in a well-known manner according industry (TAPPI) standard procedures.

30 The shape factor of the particles of the particulate kaolin according to the invention is at

least 60, preferably at least 65, in some cases at least 70 or more. The expression 'shape factor' as used herein means the average value (on a weight average basis) of the ratio of mean particle diameter to particle thickness for a population of particles of varying size and shape (i.e. in this case the particulate kaolin) as measured using the electrical conductivity method and apparatus described in GB-A-2240398, US-A-5128606 and EP-A-528078 and using the equations derived in those patent specifications.

'Mean particle diameter' is here defined as the diameter of a circle, which has the same area as the largest face of the particle. In the electrical conductivity measurement method described in the said specifications, the electrical conductivity of a fully dispersed aqueous suspension of the particles under test is caused to flow through an elongated tube. Measurements of the electrical conductivity are taken between (a) a pair of electrodes separated longitudinally along the axis of the tube and (b) a pair of electrodes separated transversely across the tube. The shape factor of the particles under test is calculated from the two conductivity measurements.

The particulate kaolin according to the first aspect of the invention is a hydrous kaolin which may be obtained from a primary or secondary (sedimentary) source and may be processed using known procedures to have the specified properties. The processing procedures may for example involve comminution, e.g. grinding or milling, and particle size

classification, e.g using screens, centrifuges, cyclones, air classifiers and the like.

The particulate kaolin according to the first aspect of the invention may be subjected to further refinement or beneficiation treatments to remove impurities and to improve properties, e.g. optical properties such as brightness. Such treatments may be known per se and may be selected for example from magnetic impurity separation, froth flotation, 5 selective flocculation, impurity leaching and 10 bleaching.

The particulate kaolin according to first aspect of the present invention may consist of at least 95% by weight kaolinite, preferably at least 15 98% by weight kaolinite.

The particulate kaolin according to the first aspect may be blended with other particulate filler materials for use in paper making compositions. Such other filler materials may be known per se and may be 20 selected for example from other hydrous kaolin, calcined kaolin, talc, calcium sulphate, titanium dioxide and alkaline earth metal carbonate, especially calcium carbonate.

According to the present invention in a second 25 aspect there is provided a blend or composition of fillers for use in compositions for making uncoated paper, especially so called wood containing or groundwood paper, comprises (a) particulate kaolin according to the first aspect and (b) a particulate 30 calcium carbonate.

The blend according to the second aspect may comprise from 5% to 95%, especially from 20% to 80%, by weight of the kaolin according to the first aspect and from 95% to 5%, especially from 80% to 20%, by weight of the particulate calcium carbonate product.

For blends according to the second aspect where the kaolin according to the first aspect has a mean particle size of 1.2 μ m or more the weight ratio of kaolin:calcium carbonate in the blend may be 50:50 or more, e.g. from 60:40 to 80:20 where the kaolin has a mean particle size greater than 1.2 μ m and not greater than 1.7 μ m.

For blends according to the second aspect where the kaolin according to the first aspect has a mean particle size of 1.2 μ m or less the weight ratio of kaolin:calcium carbonate in the blend may be 50:50 or less, e.g. from 40:60 to 20:80 where the kaolin has a mean particle size less than 1.2 μ m and not less than 0.9 μ m.

The blend according to the second aspect of the invention benefits from the enhancement of properties such as brightness provided by the calcium carbonate as well as retaining desirable properties such as gloss and print quality provided by the kaolin.

We have found, unexpectedly, that the kaolin according to the first aspect shows a superior combination of properties when used as a filler in paper making compositions, especially when used in the form of a blend with calcium carbonate, compared with prior art kaolin fillers used in a comparable

manner. Use of such fillers allows paper especially wood containing paper to be made having an improved combination of porosity, strength, sheet gloss, sheet brightness, print density and print gloss especially

5 when printed upon by a gravure printing process or an offset printing process, especially a heatset offset process. Such an improved combination of properties is obtained especially when the paper sheet made using the said filler is heavily compressed by

10 calendering, e.g. is supercalendered. The combination of properties may have a particularly good brightness when the composition is calcium carbonate rich and particularly good gloss and print quality properties when the composition is kaolin rich.

15 The papermaking composition in which the kaolin according to the first aspect or the blend according to the second aspect is used may be obtained from a groundwood pulp composition of cellulose fibres, i.e. from a pulp containing from 70% to 100% by weight of

20 a so-called mechanical pulp, which is one that has been mechanically refined, e.g. obtained from logs and ground, refined and bleached or obtained from wood chips and refined (optionally under pressure and/or at elevated temperature and/or with the use of

25 chemicals) and bleached. The composition may contain a minor percentage, e.g. up to 30% by weight, of a so called chemical pulp, i.e. one which has been chemically treated to remove lignin.

30 We have found that particularly beneficial results are obtained in use of the filler blend according to the second aspect of the invention when

the filler blend comprises calcium carbonate having (i) a mean particle size of from $0.4\mu\text{m}$ to $1.5\mu\text{m}$, especially from $0.7\mu\text{m}$ to $1.3\mu\text{m}$; and (ii) a steepness factor of at least 40, preferably at least 50, 5 especially at least 60.

The expression 'steepness factor', (sometimes referred to as 'narrowness') as used herein refers to the steepness of the particle size distribution curve as measured by the SEDIGRAPH 5100 machine in the 10 manner described earlier and is given by the expression $100x(d_{30}\div d_{70})$, where d_{30} is the value of the particle size less than which there are 30% by weight of the particles and d_{70} is the value of the particle size less than which there are 70% by weight of the 15 particles.

The said calcium carbonate may comprise a so called ground carbonate, i.e. a product obtained from natural sources, e.g. marble, chalk or limestone, and processed to have appropriate properties by known 20 treatments involving at least one grinding step.

Alternatively, the calcium carbonate may be synthesised, e.g. by chemical precipitation, e.g. by the reaction in an aqueous medium of carbon dioxide and lime (calcium hydroxide). Carbonate products made 25 in this way may be mixed materials optionally containing other fine solids, e.g. fibres or particulate solids, present in the aqueous medium when the precipitation reaction is carried out. Such other solids become bonded to the calcium carbonate 30 crystals during the precipitation of the calcium carbonate crystals. Examples of composite filler

materials produced in this way are described in our EP 892,019.

The calcium carbonate product used to form the blend according to the second aspect of the invention 5 may include a chemical additive employed to provide resistance to acidic conditions which are present in some papermaking systems. Such an additive is described for example in US 5,593,489.

The kaolin according to the first aspect and the 10 blend according to the second aspect of the invention may be employed in a paper making composition and paper sheets, especially paper sheets to be calendered and printed upon by a gravure or offset printing process, may be made using such a 15 composition all in a known manner.

Embodiments of the present invention will now be described by way of example with reference to the following Examples.

EXAMPLE 1 (Comparative)

20 A paper pulp composition was prepared using an 80:20 (by weight) blend of mechanical and chemical pulps. The composition was formed into a dilute aqueous suspension (containing less than 1% by weight solids) by addition of water. The filler consisted of 25 a 70:30 (by weight) kaolin-rich blend of kaolin and precipitated calcium carbonate (pcc). The kaolin, Kaolin 1, had the following properties:

- (i) percentage by weight of particles smaller than 2 μ m: 50%;
- 30 (ii) mean particle size: 1.6 μ m;
- (iii) shape factor 45.

The pcc, PCC1, had the following properties:

- (i) percentage by weight of particles smaller than 2 μ m: 95%;
- (ii) mean particle size: 0.9 μ m;
- 5 (iii) additive: 5% by weight (active based on the dry weight of calcium carbonate) of a neutrally buffering chemical comprising a solution of an aluminium compound and phosphoric acid.

10 Retention aid chemical commercially available under the trade name Percol 292 was added in an amount of 0.02% by weight (active based on the dry weight of solids present) to the filler containing pulp suspension.

15 Handsheets of grammage 57g.m⁻² were made from the suspension using a standard semi-automatic handsheet former according to TAPPI standard procedures. The handsheets were conditioned for 24 hours in a room at a temperature of 23°C and a 20 relative humidity of 50%. The conditioned handsheets were calendered using a laboratory soft nip calender. The calendering conditions were as follows:

- (i) roll temperature: 100°C;
- (ii) nip pressure: 300kN.m⁻²;
- 25 (iii) speed: 30m.min⁻¹;
- (iv) number of nips: 4 per side.

The properties specified in Tables 1 to 3 later of the handsheets produced were measured according to industry standard (TAPPI) procedures 30 well known to those skilled in the art. The results

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which were obtained for these measurements are also shown in Tables 1 to 3 later.

EXAMPLE 2 (Invention embodiment)

5 The procedure used in Example 1 was repeated to prepare and measure the properties of handsheets except that the kaolin used in the filler composition was a different kaolin, Kaolin 2, having the following properties:

10 (i) percentage by weight of particles smaller than 2um: 50%;
 (ii) mean particle size: 1.6 μ m;
 (iii) shape factor: 70.

15 The resulting calendered handsheets had the properties which are shown in Tables 1 to 3 later.

EXAMPLE 3 (Comparative)

20 The procedure used in Example 1 to prepare and measure the properties of handsheets was repeated except that the percentage by weight of Kaolin 1 used in the filler composition was 30%, the percentage by weight of PCC 1 being 70%.

25 The resulting calendered handsheets had the properties which are also shown in Tables 1 to 3 later.

EXAMPLE 4 (Invention embodiment)

30 The procedure used in Example 1 to prepare and measure the properties of handsheets was repeated except that (i) the percentages by weight of kaolin and pcc (PCC 1) were respectively 30% and 70% by

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weight and (ii) the kaolin used in the filler composition was a further different kaolin, Kaolin 3, having the following properties:

(ii) percentage by weight of particles smaller than 5 μm : 75%;

(ii) mean particle size: $1.0\mu\text{m}$;

(iii) shape factor: 70.

The resulting calendered handsheets had the properties which are shown in Tables 1 to 3 later.

10

Results

The results obtained for the measurements on the handsheets made in Examples 1 to 4 are given in Table 15 1 to 3 as follows.

Table 1

Example No.	Percent by weight CaCO_3	Sheet light scattering coefficient $(F8) \text{m}^2\text{kg}^{-2}$	Sheet gloss Tappi 75° %	Bendtsen porosity $\text{ml} \cdot \text{min}^{-1}$
1 (comp)	30	69	40	21
2 (inv)	30	67	42	19
3 (comp)	70	81.5	36	31
4 (inv)	70	79	43	25

20

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Table 2

Example No.	Weight Percent CaCO ₃	Rotogravure Print density	Rotogravure Print gloss	Roto Missing Dots %
1 (comp)	30	1.38	33	4.3
2 (inv)	30	1.39	34	3.5
3 (comp)	70	1.22	30	3.5
4 (inv)	70	1.24	32	3.5

Table 3

Example No.	Weight Percent CaCO ₃	Offset Print density Dry	Offset Print density litho	Offset Print Gloss Dry	Offset Print gloss litho
1 (comp)	30	1.24	1.14	41	23
2 (inv)	30	1.24	1.13	44	23
3 (comp)	70	1.25	1.17	41	18
4 (inv)	70	1.25	1.14	44	20

5

The results in Tables 1 to 3 illustrate the improved combination of properties obtained by using kaolins embodying the invention (Kaolins 2 and 3) in blends with particulate calcium carbonate.

CLAIMS

5 1. A particulate kaolin suitable for use as a
filler material in compositions for making uncoated
paper, the kaolin having a mean particle size of from
0.7 μ m to 3 μ m and a shape factor of at least 60.

2. A particulate kaolin according to claim 1 and
10 which has a mean particle size of from 0.9 μ m to
2.5 μ m.

3. A particulate kaolin according to claim 1 or
claim 2 and which has a shape factor of at least 65.

4. A composition of filler materials for use in
15 compositions for making uncoated paper, the blend
comprising the kaolin according to claim 1,2 or 3 and
one or more other fillers selected from other hydrous
kaolin, calcined kaolin, talc, calcium sulphate and
alkaline earth metal carbonate.

20 5. A composition according to claim 4 and wherein
the blend contains at least 50% by weight of the
kaolin according to claim 1,2 or 3.

6. A composition according to claim 5 and wherein
the blend contains from 60% to 80% by weight of the
25 kaolin according to claim 1,2 or 3.

7. A composition according to claim 5 or claim 6
and wherein the other filler comprises calcium
carbonate.

8. A composition according to claim 7 and wherein
30 the calcium carbonate comprises a material obtained
from a natural source and processed by grinding.

9. A composition according to claim 7 and wherein the calcium carbonate comprises a material prepared by chemical synthesis and optionally containing other solids bonded to the calcium carbonate.

5 10. A composition according to claim 7,8 or 9 and wherein the calcium carbonate has a mean particle size of from 0.5 μ m to 1.5 μ m.

11. A composition according to claim 10 and wherein the calcium carbonate has a mean particle

10 size of from 0.7 μ m to 1.3 μ m.

12. A composition according to any one of claims 7 to 11 and wherein the calcium carbonate has a steepness factor of at least 40.

13. A composition according to claim 12 and

15 wherein the calcium carbonate has a steepness factor of at least 50.

14. A composition according to any one of claims 7 to 13 and wherein the calcium carbonate is in the form of a composition containing up to 15% by weight

20 on an active basis of a chemical additive which provides stability of the carbonate in acidic conditions.

15. A composition according to any one of claims 7 to 14 and wherein the kaolin has a mean particle size

25 of 1.2 μ m or more and the weight ratio of kaolin : calcium carbonate in the blend is 50:50 or more.

16. A composition according to claim 15 and wherein the kaolin has a mean particle size of 1.2 μ m or more and not greater than 1.7 μ m and the weight ratio of

30 kaolin : calcium carbonate in the composition is from 60:40 to 80:20.

17. A composition according to any one of claims 7 to 14 and wherein the kaolin has a mean particle size of less than $1.2\mu\text{m}$ and the weight ratio of kaolin : calcium carbonate in the composition is 50:50 or 5 less.
18. A composition according to claim 17 and wherein the kaolin has a mean particle size less than $1.2\mu\text{m}$ and not less than $0.9\mu\text{m}$ and the weight ratio of kaolin: calcium carbonate is from 40:60 to 20:80.
19. A method of making uncoated paper sheets which includes the steps of preparing an aqueous paper making composition from a pulp and mineral filler particles and forming the composition into paper sheets, wherein the mineral filler particles comprise kaolin according to any one of claims 1 to 3 or a composition according to any one of claims 4 to 18.
20. A method according to claim 19 and wherein the paper sheets are calendered by a supercalender process.
21. A method according to claim 19 or claim 20 and wherein the pulp consists of at least 70% by weight of a mechanical pulp.
22. A method according to claim 19, 20 or 21 and wherein the paper sheets are for printing upon by a 25 gravure or offset printing process.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09C1/42 C01B33/40 D21H17/68

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09C C01B D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, INSPEC, COMPENDEX, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category ^o	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO 00 59840 A (HUSBAND JOHN CLAUDE ;IMERYS PIGMENTS INC (US); BROWN HARRY VINCENT) 12 October 2000 (2000-10-12) page 28, line 17 - line 18; example 2 ---	1-6, 19-22
P, X	WO 00 59841 A (IMERYS PIGMENTS INC ;PRUETT ROBERT J (US); YUAN JUN (US); BROWN HA) 12 October 2000 (2000-10-12) page 13, line 3 - line 6; claims 1,17,19; example 2 ---	1,2,4-6, 19-22
X	GB 2 310 215 A (ECC INT LTD) 20 August 1997 (1997-08-20) examples 1,2 ---	1-6, 19-22
Y	---	7-9, 14-18
		-/-



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

^o Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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INTERNATIONAL SEARCH REPORT

International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 98 56860 A (ECC INT INC) 17 December 1998 (1998-12-17) claims 1-16; example 1 ----	7-9, 14-18
A	EP 0 596 442 A (NIPPON INORGANIC COLOUR & CHEM) 11 May 1994 (1994-05-11) claims 1,6; example 2 ----	1-3
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Information on patent family members

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