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(54) **High bulk calendered paper containing vesiculated beads.**

(57) A high bulk calendered paper comprises from 2% to about 6% of the weight of the paper of highly cross-linked, titanium dioxide-pigmented, polymeric vesiculated beads having a volume average particle size of at least about 5 microns up to about 35 microns. The calendered paper preferably has a basis weight of from about 20 to about 40 pounds per ream, and the vesiculated beads are preferably used in an amount of from 4% to 6%. As a feature of the invention, it is found that the carboxyl-functional cross-linked beads used herein when used in aqueous suspension thickened with a neutralized polycarboxylic acid polymer thickener, enhance the retention of fines in the papermaking process when used in conjunction with anionic retention aids, especially carboxyl-functional acrylamide copolymers, and particularly when used in an aqueous furnish having a pH of from 4 to 6.

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PRODUCTION OF HIGH BULK PAPER AND
HIGH BULK CALENDERED PAPER
CONTAINING VESICULATED BEADS

DESCRIPTION

5 This invention is an improvement over the invention disclosed in EP-A-0 204 916.

Technical Field

This invention relates to the production of
10 high bulk paper and to high bulk calendered paper containing vesiculated beads to provide brightness, opacity and smoothness while minimizing the density of the paper.

Background Art

15 Inorganic pigments are normally introduced into the paper furnish in order that the resulting paper will possess desired brightness, opacity and printability. These inorganic pigments generally have a particle size of less than 1 micron.
20 Unfortunately, these inorganic pigments, and especially titanium dioxide, anatase, are dense and can increase the weight of the paper per unit area which is produced. Also, these very fine pigments, as well as many of the other finely divided
25 components of paper pass through the Fourdrinier wire and are lost with the "white water". While these losses are minimized by recycling, there is a limit to how much recycling can be tolerated before the paper product is damaged, so the losses are substantial and
30 some of the fines find their way back into our rivers and streams to pollute these waterways.

More particularly, conventional papermaking processes normally retain only up to about 65% of the finely divided materials which are employed,
35 including titanium dioxide, clay and carbonates, the

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remaining fines passing through the wire to be recovered or not in accordance with the recycling practices which are employed. In this invention, the retention of fines is considerably improved, usually
5 by an increase in the ash content of from 7-10 percentage points. The mechanism by which this is accomplished is not entirely clear, but it will be understood that improved retention of fines is a serious industrial problem which has plagued the
10 paper industry throughout its history.

While titanium dioxide pigments are quite effective in increasing the desirable properties of opacity and brightness of any paper, they are expensive. Printing paper is normally finished in a
15 calendering operation to improve printability and appearance for use in books, magazines, etc. Between the increased density which adds to the cost of producing each unit area, the cost of mailing, and the cost of the pigment, the conventional use of
20 titanium dioxide adds considerably to the cost of producing and using such calendered paper.

Attempts have been made to incorporate opaque cellular plastic particles into the paper furnish in order to provide the desired opacity.
25 These cellular plastic particles were thermoplastic materials, and they collapsed under the heat and force of calendering, particularly supercalendering. When the cells collapsed, the opacity and bulk which they provided was lost. The calendering force is
30 normally at least about 150 pounds per linear inch, and may be as high as about 2000 pounds per linear inch, and the temperature is at least about 100°F., more usually at least about 150°F. Since these cellular plastic particles lose their bulk and
35 opacifying power when they are collapsed, they are

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not very useful in making high bulk calendered paper.

This invention is directed toward maintaining the brightness and opacity of calendered paper while increasing its thickness (caliper) and resistance to print show through. It is also desired to minimize the need for inorganic pigments, especially titanium dioxide. As a result, the cost can be contained and the density of the calendered paper product minimized, while maintaining, or improving, smoothness and printability.

Disclosure of Invention

In accordance with this invention, all or a portion of the usual inorganic pigment, such as the titanium dioxide, anatase, normally employed in the paper furnish, is replaced by highly cross-linked, titanium dioxide-pigmented, polymeric vesiculated beads having a volume average particle size of at least about 5 microns. The final paper contains at least about 2% by weight of such beads. At about 2%, in very light paper, a minimal effect is observed. However, practical significant results require a paper have a basis weight in the range of about 20 to about 40 pounds per ream, and for these papers a proportion of bead of from about 3.5% to about 6%, preferably about 4% to 5%, provides significantly improved practical results. Below 3.5%, the effect is hard to notice in papers having the basis weight specified. Above about 6%, the incorporation of beads of the character specified herein is not economical. Below 20 pounds per ream basis weight, the papers are not quality printing papers, to which this invention relates, and above 40 pounds per ream basis weight, the bulking effect of the beads used herein becomes more difficult to observe.

In order that the calendering operation will

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produce a paper which is useful as a quality printing paper, the calendering operation must exert some considerable force upon the paper of the character which would crush most beads. This paper is
5 calendered at a pressure of at least about 150 pounds per linear inch and at a temperature of at least about 100°F to provide a calendered paper product which can qualify as a quality printing paper, and under these conditions the pigmented vesiculated
10 beads used herein provides improved bulk. It is preferred herein to provide papers suitable for offset printing to employ a calendering operation which applies a pressure of from 200 to 1200 pounds per linear inch, the improvement provided by this
15 invention being enhanced at these greater loadings. For gravure printing, a pressure of from 700 to 1200 pounds per linear inch is preferred.

More particularly, when the vesiculated beads are formed to contain titanium dioxide, it is
20 found that the calendered paper product is brighter and more opaque per unit of caliper as a result of the presence of these beads. This effect is proportional to the amount used. Moreover, it is particularly surprising to find that there is a
25 significant improvement in printing smoothness, and this superior smoothness improves the ink hold-up.

It is found that equivalent quality calendered paper can be made satisfactorily at lower basis weight. "Basis weight" is a commonly used
30 papermaking term identifying the weight per unit area. For a paper of given thickness (caliper), at a lower basis weight, the vesiculated beads have been found to provide better resistance to print show through and a smoother, more uniform surface from
35 side to side in calendered sheets than a control

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containing all mineral pigment, such as titanium dioxide.

It is stressed that the increased bulk action provided by this invention requires
5 vesiculated beads of at least about 5 microns, with larger beads providing even better bulking than the smaller ones. Beads having a diameter of up to about 35 microns can be used, but it is preferred to employ a volume average particle size in the range of from 8
10 to 30 microns. The term "vesiculated" denotes the presence of a plurality of vesicles or cells. An average of at least about 5 cells per bead is contemplated herein, preferably at least about 10 cells per bead. It appears that the presence of a
15 large number of cells in each bead is what allows the bead to avoid collapse when paper containing the same is compressed under the considerable force imposed in the calendering operation.

Thus, with beads of the size specified, the
20 bulking improvement after calendering is about 5-15%, where the improvement in bulking indicates the extent of thickness increase in paper having the same weight. With paper having a lower basis weight, e.g., below about 35 pounds per ream (typically 30
25 pounds per ream), the smaller beads having a particle size below about 15 microns appear to perform more efficiently. With paper having a higher basis weight, e.g., above about 35 pounds per ream (typically 40 pounds per ream), beads having an
30 average particle size above about 15 microns perform better (more of the bulking action is retained on calendering).

Typical machine calendering conditions which have been investigated involved calender stack
35 pressures of 150 and 900 pounds per linear inch. at

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normal papermaking temperatures at this point in the process, e.g., about 150°F. Calendering temperatures of less than about 200°F. are preferred.

In the production of the papers which are
5 calendered in this invention, the vesiculated beads may be used in aqueous medium, as produced, or they can be dried prior to use, but in preferred practice the aqueous suspension of beads is modified by the introduction of a neutralized polycarboxylic acid
10 polymer, such as an ammonia-neutralized polyacrylic acid, to thicken the aqueous medium and thereby hold the beads in stable suspension. It is found that when the aqueous bead suspension is stabilized, as described, that the the papermaking process is
15 substantially altered because there is a reduction in the proportion of fines which pass through the wire into the white water. This action is particularly effective in combination with the inclusion of an effective amount of an anionic
20 retention aid in the furnish, the proportion of such anionic retention aid being of secondary significance because the normal proportions thereof as presently used remain effective herein.

It is stressed that the vesiculated beads
25 used herein are cross-linked carboxyl-function beads in order that they might participate in improving the retention of fines. The presence of titanium dioxide pigmentation in these beads is not required for fine retention, but is only an aspect of the capacity of
30 the beads to improve calendered paper.

It is of interest to note that the neutralized polycarboxylic acid polymer which thickens the aqueous bead suspension to stabilize the same apparently chemically coacts with the carboxyl
35 functionality in the beads. This is evidenced by the

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fact that these neutralized polymers are effective to stabilize the suspension at a lower viscosity than other thickeners, so more is involved in providing stability than merely the viscosity of the aqueous
5 medium.

Also, there appears to be a chemical coaction with the anionic retention aid. This is evidenced by the fact that the anionic retention aid is selected and used in a proportion which maximizes
10 retention on a practical basis. The amount of neutralized thickener, which is chemically similar to the anionic retention aid, which is added with the bead suspension is far too small to account for any detectable increase in retention. It is thought that
15 the amine or ammonia used to neutralize the carboxyl functionality in the anionic retention aid, the carboxyl functionality in the thickener and the carboxyl functionality in the beads, serves to effectively couple the retention aid to the beads.
20 As a result, when the retention aid couples with a finely divided particle which would normally pass through the wire, that retention aid may also be coupled with a bead. This bead is much larger than the finely divided particle, and this increases the
25 chance that the much larger conglomerate including the bead will be retained on the wire.

In summary, it is found that the vesiculated beads, when used in aqueous suspension which has been thickened with a neutralized polycarboxylic acid
30 polymer thickening agent to prevent settling of the suspension, are effectively retained in the paper together with an increased proportion of the fines and mineral filler which normally pass through the Fourdrinier wire in conventional papermaking.

35 Bead retention is enhanced when conventional

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retention aids are employed, both anionic and cationic retention aids being useful to increase the proportion of the beads which is retained. However, anionic retention aids are more efficient and the
5 combination of carboxyl-functional cross-linked beads preassociated with a neutralized polycarboxylic acid polymer thickening agent and anionic retention aid functions to also increase the retention of all fines in the papermaking process.

10 The vesiculated beads bulk the paper even when they are not pigmented. But the pigmented vesiculated beads withstand the heat and pressure of calendering, and despite their much larger size (in comparison with mineral filler), these beads bulk the
15 calendered paper and serve to maintain its opacity and brightness while the smoothness of the calendered paper is improved. At the same time, the proportion of titanium dioxide pigment can be substantially reduced. This is surprising. While the titanium
20 dioxide pigment need not be reduced, larger proportions of this pigment can be omitted when larger proportions of titanium dioxide are included in the vesiculated beads which are used.

 The retention aids which have been found to
25 be useful herein are themselves well known, and many are available in commerce. Acrylamide and methacrylamide copolymers with monoethylenic acids or monoethylenic amines are preferred, these generally containing from 5% to 50% of the acid or amine
30 monomer, balance the amide monomer. The anionic copolymers which are preferred will usually contain acrylic or methacrylic acid as the acid component, and these are rendered anionic with the aid of an amine, which is preferably ammonia. Thus, a
35 copolymer of 20% methacrylic acid with 80% acrylamide

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is illustrative of a preferred anionic retention aid.

The cationic amide copolymers are illustrated by copolymers of acrylamide with diethyl aminoethyl methacrylamide.

5 Various other anionic and cationic resins which may be used as the retention aid are discussed in the Kirk Othmer "Encyclopedia of Chemical Technology, third edition" Volume 16, at page 804 which points out that the usual fillers having a size
10 up to 5 microns are not effectively retained because they are so small, thus provoking the use of retention aids in the paper furnish. The beads used herein are generally much larger, but their retention on the Fourdrinier wire is enhanced by the
15 conventional retention agents nonetheless.

The preferred retention aids are thus anionic and are constituted by carboxyl functional copolymers which are dispersed in the aqueous furnish because they are solubilized with a base, usually
20 ammonia or a volatile amine. The vesiculated beads which are used herein are constituted by cross-linked polyester resin which carry unreacted carboxyl groups. These carboxyl groups are also associated with a base since a base is always present when the
25 beads are made.

The polyacrylic acid thickeners are well known materials and are of relatively high molecular weight as is produced by polymerization in aqueous emulsion. Acrylic acid or methacrylic acid are
30 usually employed, the selected acid, or mixture thereof, being substantially the only monomer, though up to about 10% of other monoethylenically unsaturated monomers, such as ethyl acrylate, may be present. Up to about 2% of a polyethylenic monomer,
35 like divinyl benzene or ethylene glycol diallyl

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ether, may be present during the copolymerization to increase the molecular weight or to introduce limited cross-link density. Ammonia or volatile amine, like monoethanol amine, can be used for the neutralization
5 which thickens the aqueous medium containing the polymer. Ammonia is the preferred base. Usually 0.1% to 2% of the polyacrylic acid polymer will provide all the thickening which is needed (after neutralization) to stabilize a bead suspension
10 containing from 10% to 50% of free water. Exact neutralization is not required, the achievement of desired thickening determining the amount of base which should be used.

It is preferred in the process of this
15 invention to employ an aqueous furnish having a pH of from 4 to 6, an acid such as sulfuric acid being added to achieve this result. This is because this pH range maximizes the retention of fines.

It is of interest to note that anionic
20 retention aids are usually added at or near the head box to minimize the agitation they are subjected to, and this conventional procedural device is also preferably used herein (the vesiculated beads are added with the retention aids) in order to maintain
25 the associations between the anionic groups which are added and the fines and fibers which are present in the furnish. More particularly, it is preferred to add the beads and the anionic retention aid to the furnish just prior to the headbox and after pumping
30 and centrifugal screening pressures have been applied so as to minimize the shear which is encountered by the anionic retention aid and the anionic beads which are used herein.

In a specific comparison with the use of
35 titanium dioxide, anatase, at the 7.5% level in a

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typical opacified paper, it is found that the combination of 2.5% titanium dioxide, anatase, and 5% pigmented vesiculated beads provides a calendered paper of the same basis weight having equal strength, higher bulk, equal opacity and better smoothness. About the same situation applies when one uses only pigmented vesiculated beads in the absence of the titanium pigment. Using only titanium dioxide pigmented vesiculated beads in the absence of additional titanium pigment in place of the same weight proportion of titanium pigment provides, for the same basis weight paper, a bulkier paper having comparable brightness and opacity and a smoother surface than the titanium dioxide control. The titanium dioxide-pigmented beads are used for the further reason that the presence of the finely divided pigment in the cell walls of the vesiculated beads provides greater resistance to collapse during the calendering operation.

While pigmented vesiculated beads are important in the production of calendered paper, the effect of increasing the retention of fines in the papermaking process does not appear to require the presence of pigment in the cell walls of the beads, so pigmented beads are not an essential factor in the new process of this invention.

While excellent properties are obtained in the absence of free titanium dioxide, it is desirable for some purposes to include a smaller than usual proportion of such inorganic pigment. Thus, the normal proportion of titanium dioxide, anatase, in opacified calendered printing paper is about 7.5%, and this is reduced herein to 0.5% to 5%, preferably from 1% to 4%.

The preferred vesiculated beads are

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styrene-cross-linked unsaturated polyester resins. These are made into a vesiculated bead in conventional fashion, as illustrated by U.S. Pat. No. 3,879,314. The size of the vesiculated beads under
5 consideration may vary considerably, but is generally larger than a volume average of about 5 microns in diameter. For example, beads having a volume average diameter of from 8 to 30 microns are conveniently prepared and fully useful in this invention. As the
10 bead size increases above about 30 microns, it becomes progressively harder to produce beads of good quality. The beads are obtained in aqueous suspension and normally retain within themselves about 55% to 60% of their own weight of water. The
15 suspensions contain more water than the beads can retain in a dry-appearing cake, so that the suspensions will contain 15% to 35% of bead solids, balance water. These are typically thickened with ammonia-neutralized polyacrylic acid or
20 polymethacrylic acid using enough to provide a stable suspension, but exact proportions are not critical because poorly stable suspensions are still useful while excess thickener can be tolerated.

Various other patents are of interest to the
25 formation of vesiculated beads useful in this invention, particular attention being directed to U.S. patents Nos. 3,822,224, 3,923,704 and 3,933,579. This last-named patent describes the vesiculated beads which are preferred herein, namely,
30 those having a ratio of granular diameter to mean vesicle diameter of at least 5:1, a vesicle volume of from 5% to 95% of the volume of the granule, and not more than about 60% pigment, by volume.

The vesiculated beads used herein have a
35 highly cross-linked polymeric body which is

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preferably constituted by a carboxyl-functional unsaturated polyester resin cross-linked with an ethylenically unsaturated monomer copolymerizable therewith. The unsaturation in the polyester is
5 preferably maleate unsaturation, these polyesters being themselves well known and illustrated hereinafter. These polyesters are carboxyl-functional materials, and it is preferred that the polyester have an acid value of 10 to 45 mgm
10 KOH per gm., more usually 15 to 25.

The unsaturated monomers used for cross-linking are also well known and are water insoluble monomers typically illustrated by styrene or vinyl toluene. The polyesters and monomers are
15 more fully discussed in U.S. Pat. No. 3,879,314 which shows the production of vesiculated beads using a water-soluble polyamine containing at least three amine groups per molecule and having a dissociation constant in water (pKa value) of 8.5-10.5, typically
20 illustrated by diethylene triamine. The polyamine is used in a concentration providing 0.3 to 1.4 amine groups per polyester carboxyl group. It is preferred to have from 35% to 45% of the unsaturated polyester cross-linked with from 55% to 65% of styrene. The
25 beads are normally used without drying, and thus contain much of the water and the amines which were used in their production.

The invention is illustrated as follows, it being understood that all parts and proportions are
30 by weight, unless otherwise specified.

Suitable pigmented vesiculated beads in accordance with this invention are illustrated in U.S. Patent No. 3,879,314 issued April 22, 1975, see particularly Example II. By proceeding in accordance
35 with said Example II and using a polyester of 18%

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phthalic anhydride, 37% maleic anhydride and 45% propylene glycol dissolved in styrene to form a solution containing 41.8% of the polyester, vesiculated beads pigmented with titanium dioxide, anatase, to contain about 43.2% pigment are provided. The polyester is a carboxyl-functional product and this carboxyl functionality is largely in salt form with the amines used in the production of the beads. These beads have an average size of about 25 microns and contain an average of more than 10 cells per bead.

These beads are incorporated into a paper furnish in which 88 pounds of softwood kraft, 132 pounds of hardwood kraft, 44 pounds of clay, 5 pounds of calcined clay, and 3.4 pounds of alum is mixed into water to provide 500 gallons of mixture to which is added 300 cc of concentrated sulfuric to provide a pH in the range of 4.5 to 6.5. This furnish is modified to include 4% or 6% of the vesiculated beads and 1.5% of titanium dioxide, anatase, based on solids content, and is supplied to the head box by passing the mixture through a valve in which the solids concentration is reduced to 2.5%.

The paper made from this furnish had a basis weight in the range of 37 to 40 pounds per ream and was calendered at either 150 or 900 pounds per linear inch at a temperature of about 150°F. Compared with the same furnish containing 6.5% titanium dioxide, anatase, a 5-15% increase in the caliper of the calendered paper at any given basis weight was observed at both of the 4% and 6% bead inclusion levels which were investigated.

The paper produced, with and without the beads, was passed through a size press in conventional fashion and then calendered under the

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conditions noted to provide the final paper which was tested. The paper containing the pigmented vesiculated beads had greater caliper and greater resistance to print show through than the
5 conventional titanium dioxide-pigmented paper. This establishes that printing paper of lesser weight and the same resistance to print show through can be provided by this invention.

The vesiculated beads in the form of an
10 ammonia-neutralized polyacrylic acid-thickened stable aqueous suspension can be added together with an anionic retention aid constituted by a copolymer of 20% methacrylic acid and 80% acrylamide in an amount of 1% based on the weight of solids present in the
15 furnish. These are added to the furnish together with the water used to dilute the furnish to the desired solids content immediately prior to the head box so as to minimize shear. In comparison with the use of the anionic retention aid alone, a substantial
20 reduction in fines passing through the wire into the white water is experienced, as evidenced by the lowering of the zeta potential of that white water. From the standpoint of ash content, it is found that the normal retention as evidenced by comparing the
25 theoretical ash content with the actual ash content increases from about 67-68% to about 76-77% when this aspect of the invention is practiced.

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WHAT IS CLAIMED IS:

1. A high bulk calendered paper comprising from 2% to about 6% of the weight of the paper of highly cross-linked, titanium dioxide-pigmented, polymeric vesiculated beads having a volume average particle size of at least about 5 microns up to about 35 microns, said calendered paper having a basis weight of up to about 40 pounds per ream.

2. A high bulk calendered paper as recited in claim 1 in which said vesiculated beads are present in an amount of at least about 3.5%, and said calendered paper has a basis weight of at least about 20 pounds per ream to provide a quality printing paper and said vesiculated beads have a volume average particle size in the range of from 10 to 30 microns.

3. A high bulk calendered paper as recited in claim 2 in which said vesiculated beads are present in an amount of from about 4% to about 5% and said vesiculated beads contain an average of at least 5 cells per bead, have a ratio of granular diameter to mean vesicle diameter of at least 5:1, a vesicle volume of from 5% to 95% of the volume of the granule, and not more than about 60% pigment, by volume.

4. A high bulk calendered paper as recited in claim 3 in which the polymeric body of said beads is constituted by a carboxyl-functional unsaturated polyester resin cross-linked by an ethylenically unsaturated monomer copolymerizable therewith and are incorporated in the furnish and retained with the aid of an anionic retention aid.

5. A high bulk calendered paper as recited in claim 4 in which from 35% to 45% of unsaturated polyester containing maleate unsaturation is

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cross-linked with from 55% to 65% of styrene and said polyester has an acid value of 10 to 45 mgm KOH per gm.

6. A high bulk calendered paper as recited in claim 1 in which said paper is calendered at a pressure of at least about 150 pounds per linear inch using a temperature of at least about 100°F.

7. A high bulk calendered printing paper as recited in claim 1 in which the calendering pressure is in the range of 700 to 1200 pounds per linear inch and the calendering temperature is at least about 150°F.

8. A high bulk calendered printing paper as recited in claim 16 in which the proportion of titanium dioxide, anatase, not in said beads is from 1% to 4%.

9. A method of making paper as recited in claim 1 comprising adding to the aqueous furnish an aqueous suspension of carboxyl-functional highly cross-linked, polymeric vesiculated beads having a volume average particle size of at least about 5 microns together with an anionic retention aid, said beads being preassociated with a neutralized polycarboxylic acid polymer thickener, to thereby reduce the proportion of fines which pass through the wire into the white water.

10. A method of making paper as recited in claim 9 in which and said polyester has an acid value of 10 to 45 mgm KOH per gm. and said anionic retention aid is a copolymer of acrylamide with from 5% to 50% of a monoethylenically unsaturated carboxylic acid. said polyester has an acid value of 15 to 25 mgm KOH per gm., said thickener is a polyacrylic acid, and said anionic retention aid and said thickener being neutralized with ammonia.



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
D,P X	EP-A-0 204 916 (DeSOTO) * Whole document * ---	1-8	D 21 H 3/82 D 21 D 3/00
D,X	US-A-3 933 579 (R.W. KERSHAW et al.) * Examples 7,29; column 3, lines 26-52 *	1-5	
A	ABSTRACT BULLETIN OF THE INSTITUTE OF PAPER CHEMISTRY, vol. 56, no. 1, July 1985, page 72, abstract no. 469, Appleton, Wisconsin, US; K. KUBOSHIMA: "On functional fillers for papermaking. (1). Highly filler-containing paper", & ANN. HIGH PERFORMANCE PAPER SOC. (JAPAN) no. 21:31-38 (October 1982) * Whole abstract * ---	1,9	
A	GB-A-1 405 751 (BPB INDUSTRIES) * Page 1, lines 24-91; example 2 * ---	9,10	
A	ABSTRACT BULLETIN OF THE INSTITUTE OF PAPER CHEMISTRY, vol. 53, no. 1, July 1982, page 75, abstract no. 465, Appleton, Wisconsin, US; V.V. LAPIN et al.: "Increasing ash content of paper without lowering its mechanical strength", & BUMAZH. PROM. no. 2: 4-6 (February 1981) * Whole abstract * ---	9	TECHNICAL FIELDS SEARCHED (Int. Cl.4) D 21 D D 21 H
A	US-A-4 272 297 (K. BROOKS et al.) -----		
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 10-02-1988	Examiner NESTBY K.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document			