(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 740 014 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
30.10.1996 Bulletin 1996/44

(51) Int Cl.6: **D21C 9/08**, D21H 21/02

(21) Application number: **96301664.7**

(22) Date of filing: **12.03.1996**

(84) Designated Contracting States:
AT BE DE DK ES FI FR GB IT NL PT SE

(30) Priority: **16.03.1995 GB 9505323**

(71) Applicant: **ECC INTERNATIONAL LIMITED**
Theale, Reading, Berkshire RG7 4SA (GB)

(72) Inventors:
- **Rogan, Keith Robert**
  Par, Cornwall PL24 2SQ (GB)
- **Plasted, Roderick Michael**
  Par, Cornwall PL24 2SQ (GB)
- **Adams, John Michael**
  Par, Cornwall PL24 2SQ (GB)
- **Rey, Paul Alan**
  Pittsburgh, Pennsylvania 15205 (US)

(74) Representative: **McCormack, Derek James**
English China Clays plc
1015 Arlington Business Park
Theale
Reading, Berkshire RG7 4SA (GB)

(54) Improved pitch control agent

(57) A method of controlling the deposition of pitch in a pulping and/or paper making process which comprises adding a pitch control agent to a stream or a slurry of cellulosic fibres is characterised in that the pitch control agent comprises a particulate inorganic material comprising at least one silicon-containing compound whose particles are coated with a nitrogen-containing polymer having one or more triazine rings.

The pitch control agent may comprise a kandite clay whose particles are coated with a homo- or co-polymer comprising melamine formaldehyde. The pitch control agent may be added together with particulate filler material to the cellulosic fibres being processed. A method of preparing a suitable pitch control agent is also described comprising mixing an aqueous suspension of a particulate inorganic material comprising at least one silicon-containing compound with a solution containing a nitrogen-containing polymer having one or more triazine rings, the pH of the mixture formed being in the range pH1 to pH7.

Printed by Jouve, 75001 PARIS (FR)

Description

This invention relates to a pitch control agent suitable for incorporation in cellulose pulp compositions, to reduce the adverse effects of the deposition of pitch derived from wood pulp in the manufacture of paper and board, and to a process for controlling the deposition of pitch.

Pitch is the name given by paper manufacturers to the substance, derived from colloidally dispersed components of wood resin, which deposits on the wire mesh belts, or "wires", of paper making machines and on the rolls and dewatering felts.

The components of wood resin are released into pulp and paper mill circulatory waters at the pulping stage of the papermaking process. In these waters they have a transitory existence as an unstable oil-in-water emulsion. In a short time coalescence occurs followed by deposition. The pitch deposits are sticky and can block holes in the wire thus reducing drainage through the wire, and can also reduce the absorptive capacity of the felt. They can pick fibres from the formed paper web, often causing holes or weak areas, and occasionally appear in the paper as brown lumps or patches.

Pitch is a mixture of chemical compounds of which the principal components which can be extracted by means of organic solvents are organic acids, for example fatty and resin acids (such as oleic acid), and neutral organic material, for example fats (such as triolein).

The effectiveness of a pitch control agent can be determined in the laboratory by investigating the uptake of triolein and/or oleic acid by the agent.

Both hardwoods and softwoods contain fatty acids and neutral organic materials, but only softwoods contain significant amounts of resin acids. This latter material occurs in wood mainly in the ray cells and resin canals or ducts. Therefore, softwoods or gymnosperms such as pine, spruce and fir, in general cause more serious pitch problems than hardwoods, such as birch, maple, oak and poplar. Certain species of pine are particularly rich in resin acids.

The process by which the paper pulp is prepared is also important. The wood may be reduced to pulp by mechanical grinding alone, or with the aid of a chemical cooking process. The two most important chemical cooking processes are the sulphite process in which the ground wood is cooked in an acid solution of calcium bisulphite saturated with sulphur dioxide, and the sulphate or Kraft process in which the cooking is performed in an alkaline solution comprising sodium hydroxide, sodium sulphide and sodium hydrosulphide. When pulp is prepared by the sulphate process the pitch problem is less severe than when the pulp is prepared by the mechanical or sulphite processes because, in the sulphate process, the cooking solution is alkaline and most of the pitch-forming material is saponified and removed in solution by washing.

Two methods have been used for controlling pitch in preparing paper pulp and in paper making. In the first method an adsorbent material is introduced which will adsorb the pitch in the form of small droplets, generally smaller than about 2µm in diameter. Adsorbent materials used for this purpose include bentonite, talc and diatomaceous silica. In the second method the pitch is chemically stabilised so that it remains in suspension in process water and is removed from the process.

EP-A-0569085 describes a method for inhibiting the deposition of pitch and "stickies" on the surfaces of pulping and paper making machinery and/or for removing the deposits therefrom, wherein an effective amount of a melamine-aldehyde type polymer is added to a pulp slurry or furnish in contact with the machinery.

EP-A-0232015 describes a method for the control of pitch in an aqueous system used during pulp or paper making wherein there is added to the system or to the pulp or paper making machinery a water-soluble, polyquaternary branched polymer derived from (a) an epihalohydrin, a diepoxide or a precursor for an epihalohydrin or a diepoxide; (b) an alkyl amine having a functionality with respect to an epihalolydrin of 2; and (c) an amine which has a functionality with respect to a epihalolydrin greater than 2 and which does not posses any carbonyl groups.

US-3582461 concerns the use as a pitch control agent of water-soluble di-cyandiamide-formaldehyde condensates.

Examples of attempts to control pitch with other types of compounds or processes are found in U.S. Patent Nos. 3,812,055; 3,895,164; 3,896,046; 3,992,249; 4,313,790.

Zirconium chemicals have also been used to control pitch. See, for example, U.S. Pat. No. 4,950,361.

The purpose of the present invention is to provide a pitch control agent which is more effective than the agents used in the prior art in the control of pitch in a pulping and/or paper making process.

According to a first aspect of the present invention there is provided a method of controlling the deposition of pitch in a pulping and/or paper making process which comprises adding a pitch control agent to a stream or slurry of cellulosic fibres and characterised in that the pitch control agent comprises a particulate inorganic material comprising at least one silicon-containing compound whose particles are coated with a coating material comprising a nitrogen-containing polymer having one or more triazine rings.

In this specification "paper" includes all paper related products made in a manner similar to paper by processing of cellulosic fibres derived from pulp.

According to a second aspect of the present invention there is provided a pitch control agent for use in the method according to the first aspect which agent comprises a particulate inorganic material comprising at least one silicon-containing compound whose particles are coated with a coating material comprising a nitrogen-containing polymer having one or more triazine rings.

The method according to the first aspect may provide inhibition of pitch deposits on and/or removal of pitch deposits from pulping and/or paper making machinery or equipment. The stream or slurry to which the said pitch control agent is added may comprise for example a furnish, stock or other paper making stream or slurry which contacts the surface of the machinery or equipment to be protected from pitch build-up.

The said nitrogen-containing polymer may comprise a homopolymer or alternatively it may comprise a co-polymer comprising one or more nitrogen-containing monomer units and one or more other cationic monomer units. Any suitable cationic monomer unit may be used; an example is diallyldimethylammonium chloride (dadmac).

With the exception of talc, which has a naturally hydrophobic surface, inorganic silicon-containing compounds are relatively ineffective as pitch control agents in pulping and paper making. Also, polymers containing triazine rings generally have only a moderate capacity for adsorbing pitch. However, it has now been discovered that, when such a polymer is coated onto the surface of a particulate inorganic material comprising one or more silicon-containing compounds, especially onto the surface of a kandite clay, the capacity of the polymer to adsorb pitch is unexpectedly increased to a large degree.

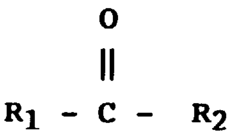
The particulate inorganic material should have surfaces which provide negatively charged sites which ionically bond with positively charged sites on the polymer molecule to provide suitable particle coatings.

The silicon-containing compound or compounds may be silica or a silicate of, for example, calcium, magnesium or aluminium. The compound(s) may be provided by a naturally-occurring mineral, eg. selected from talc, clay minerals, mica or wollastonite, and/or may be synthetic. Preferably the or each silicon-containing compound present is an aluminosilicate, for example a clay mineral of the kandite or smectite type. Clay minerals of the kandite group, for example kaolinite, dickite, nacrite and halloysite, have been found to be particularly advantageous. The kandite clay mineral may be used in its natural hydroxylated or hydrous state, or may be calcined to drive off chemically combined water. Such a mineral may comprise a mixture of clay compounds.

Desirably, kaolin either calcined or uncalcined, having a particle size distribution such that at least 80%, preferably at least 90% by weight, have an equivalent spherical diameter of less than 2 microns (micrometres) is employed to provide the particulate inorganic material. Kaolin which has not been treated during processing by chemical additives, eg. dispersants, is prefered. Desirably, the particles of the kaolin or other silicon-containing inorganic particulate material to be polymer-coated have a specific surface area which is greater than 12m^2/gm in order to maximise the surface area to be coated by the polymer.

The amount of the nitrogen-containing polymer material used to coat the particulate inorganic material has been found to be critical, but varies according to the nature of the inorganic material. For example, kandite clays, which are of relatively low cation exchange capacity, require from 0.5 to 1.5% by weight, preferably from 0.7 to 1.3% by weight, based on the weight of the clay(s) present, of the nitrogen-containing polymer.

In a preferred embodiment, at least one of the triazine rings of the nitrogen-containing polymer employed in or as the polymer material is symmetric, although at least one of the triazine rings may be non-symmetric. The nitrogen containing polymer may be a polymer of the melamine-aldehyde type. As used herein, a melamine-aldehyde type polymer is a polymer formed from: (a), melamine or a substituted melamine; and (b) a compound described by the following formula:



$$R_1 - \overset{\overset{\displaystyle O}{\|}}{C} - R_2$$

wherein R_1 and R_2, which may be the same or different, are selected from the group consisting of H and straight or branched C_{1-4} alkyl groups. The preferred compounds of (b) comprise aldehydes, wherein R_1=H, with methanal (formaldehyde), ethanal and propanal being especially preferred; the most preferred aldehyde is formaldehyde. Also, moderate amounts of additional moieties, including, for example, urea and/or dicyandiamide, may be present in the melamine-aldehyde type polymer.

EP-A-0569085 gives examples of suitable polymers.

The nitrogen-containing polymer preferably comprises the amino derivative of a triazine and the aldehyde in a molar ratio of 1:1 to 1:6. The molecular weight (which is the weight average molecular weight) of the polymer is preferably in the range from 500 to 50,000, most preferably in the range from 500 to 5,000. Suitable melamine aldehyde-type polymers are commercially available from Calgon Corporation, Pittsburgh USA, under the tradenames CA-289 and WT-2511 and SURROUND. These products have molecular weights of about 2,000 to 5,000.

The nitrogen-containing polymer will have a cationicity which varies with pH. This will affect the physical form of the polymer. At very low pH values the polymer will exist for months as discrete, highly stable colloidal particles with a high level of hydrophilicity. On the other hand, at high pH values the catonicity of the polymer is insignificant giving a very low level of hydrophilicity (ie., a high level of hydrophobicity). This produces almost instantaneously a network of flocculated particles. In consequence, the uptake of the polymer by the anionic sites present on the particles of the inorganic particulate material will vary with pH. Significant uptake will occur over a pH range which will be generally from pH1 to pH7. This is the pH at which the polymer contacts the particles of the inorganic material. The uptake will reach a maximum at a particular pH value in this range. For example, the up take of melamine formaldehyde by kaolin is significant over the range pH3 to pH7 and reaches a maximum at about pH5.

Thus, the coating of the inorganic particulate material by the nitrogen-containing polymer should be carried out using a process in which the pH of the polymer when it contacts the inorganic particulate material is maintained in the range pH1 to pH7. The polymer may be present in a medium having a lower pH, eg. in the range pH1 to pH4, when it is applied to coat the inorganic particulate material so that it is in an appropriate colloidal form. The polymer may be added in the form of a colloidal suspension in a suitable acidic aqueous medium.

Although various prior patent specifications eg. EP568720, EP281134, EP132132 and JP6016980 describe aqueous based media containing both a clay and a melamine-aldehyde type polymer for various purposes none of these media would be suitable for, and none is suggested for use in, pitch control in paper making. This is because the pH employed in the media described would not be suitable for the polymer to coat the clay as described hereinbefore to provide an effective pitch control agent.

According to a third aspect of the present invention, there is provided a method of preparing a pitch control agent having a particulate inorganic material comprising at least one silicon-containing compound coated with a nitrogen-containing polymer having one or more triazine rings, which method comprises mixing an aqueous suspension of the particulate inorganic material with a solution or suspension comprising the nitrogen containing polymer.

Preferably, the pH of the solution or suspension comprising the nitrogen-containing polymer is adjusted to a value such that the polymer is present in the form of colloidal particles before the solution or suspension is added to the aqueous suspension. The pH may for example be not greater than than pH4, eg. pH1 to pH4. The polymer may be present as a colloidal suspension in an acidic aqueous medium.

The polymer may form from 1% to 20%, eg. from 5% to 15%, by weight of the solution or suspension containing it (prior to addition to the suspension containing the inorganic particulate material).

The aqueous suspension of the particulate inorganic material may include one or more additives normally employed in the preparation of such suspensions. For example, the suspension may incorporate a dispersing agent such as a sodium polyacrylate (up to about 2% by weight of the dry weight of particulate material present).

The product formed by mixing of the two components, ie. suspension of particulate inorganic material and solution or suspension of nitrogen-containing polymer, may be further treated to enhance the pitch control capacity of the product.

For example, the product of the said mixing step may be dewatered and/or dried so that the water content of the polymer-coated inorganic particulate material is preferably less than 10%, most preferably less than 2% by weight. Dewatering may be achieved in one of a number of ways well known to those skilled in the art, eg. filtration or centrifugation. Drying may conveniently be performed at an elevated temperature, eg. in the range 30°C to 150°C using a current of gas, eg. air or an inert gas such as nitrogen.

In another example, the product of the said mixing step in the method of the third aspect may be heated without incurring substantial loss of water therefrom.

Thus, the capacity of the polymer coated particulate inorganic material to adsorb pitch is likewise increased still further when the nitrogen-containing polymer has been coated on to the particulate inorganic material by a process which includes a step in which a suspension of a mixture of the two components is subjected to heating. This heating step is conveniently performed at a temperature in the range of from 30°C to 100°C, and without substantial loss of water from the suspension, such that the solids content of the suspension remains substantially constant throughout the heating step. The heating step is most preferably performed at a temperature in the range of form 35°C to 75°C.

In another example, the product'of the mixing step in the second aspect may be heated with the loss of some of the water present in the suspension (but without application of a current of gas). Thus, the capacity of the polymer coated inorganic particulate material to adsorb pitch is likewise increased still further when the nitrogen-containing polymer has been coated on to the inorganic particulate material by a process which includes a step in which a suspension of a mixture of the two components is subjected to heating. In this example of the method, the heating step is conveniently performed at a temperature in the range of from 30°C to 75°C. The solids content of the suspension after the heating step is preferably in the range of from 30% to 100% by weight.

The pitch control agent according to the second aspect of the present invention may be added to the pulp being produced or processed to make paper in various ways and at various points of addition. Generally, the pitch control agent will be used in the same way as known inorganic pitch control agents such as talc. The pitch control agent can be added at early stages of the process of pulp producing or processing but it is preferred that it is added later in the process eg. at a stage together with filler particles where such particles are mixed with water to form an aqueous suspension or in a tank in which a suspension of the filler particles is mixed with the pulp or paper making cellulosic fibres or in a so-called head box.

Further examples of locations where addition of the pitch control agent may be made are described hereinafter (with reference to Figure 3 of the accompanying drawings).

The pitch control agent may be added in batches at one or more locations in the pulp or paper making plant or, alternatively, in one or more continuous additions. Samples of the wood pulp or fibres being treated may be analysed (prior to treatment) to determine the amount of pitch control agent required. Alternatively, the pitch control agent may be added only when pitch deposition is detected.

In the method according to the first aspect, the pitch control agent may be added so as to allow maximum contact between the pitch control agent and the pitch to be controlled. Multiple points of addition may be used.

The pitch control agent may conveniently be added to a paper making stock suspension, which generally comprises an aqueous suspension containing from about 0.5% to about 1% by bone dry weight of cellulosic fibres. The amount of the pitch control agent added is generally in the range from 0.5% to 25% by weight, based on the bone dry weight of cellulosic fibres.

Conveniently, the pitch control agent according to the second aspect of the present invention is added in the paper making process together with particulate filler material added to fill the paper composition. Materials useful as filler materials are well known in the art and comprise for example one or more of materials selected from clay (eg., calcined or uncalcined kaolin), calcium carbonate, calcium sulphate. The pitch control agent added in this way, optionally together with one or more other pitch control agents, eg. talc, will act as a paper filler material.

According to the present invention in a fourth aspect a paper composition includes cellulosic fibres and inorganic particulate material as filler and is characterised in that the inorganic particulate material includes a pitch control agent according to the second aspect of the present invention.

The pitch control agent according to the second aspect of the present invention may form up to 30% by weight of the added filler material in the said paper composition, preferably from 10% to 25% of the added filler material. As will be apparent to those skilled in the art, the amount of filler added with depend upon the type of paper being produced.

The said paper composition will also include pitch adsorbed by the pitch control agent. Since the amount of pitch is likely to be less than 0.3% of the weight of the paper composition it will not have an adverse effect on the paper quality. Generally, the amount of pitch adsorbed by the pitch control agent will be up to about 20% by weight of the pitch control agent present.

Embodiments of the present invention will now be described by way of example only with reference to the accompanying drawings, in which:

Figure 1 is a graphical plot of the amount of triolein controlled by a number of different pitch control agents. Curves A to F represent the pitch control agents of the same designations in Example 1 below. For curve E in Figure 1 the amount of pitch control is in μmol per 100mg of pitch control agent. For the other curves in Figure the amount of pitch controlled is in μmol per gramme.

Figure 2 is a graph illustrating the effectiveness of pitch control agents embodying the invention as a function of amount of polymer used for particle coating.

Figure 3 is a schematic flow sheet illustrating a paper making process.

Example 1: Samples to simulate pitch containing a high proportion of neutral organic material were prepared by mixing various different amounts of triolein, measured in micromols, with 10cm^3 of ethanol. Each 10cm^3 sample of solution of triolein in ethanol was mixed with 99g of water, to give a triolein oil-in-water emulsion, and there were then added thereto 1g samples of each of a series of pitch control agents described below.

In each case, the pitch control agent was shaken with the oil-in-water emulsion of triolein for 15 minutes, after which the solid component of the mixture was removed by means of a centrifuge and the triolein which remained in the aqueous phase unadsorbed by the pitch control agent was extracted first with 10cm^3 of hexane and then with three successive 10cm^3 aliquots of chloroform. The hexane and chloroform solutions were combined together in a vessel and the solvents were removed by passing a current of air over the mixed solutions at 60°C to leave a deposit of fat on the walls of the vessel. This fat deposit was then extracted with 20cm^3 of the mobile phase of a high performance liquid chromatography (HPLC) system and the solution shaken for 30 minutes. A small quantity of the solution was then injected into an HPLC column and the quantity of triolein measured by determining the area of the appropriate peak. The difference between the original quantity of triolein introduced and the quantity of triolein present in the hexane and chloroform solvents gave the quantity which had been controlled (i.e. adsorbed) on the pitch control agent.

For each pitch control agent, a graph was plotted of the amount of triolein controlled in μmol per gram of pitch control agent against the concentration of triolein remaining in the aqueous phase. In most cases, a plateau value was reached for the amount of triolein controlled, which remained substantially constant as the concentration of triolein in the aqueous phase was increased. This plateau value was recorded as an indicator of the pitch controlling capacity of the agent.

The pitch control agents were prepared as follows:-

A. (Invention) 45g of a dry kaolin clay from Georgia, U.S.A., having a particle size distribution such that 91% by weight consisted of particles having an equivalent spherical diameter smaller than 2µm and the specific surface area as measured by the BET nitrogen adsorption method was $15.8m^2.g^{-1}$, was added to 105g of distilled water in the stainless steel mixing pot of a Waring Blendor laboratory mixer. The kaolin clay had been prepared without the use of chemical dispersing agents. The resultant suspension, which contained 30% by weight of dry kaolin, was stirred for 1 hour to allow the clay surface to rehydrate fully. The pH of the suspension on completion of this mixing was 8.5. 5.625g of an 8% by weight solution of a melamine-formaldehyde polymer acidified with hydrochloric acid to a pH value of 1.9, and thus converted into the form of a colloid, was added dropwise to the kaolin suspension which was continuously stirred in the Waring Blendor. The stirring was continued for a further 30 minutes after the addition of the melamine-formaldehyde polymer had been completed. The pH of the mixture was then found to be 3.1. The suspension was filtered on a Whatman No.542 hardened ashless filter paper and the cake of solid material was dried in a current of air in a fan oven at about 35 ± 3°C for 16 hours. The dried cake was then pulverised before being added to the triolein oil-in-water emulsions.

B. (Invention) 45g of a dry kaolin clay which was identical to that used in the preparation of pitch control agent A, except that a sodium polyacrylate dispersing agent had been used in its preparation, was coated with the same melamine-formaldehyde polymer and by exactly the same procedure as is described for pitch control agent A.

C. (Invention) 45g of a calcined kaolin clay from Georgia, U.S.A., having a particle size distribution such that 90% by weight consisted of particles having an equivalent spherical diameter smaller than 2µm was coated with the same melamine-formaldehyde polymer and by exactly the same procedure as is described for pitch control agent A.

D. (Comparative) Finely ground talc having a particle size distribution such that the mean particle diameter was 1.65µm and the specific surface area, as measured by the BET nitrogen adsorption method, was $13.6m^2.g^{-1}$. This was considered to be the most effective conventional pitch control agent currently available.

E. (Comparative). The melamine-formaldehyde polymer which was used to prepare pitch control agents A, B and C, but in this case used on its own, in a precipitated form, rather than as a coating on an inorganic silicon-containing compound; the polymer was precipitated prior to the addition of the triolein by the raising of the pH of the water to a value above pH 5 by the addition of $7cm^3$ of a 1% (wt./vol.) solution of $NaHCO_3$. In this case, the amount of the polymer used was 100mg, rather than 1g as in the case of pitch control agents A-D. This amount (100mg) of polymer compares with the 10mg of the polymer which is present on the surface of the 1g of the silicon-containing compound in each of pitch control agents A, B and C.

F. (Comparative). 8.85g of the quaternary ammonium compound dimethyl dihydrogenated tallow ammonium chloride was added, in the form of a hot (ca. 70°C) concentrated (92% by weight) solutien, to 45.45g of dry bentonite clay having an average particle size diameter of ca. 250nm, an approximate mineralogical analysis of 95% by weight of montmorillonite and a cation exchange capacity of 101mequiv./100g. The bentonite and added quaternary ammonium compound were mixed in a blender for 2 minutes. In this-way, the actual dose of the compound on the bentonite was, by weight, 19.5% which corresponded to an equivalents-dose of 30mequiv./100g.

G. (Comparative). The dry kaolin clay which was used to prepare pitch control agent A, but in this case used per se, rather than with a coating of the melamine formaldehyde polymer.

H. (Comparative). The melamine formaldehyde polymer which was used to prepare the pitch control agent E, but in this case used in its colloid form at low pH; the polymer was kept in its colloid form prior to the addition of the triolein by the maintenance of the pH of the water below pH 5 by the addition of less than $3cm^3$ of a 1% (wt./vol.) solution of $NaHCO_3$.

I. (Comparative). The $NaHCO_3$ which was used to prepare the pitch control agents E and H, but in this case used on its own, rather than with the melamine formaldehyde polymer.

The plateau values for the amount of triolein controlled by the different pitch control agents, where measurable, are given in the following Table.

Table

Triolein control data		
Pitch Control agent	Triolein controlled by pitch control agent	
	Expressed as µmol of triolein per g. of pitch control agent	Expressed as a percentage of added triolein, at addition level of 110µmol
A	Too high to measure	99
B	192	99
C	209	99
D	393	95
E	168 µmol. (100mg)$^{-1}$	94
F	120	89
G	<2	<1
H	none (pitch control agent behaved like hydrophobic pitch)	0
I	0	0

The accompanying Figure shows a graphical plot of the amount of triolein controlled in µmol.g^{-1} against the concentration of triolein remaining in the aqueous phase, and the superiority, in particular, of pitch control agent A, as compared with conventional pitch control agent D, can be clearly seen.

EXAMPLE 2

Five pitch control agents were prepared using a dry kaolin clay of the type described under "B" in Example 1 and the method of preparation described under "A", except that a different amount of the acidified colloidal suspension of the melamine-formaldehyde polymer was used in each case.

A 1g sample of each pitch control agent was shaken for 15 minutes with a triolein oil-in-water emulsion prepared by mixing 10ml of a solution of 220µmol of triolein in 10cm^3 of ethanol with 99g of water.

As a comparison, aliquots of triolen oil-in-water emulsion prepared exactly as described above were shaken with amounts of the melamine-formaldehyde polymer which were equivalent to the amounts present in the pitch control agents prepared as described above, but the melamine-formaldehyde was added in a precipitated form, as described under "E" in Example 1, rather than as a coating on an inorganic silicon-containing compound.

In each case the amdunt of triolein controlled in µmol per gram of pitch control agent was determined for each sample by the method described in Example 1. The results are set forth in Table 2 below:

Table 2

Amount of triolein controlled at a triolein addition of 220 µmol by			
Wt. of polymer present in 1.000g of pitch control agent	% by weight of polymer based on weight of mineral	1.000g of pitch control agent (µmol.g^{-1})	Equivalent weight of polymer used alone (µmol. g^{-1})
0.0000	0	32	0
0.0050	0.5	199	8
0.0099	1.0	190	15
0.0133	1.35	210	20
0.0478	5.0	215	73

These results show that as little as 0.5% by weight of the polymer, when coated on to the silicon-containing mineral, is effective for controlling pitch, but that there is little advantage in using more than about 1.5% by weight of the polymer, based on the weight of the mineral. The polymer when coated on to the silicon-containing mineral is very much more effective in controlling pitch than an equivalent weight of the polymer used on its own.

EXAMPLE 3

A first pitch control agent (J) was provided identical to that used under heading "B" in Example 1, the amount of the melamine-formaldehyde polymer which was coated on to the kaolin clay being 1% by weight, based on the weight of dry clay.

A second pitch control agent (K) was prepared using the kaolin clay described under "B" in Example 1, but, in the method of preparation, the steps of filtering, drying and pulverising, which were described under "A" in Example 1, were omitted. Instead, the pitch control agent was made available as a suspension containing 28.3% by weight of dry solids.

1g dry weight samples of each pitch control agent were shaken for 15 minutes with aliquots of oil-in-water emulsions containing different weights of triolein, and the plateau values for the amount of triolein controlled by the two pitch control agents were measured by the method described in Example 1, and are set forth in Table 3 below:

Table 3

Pitch control agent	µmol of triolein controlled per gram of pitch control agent
J	192
K	124

These results show that, in order to achieve the best results it is preferred to dewater and dry the polymer coated silicon-containing compound before use as a pitch control agent.

EXAMPLE 4

A first pitch control agent (L) was prepared using the kaolin clay described under "B" in Example 1, but, in the method of preparation, the steps of filtering, drying and pulverising, which were described under "B" in Example 1, were omitted. Instead, the suspension at the relatively low pH value of 3.1 was transferred from the stainless steel mixing pot of the Waring Blendor laboratory mixer to a 1 litre round-bottomed flash with a ground glass neck. The suspension was then heated at 35°C for 16 hours with a reflux condenser inserted into the neck of the round-bottomed flask to ensure that substantially no water was lost from the suspension. In this way, the solids content of the suspensions was kept at about 30% by weight. The suspensions was allowed to cool to room temperature before being added to the triolein-in-water emulsions.

A second pitch control agent (M) was prepared using the kaolin clay described under "B" in Example 1, and the method described above under "L", except that the suspension at a pH value of 3.1 was heated to 70°C instead of to 35°C.

1g dry weight samples of each pitch control agent were shaken for 15 minutes with aliquots of oil-in-water emulsions containing different weights of triolein, and the plateau values for the amount of triolein controlled by the two pitch control agents, "L" and "M", were measured by the method described in Example 1, and are set forth in Table 4 below:

TABLE 4

Pitch control agent	**µmol of triolein controlled per gram of pitch control agent**
M	212
L	200

These results, when compared with those in Table 3, show that heating the suspension to between 35°C and 70°C produces a pitch control agent which has a very similar pitch controlling performance to that of a pitch control agent produced by dewatering and drying the suspension. Thus, in order to achieve the best results, it is preferred to either a) heat the suspension of the polymer-coated silicon-containing compound to between 35°C and 70°C for 16 hours before use as a pitch control agent, or b) dewater and dry the suspension of the polymer-coated silicon-containing compound before use as a pitch control agent.

Figure 2 illustrates how the amount of melamine aldehyde polymer coated onto the surface of an inorganic particulate material can affect the pitch adsorbing ability of the coated material. In this case, the coated material is kaolin coated with a melamine formaldehyde polymer to different coating thicknesses. The kaolin and polymer are as in Example 1 (Pitch Control Agent "B"). The pitch adsorbing ability is represented by the ability of the various coated materials to adsorb triolein. As seen in Figure 2, the triolein adsorption increases rapidly as the weight percentage of the polymer coating on the kaolin is increased from zero to about 0.25%. For coating weight percentages in the range from about 0.25% to about 1.25% the triolein adsorption continues to increase (at a rate which decreases with increasing coating weight). For coating weight percentages above about 1.25% the adsorption of triolein shows little increase with increasing coating weight percentage. A particular coating weight percentage, indicated in Figure 2 by a dotted vertical line labelled "X", corresponds to a coating weight percentage value calculated from theory which is the amount of the polymer just required to satisfy the negatively charged sites present on the surface of the kaolin. The value X can be considered to be the optimum theoretical coating weight percentage required.

EXAMPLE 5

The efficacy of the materials embodying the invention was measured by a different laboratory method, using tall oil as a synthetic pitch (rather than triolein) as described below. Tall oil contains oleic acid.

The synthetic pitch solution was prepared by adding 40 g potassium hydroxide and 600 g denatured ethanol to 160 g distilled tall oil, and stirring until the potassium hydroxide is completely dissolved.

To 1 litre of water in a beaker at pH 8.5 is added 1040 ppm of synthetic pitch solution, sufficient of 10% calcium chloride solution to attain a hardness of 1020 ppm (as $CaCO_3$)and a selected quantity of the deposit control treatment. Throughout these additions and for 8 minutes thereafter, the mixture is stirred at 160 rpm using square mixing blades. Mixing is then stopped, the beaker emptied and the mixing blades rinsed lightly. Beakers and blades are then oven dried for 15 minutes at 60°C. The weight difference between beaker and blades before and after the experiment is recorded as mg pitch deposited.

The pitch control materials employed were:

P (Comparative)	A finely ground talc (The same as D in Example 1)
Q (Comparative)	A melamine formaldehyde polymer (The same as E in Example 1)
R (Invention)	A clay treated with melamine formaldehyde as follows:

A sample at 27% solids of the same clay as in Example 1, B, was mixed with 8% by weight solution of melamine formaldehyde polymer such that the ratio of active polymer:dry clay was 1:100. After mixing, the pH was 4.5. Sulphuric acid was then added to reduce the pH to 2.8. The flocculated mixture was then filtered to 55-60% solids, and was dried at 220 °C. The dried cake was then pulverised before being subjected to pitch control tests.

The results obtained were as in Table 5 as follows:

TABLE 5

Agent	Dose (ppm)	Polymer Dose (ppm)	Deposit wt (mg)
P	800	-	643
Q	8	8	751
R	800	8	142
None			950

Comparison of the deposit values in Table 3 shows that the amount of pitch deposited is minimised by use of the pitch control agent R embodying the invention.

Figure 3 illustrates a paper making process in which a pitch control agent embodying the present invention, herein "PCA", is used. The PEA may be one of the materials prepared above, eg. as in Example 1.

An aqueous stock containing 2% by weight of cellulosic fibres (obtained by beating and refining a bleached sulphite pulp) is mixed in a stirred tank 1 with 1.5% by weight, based on the weight of dry cellulosic fibres, of fortified rosin size and 3.0% by weight of powdered aluminium sulphate. The resulting stock of sized fibres is delivered by a pump 2 through a conduit 3 to a constant head tank 4 from which the overflow is returned to tank 1 through a conduit 5. Clean water is supplied via a conduit 16 to a second constant head tank 6 from which the overflow is passed through a conduit 7 to a reservoir (not shown).

The stock of sized fibres flows from tank 4 through a conduit 8, and water flows from tank 6 through a conduit 9, to a tank 10 where they are mixed in the proportions 3 parts by weight of water to 1 part by weight of suspension to dilute the stock to 0.5% by weight of cellulosic fibres. In a tank 11 provided with an impeller there are mixed together in batches of approximately 8 litres total volume water, filler including PCA (in an amount as specified hereinbefore) and other optional additives eg. cationic starch as a retention aid. The speed of the impeller is such that a vortex is first formed in the tank 11. The mixture so formed is run through a conduit 12 to the tank 10 and is mixed therein with the stock of sized fibres to give a uniform mixture. The resulting mixture is run through a conduit 13 to the head box

14 of a paper making machine 15 where for each loading of the suspension formed in the tank 11 a web of paper is formed on the wire of the machine 15 and then dewatered and thermally dried.

Alternatively, or in addition, the PCA may be added to the pulp when it is formed, before its addition to the tank 1 or in any one or more of the tank 1, tank 4, tank 6, tank 10 or head box 14.

The paper produced in the manner described with reference to Figure 3 contains amongst other things PCA and pitch (adhered thereto) in quantities in the ranges specified above.

The melamine-formaldehyde polymer used in the above Examples was material supplied under the product name SURROUND (Trade Mark) by Calgon Corporation of Pittsburgh, USA. It has a weight average molecular weight of about 4300 and a melamine to formaldehyde molar ratio of from 3.2:1 to 3.5:1.

Claims

1. A method of controlling the deposition of pitch in a pulping and/or paper making process which comprises adding a pitch control agent to a stream or a slurry of cellulosic fibres and characterised in that the pitch control agent comprises a particulate inorganic material comprising at least one silicon-containing compound whose particles are coated with a nitrogen-containing polymer having one or more triazine rings.

2. A method as claimed in claim 1 and wherein the particulate inorganic material comprises an aluminosilicate and the polymer comprises a melamine-aldehyde type polymer.

3. A method as claimed in claim 1 or claim 2 and wherein the polymer comprises a co-polymer comprising one or more nitrogen-containing monomer units and one or more other cationic monomer units.

4. A method as claimed in claim 1, claim 2 or claim 3 and wherein the pitch control agent comprises kandite clay whose particles are coated with a homo-or co-polymer comprising melamine formaldehyde.

5. A method as claimed in Claim 1, claim 2, claim 3 or claim 4 and wherein the pitch control agent is added together with particulate filler material to the cellulosic fibres.

6. A method of preparing a pitch control agent for use in the method of any one of claims 1 to 4 which comprises mixing an aqueous suspension of a particulate inorganic material comprising at least one silicon-containing compound with a solution containing a nitrogen-containing polymer having one or more triazine rings, the pH of the mixture formed being in the range pH1 to pH7.

7. A method as claimed in claim 6 and wherein the pitch control agent comprises kandite clay coated with a melamine formaldehyde homo- or co-polymer and the pH of the mixture is in the range pH4 to pH6.

8. A method as claimed in claim 6 or claim 7 and which includes dewatering and/or drying the product of the said mixing so that the water content of the polymer-coated particulate inorganic material is less than 10% by weight.

9. A method as in claim 6 or claim 7 and which includes heating the product of the said mixing without substantial loss of water.

10. A method as in claim 6 or claim 7 and which includes heating the product of the said mixing with some loss of the water present.

11. A method claimed in any one of claims 6 to 10 and wherein the weight of the nitrogen-containing polymer which coats the particles of the particulate inorganic material is in the range of from 0.5% to 1.5% of the weight of the particulate inorganic material.

12. A pitch control agent for use in the method claimed in any one of claims 1 to 5 and which is the product with or without further treatment of the method of preparation claimed in any one of claims 6 to 10.

13. A paper composition including cellulosic fibres and particulate filler material and characterised in that the particulate filler material includes a pitch control agent comprising a particulate inorganic material whose particles are coated with a polymer material comprising a nitrogen-containing polymer having one or more triazine rings.

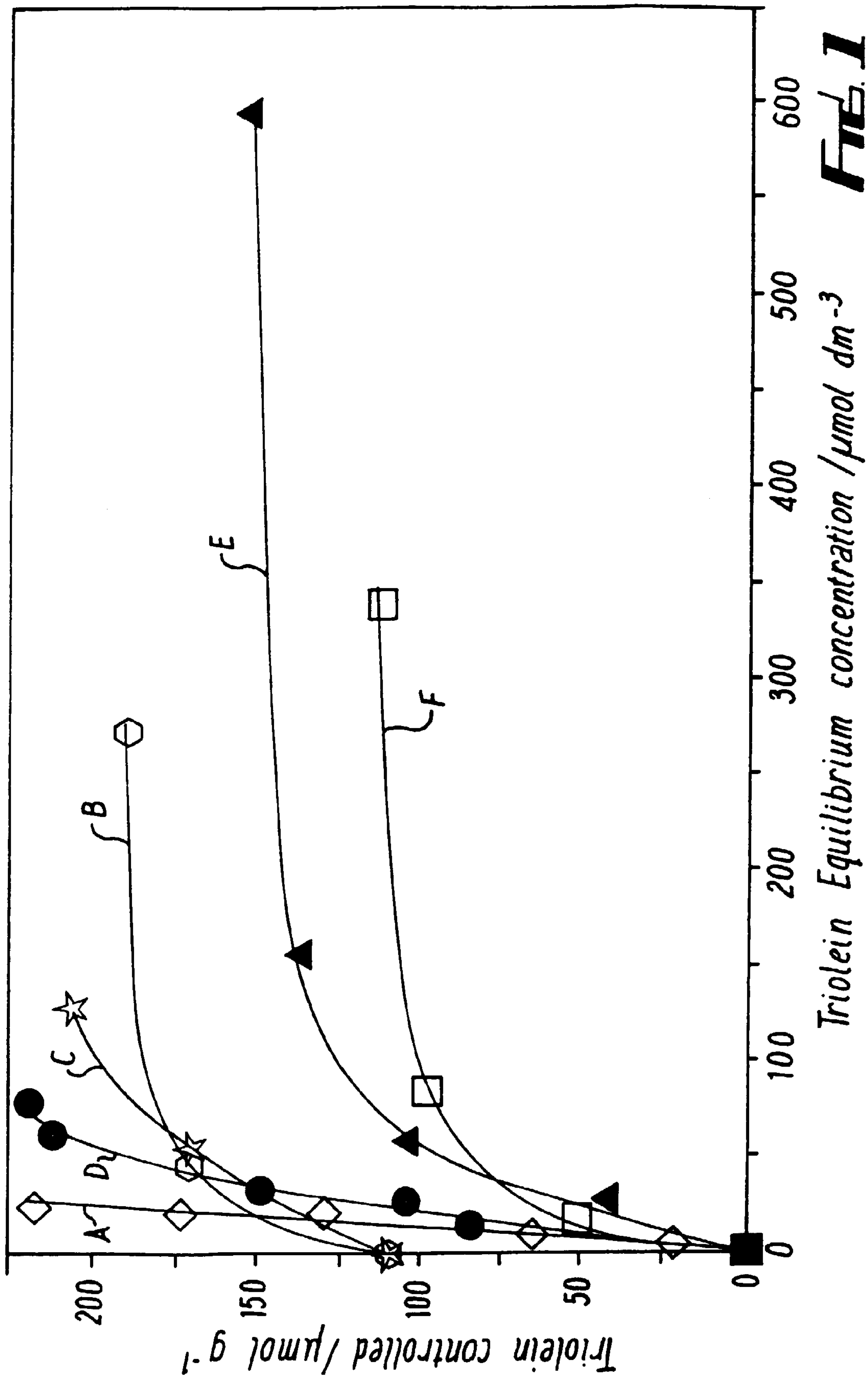

Triolein controlled /μmol g-1
0
50
100
150
200
Triolein Equilibrium concentration /μmol dm-3
0
100
200
300
400
500
600
A
B
C
D
E
F

FIG. 1

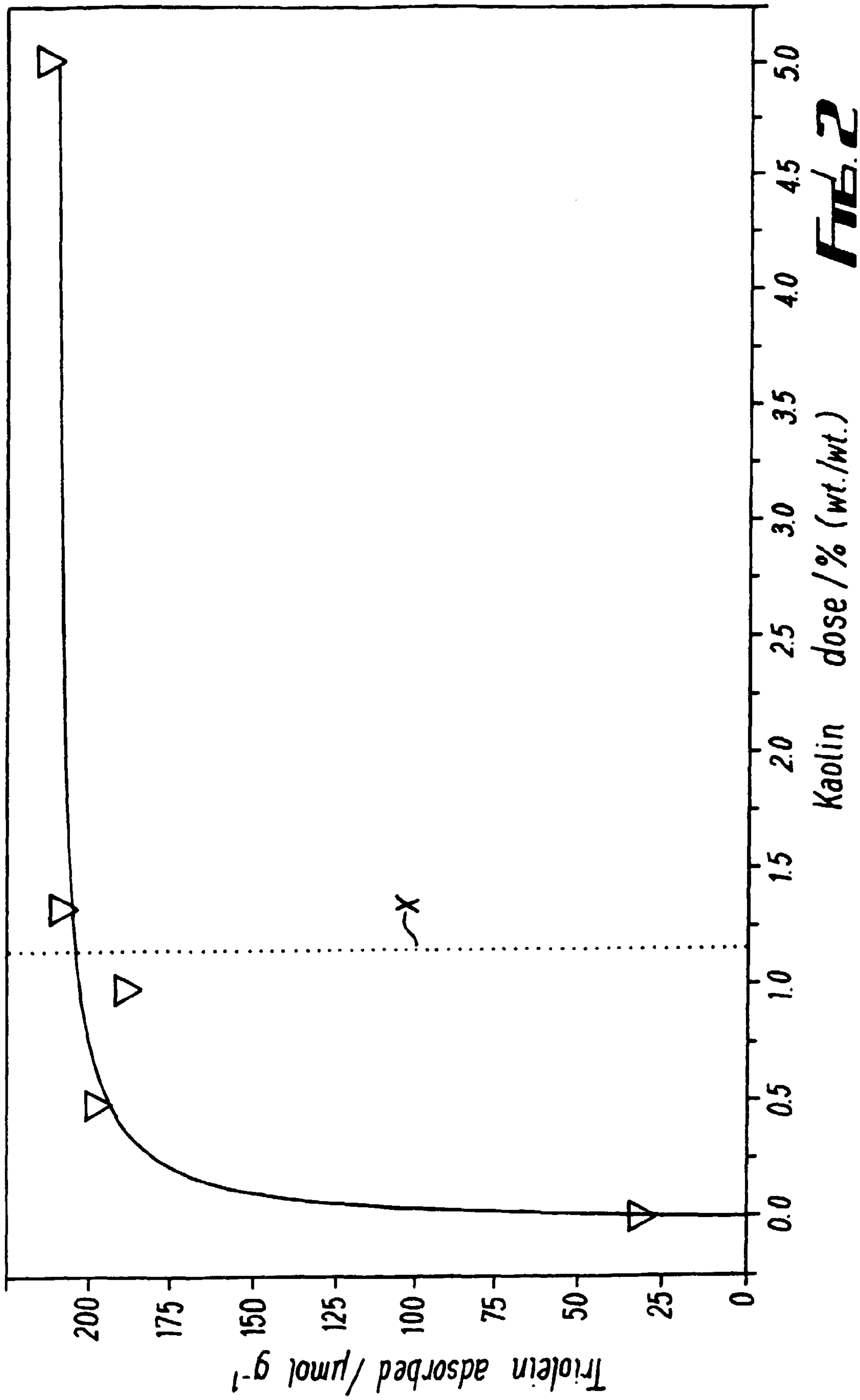

Triolein adsorbed /µmol g⁻¹
0
25
50
75
100
125
150
175
200
Kaolin dose /% (wt./wt.)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
X

FIG. 2

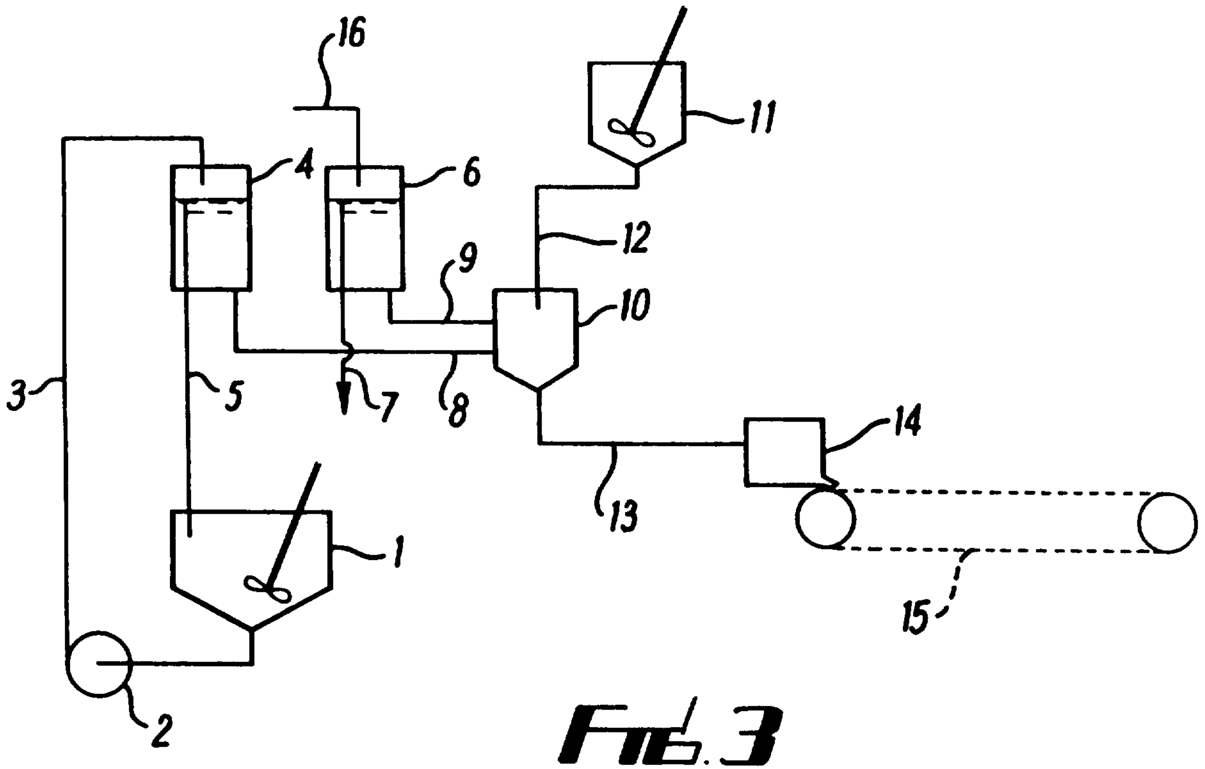


FIG. 3

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 30 1664

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.6)
Y	WO-A-89 06294 (CYPRUS IND MINERALS COMPANY) 13 July 1989 * page 12, line 19 - page 13, line 3 * * page 14, line 34 - page 15, line 23 *	1,2,4,5	D21C9/08 D21H21/02
A		6,7, 11-13	
D,Y	EP-A-0 569 085 (CALGON CORP) 10 November 1993 * the whole document *	1,2,4,5	
D,X	EP-A-0 132 132 (DU PONT) 23 January 1985 * the whole document *	13	
A		6,11	
A	EP-A-0 349 311 (ECC INT LTD) 3 January 1990 * the whole document *	1-13	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)
D21C
D21H

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	15 July 1996	Bernardo Noriega, F

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

EPO FORM 1503 03.82 (P04C01)