

(19)



(11)

**EP 1 406 711 B1**

(12)

**EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention  
of the grant of the patent:  
**18.11.2009 Bulletin 2009/47**

(51) Int Cl.:  
**B01D 1/00** <sup>(2006.01)</sup> **B01D 37/02** <sup>(2006.01)</sup>  
**C02F 11/00** <sup>(2006.01)</sup> **C02F 1/00** <sup>(2006.01)</sup>

(21) Application number: **00967147.0**

(86) International application number:  
**PCT/US2000/026925**

(22) Date of filing: **28.09.2000**

(87) International publication number:  
**WO 2002/026340 (04.04.2002 Gazette 2002/12)**

**(54) METHODS OF USING NATURAL PRODUCTS AS DEWATERING AIDS FOR FINE PARTICLES**

VERFAHREN ZUR VERWENDUNG VON NATÜRLICHEN PRODUKTEN ALS  
ENTWÄSSERUNGSHILFEN FÜR FEINE TEILCHEN

PROCEDES PERMETTANT D'UTILISER DES PRODUITS NATURELS COMME AUXILIAIRES DE  
DESHYDRATATION DE PARTICULES FINES

(84) Designated Contracting States:  
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE**

(74) Representative: **Kierdorf, Theodor**  
**Intecpatent**  
**Postfach 40 01 53**  
**51410 Bergisch Gladbach (DE)**

(43) Date of publication of application:  
**14.04.2004 Bulletin 2004/16**

(56) References cited:  
**US-A- 4 207 186 US-A- 4 210 531**  
**US-A- 4 278 208 US-A- 4 561 953**  
**US-A- 5 346 630 US-A- 5 670 056**  
**US-A- 5 814 210**

(73) Proprietor: **Yoon, Roe-Hoan**  
**Blacksburg, VA 24060 (US)**

(72) Inventor: **Yoon, Roe-Hoan**  
**Blacksburg, VA 24060 (US)**

**EP 1 406 711 B1**

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

## Description

## BACKGROUND

**[0001]** Many particulate materials are produced and processed in aqueous media. Before they are sold to customers or further processed, it is often necessary to remove the water. Dewatering can be achieved by either mechanical methods (e.g., filtration and centrifugation) or thermal drying. In general, the former is cheaper than the latter. However, mechanical dewatering becomes inefficient with finer particles. Dewatered products contain high moistures, often requiring thermal drying to meet specifications.

**[0002]** In a given mechanical dewatering process, bulk of the water is removed rather quickly. What is difficult to remove is the water adhering to the surface of the particulate material. Thus, the amount of the residual water left in the product is approximately proportional to its surface area. For a given material, specific surface area is inversely proportional to the square of its particle size. Therefore, the residual moistures in filtered products increase accordingly with decreasing particle size. A more quantitative explanation for the difficulty in dewatering fine particles by filtration may be given by the Laplace equation:

$$\Delta p = \frac{2\gamma \cos \theta}{r}, \quad [1]$$

in which  $\Delta p$  is the pressure of the water inside a capillary (formed between the particles present in a filter cake),  $r$  is the capillary radius,  $\gamma$  is the surface tension of water, and  $\theta$  is the contact angle of the particles in the cake. The contact angle is a measure of the hydrophobicity (water-hating property) of the particles. Eq. [1] shows that the pressure required to blow the water out of a capillary increases with decreasing capillary radius. Considering that finer particles form smaller capillaries, one can see the difficulty in dewatering fine particles. With a given filter cake, which consists of particles of different sizes, there must be a distribution of capillaries of various radii. At a given pressure drop applied across a filter cake, it would be difficult to blow the water out of the capillaries whose radii are below certain critical value. Thus, the number of capillaries, whose radii are below the critical radius, should determine the final cake moisture.

**[0003]** Various polymeric flocculants are used to enlarge the particle size and, hence, minimize the number of smaller capillaries. Electrolytic coagulants can also be used to enlarge particles. Groppo and Parekh (Coal Preparation, 1996, vol. 17, pp. 103-116) showed that fine coal dewatering improves considerably in the presence of divalent and trivalent cations. They found this to be the case when using cationic, anionic and nonionic surfactants.

**[0004]** Eq. [1] suggests also that capillary pressure should decrease with decreasing surface tension and increasing contact angle. Various surfactants are used to decrease the surface tension. Most of the dewatering aids used for this purpose is ionic surfactants with high hydrophile-lipophile balance (HLB) numbers. Sodium laurylsulfate and sodium dioctylsulfosuccinate, whose HLB numbers are 40 and 35.3, respectively, are typical examples. Singh (Filtration and Separation, March, 1977, pp. 159-163) suggested that the former is an ideal dewatering aid for coal because it does not adsorb on the surface, which in turn allows for the reagents to be fully utilized in lowering surface tension. The U.S. Patent No. 5,346,630 teaches a method of pressure spraying a solution of a dewatering aid from a position within the filter cake forming zone of a filter just prior to the disappearance of the supernatant process water. This method, which is referred to as torpedo-spray system, ensures even distribution of the dewatering aid without becoming significantly diluted by the supernatant process water.

**[0005]** It is well known that high HLB surfactants can actually cause an increase in moisture in dewatering hydrophobic materials such as coal. Due to the high polarity of its head group, high HLB surfactants adsorb on hydrophobic surfaces with inverse orientation, i.e., with hydrocarbon tails in contact with the surface and the polar heads pointing toward the aqueous phase. Such an adsorption mechanism should decrease the hydrophobicity and, hence, cause an increase in cake moisture. Most of the flocculants used as dewatering aids also dampen the hydrophobicity, and cause an increase in moisture.

**[0006]** There are several U.S. patents, which disclosed methods of using low HLB surfactants as dewatering aids. The U.S. patent Nos. 4,447,344 and 4,410,431 disclosed methods of using water insoluble nonionic surfactants with their HLB numbers in the range of 6 to 12. These reagents were used together with reagents (hydrotropes) that are capable of keeping the surfactants in solution or at the air-water interface rather than at the solid-liquid interface, so that they can be fully utilized in lowering surface tension. The advantage of using low HLB surfactants may be that unlike the high HLB surfactants they do not have the deleterious effects of hydrophobicity dampening.

**[0007]** The U.S. Patent No. 5,670,056 teaches a method of using non-ionic low HLB surfactants and polymers as hydrophobizing agents that can increase the contact angle above 65° and, thereby, reduce the cake moisture. Monounsaturated fatty esters, fatty esters whose HLB numbers are less than 10, and water-soluble polymethylhydrosiloxanes

were used as hydrophobizing agents. The fatty esters were used with or without using butanol as a carrier solvent for the low-HLB surfactants. This invention disclosure lists a group of particulate materials that can be dewatered using these reagents. These include coals, clays, sulfide minerals, phosphates, metal oxide minerals, industrial minerals and waste materials, most of which are hydrophilic. The use of the low HLB surfactants disclosed in the U.S. Patent No. 5,670,056 may be able to increase the contact angles of the materials that are already hydrophobic but not for the hydrophilic particles.

**[0008]** The U.S. Patent No. 2,864,765 teaches a method of using a polyoxyethylene ether or a hexitol anhydride partial long chain fatty acid ester, functioning alone or as a solution in kerosene. However, the disclosure does not mention that the nonionic surfactant increases the hydrophobicity of moderately hydrophobic particles. Furthermore, the compounds disclosed are essentially not adsorbed upon the solid surface of the ore particles and remain in the filtrate, as noted in the U.S. Patent No. 4,156,649. In the latter patent and also in the U.S. Patent No. 4,191,655, methods of using linear or branched alkylethoxylated alcohols as dewatering aids were disclosed. They were used in solutions of hydrocarbon solvents but in the presence of water-soluble emulsifiers such as sodium dioctylsulfosuccinate. As has already been discussed, the use of such a high HLB surfactant can dampen the hydrophobicity and cause an increase in moisture.

**[0009]** The U.S. Patent No. 5,048,199 disclosed a method of using a mixture of a non-ionic surfactant, a sulfosuccinate, and a deforming agent. The U.S. Patent No. 4,039,466 disclosed a method of using a combination of nonionic surfactant having a polyoxyalkylene group and an anionic surfactant. The U.S. Patent No. 5,215,669 teaches a method of using water-soluble mixed hydroxyether, which is supposed to work well on both hydrophobic (coal) and hydrophilic (sewage sludge) materials. The U.S. Patent No. 5,167,831 teaches methods of using non-ionic surfactants with HLB numbers of 10 to 14. This process is useful for dewatering Bayer process alumina trihydrate, which is hydrophilic. The U.S. Patent No. 5,011,612 disclosed methods of using C<sub>8</sub> to C<sub>20</sub> fatty acids, fatty acid precursors such as esters or amides, or a fatty acid blend. Again, these reagents are designed to dewater hydrophilic alumina trihydrate.

**[0010]** The U.S. Patent No. 4,206,063 teaches methods of using a polyethylene glycol ether of a linear glycol with its HLB number in the range of 10 to 15 and a linear primary alcohol ethoxylate containing 12 to 13 carbon atoms in the alkyl moiety. These reagents were used to dewater mineral concentrates in conjunction with hydrophobic alcohols containing 6 to 24 carbon atoms. The composition of this invention was preferably used in conjunction with polymeric flocculants. Similarly, the U.S. Patent No. 4,207,186 disclosed methods of using a hydrophobic alcohol and a non-ionic surfactant whose HLB number is in the range of 10 to 15.

**[0011]** It is well known that oils can enhance the hydrophobicity of coal, which is the reason that various mineral oils are used as collectors for coal flotation. The U.S. Patent No. 4,210,531 teaches a method of dewatering mineral concentrates using a polymeric flocculant, followed by a combination of an anionic surfactant and a water-insoluble organic liquid. The use of flocculant and ionic surfactants may be beneficial in dewatering, but they could dampen the hydrophobicity of the particles and, hence, adversely affect the process. The U.S. Patent No. 5,256,169 teaches to treat a slurry of fine coal with an emulsifiable oil in combination with an elastomeric polymer and an anionic and nonionic surfactant, dewatering the slurry and drying the filter cake, where the oil reduces the dissemination of fugitive dusts. The U.S. Patent No. 5,405,554 teaches a method of dewatering municipal sludges, which are not hydrophobic, using water-in-oil emulsions stabilized by cationic polymers. The U.S. Patent No. 5,379,902 disclosed a method of using heavy oils in conjunction with two different types of surfactants, floating the coal-emulsion mixture, dewatering the flotation product and drying them for reconstitution. The U.S. Patent No. 4,969,928 also teaches a method of using heavy oils for dewatering and reconstitution.

**[0012]** The U.S. Patent No. 4,770,766 disclosed methods of increasing the hydrophobicity of oxidized and low-rank coals using additives during oil agglomeration. The main objective of this process is to improve the kinetics of agglomeration and ultimately the separation of hydrophilic mineral matter from coal. The additives disclosed in this invention include a variety of heavy oils and vegetable oils, alcohols containing 6 or more carbon atom, long-chain fatty acids, etc. When these additives were used, the product moisture was lower than would otherwise be the case. However, the process requires up to 150 kg/t (300 lb/ton) of additives and uses very large amounts (45 to 55% by volume of a coal to be cleaned) of an agglomerant, which is selected from butane, hexane, pentane and heptane.

**[0013]** The U.S. Patent Nos. 5,458,786 disclosed a method of dewatering fine coal by displacing water from the surface with a very large amount of liquid butane. The spent butane is recovered and recycled. The U.S. Patent No. 5,587,786 teaches methods of using liquid butane and other hydrophobic liquids for dewatering other hydrophobic particles.

## OBJECTS OF THE INVENTION

**[0014]** It is an object of the present invention to provide novel methods of decreasing the moisture of fine particulate materials during mechanical dewatering processes such as vacuum and pressure filtration and centrifugation.

**[0015]** Another important objective of the invention is the provision of improving the rate at which water is removed so that given dewatering equipment can process higher tonnages of particulate materials.

**[0016]** An additional objective of the present invention is the provision of novel fine particle dewatering methods that

can reduce the moisture so low that no thermal drying is necessary.

**[0017]** Still another object of the instant invention is the provision of a novel dewatering method that creates no adverse effects on up- and downstream processes when the water removed from the dewatering processes disclosed in the present invention is recycled

**[0018]** Yet another object of the invention is the provision of methods of controlling the frothing properties of the flotation product.

**[0019]** Perhaps the most important object of the instant invention is to achieve all of the above objects using low-cost affordable dewatering aids that have no harmful effects on the environment and the human health.

## SUMMARY OF THE INVENTION

**[0020]** It is the object of this invention to provide an efficient method of dewatering fine particulate materials. This is achieved by destabilizing the water on the surface of the particles to be dewatered by rendering the surface substantially hydrophobic. The particles are hydrophobized in two steps. Initially, surfactants, preferably of high hydrophile-lipophile balance (HLB) numbers, or collectors are used to render a particulate material moderately hydrophobic. The material is subsequently treated with a lipid, which is a naturally occurring hydrophobic substance, to further enhance its hydrophobicity close to or above the water contact angle of  $90^\circ$ . This will greatly weaken the bonds between the water molecules and the surface of the particulate material and, thereby, 'liberate' the surface water. The liberated surface water is then removed from the particulate material by using various mechanical dewatering devices.

**[0021]** The key to the methods of dewatering described in the present invention disclosure is the hydrophobicity enhancement step. According to the Laplace equation, a relatively small increment in hydrophobicity (above the level that can normally be achieved using a high HLB surfactant in the first hydrophobization step) can bring about a large decrease in capillary pressure and, hence, a large decrease in surface moisture.

**[0022]** The lipids used in the second hydrophobization step of the instant invention are insoluble in water; therefore, they are used as solutions in appropriate solvents, which include but not limited to light hydrocarbon oils and short-chain alcohols. When used in conjunction with an appropriate solvent, lipid molecules may act as nonionic surfactants that can greatly enhance the hydrophobicity of the particulate material to be dewatered. Since lipids are naturally occurring reagents, their use offers a low cost means of improving mechanical dewatering processes.

**[0023]** The dewatering methods disclosed in the instant invention are capable of not only reducing the final cake moistures but also of increasing the kinetics of dewatering substantially. By virtue of the latter, the instant invention can greatly increase the throughput of a dewatering device. Furthermore, the dewatering aids of the present invention have the characteristics of anti-forming agents, which is very important for processing the particulate materials produced from flotation processes. Also, most of the reagents added as dewatering aids and blends thereof adsorb on the surfaces of minerals and coal so that the plant water does not contain significant amounts of residual reagents.

## DETAILED DESCRIPTION OF THE INVENTION

**[0024]** The difficulty in removing water from the surface of fine particles may be attributed to the fact that water molecules are held strongly to the surface *via* hydrogen bonding. It is possible to break the bonds and remove the water by subjecting the wet particles to intense heat, highpressure filters and high-G centrifuges. However, the use of such brute forces entails high energy costs and maintenance problems. A better solution would be to destabilize the surface water by appropriate chemical means, so that it can be more readily removed by using mechanical dewatering devices with minimum energy and maintenance requirements.

**[0025]** The state of the water adhering to a surface may be best represented by the hydrophobicity (water-hating property). The stronger the hydrophobicity, the weaker the bonds between the water and the surface. Therefore, the key to finding appropriate chemical means to destabilize surface water is to increase the hydrophobicity of the particles to be dewatered. A more traditional measure of surface hydrophobicity is water contact angle. In the sessile drop technique, contact angles are measured by placing droplets of water on the surface of the solids of interest. The contact angle, which is measured through the aqueous phase, increases with increasing hydrophobicity.

**[0026]** More recently, scientists developed methods of measuring the forces between two macroscopic surfaces approaching to each other in water. They discovered a hitherto unknown attractive force, which is generally referred to as hydrophobic force. Many researchers showed that the new attractive force is 10 to 100 times stronger than the omnipresent van der Waals force. Yoon and Ravishankar (J. Colloid and Interface Science, vol. 179, p. 391, 1996) showed that the hydrophobic force increases sharply when the contact angles of two interacting mica surfaces approach  $90^\circ$ . According to Eq. [1], capillary pressure becomes negative at contact angles above this value. Thus, if one can increase the hydrophobicity of a particulate material to the extent that its water contact angle exceeds  $90^\circ$ , water should be removed spontaneously. This may be achieved using appropriate surfactants. According to Flinn, et al. (Colloids and Surfaces A, vol. 87, p. 163, 1994), the hydrocarbon tails of octadecylchlorosilane begin to stand up vertically and form

a close-packed monolayer on the surface of silica at a contact angle close to or above 90°. Also, Yoon and Ravishankar observed long-range hydrophobic forces only when close-packed monolayers were formed on mica surfaces. It appears, therefore, that the key to achieving spontaneous dewatering may be to find appropriate surfactants or combinations thereof that can form close-packed monolayers of hydrophobes on the surfaces of the particles to be dewatered.

**[0027]** In the instant invention, the particulate materials in a slurry are hydrophobized in two steps. In *the first step*, an appropriate surfactant or collector is added to the slurry, so that it can adsorb on the surface of the particles and render them moderately hydrophobic. For hydrophilic particles such as silica and clay, ionic surfactants of high HLB numbers may be used for the initial hydrophobization. For sulfide minerals, short-chain thiols may be used. These reagents adsorb on the surface with their polar heads in contact with the surface and their hydrocarbon tails directed toward the aqueous phase. For naturally hydrophobic materials of moderate hydrophobicity, hydrocarbon oils and short-chain alcohols may be used to enhance the hydrophobicity. In *the second step*, a lipid dissolved in an appropriate solvent or a mixture of solvents is added to the slurry to further increase the hydrophobicity of the particulate materials, so that the surface water can be removed more readily by mechanical dewatering processes of low energy consumption.

**[0028]** As a result of the first hydrophobization step, the contact angle of the particulate material to be dewatered is increased to the range of 25° to 60°. It is difficult, but not impossible, to obtain contact angles above this range using a high HLB surfactant alone. High HLB surfactants and thiols adsorb only on specific surface sites. The population of the surface sites, at which the adsorption can occur, is usually well below what is needed to form a close-packed monolayer of the adsorbed surfactant molecules. The reagents added in the second hydrophobization step, i.e., the lipids dissolved in appropriate solvents, may adsorb in between the sparsely populated hydrocarbon tails of the high HLB surfactants and thiols, so that the surface is more fully covered by a close-packed monolayer of hydrophobes. This will increase the contact angle over 60° and more desirably close to or over 90°, so that water can be readily removed from the capillaries formed between finer particles.

**[0029]** Although the Laplace equation suggests that contact angle must exceed 90° for spontaneous dewatering, increasing contact angles close to but not exceeding this value can bring about sufficient advantages. A close examination of Eq. [1] reveals that an increase in contact angle beyond what can be achieved in the first hydrophobization step can bring about a substantial decrease in capillary pressure and, hence, a reduction in cake moisture. Consider a case where contact angle is increased from zero to 60° in the first hydrophobization step. This should decrease capillary pressure by only one half. If the angle is further increased from 60° to 85° in the second hydrophobization step, the capillary pressure decreases further by 5.7 times. This is a substantial gain that can be achieved by a seemingly a modest increment in contact angle. Thus, the second hydrophobization step disclosed in the instant invention offers a highly efficient means of substantially lowering capillary pressures and, thereby, achieving very low cake moistures.

**[0030]** Lipids are naturally occurring organic molecules that can be isolated from plant and animal cells (and tissues) by extraction with nonpolar organic solvents. Large parts of the molecules are hydrocarbons (or hydrophobes); therefore, they are insoluble in water but soluble in organic solvents such as ether, chloroform, benzene, or an alkane. Thus, the definition of lipids is based on the physical property (i.e., hydrophobicity and solubility) rather than by structure or chemical composition. Lipids include a wide variety of molecules of different structures, i.e., triacylglycerols, steroids, waxes, phospholipids, sphingolipids, terpenes, and carboxylic acids. They can be found in various vegetable oils (e.g., soybean oil, peanut oil, olive oil, linseed oil, sesame oil), fish oil, butter, and tallow. Animal fats and vegetable oils are the most widely occurring lipids. Although fats and oils appear different, that is, the former are solids and the latter are liquids at room temperature, their structures are closely related. Chemically, both are triacylglycerols; that is, triesters of glycerol with three long-chain carboxylic acids. They can be readily hydrolyzed to fatty acids. Corn oil, for example, can be hydrolyzed to obtain mixtures of fatty acids, which consists of 35% oleic acid, 45% linoleic acid and 10% palmitic acid. The hydrolysis products of olive oil, on the other hand, consist of 80% oleic acid. Waxes can also be hydrolyzed, while steroids cannot. Vegetable fats and oils are usually produced by expression and solvent extraction or a combination of the two. Pentane is widely used for solvent, and is capable of extracting 98% of soybean oil. Some of the impurities present in crude oil, such as free fatty acids and phospholipids, are removed from crude vegetable oils by alkali refining and precipitation. Animal oils are produced usually by rendering fats.

**[0031]** In the instant invention, the lipids may act as natural surfactants that can enhance the hydrophobicity of the particles to be dewatered. Each triacylglycerol, for example, consists of one head group, i.e., glycerol, and three hydrocarbon tails. For steroids, hydroxyl groups may act as polar head, while the ester linkages serve as the head groups with waxes. They may act effectively as nonionic surfactants of low hydrophile-lipophile balance (HLB) numbers. The HLB numbers of soybean oil and corn oil are 6 and 8, respectively, while that of castor oil is 14. They may adsorb in between or on top of the hydrocarbon chains of the surfactants and thiols that are present on the surface of fine particles as a result of the first hydrophobization step and, thereby, enhance the hydrophobicity.

**[0032]** Since the lipids have low HLB numbers, they are used as solutions of appropriate solvents including but not limited to short-chain alcohols and light hydrocarbon oils. Typically, one part by volume of a lipid, which may be termed as active ingredient(s), is dissolved in two parts of a solvent before use. The two may be mixed in different ratios. As an example, three parts of an active ingredient may be mixed with one part of a solvent. In another, one part of an active

ingredient may be mixed with 20 parts of a solvent.

**[0033]** For example, selected mineral (or coal) constituents of an ore (or coal) are selectively hydrophobized using appropriate reagents (e.g., high HLB surfactants, thiols, light hydrocarbon oils and short-chain alcohols) and floated away from hydrophilic mineral constituents as a means of separation and upgrading. The particulate material to be dewatered must be moderately hydrophobic for the second hydrophobization step disclosed in the instant invention to work. Otherwise, the hydrophobic lipids disclosed cannot adsorb on the surface via hydrophobic attraction and enhance its hydrophobicity. Frequently, the naturally hydrophobic materials or mineral concentrates become considerably less hydrophobic by the time they reach the dewatering step due to superficial oxidation, aging, or exposure to plant water containing hydrophilic polymers. In such cases, they may be re-hydrophobized using the high HLB surfactants and other reagents noted above before adding the reagents identified in the instant invention for the second hydrophobization step.

**[0034]** It may be useful to note here that mineral and coal concentrates obtained by flotation is not hydrophobic enough to be dewatered efficiently. The reason is that the thermodynamic requirement for bubble-particle adhesion, which is a prerequisite for flotation, is that contact angle be larger than zero, while the thermodynamic requirement for spontaneous dewatering is  $90^\circ$ , as discussed above. Therefore, the second hydrophobization step is essential to reduce the cake moisture beyond the levels usually achieved using the currently available dewatering aids and methods. The use of lipids in the second hydrophobization step provides a low-cost means of increasing the contact angle close to or above  $90^\circ$ .

**[0035]** For a given particulate material, parts of the surface must be more hydrophobic than the rest. When using a lipid as dewatering aid, most of the molecules may adsorb on the more hydrophobic parts of the surface, thereby increasing the packing density of hydrophobes on the surface and further increasing its hydrophobicity. The driving force for the adsorption mechanism may be one of hydrophobic attraction. On the other hand, some of the lipid molecules may adsorb on less hydrophobic parts of the surface, with the oxygens in the head groups in contact with the less hydrophobic parts of the surface, possibly via acid-base interactions, while the hydrocarbon tails are pointed toward the aqueous phase. The net result of this adsorption mechanism would be a conversion of the less hydrophobic parts of a surface to more hydrophobic ones. Both of these adsorption mechanisms, i.e., one based on hydrophobic interaction and the other based on acid-base interactions, should help increase the surface hydrophobicity substantially, with its contact angle approaching or exceeding  $90^\circ$ .

**[0036]** The light hydrocarbon oils used as solvents for lipids may also adsorb on the surface of the particulate material to be dewatered *via* hydrophobic interaction, and further enhance its hydrophobicity. In effect, the lipid molecules may act as nonionic surfactants and help spread the light hydrocarbon oils on the surface by modifying the interfacial tensions involved. The lipid molecules should increase the interfacial tension at the solid/water interface, as a consequence of rendering the surface more hydrophobic, while causing a decrease in the interfacial tensions at the oil/water and solid/oil interfaces. Improved spreading of the light hydrocarbon oil should contribute to enhancing the surface hydrophobicity close to or above  $90^\circ$ . Furthermore, all of the reagents used in the present invention may also serve as surface tension lowering agents. The surface tensions of the lipids, hydrocarbon oils and short-chain alcohols are substantially lower than that of water. Their presence at the air-water interface by virtue of their hydrophobicity should reduce the surface tension, and thereby help reduce cake moistures according to the Laplace equation.

## TEST PROCEDURE

**[0037]** Many different samples were used for dewatering tests. These include fine silica, kaolin clay from middle Georgia (60% finer than  $2\ \mu\text{m}$ ), various coal samples from different sources, and sulfide mineral concentrates. A hydrophilic material such as silica and kaolin was hydrophobized in two steps: first using a high HLB surfactant to render the surface moderately hydrophobic and then using a lipid to further enhance its hydrophobicity. Since lipids are insoluble in water, they were used after dissolution in suitable solvents. When sulfide mineral concentrates were received from abroad, they were superficially oxidized and became hydrophilic. As a means of regenerating fresh hydrophobic surfaces, they were re-floated using a thiol collector and methylisobutyl carbinol (MIBC) as a frother. This was necessary because lipids do not adsorb on hydrophilic surfaces.

**[0038]** Some of the coal samples were used as received. Most of the tests were conducted, however, after re-flotation using standard flotation reagents such as kerosene and MIBC. When a sample became hydrophilic due to aging or superficial oxidation during transportation, it was wet-ground in a ball mill for a short period of time to remove the oxidation products and regenerate fresh, moderately hydrophobic surfaces. Lipids adsorb on the surface and enhance its hydrophobicity. To minimize the problems concerning oxidation, some of the tests were conducted using coarse dense-medium products. They were crushed, pulverized, wet-ground in a ball mill, and floated using kerosene and MIBC. The float product was placed in a container and agitated. A known volume of the slurry was removed and transferred to an Elenmeyer flask. After adding known amounts of reagent(s), the flask was hand-shaken for 2 minutes. The conditioned slurry was poured into a filter to initiate a dewatering test. After a preset drying cycle time (usually 2 minutes), the product was removed from the filter, dried in an oven for overnight, and then weighed to determine the cake moisture. In each test, cake formation time and cake thickness were recorded. The cake formation time is defined as the time it takes for

bulk of the water is drained and a cake is formed on a filter medium. For vacuum filtration, a 6.35 cm (2.5-inch) diameter Buchner funnel with a medium porosity glass frit was used. When it was desired to conduct tests at large cake thicknesses, the height of the Buchner filter was extended. For pressure filtration, a 6.35 cm (2.5-inch) diameter air pressure filter with a cloth fabric medium was used. It was made of Plexiglas so that the cake formation time could be determined by visual observation.

## EXAMPLES

### Example 1

**[0039]** A fine silica sample from Tennessee was wet-ground in a ball mill and screened to obtain a 0.074 mm x 0 fraction. It was subjected to two sets of vacuum filtration tests, using varying amounts of a lipid (sunflower oil) with and without the first hydrophobization step. Dodecylammonium hydrochloride was used in the amount of 0.2 kg/t (0.4 lb/ton) at pH 9.5 for the initial hydrophobization. The sunflower oil was used as a 33.3% solution in diesel. All tests were conducted using a 6.35 cm (2.5-inch) diameter Buchner funnel at 1.143 cm (0.45 inches) of cake thickness, 2 minutes of drying cycle time, and a vacuum pressure of 635 mm (25-inches) Hg.

**[0040]** The control test conducted without any reagent gave 21.2% by weight of cake moisture and 104 seconds of cake formation time, as shown in Table 1. When the tests were conducted using sunflower oil without the initial hydrophobization step, both the moisture and the cake formation time decreased only slightly. These findings suggest that lipids do not adsorb on the hydrophilic silica surface and, therefore, cannot work as efficient dewatering aids. When test was conducted after the initial hydrophobization step but without the second hydrophobization step, the cake moisture was reduced to 15.3% and the cake formation time to 21 seconds.

**[0041]** When the silica sample was hydrophobized in two stages as disclosed in the instant invention, substantial reductions in cake moisture were achieved. For example, the process involving an initial hydrophobization step of using 0.2 kg/t (0.4 lb/ton) of a high HLB surfactant (dodecylammonium hydrochloride) and a hydrophobicity-enhancement step of using 1 kg/t (2 lb/ton) sunflower oil reduced the cake moisture from 21.2% to 6.2% and the cake formation to from 104 seconds to 11 seconds.

Table 1 Effects of Using Sunflower Oil as a Dewatering Aid for the Filtration of a 0.074 mm x 0 Silica Sample at 635 mm (25 in.) Hg Vacuum Pressure

Reagent Dosage kg/t (lb/ton)	w/o 1 <sup>st</sup> Hydrophobization Step		w/ 1 <sup>st</sup> Hydrophobization Step <sup>1</sup>	
	Moisture Content (%wt)	Cake Form. Time (sec)	Moisture Content (%wt)	Cake Form. Time (sec)
0 (0)	21.2	104	15.3	21
0.25 (0.5)	20.8	101	9.0	16
0.5 (1)	20.6	98	7.1	12
1.0 (2)	19.7	97	6.2	11

<sup>1</sup> with 0.2 kg/t (0.4 lb/ton) dodecylammonium hydrochloride

**[0042]** Tests were also conducted with a finer (0.034 mm x 0) silica sample. A control test gave a cake moisture of 26.4% and a cake formation time of 161 seconds. With a single-stage hydrophobization process of using 0.2 kg/t (0.4 lb/ton) of dodecylammonium chloride at pH 9.5, the cake moisture was reduced to 19.2% and the cake formation time to 26 seconds. With the two-stage hydrophobization process of using 0.2 kg/t (0.4 lb/ton) of the high HLB surfactant in the first stage and 1 kg/t (2 lb/ton) of a lipid (sunflower oil) in the second stage, the cake moisture was substantially reduced to 8.9% and the cake formation time to 11 seconds.

### Example 2

**[0043]** High-brightness kaolin clays are produced by reverse flotation, i.e., colored impurities are hydrophobized by appropriate collectors and floated away from the clay which remain hydrophilic. The product is usually in the form of 25 to 35% solids, and is dewatered by vacuum filtration to obtain a cake containing 50-55% moisture. Part of the filter cake is thermally dried and then mixed with the remaining wet cake to further reduce the moisture to 25 to 30% range. In this example, a series of filtration tests were conducted on a Middle Georgia kaolin clay (60% finer than 2 $\mu$ m) to demonstrate that the method of dewatering as described in the instant invention disclosure can dewater clay by vacuum filtration to a desired level without thermal drying. All tests were conducted using a 6.35 cm (2.5-inch) diameter Buchner funnel at

635 mm (25 inches) Hg, 0.41 cm (0.16 inches) cake thickness, and 3 min drying cycle time.

**[0044]** When test was conducted without any reagent, it was not possible to form a cake even after a long filtration time. When a test was conducted after hydrophobizing the clay with 0.7 kg/t (1.4 lb/ton) dodecylammonium hydrochloride at pH 9.3, the moisture was reduced to 32.3%. The cake formation time was 13.4 minutes. When the hydrophobicity was enhanced using varying amounts of sunflower oil, the moisture was further reduced as shown in Table 2. At 1.5 kg/t (3 lb/ton) sunflower oil, the moisture content was reduced to 22.4% and the cake formation time to 10.5 minutes. The lipid was used as a 33% solution in diesel oil.

Table 2 Effect of Using Sun Flower Oil on the Dewatering of a Middle Georgia Kaolin Clay

Reagent Dosage kg/t (lb/ton)	Moisture Content (%wt)	Cake Form. Time (Min.)
0 (0)	32.3	13.4
0.5 (1)	27.6	12.2
1.0 (2)	24.0	11.3
1.5 (3)	22.4	10.5

### Example 3

**[0045]** A bituminous coal sample from Blackwater Mine, Australia, was subjected to a series of laboratory vacuum filtration tests. The sample was a flotation product and was received in the form of slurry. Since bituminous coals are naturally hydrophobic, the tests were conducted without the initial hydrophobization. However, the moisture reduction was relatively poor, most probably due to the superficial oxidation of the sample during transportation. As a means of removing the oxidation product from the surface and thereby restoring its hydrophobicity, the coal sample was wet-ground for 1.5 minutes and re-floated using a standard reagent package (i.e., 0.5 kg/t (1 lb/ton) of kerosene as collector and 0.1 kg/t (0.2 lb/ton) methylisobutylcarbinol (MIBC) as frother). The process of grinding and flotation may be considered to be the first hydrophobization step disclosed in the present invention.

**[0046]** The flotation product was then conditioned for two minutes with various reagents that can further increase its hydrophobicity and, thereby, improve dewatering. Three different reagents were used as hydrophobicity enhancing reagents and the results are compared. These include a vegetable lipid (soybean oil), diesel oil, and mixtures of the two. After the second hydrophobization step, the coal sample was subjected to a series of vacuum filtration tests using a 6.35 cm (2.5-inch) diameter Buchner funnel at 635 mm (25 inches) Hg vacuum pressure 1.14 cm (0.45-inch) cake thickness, and 2 min drying cycle time. Table 3 compares the results. A control test, in which the second hydrophobization step was not employed, gave a cake moisture of 25.2%. Using 0.5 kg/t (1 lb/ton) of soybean oil in the second hydrophobization step, the moisture was reduced to 20.2%. At higher dosages of the reagent, no further improvement in moisture reduction was obtained. Use of diesel oil in the second hydrophobization step gave similar results. Using 1:2 mixtures of the two oils gave greater degrees of moisture reductions. In this case, the reagent dosages given in the first column of Table 3 refer to the dosages of soybean oil (active ingredient) alone rather than the sum of the two oils. One may suggest, therefore, that the performance of 0.5 kg/t (1 lb/ton) of the mixture should be compared with the performance of 1.5 kg/t (3 lb/ton) of soybean oil alone or diesel oil alone. Note, however, that the soybean oil-diesel oil mixtures outperformed either soybean oil or diesel oil individually even when they were compared on the basis of total amounts of the reagents used in the filtration experiments. For example, the use of 0.5 kg/t (1 lb/ton) soybean oil and 1 kg/t (2 lb/ton) diesel oil mixture gave 17.1% moisture, while 1.5 kg/t (3 lb/ton) of soybean oil alone and diesel oil alone gave 20.5 and 20.1% cake moistures, respectively. Thus, there exists a synergistic effect of using the mixture. The synergism increased with increasing reagent dosage. As shown in Table 3, continued increase in the dosages of soybean oil alone and diesel oil alone did not significantly decrease the cake moisture, while an increase in the dosages of the soybean oil-diesel oil mixtures substantially improved the moisture reduction. At 1.5 kg/t (3 lb/ton) soybean oil as an active ingredient, the cake moisture was reduced to as low as 14.3%. From a practical point of view, diesel oil is substantially cheaper than soybean oil; therefore, one may consider using the mineral oil as a low-cost facilitator, which can greatly enhance the performance of the lipid, i.e., soybean oil.

**[0047]** The reasons for the synergistic effect are not clear. It is possible that the triacylglycerols present in the soybean oil act as large surfactant molecules with one head group (glycerol) and three hydrocarbon tails. Since they are water insoluble, it will form large globules in water and would act as a hydrocarbon oil just like diesel oil. When soybean oil and diesel oil were used together, however, the latter serves as a solvent for triacylglycerols and help distribute them evenly on the surface of the coal particles. Triacylglycerols may adsorb on the surface of coal *via* hydrophobic interaction, and enhance its hydrophobicity. The contact angles may be increased close to or over 90°, which is conducive to achieving high degrees of moisture reduction. Another possible explanation may be that the triacylglycerols present in



soybean oil facilitate the spreading of diesel oil on coal. This can be achieved if the surfactant can reduce the interfacial tensions at the diesel oil/water and oil/coal interfaces, while increasing the interfacial tension at the solid/water interface. The net results of the two possible mechanisms are the same, that is, the hydrophobicity of coal increases by the combined use of a lipid of vegetable origin and a light hydrocarbon oil.

Table 3 Synergistic Effect of Using Soybean Oil and Diesel Oil for the Vacuum Filtration of a Blackwater Coal Sample (0.85 mm x 0)

Reagent Addition kg/t (lb/ton)	Moisture Content (% wt.)		
	Soybean Oil	Diesel Oil	Combination <sup>1</sup>
0 (0)	25.8	25.8	25.8
0.5 (1)	20.2	22.5	17.1
1.0 (2)	19.6	20.8	15.5
1.5 (3)	20.5	20.1	14.3
2.5 (5)	21.5	19.7	13.7
3.5 (7)	20.9	19.9	14.4

<sup>1</sup> part soybean oil mixed with 2 parts of diesel oil by volume; The reagent dosages for the combination refer to soybean oil alone.

#### Example 4

**[0048]** A coarse Pittsburgh coal sample from a dense-medium separator was pulverized by means of a jaw crusher and a roll crusher, and then wet-ground in a ball mill. The advantage of using a freshly pulverized coal sample may be that the harmful effect of surface oxidation is minimized. The ball mill product was screened at 0.5 mm, and the screen underflow was floated using 0.5 kg/t (1 lb/ton) kerosene and 0.1 kg/t (0.2 lb/ton) MIBC. The process of flotation may be considered to be the first hydrophobization step disclosed in the instant invention. The product was subjected to a second hydrophobization step, in which a lipid (soybean oil) was used as a hydrophobicity-enhancing reagent. Since lipids are water insoluble, it may be beneficial to use them in conjunction with various solvents. In this example, several light hydrocarbon oils and a short-chain alcohol were used as solvents. The filtration tests were conducted using a 6.35 cm (2.5-inch) vacuum filter at 1.14 cm (0.45-inch) cake thickness, 2-minute drying cycle time, and 635 mm (25-inch) cake thickness. The results are given in Table 4. With the particular coal sample used in this example, mineral oils gave better results than butanol. Soybean oil dissolves better in the former. On the other hand, butanol is water-soluble, while mineral oils are not. Therefore, it is not clear what makes a better solvent for soybean oil.

Table 4 Effects of Using Soybean Oil as a Dewatering Aid in Various Solvents on the Vacuum Filtration of a Pittsburgh Coal Sample (0.5 mm x 0)

Reagent Dosage kg/t (lbs/ton)	Cake Moisture (% wt)				
	Diesel Oil	Kerosene	Fuel Oil No. 4	Gasoline	Butanol
0 (0)	25.1	25.1	25.1	25.1	25.1
0.5 (1)	16.8	17.0	17.5	17.6	19.8
1.5 (3)	14.3	14.4	15.4	16.1	18.6
2.5 (5)	13.7	13.5	14.7	14.8	17.1

#### Example 5

**[0049]** A flotation product from Peak Downs Mine, Australia, was received in the form of slurry. The sample was superficially oxidized during transportation. It was, therefore, wet-ground in a ball mill for 1.5 minutes and re-floated using 0.5 kg/t (1 lb/ton) of kerosene and 0.1 kg/t (0.2 lb/ton) MIBC. The flotation product was conditioned with a lipid of animal origin (fish oil) to enhance its hydrophobicity. The lipid was used as a 33.3% solution in diesel oil. The conditioned coal sample was subjected to a series of filtration tests at 200 kPa air pressure and 2 min drying cycle time. The results are given in Table 5. At 0.64 cm (0.25-inch) cake thickness and 2.5 kg/t (5 lb/ton) fish oil, the moisture was reduced from 23.4 to 9.4%, which represents a 59.8% moisture reduction. At lower reagent dosages and higher cake thicknesses,

the moisture reduction became less substantial.

Table 5 Effects of Using Fish Oil on the Filtration of a Coal Sample (0.6 mm x 0) from the Peak Downs Mine, Australia, at 200 kPa of Air Pressure

Reagent Addition kg/t (lb/ton)	Moisture Content (% wt.)		
	Cake Thickness (inch) cm		
	(0.25) 0.64	(0.50) 1.27	(0.85) 2.16
0 (0)	23.4	25.8	26.7
0.5 (1)	14.8	16.2	18.8
1.5 (3)	10.1	13.7	17.2
2.5 (5)	9.4	12.4	15.6

#### Example 6

**[0050]** Table 6 shows the results of the vacuum filtration tests conducted on a Pittsburgh coal sample using fish oil as a dewatering aid. It was used as a 1:2 mixture by volume with diesel oil. The coal sample was a dense-medium product, which was pulverized, ball-mill ground and screened at 0.5 mm. The screen underflow was floated using 0.5 kg/t (1 lb/ton) kerosene and 0.1 kg/t (0.2 lb/ton) MIBC before filtration. The filtration tests were conducted using a 6.35 cm (2.5-inches) diameter Buchner funnel at 635 mm (25-inches) Hg of vacuum pressure and 1.14 cm (0.45 inches) of cake thickness. At 1.5 kg/t (3 lb/ton) of fish oil, moisture was reduced from 28.2 to 15.4%.

**[0051]** Also shown in the table are the equilibrium contact angles of the Pittsburgh coal sample treated under different reagent conditions. In the absence of any reagent, the coal sample gave a contact angle of 12° only, which should give rise to a relatively high capillary pressures and, hence, a high cake moisture. At 0.5 kg/t (1 lb/ton) kerosene, contact angle increased to 44°. According to the Laplace equation, the increase in contact angle from 12° to 44° should reduce the capillary pressure by 1.36 time, which may be responsible for the modest reduction in cake moisture from 28.2 to 24.9%. These results may be considered to be the consequence of the first hydrophobization step disclosed in the instant invention. In the presence of fish oil, contact angle increased close to 90° as shown in Table 6. At 1 kg/t (2 lb/ton), it increased to 86°, which should reduce the capillary pressure by 14 times as compared to the case of untreated coal. Such a large decrease in capillary pressure may be responsible for the substantial decrease in moisture from 28.2 to 16.2%. The results obtained after conditioning with fish oil may be considered to be the consequence of the second hydrophobization step disclosed in the instant invention. Table 6 also shows the surface tensions of the filtrates. The decrease in surface tension with increasing reagent addition may be another factor in the observed decrease in cake moisture.

Table 6 Effects of Kerosene and Fish Oil on the Contact Angle of a Pittsburgh Coal Sample, Filtrate Surface Tension, and the Final Cake Moisture

Reagents Added	Reagent Dosages kg/t (lb/ton)	Contact Angle (Degree)	Filtrate Surface Tension (mN/m)	Moisture Content (%wt)
None	0 (0)	12	71	28.2
Kerosene	0.5 (1)	44	69	24.9
	0.5 (1)	73	65	18.4
Fish	1.0 (2)	86	62	16.2
Oil	1.5 (3)	89	63	15.4
	2.5 (5)	91	56	15.5

#### Example 7

**[0052]** The various lipids of vegetable and animal origins should work with any moderately hydrophobic solid. Therefore, filtration tests were conducted on a zinc (sphalerite) concentrate (0.105 mm x 0) obtained by flotation. The sample was received from a zinc mine in Europe. It was found, however, that the sample was superficially oxidized when it was delivered. Therefore, the sample was re-floated using 0.05 kg/t (0.1 lb/ton) sodium isopropyl xanthate and 0.075 kg/t

(0.15 lb/ton) MIBC as a means of regenerating fresh, hydrophobic surface. The filtration tests were conducted using a 6.35 cm (2.5-inch) diameter pressure filter at 100 kPa air pressure and 2 min drying cycle time. The tests were conducted at various dosages of a lipid (fish oil) and cake thicknesses. One part by volume of fish oil was mixed with 2 parts of diesel oil before use. At 1.5 kg/t (3 lb/ton) fish oil, the moisture reductions were 46, 43 and 41% at 0.51 (0.2), 0.76 (0.3) and 1.52 cm (0.6 inches) of cake thicknesses, respectively. At 2.5 kg/t (5 lb/ton), the moisture reductions did not improve significantly further.

Table 7 Effects of Using Fish Oil for the Filtration of a Zinc Concentrate at 100 kPa of Air Pressure

Reagent Dosage kg/t (lbs/ton)	Moisture Content (% wt.)		
	Cake Thickness (inch) cm		
	(0.2) 0.51	(0.3) 0.76	(0.6) 1.52
0 (0)	13.7	14.6	17.3
0.5 (1)	8.7	9.5	11.8
1.5 (3)	7.4	8.3	10.2
2.5 (5)	7.6	8.2	9.8

**Example 8**

**[0053]** As another example, soybean oil was used as dewatering aid for copper (chalcopyrite) concentrate (150 mm x 0). The lipid was used as a 33.3% solution in diesel oil. The sample was a flotation product, which was superficially oxidized during transportation. As a means of regenerating hydrophobic surfaces, the sample was wet-ground in a ball mill and re-floated using 0.05 kg/t (0.1 lb/ton) sodium isopropyl xanthate and 55 g/t (50 g/ton) MIBC. The flotation product was subjected to vacuum filtration tests using a 6.35 cm (2.5-inch) Buchner funnel at 635 mm (25-inches) Hg and 2 min drying cycle time. The %moisture reductions were 55, 43, and 43.4% at 0.38 (0.15), 0.76 (0.3) and 1.52 cm (0.6 inches) of cake thickness, respectively. Reagent additions above 1.5 kg/t (3 lb/ton) did not significantly further the moisture reduction. These results are comparable to those obtained in the plant using a highpressure filter followed by a thermal dryer.

Table 8 Effects of Using Soybean Oil for the Vacuum Filtration of a Copper Concentrate

Reagent Dosage kg/t (lb/ton)	Moisture Content (%wt)		
	Cake Thickness (inch) cm		
	(0.15) 0.38	(0.30) 0.76	(0.60) 1.52
0 (0)	9.8	10.7	12.2
0.5 (1)	5.7	6.7	8.3
1.0 (2)	4.9	6.4	7.2
1.5 (3)	4.4	6.1	6.9
2.5 (5)	4.1	5.8	6.7

**Example 9 (not an example of the present invention)**

**[0054]** Table 9 shows a set of vacuum filtration tests conducted on a bituminous coal sample (0.6 mm x 0) from Elkview Mine, British Columbia, Canada. The sample was received in the form of slurry and used as received. The tests were conducted using a 6.35 cm (2.5-inch) diameter Buchner funnel at 635 mm (25 inches) Hg of vacuum pressure with 2 min drying cycle time and 1.02 cm (0.4 inches) of cake thickness. Three different vegetable oils were used as dewatering aids, and the results are compared. These oils were used as 10% solutions in butanol. Both sesame oil and peanut oil reduced the cake moisture by nearly 50% at 1 kg/t (2 lb/ton) of reagent addition.

# EP 1 406 711 B1

Table 9 Effects of Using Different Vegetable Oils for the Vacuum Filtration of Elkview Coal

Reagent Addition kg/t (lb/ton)	Moisture Content (% wt.)		
	Sesame Oil	Peanut Oil	Corn Oil
0 (0)	24.4	24.4	24.4
0.25 (0.5)	14.1	14.4	15.6
0.5 (1)	13.3	13.5	15.8
1.0 (2)	12.0	12.6	14.6
1.5 (3)	11.9	11.9	14.2

## Example 10

**[0055]** A flotation product (0.85 mm x 0) from Massey Coal Company, West Virginia, was used for filtration tests, in which a 6.35 cm (2.5-inch) diameter pressure filter was used at 200 kPa air pressure and 2 min drying cycle time. The coal sample was wet-ground in a ball mill for 1.5 minutes and re-floated using 0.5 kg/t (1 lb/ton) kerosene and 0.1 kg/t (0.2 lb/ton) MIBC. Varying amounts of coconut oil were used at different cake thicknesses. It was used as a 1:2 mixture with diesel oil. The moisture reductions were 64.7, 58.5, and 51.2% at 0.51 (0.2), 1.02 (0.4) and 2.03 cm (0.8 inches) cake thicknesses, respectively.

Table 10 Effects of Using Coconut Oil for the Filtration of a Bituminous Coal at 200 kPa of air Pressure

Reagent Addition kg/t (lb/ton)	Moisture Content (% wt.)		
	Cake Thickness (inch) cm		
	(0.2) 0.51	(0.4) 1.02	(0.8) 2.03
0 (0)	21.8	23.4	24.8
0.5 (1)	12.4	14.2	16.2
1.0 (2)	10.1	11.9	14.5
1.5 (3)	9.0	10.4	12.8
2.5 (5)	7.7	9.7	12.1

## Example 11

**[0056]** The dewatering aids disclosed in the present invention works well with hydrophobic particles. Talc is a naturally hydrophobic mineral that is used for a variety of applications including paper coating and removal of sticky materials from wood pulp. Table 11 shows the results obtained in a series of filtration tests conducted using sunflower oil as a dewatering aid. The reagent was used as a 33.3% solution in diesel oil. The tests were conducted using a 6.35 cm (2.5-inch) diameter pressure filter at 200 kPa air pressure and 2 min drying cycle time. The sample was received from Luzenac America, and was floated using 0.1 kg/t (0.2 lb/ton) MIBC just before filtration. Better than 50% moisture reductions were achieved at 0.51 (0.2) and 1.02 cm (0.4 inches) cake thicknesses. At 2.03 cm (0.8-inch) cake thickness, the moisture was reduced from 28.4% to 16.3% using 2.5 kg/t (5 lb/ton) sunflower oil.

Table 11 Effects of Using Sun Flowen Oil for the Filtration of a Talc (0.15 mm x 0) Sample at 200 kPa of Air Pressure

Reagent Dosage kg/t (lbs/ton)	Moisture Content (%wt)		
	Cake Thickness (inch) cm		
	(0.2) 0.51	(0.4) 1.02	(0.8) 2.03
0 (0)	25.2	26.9	28.4
0.5 (1)	14.2	17.3	18.9
1.5 (3)	12.6	14.7	17.5
2.5 (5)	11.8	13.4	16.3

## Example 12

**[0057]** In this example, a clean spiral product was wet-ground in a ball mill. The fines fraction (0.85 mm x 0) was floated using 0.5 kg/t (1 lb/ton) kerosene and 0.1 kg/t (0.2 lb/ton) MIBC as a means of initial hydrophobization. The hydrophobicity of the flotation product was enhanced using a lipid of animal origin (lard) and then subjected to filtration tests. Two sets of tests were conducted at 100 and 200 kPa of air pressures. Varying amounts of the lipid were used as 25% solutions in diesel oil. The tests were conducted using a 6.35 cm (2.5-inch) diameter filter at 2 min drying cycle time. As shown in Table 12, lard oil works well as a dewatering aid. The moisture reduction improves with increasing reagent dosage and air pressure. Moisture reductions of 50 to 60% were obtained at lower cake thicknesses and at the higher air pressure. Even at the thicker cake, moisture reductions approaching 50% were obtained at higher reagent dosages.

Table 12 Effects of Using Lard Oil for the Filtration of a 0.85 mm x 0 Massy Coal Sample at 100 and 200 kPa of Air Pressures

Applied Pressure (kPa)	Reagent Addition kg/t (lb./ton)	Moisture Content (% wt.)		
		Cake Thickness (inch) cm		
		(0.2) 0.51	(0.4) 1.02	(0.8) 2.03
100	0 (0)	24.6	26.4	27.1
	0.5 (1)	14.0	16.3	19.1
	1.5 (3)	12.3	14.1	15.2
200	0 (0)	22.4	24.1	25.4
	0.5 (1)	10.8	12.6	14.3
	1.5 (3)	8.7	10.8	12.8

## Example 13

**[0058]** In this example, one part by volume of sunflower oil was blended with one part of sorbitan monooleate (Span 80) and four parts of diesel oil and used as dewatering aid. The HLB number of sorbitan monooleate is 4.3; therefore, it blends well with the other two components. Dewatering tests were conducted on a bituminous coal sample from Massey Coal Company, West Virginia. It was a dense-medium product, which was crushed, ground, and screened to obtain 0.6 mm x 0 fraction, which was floated using 0.5 kg/t (1 lb/ton) kerosene and 110 g/t (100 g/ton) MIBC. Dewatering tests were conducted using a 6.35 cm (2.5-inch) diameter pressure filter at 150 kPa air pressure at 2 min drying cycle time and 1.27 cm (0.5 inches) cake thickness. The tests were conducted by varying the reagent dosage.

**[0059]** The results obtained with the sunflower oil-sorbitan monooleate blend were compared with those obtained with its individual components. Sunflower oil gave considerably inferior results to those obtained with sorbitan monooleate. However, the results obtained with a blend of the two were comparable to those obtained with sorbitan monooleate. This finding suggest that blending an appropriate lipid and a low HLB surfactant provides a means of reducing reagent cost, because the former is cheaper than the latter.

Table 13 Effects of Using a Sunflower Oil-Sorbitan Monooleate Blend for the Filtration of a Bituminous Coal Sample at 150 kPa Air Pressure

Reagent Addition kg/t (lb/ton)	Moisture Content (% wt)		
	Sunflower Oil	Sorbitan Monooleate	Combination
0 (0)	25.7	25.7	25.7
0.5 (1)	16.2	13.4	13.0
1.0 (2)	14.2	10.3	10.4
1.5 (3)	12.0	9.5	9.3
2.5 (5)	11.7	9.0	8.7

## Example 14

**[0060]** Although the results obtained using the dewatering aids disclosed in the present invention produced results far superior to those obtainable using conventional dewatering aids, their effectiveness decrease with increasing cake thickness. This is probably a reflection of the difficulty in transporting the water molecules liberated by the dewatering aids disclosed in the instant invention through filter cake. One solution to the problem may be to apply a mechanical vibration to the filter cake during drying cycle time. Table 14 shows the results obtained with and without using vibration when sunflower oil was used as dewatering aid for the filtration of a coal sample (0.6 mm x 0) from Virginia. The reagent was used as a 33.3% solution in diesel oil. The coal sample was a dense-medium product, which was crushed, ground and floated using 0.5 kg/t (1 lb/ton) kerosene and 0.1 kg/t (0.2 lb/ton) MIBC. The filtration experiments were conducted using a 6.35 cm (2.5-inch) diameter Buchner funnel at 635 mm (25-inch) Hg vacuum pressure. An ultrasonic probe was placed at the conical part of the Buchner funnel during the 5 minute drying cycle time. When the vibration was applied without the dewatering aid, the cake moisture was reduced from 22.6 to 19.2%. When 1 kg/t (2 lb/ton) of the dewatering aid was used in conjunction with the vibration, the cake moisture was reduced to 9.2% at 1.02 cm (0.4-inch) cake thickness. At 2.5 kg/t (5 lb/ton), the moisture was reduced to as low as 7.7%.

Table 14 Effects of Vibration on the Filtration of a Virginia Coal Using Sunflower Oil as a Dewatering Aid

Reagent Addition kg/t (lb/ton)	Cake Moisture (% wt.)			
	Cake Thickness (inches) cm			
	(0.2) 0.51		(0.4) 1.02	
	w/o Vibration	w/ Vibration	w/o Vibration	w/ Vibration
0 (0)	19.6	16.1	22.6	19.2
0.5 (1)	12.5	10.7	14.3	10.7
1.0 (2)	10.2	7.3	12.6	9.2
1.5 (3)	9.6	6.0	12.0	8.3
2.5 (5)	8.2	4.8	11.7	7.7

## Example 15

**[0061]** Various surfactants are used to lower the surface tension of the water that is to be removed by filtration. According to the Laplace equation, this should reduce the pressure of the water trapped in the capillaries present in a filter cake and, hence, help reduce the residual cake moisture. It should be, noted, however, that bulk of the water is removed easily during the cake formation time or through the larger capillaries present in the cake. In this regard, the amount of the reagent dissolved in the portion of the water that is easily removed may be considered to be a waste. It would be more economical to add the reagent after a cake has been formed. This will serve as a means of adding the reagent when it is really needed.

**[0062]** In this example, a series of dewatering tests were performed by spraying butanol directly on to a filter cake. Approximately 1 kg/t (2 lb/ton) of the reagent was added immediately after cake formation time. The surface tension of butanol is 20.6 mN/m at 20°C, which is much lower than that of water. Therefore, the role of butanol may be to reduce the surface tension of the water trapped in the finer capillaries. The coal sample used in this example was a Middle Fork dense-medium product, which was crushed, ground, and floated using 0.5 kg/t (1 lb) kerosene and 0.075 kg/t (0.15 lb/ton) MIBC. The flotation product was conditioned with varying amounts of a lipid (sunflower oil) prior to filtration. The filtration tests were conducted using a 6.35 cm (2.5-inch) diameter Buchner funnel at 635 mm (25-inch) Hg vacuum pressure, 2-min drying cycle time, and 1.65 cm (0.45-inch) cake thickness. As shown in Table 15, the spray technique reduced the cake moisture by 4 to 5% beyond what can be achieved using the lipid as a hydrophobicity-enhancing reagent. Thus, the technique of using lipids and butanol spray provides a means of achieving deep moisture reductions. Any other surface tension lowering reagents may be sprayed in place of the butanol used in this example. One should be careful, however, not to use the surfactants that can dampen the hydrophobicity of the particles to be dewatered.

Table 15 Effects of Combining the Techniques of Using Sunflower Oil and Butanol Spray to Achieve Deep Moisture Reductions at 1.65 cm (0.45-inch) Cake Thickness

Reagent Dosage kg/t (lb/ton)	Moisture Content (%wt)	
	w/o Spray	w/ Spray
0 (0)	22.2	18.0
0.5 (1)	15.3	11.2
1.0 (2)	13.2	9.4
1.5 (3)	12.7	8.3
2.5 (5)	12.5	7.6

#### Example 16

**[0063]** It is the objective of the present example to demonstrate that combining the methods of using a lipid to enhance the hydrophobicity and of spraying butanol to lower the surface tension can achieve deep moisture reductions at a large cake thickness. Vacuum filtration tests were conducted on a bituminous coal sample from Massey Coal Company, West Virginia, at a 3.56 cm (1.4-inch) cake thickness. The coal sample was a dense-medium product, which was crushed, ground, and screened to obtain a 0.6 mm x 0 fraction. The screen underflow was floated using 0.5 kg/t (1 lb/ton) kerosene and 0.075 kg/t (0.15 lb/ton) MIBC. The filtration tests were conducted using a 6.35 cm (2.5-inch) diameter Buchner funnel with a 16.5 cm (6.5-inch) height at a 635 mm (25-inch) Hg vacuum pressure and 2-min drying cycle time. The control test, which was conducted on the flotation product without lipid and butanol spray, gave 25.8% cake moisture as shown in Table 16. At 1.5 kg/t (3 lb/ton) sunflower oil and 1 kg/t (2 lb/ton) butanol spray, the cake moisture was reduced from 25.8 to 13%.

Table 16 Effects of Combining the Techniques of Using Sunflower Oil and Butanol Spray to Achieve Deep Moisture Reductions at 3.56 cm (1.4-inch) Cake Thickness

Reagent Dosage kg/t (lbs/ton)	Moisture Content (%wt)	
	No Spray	Butanol Spray
0 (0)	25.8	22.5
0.5 (1)	19.6	16.5
1.0 (2)	17.4	14.2
1.5 (3)	16.5	13.0
2.5 (5)	15.8	12.7

#### Example 17

**[0064]** A rather surprising observation was made when aluminum ( $Al^{3+}$ ) ions were used in conjunction with the dewatering aids disclosed in the present invention. It has been found that in the presence of the well-known coagulant for negatively charged particles, the amounts of lipids required to achieve desired cake moistures were substantially reduced. The second and third column of Table 17 compare the results obtained with and without using  $Al^{3+}$  ions before filtration. In each experiment, a coal slurry was conditioned in the presence of 0.01 kg/t (0.02 lb/ton) aluminum chloride for 2 minutes before adding a desired amount of sunflower oil. The coal sample was a dense-medium product from the Middle Fork coal preparation plant, Virginia. It was crushed, ground, and screened to obtain a 0.6 mm x 0 fraction, which was floated using 0.5 kg/t (1 lb/ton) kerosene and 0.1 kg/t (0.2 lb/ton) MIBC. The flotation product was filtered using a 6.35 cm (2.5-inch) diameter Buchner filter at 1.70 cm (0.67-inch) cake thickness and 5 min drying cycle time. As shown, the cake moisture obtained using both  $Al^{3+}$  ions and a lipid (sunflower oil) are much lower than the case of using the latter alone. Consequently, the amount of sunflower oil needed to achieve a given level of cake moisture was reduced substantially in the presence of  $Al^{3+}$  ions. For example, 2.5 kg/t (5 lb/ton) of sunflower oil was needed to achieve 12.3% cake moisture in the absence of  $Al^{3+}$  ions. In the presence of  $Al^{3+}$  ions, however, only 0.25 kg/t (0.5 lb/ton) sunflower oil was needed to achieve a 12.6% cake moisture. When 1 kg/t (2 lb/ton) butanol was sprayed, dewatering became even more effective: The amount of sunflower oil needed to achieve a 12.3% cake moisture was further reduced to 0.125 kg/t (0.25 lb/ton), as shown in the third column of Table 16.

**[0065]** Dewatering became even more efficient when filter cake was vibrated during the 5 min drying cycle time. As

shown in the last column of Table 17, the cake moisture was reduced to 10.3% at 0.125 kg/t (0.25 lb/ton) sunflower oil. At higher dosages of sunflower oil, single digit cake moistures were obtained. Thus, proper combinations of: i) using the dewatering aids disclosed in the present invention, ii) conditioning the slurry with trivalent (or divalent) cations, iii) spraying appropriate surface tension lowering agent(s) during drying cycle time, and iv) applying mechanical vibration during drying cycle time, can help achieve deep levels of moisture reduction using small amounts of lipids as dewatering aids.

Table 17 Effects of Combining the Techniques of Using Sunflower Oil, Al<sup>3+</sup> Ions, Butanol Spray, and Vibration to Achieve Deep Moisture Reductions at a 1.70 cm (0.67-inch) Cake Thickness

Reagent Addition kg/t (lb./ton)	Cake Moisture (% wt.)			
	None	Al <sup>3+</sup> Ion	Al <sup>3+</sup> ions and Butanol Spray	Al <sup>3+</sup> ions, Butanol Spray and Vibration
0 (0)	23.8	20.4	18.8	17.0
0.125 (0.25)	17.1	14.3	12.3	10.4
0.25 (0.5)	16.3	12.6	10.7	8.7
0.5 (1)	14.4	11.7	9.5	7.5
1.0 (2)	13.7	11.2	9.1	7.1
1.5 (3)	13.1	10.9	8.8	6.8
2.5 (5)	12.3	10.8	8.5	6.2

## Claims

1. A process for dewatering a slurry of fine particulate material being smaller than 2 mm in diameter, which process comprises the steps of:
  - i) rendering the fine particulate material moderately hydrophobic by increasing its contact angle to the range of 25° to 60° in an initial hydrophobization step,
  - ii) adding a lipid dissolved in an appropriate solvent or mixtures of solvents,
  - iii) agitating the slurry to allow for the lipid molecules to adsorb on the surface of the moderately hydrophobic material so that its hydrophobicity is enhanced and the contact angle is increased over 60°, and then
  - iv) subjecting the conditioned slurry containing the particulate material, whose water contact angle has been increased, to a suitable mechanical method of dewatering.
2. The process of claim 1 wherein the initial hydrophobization in (i) is achieved using appropriate surfactants and collectors.
3. The process of claim 1 wherein the initial hydrophobization step (i) involves creating fresh surfaces by comminution and/or attrition, when the fine particulate material to be dewatered is coal or other naturally hydrophobic material.
4. The process of claim 1 wherein the fine particulate material to be dewatered is a material whose surface has become less hydrophobic due to aging or superficial oxidation.
5. The process of claim 1 wherein the fine particulate material includes minerals, coal, inorganic pigments, plastics, metals, metal powders, fly ash, and biological materials.
6. The process of any of the preceding claims wherein the said suitable mechanical method of dewatering includes vacuum filtration, pressure filtration, centrifugal filtration, and centrifugation.
7. The process of any of the preceding claims wherein the lipid is selected from various vegetable oils, plant oils, fish and animal oils, fats, steroids, and waxes.
8. The process of any of the preceding claims wherein the lipid is blended with a nonionic surfactant of hydrophile-lipophile balance number of less than 15.
9. The process of any of the preceding claims wherein the said appropriate solvents include light hydrocarbon oils, short-chain alcohols, and ethers.



10. The process of claim 2 wherein the said appropriate surfactants are high HLB surfactants, whose polar heads can interact with the surface of the particulate materials.

11. The process of claim 2 wherein the said collectors are thiols for sulfide minerals and metals.

12. The process of claim 2 wherein the said collectors are hydrocarbon oils when the particulate material is coal or other naturally hydrophobic substance.

13. The process of any of the preceding claims wherein an electrolyte or mixture of electrolytes selected from salts of monovalent, divalent and trivalent cations and anions is added after the initial hydrophobization step (i) and before step (ii), so that the amount of lipids required to achieve a desired moisture of the particulate material is substantially reduced.

14. The process of claim 13 wherein the said electrolytes are the salts of aluminum ions.

15. The process of claim 13 or 14 wherein the reagents used in step (i) and step (ii) and said electrolyte or mixture of electrolytes can be added in a single step.

16. The process of any of claims 1 to 12 wherein the suitable mechanical method of dewatering is a filtration process in which the filter cake is subjected to an appropriate vibratory means, so that a higher degree of moisture reduction is achieved at a given cake thickness.

17. The process for claim 16 wherein the appropriate vibratory means include ultrasonic, mechanical and acoustic means.

18. The process of any of claims 1 to 12 wherein the suitable mechanical method of dewatering is a filtration process in which a suitable surface tension lowering reagent is added to the filter cake in the form of fine mist or spray, so that a higher degree of moisture reduction is achieved at a given cake thickness.

19. The process for claim 18 wherein the suitable surface tension lowering agent is selected from short-chain alcohols, light hydrocarbon oils, and appropriate surfactants.

20. A process of any of claims 13 to 15 wherein the suitable mechanical method of dewatering is a filtration process in which a suitable surface tension lowering reagent is added to the filter cake in the form of fine mist or spray and, at the same time, the filter cake is subjected to an appropriate vibratory means, so that a substantial moisture reduction is achieved at high cake thicknesses using minimum amounts of reagents.

## Patentansprüche

1. Verfahren zur Entwässerung einer Aufschlämzung von feinem teilchenförmigen Material, das im Durchmesser kleiner als 2 mm ist, wobei das Verfahren die Schritte umfasst:

i) moderates Hydrophobieren des feinen teilchenförmigen Materials, durch Erhöhung seines Kontaktwinkels auf einen Bereich von 25° bis 60° in einem anfänglichen Hydrophobierungsschritt,

ii) Hinzufügen eines Lipids, das in einem geeigneten Lösungsmittel oder einer Mischung von Lösungsmitteln gelöst ist,

iii) Rühren der Aufschlämzung, um die Fettmoleküle an die Oberfläche des moderat hydrophoben Materials adsorbieren zu lassen, so dass seine Hydrophobie erhöht und der Kontaktwinkel über 60° vergrößert wird, und dann

iv) Unterziehen der konditionierten Aufschlämzung, die das teilchenförmige Material, dessen Wasserkontaktwinkel vergrößert worden ist, enthält, einem geeigneten mechanischen Verfahren zur Entwässerung.

2. Verfahren nach Anspruch 1, wobei die anfängliche Hydrophobierung in (i) unter Verwendung von geeigneten oberflächenaktiven Substanzen und Sammlern erzielt wird.

3. Verfahren nach Anspruch 1, wobei der anfängliche Hydrophobierungsschritt (i) das Erzeugen frischer Oberflächen durch Zerkleinerung und/oder Zerreißung beinhaltet, wenn das feine teilchenförmige Material, das zu entwässern

ist, Kohle oder ein anderes natürliches hydrophobes Material ist.

4. Verfahren nach Anspruch 1, wobei das feine teilchenförmige Material, das zu entwässern ist, ein Material ist, dessen Oberfläche aufgrund von Alterung oder Oberflächenoxidation weniger hydrophob geworden ist.
5. Verfahren nach Anspruch 1, wobei das feine teilchenförmige Material Mineralien, Kohle, anorganische Pigmente, Kunststoffe, Metalle, Metallpulver, Flugasche und biologische Materialien umfasst.
6. Verfahren nach einem der vorstehenden Ansprüche, wobei das geeignete mechanische Verfahren zur Entwässerung Vakuumfiltration, Druckfiltration, Zentrifugalfiltration und Zentrifugation umfasst.
7. Verfahren nach einem der vorstehenden Ansprüche, wobei das Lipid aus verschiedenen Pflanzenölen, pflanzlichen Ölen, Fisch- und tierischen Ölen, Fetten, Steroiden und Wachsen ausgewählt ist.
8. Verfahren nach einem der vorstehenden Ansprüche, wobei das Lipid mit einer nichtionischen oberflächenaktiven Substanz mit einem Hydrophilie-Lipophilie-Gleichgewicht von weniger als 15 vermischt wird.
9. Verfahren nach einem der vorstehenden Ansprüche, wobei diese geeigneten Lösungsmittel leichte Kohlenwasserstofföle, kurzkettige Alkohole und Ether umfassen.
10. Verfahren nach Anspruch 2, wobei diese geeigneten oberflächenaktiven Substanzen oberflächenaktive Substanzen mit hohem HLB-Wert sind, deren polare Köpfe mit der Oberfläche der teilchenförmigen Materialien wechselwirken können.
11. Verfahren nach Anspruch 2, wobei diese Sammler Thiole für Sulfidminerale und Metalle sind.
12. Verfahren nach Anspruch 2, wobei diese Sammler Kohlenwasserstofföle sind, wenn das teilchenförmige Material Kohle oder eine andere natürlich hydrophobe Substanz ist.
13. Verfahren nach einem der vorstehenden Ansprüche, wobei ein Elektrolyt oder eine Mischung von Elektrolyten, ausgewählt aus Salzen von monovalenten, divalenten und trivalenten Kationen und Anionen, nach dem anfänglichen Hydrophobierungsschritt (i) und vor Schritt (ii) zugegeben wird, so dass die Menge an Lipiden, die benötigt wird, um die gewünschte Feuchte des teilchenförmigen Materials zu erreichen, erheblich reduziert wird.
14. Verfahren nach Anspruch 13, wobei diese Elektrolyte die Salze von Aluminiumionen sind.
15. Verfahren nach Anspruch 13 oder 14, wobei die Reagenzien, die in Schritt (i) und Schritt (ii) verwendet werden, und dieser Elektrolyt oder diese Mischung von Elektrolyten in einem einzigen Schritt zugegeben werden können.
16. Verfahren nach einem der Ansprüche 1 bis 12, wobei das geeignete mechanische Verfahren zur Entwässerung ein Filtrationsprozess ist, in welchem der Filterkuchen geeigneten vibrierenden Mitteln ausgesetzt wird, so dass ein höherer Grad an Feuchtigkeitsreduzierung bei einer gegebenen Kuchendicke erreicht wird.
17. Verfahren nach Anspruch 16, wobei die geeigneten vibrierenden Mittel Ultraschall-, mechanische und akustische Mittel umfassen.
18. Verfahren nach einem der Ansprüche 1 bis 12, wobei das geeignete mechanische Verfahren zur Entwässerung ein Filtrationsprozess ist, in welchem ein geeignetes Reagenz zur Verringerung der Oberflächenspannung zu dem Filterkuchen in Form von feinem Nebel oder Spray gegeben wird, so dass ein höherer Grad an Feuchtigkeitsreduktion bei einer gegebenen Kuchendicke erreicht wird.
19. Verfahren nach Anspruch 18, wobei das geeignete Mittel zur Verringerung der Oberflächenspannung aus kurzkettigen Alkoholen, leichten Kohlenwasserstoffölen und geeigneten oberflächenaktiven Substanzen ausgewählt ist.
20. Verfahren nach einem der Ansprüche 13 bis 15, wobei das geeignete mechanische Verfahren zur Entwässerung ein Filtrationsprozess ist, in welchem ein geeignetes Reagenz zur Verringerung der Oberflächenspannung zu dem Filterkuchen in Form von feinem Nebel oder Spray gegeben wird und gleichzeitig der Filterkuchen geeigneten vibrierenden Mitteln ausgesetzt wird, so dass eine wesentliche Feuchtigkeitsreduktion bei hohen Kuchendicken

unter Verwendung minimaler Mengen von Reagenzien erreicht wird.

## Revendications

1. Procédé de déshydratation d'une pâte de matériau particulaire fin ayant un diamètre inférieur à 2 mm, ledit procédé comprenant les étapes consistant à :
  - i) rendre le matériau particulaire fin modérément hydrophobe en augmentant son angle de contact dans la gamme de 25° à 60° dans une étape d'hydrophobisation initiale ;
  - ii) ajouter un lipide dissous dans un solvant ou des mélanges de solvants appropriés ;
  - iii) agiter la pâte pour permettre aux molécules de lipides d'adsorber sur la surface du matériau modérément hydrophobe, de sorte que son hydrophobie soit accrue et que l'angle de contact soit accru sur 60°, puis
  - iv) soumettre la pâte conditionnée contenant le matériau particulaire dont l'angle de contact de l'eau a été accru, à un procédé mécanique adapté de déshydratation.
2. Procédé selon la revendication 1, dans lequel l'hydrophobisation initiale en (i) est réalisée en utilisant des tensioactifs et collecteurs appropriés.
3. Procédé selon la revendication 1, dans lequel l'étape d'hydrophobisation initiale (i) implique la création de surfaces fraîches par broyage et/ou frottement, quand le matériau particulaire fin à déshydrater est du charbon ou un autre matériau naturellement hydrophobe.
4. Procédé selon la revendication 1, dans lequel le matériau particulaire fin à déshydrater est un matériau, dont la surface est devenue moins hydrophobe du fait du vieillissement ou de l'oxydation superficielle.
5. Procédé selon la revendication 1, dans lequel le matériau particulaire fin comprend des minéraux, du charbon, des pigments inorganiques, du plastique, des métaux, des poudres métalliques, des cendres volantes et des matériaux biologiques.
6. Procédé selon l'une quelconque des revendications précédentes, dans lequel ledit procédé mécanique adapté de déshydratation comprend une filtration sous vide, une filtration sous pression, une filtration centrifuge et une centrifugation.
7. Procédé selon l'une quelconque des revendications précédentes dans lequel le lipide est choisi parmi différentes huiles végétales, huiles de plantes, huiles de poisson et animales, graisses, stéroïdes et cires.
8. Procédé selon l'une quelconque des revendications précédentes, dans lequel le lipide est mélangé à un tensioactif non-ionique ayant un indice d'équilibre hydrophile-lipophile inférieur à 15.
9. Procédé selon l'une quelconque des revendications précédentes, dans lequel lesdits solvants appropriés comprennent des huiles hydrocarbures légères, des alcools à chaîne courte, et des éthers.
10. Procédé selon la revendication 2, dans lequel des tensioactifs appropriés sont des tensioactifs HLB élevés dont les têtes polaires peuvent interagir avec la surface des matériaux particuliers.
11. Procédé selon la revendication 2, dans lequel lesdits collecteurs sont des thiols pour les minéraux de sulfures et les métaux.
12. Procédé selon la revendication 2, dans lequel lesdits collecteurs sont des huiles hydrocarbures, quand le matériau particulaire est le charbon ou une autre substance naturellement hydrophobe.
13. Procédé selon l'une quelconque des revendications précédentes, dans lequel un électrolyte ou un mélange d'électrolytes choisis parmi des sels de cations monovalents, divalents et trivalents et des anions est ajouté après l'étape d'hydrophobisation initiale (i) et avant l'étape (ii), de sorte que la quantité de lipides requise pour atteindre une humidité souhaitée du matériau particulaire soit sensiblement réduite.
14. Procédé selon la revendication 13, dans lequel lesdits électrolytes sont des sels d'ions aluminium.

15. Procédé selon la revendication 13 ou 14, dans lequel les réactifs utilisés dans l'étape (i) et l'étape (ii) et ledit électrolyte ou mélange d'électrolytes peuvent être ajoutés en une seule étape.

16. Procédé selon l'une quelconque des revendications 1 à 12, dans lequel le procédé mécanique adapté de déshydratation est un procédé de filtration dans lequel le gâteau de filtration est soumis à un système vibratoire approprié, de sorte qu'un degré supérieur de réduction de l'humidité soit atteint à une épaisseur de gâteau donnée.

17. Procédé selon la revendication 16, dans lequel le système vibratoire approprié comprend un système à ultrasons, mécanique et acoustique.

18. Procédé selon l'une quelconque des revendications 1 à 12, dans lequel le procédé mécanique adapté de déshydratation est un procédé de filtration, dans lequel un réactif réducteur de tension de surface adapté est ajouté au gâteau de filtration, sous la forme d'un brouillard fin ou d'une vaporisation, de sorte qu'un degré supérieur de réduction d'humidité soit atteint à une épaisseur de gâteau donnée.

19. Procédé selon la revendication 18, dans lequel l'agent réducteur de tension de surface adapté est choisi parmi des alcools à chaîne courte, des huiles hydrocarbures légères, et des tensioactifs appropriés.

20. Procédé selon l'une quelconque des revendications 13 à 15, dans lequel le procédé mécanique adapté de déshydratation est un procédé de filtration, dans lequel un réactif réducteur de tension de surface adapté est ajouté au gâteau de filtration, sous la forme d'un brouillard fin ou d'une vaporisation et, en même temps, le gâteau de filtration est soumis à un système vibratoire approprié, de sorte qu'une réduction sensible de l'humidité soit atteinte à des épaisseurs de gâteau élevées, en utilisant des quantités minimales de réactifs.

## REFERENCES CITED IN THE DESCRIPTION

*This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.*

### Patent documents cited in the description

- |                       |                       |
|-----------------------|-----------------------|
| • US 5346630 A [0004] | • US 5011612 A [0009] |
| • US 4447344 A [0006] | • US 4206063 A [0010] |
| • US 4410431 A [0006] | • US 4207186 A [0010] |
| • US 5670056 A [0007] | • US 4210531 A [0011] |
| • US 2864765 A [0008] | • US 5256169 A [0011] |
| • US 4156649 A [0008] | • US 5405554 A [0011] |
| • US 4191655 A [0008] | • US 5379902 A [0011] |
| • US 5048199 A [0009] | • US 4969928 A [0011] |
| • US 4039466 A [0009] | • US 4770766 A [0012] |
| • US 5215669 A [0009] | • US 5458786 A [0013] |
| • US 5167831 A [0009] | • US 5587786 A [0013] |

### Non-patent literature cited in the description

- |   |   |
|---|---|
| • <b>Groppo ; Parekh.</b> <i>Coal Preparation</i> , 1996, vol. 17, 103-116 [0003] | • <b>Yoon ; Ravishankar.</b> <i>J. Colloid and Interface Science</i> , 1996, vol. 179, 391 [0026] |
| • <i>Filtration and Separation</i> , March 1977, 159-163 [0004]                   | • <b>Flinn et al.</b> <i>Colloids and Surfaces A</i> , 1994, vol. 87, 163 [0026]                  |