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(54) Title: SULFONATED SOLVENT DEASPHALTING RESIDUES, PROCESS FOR PRODUCTION THEREOF AND THEIR USE

(57) Abstract: Bitumen-upgrading residues are extracted with solvent to remove any remaining fuel value. The resultant insoluble solvent- deasphalted (SDA) residue is rendered useful as a dispersant (e.g. for cement) by sulfonation with oleum or sulfur trioxide to yield a sulfonated, solvent-deasphalted, bitumen upgrading residue.



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SULFONATED SOLVENT DEASPHALTING RESIDUES, PROCESS FOR PRODUCTION THEREOF AND THEIR USE

Field of the Invention

The present invention relates to sulfonated solvent deasphalting residues
5 and their use as dispersants or superplasticizers, and more particularly, the
present invention relates to a process and product for formulating a water
requirement reducing admixture for cement-based mixtures formed by sulfonation
of solvent deasphalted bitumen upgrading residues.

Description of Related Art

10 Non-distillable bitumen fractions such as those from conventional
petroleums or from heavy oils and tar sands require pyrolytic processes to produce
distillable products. Common pyrolytic processes are coking and hydrocracking.
There are various versions of both of these processes.

In coking, the products are volatile fractions and coke. However, the
15 volatile fractions contain heavy components and these heavy components can be
recycled to the coker for further cracking to produce suitable distillable products.
These heavy components are called coker recycle. In hydrocracking, the
bitumens are pyrolyzed in the presence of hydrogen and produce larger yields of
distillable components than coking. However, depending on the hydrocracking
20 severity, some non-distillable residues remain. Collectively, coker products, such
as coker recycle, and hydrocracking residue may be referred to as bitumen
upgrading residues.

Hydrocracking residue and coker recycle have very low value as fuels,
therefore it is desirable to be able to use them in some way. To this end,
25 Sawatzky et al, in United States Patent No. 5,584,920 issued December 17, 1996,
discloses a process whereby a hydrocracking residue is sulfonated to form a water
requirement reducing product for concrete mixtures. Although this process is
useful, it has disadvantages. For example, hydrocracking residues still have some

fuel value which is lost in this process. When sulfuric acid or oleum is used as a sulfonation agent, this process involves separation of a neutralized sulfonation product from a large amount of sulfate, which separation is not entirely successful. Efficiency of this process is limited by a methanol extraction step in which a
5 significant amount of the sulfonation product is not recovered.

One way of recovering the fuel value from bitumen upgrading residue is to extract the bitumen upgrading residue with an organic solvent, for example hexanes. Such an extraction is termed solvent deasphalting. Much of the bitumen upgrading residue can be extracted in this manner leaving some insoluble
10 material, called solvent deasphalting (SDA) residue. Thus, there is a need in the art to find a use for SDA residues.

Summary of the Invention

It has now been found that solvent deasphalting (SDA) residues may be sulfonated to produce a dispersant for aqueous dispersions, especially a water
15 requirement reducing product for cement-based mixtures.

According to an aspect of the invention, there is provided a sulfonated solvent deasphalting residue of a solvent deasphalted bitumen upgrading residue.

According to yet another aspect of the invention, there is provided a process for preparing a sulfonated solvent deasphalting residue, the process
20 comprising providing a solvent deasphalting residue and contacting the solvent deasphalting residue with a sulfonating agent.

According to still yet another aspect of the invention, there is provided a process for preparing sulfonated solvent deasphalting residue, the process comprising: providing a solvent deasphalting residue; providing a sulfonating
25 agent; contacting the solvent deasphalting residue with the sulfonating agent to produce a sulfonated solvent deasphalting residue; and neutralizing the sulfonated solvent deasphalting residue with a base.

It has now been found that sulfonated solvent deasphalting residues are excellent superplasticizers for aqueous solid dispersions. In particular, they are excellent water requirement reducing admixtures for cement-based mixtures. They provide improved performance over prior art admixtures such as sulfonated hydrocracking residues disclosed in US 5,584,920, and improved economics.

Product and Process:

The solvent deasphalting (SDA) residue may be prepared from any suitable bitumen upgrading residue, for example thermal, catalytic and conventional hydrocracking residues or coker product. Preferably, the bitumen upgrading residue has a weight average molecular weight of at least 200 g/mol. In some instances the bitumen upgrading residue will be depleted in branched long chain aliphatics. In some instances the bitumen upgrading residue is enriched in aromatic ring containing molecules. In some instances, the bitumen upgrading residue has a carbon content of 80 wt% or greater. One thermal hydrocracking residue, generally referred to as the CANMET from PetroCanada, is a 64% conversion residue provided from cracking vacuum tower bottoms using iron based additives. Another particular hydrocracking residue, referred to as HRI residue, is obtained from a Husky oil catalytic cracking process. One particular coker product, referred to as Syncrude coker recycle, is obtained from the Syncrude flexi-coking process.

Bitumen upgrading residue is deasphalted (extracted) with an organic solvent to yield a solid phase comprising solvent insoluble residue, i.e. the SDA residue, and a liquid phase comprising the organic solvent and a solvent soluble fraction. The solvent with the solvent soluble phase may be further treated to recover fuel values, e.g. oils. The organic solvent is preferably an aliphatic solvent, more preferably a solvent comprising an alkane. In some instances a C₃-C₂₀ alkane is used. In some instances a C₃-C₁₅ alkane is used. In some instances a C₃-C₈ alkane is used. In some instances the alkane is linear. Paraffinic solvents, e.g. propane, butanes, pentanes and hexanes, are specific examples. Hexanes is particularly suitable for many purposes. The use of more

solvent provides cleaner separation but may lead to major utility costs in solvent recovery, greater environmental impact and might lead to sulfonation difficulties. A solvent:hydrocracking residue ratio of 2:1 or greater is preferred in the deasphalting of the hydrocracking residue.

5 The SDA residue comprises asphaltenes and other solvent insoluble materials (e.g. sulfur and heavy metals (e.g. Ni and V)). The SDA residue may have a weight average molecular weight of 200 g/mol or greater. In some instances, the weight average molecular weight may be 600 g/mol or greater. Higher molecular weight SDA residues may lead to better performance. In some
10 instances the SDA residue comprises 75-90 wt% of carbon. In some instances the SDA residue comprises 5-10 wt% of hydrogen. In some instances the SDA residue comprises 4-7 wt% of sulfur. The SDA residue may comprise 75-90 wt% of carbon, 5-10 wt% of hydrogen and 4-7 wt% of sulfur. The SDA residue may have lower alkyl content than the bitumen upgrading residue from which the SDA
15 residue is produced. Lower alkyl content ultimately leads to less air entrainment in cement-based mixtures.

Sulfonation of the SDA residue may be achieved with any suitable sulfonating agent, for example, sulfuric acid, fuming sulfuric acid (oleum) and sulfur trioxide. Oleum and sulfur trioxide are of particular note.

20 Sulfonation is achieved by contacting the SDA residue with the sulfonating agent, or with a source of the sulfonating agent. Sulfonation may be achieved with or without the use of solvents. Without a solvent, solid or liquid SDA residue may be contacted with sulfonating agent, e.g. liquid oleum, liquid or gaseous sulfur trioxide). With a solvent, one or both of the SDA residue and the sulfonating agent
25 may be dissolved in a solvent prior to reaction. In one embodiment, the SDA residue is dissolved in a solvent and the sulfonating agent is contacted with the SDA residue in the solvent. In another embodiment, the sulfonating agent is dissolved in a solvent and the SDA residue is contacted with the sulfonating agent in the solvent. In yet another embodiment, the SDA residue and sulfonating agent
30 are dissolved independently in solvents and the two resulting solutions contacted

with each other. When a solvent is used, the sulfonated product is generally insoluble in the solvent, and thus precipitates out as a solid. Removal of the supernatant liquid by centrifugation or other solid/liquid separation techniques may be used to isolate the solid sulfonated product and get rid of excess sulfonating agent after the reaction is complete.

Solvents are preferably inert to or only minimally reactive with one or both of the sulfonating agent and SDA residue, more preferably inert to or only minimally reactive with both. Organic solvents are preferred. Organic solvents having a boiling point from 30°C to 130°C are preferred. Some examples of suitable organic solvents include chlorinated organic solvents (e.g. methylene chloride, tetrachloroethylene, tetrachloroethane, etc.).

There is no upper limit to the amount of sulfonating agent that can be used with a given amount of SDA residue. The greater the amount of sulfonating agent, the more the equilibrium is shifted to higher sulfonation, but the more excess sulfonating agent will remain. Conversely, the use of too low an amount of sulfonating agent will not yield a viable water requirement reducing admixture with low surfactant properties. Thus, the weight ratio of sulfonating agent to SDA residue is preferably not lower than about 0.5:1. More preferably, the weight ratio of sulfonating agent to SDA residue is greater than or equal to about 1:1. Diminishing returns occur at a weight ratio of sulfonating agent to SDA residue of about 3:1 and higher.

There are trade-offs with respect to reaction time, temperature, solvent volumes (if used), degree of acid removal, etc. The temperature is preferably low enough to avoid boiling away any solvent and/or reactants. Very good mixing leads to better sulfonation of the SDA residue. Further, in solvents, as the ratio of sulfur trioxide (SO₃) to SDA residue is increased, there may be a tendency for sulfonated SDA residue to deposit on solid surfaces, which may cause some hindering of contact of SO₃ with the incompletely sulfonated product. A stepwise feed, i.e. adding equal amounts of SDA residue and SO₃, then adding more SO₃ later, permits the use of less SO₃ to obtain good products.

In contacting the sulfonating agent with the SDA residue, a sulfonated SDA residue is produced. If the sulfonation was conducted in a solvent, it advantageous to remove the solvent, for example by evaporation, centrifugation or other techniques, before further processing. Further processing may be, for example, neutralization and/or isolation of the sulfonated SDA residue.

If sulfonation takes place without a solvent, the sulfonated product is preferably separated from the sulfonating agent. Separation from liquid sulfonating agents (e.g. oleum) may be accomplished with the selection of an appropriate technique, for example, selection of an appropriate membrane for membrane separation, washing the reaction mixture with water to remove excess sulfur trioxide as sulfuric acid, etc.

The sulfonated SDA residue is preferably neutralized before using it as a water requirement reducing admixture. Neutralization may be achieved with any suitable base. Some examples of suitable bases include alkali metal hydroxides (e.g. NaOH, KOH, etc.), alkali metal carbonates (e.g. Na₂CO₃, NaHCO₃, etc.), alkaline earth metal hydroxides (e.g. Ca(OH)₂, Mg(OH)₂, etc., alkaline earth metal carbonates (e.g. CaCO₃), etc., and mixtures thereof. Preferably, the base comprises NaOH, Ca(OH)₂, CaCO₃, or mixtures thereof.

Unless the sulfuric acid is removed prior to neutralization (e.g. with a membrane), then the neutralization of the sulfonated SDA residue produces sulfates as a by-product (which is undesirable in most, but not all, cases). In this situation, the base preferably comprises a counter-cation which forms an insoluble salt with sulfate, for example calcium (Ca²⁺). Calcium-containing bases preferably comprise Ca(OH)₂ (lime) and/or CaCO₃ (limestone). Precipitation of insoluble sulfates facilitates separation of sulfate impurities from sulfonated SDA residues.

More preferably, the base comprises a mixture of NaOH together with Ca(OH)₂ and/or CaCO₃. Separation of sodium sulfate may also be achieved by membrane separation techniques. Neutralization is preferably performed in a polar solvent, for example water, alcohol or mixtures thereof. Water is preferred.

One advantage of the present process is that the use of alcohol, e.g. methanol, may be avoided if desired.

In some situations, calcium salts of the sulfonated SDA residue may be desired, in which case complete neutralization with calcium hydroxide or calcium carbonate is preferred. In other situations, the neutralized sulfonated SDA residue is preferably a sodium salt, which is accomplished by the use of sodium hydroxide once the sulfonated SDA residue is separated from excess sulfate. If separation from excess sulfate was accomplished through precipitation of calcium sulfate, the calcium salts of the sulfonated SDA residue may not be readily displaced by sodium ions from the sodium hydroxide. In this instance, a soluble salt with a counter-anion that produces an insoluble calcium salt, for example soluble bicarbonate (e.g. sodium bicarbonate), may be used to ensure removal of calcium. Additionally, in this case, the use of limestone rather than lime for separating excess sulfates is preferred as it minimizes Ca^{2+} uptake in the final product.

The neutralized sulfonated SDA residue may be isolated or not depending on the intended use. Preferably, the neutralized sulfonated SDA is isolated before being used as a water requirement reducing admixture. Isolation of the sulfonated SDA residue may be accomplished by generally known techniques, for example, centrifugation, filtration, extraction, evaporation, etc., and combinations thereof. Isolation steps may be employed before, during and/or after neutralization.

The sulfonated SDA residue preferably has a weight average molecular weight of 600 g/mol or greater. In some instances, the weight average molecular weight is 1000 g/mol or greater. In some instances, the sulfonated SDA residue comprises about 50 wt% aromatic components. In some instances, the sulfonated SDA residue comprises 15-40 wt% carbon. In some instances, the sulfonated SDA residue comprises 1-4 wt% hydrogen. In some instances, the sulfonated SDA residue comprises 5-20 wt% sulfur. In some instances, the sulfonated SDA residue comprises 20-35 wt% oxygen. The sulfonated SDA residue may comprise 15-40 wt% carbon, 1-4 wt% hydrogen, 5-20 wt% sulfur and 20-35 wt% oxygen.

Uses:

The sulfonated solvent deasphalting residue described above may be used as a water requirement reducing admixture in cement-based mixtures. Cement-based mixtures include cement, mortar, concrete, etc. Cement is generally formulated by mixing water with dry powder cementitious material. Mortar is generally formulated by mixing water with dry powder cementitious material and fine aggregate (e.g. sand). Concrete is generally formulated by mixing water with dry powder cementitious material and both fine aggregate (e.g. sand) and coarse aggregate (e.g. stone). Cementitious material includes, for example, Portland cement, high alumina cement, magnesium phosphate cement, gypsum, etc.

Other chemical admixtures may be present in the cement-based mixture, for example, pozzolanic materials (e.g. fly ash, slag, silica fume, lime, etc.) to supplement or replace cementitious materials, accelerators for reducing set time, set retarders for delaying set time, air-entrainers for freeze-thaw resistance, corrosion inhibitors, expansive admixtures for minimizing shrinkage, shrinkage reducing admixtures, water repelling admixtures, mixtures thereof, etc.

The presence of the sulfonated SDA residue in a wet cement-based mixture increases the fluidity of the mixture, thus reducing the amount of water required to make up the cement-based mixture having a given initial workability, thus increasing compressive strength of the cement-based mixture.

Sulfonated SDA residues of the present invention are particularly advantageous. For example, they have a significantly lower degree of surfactant properties, leading to reductions in air entrainment and retardation of set in cement-based mixtures, especially in comparison with sulfonated hydrocracking residues disclosed in US 5,584,920. Without being held to any particular mode of action, it is thought that sulfonated SDA residues have less alkyl group content in comparison to sulfonated hydrocracking residues. Alkyl groups attached to sulfonated aromatics cause surface activity leading to undesired air entrainment.

Brief Description of the Drawings

In order that the invention may be more clearly understood, preferred embodiments thereof will now be described in detail by way of example, with reference to the accompanying drawings, in which:

- 5 Fig. 1 is a graph of time (h) vs. reaction rate (mW/g) for conduction calorimetry experiments conducted on water requirement reducing admixtures.

Detailed Description of Preferred Embodiments

Table 1 lists materials used in the Examples below.

Table 1

<u>Material</u>	<u>Supplier</u>
CANMET hydrocracking residue	PetroCanada
Husky catalytic hydrocracking residue	Husky Oil
Syncrude fluid coking recycle	Syncrude
Hexane	Caledon
Sulfuric acid (H ₂ SO ₄)	Fisher
Oleum	Made from SO ₃ and H ₂ SO ₄
Sulfur trioxide (SO ₃)	Dupont
Methylene chloride	Aldrich
Tetrachloroethylene	Aldrich
Sodium hydroxide (NaOH)	Anachemia
Calcium carbonate (CaCO ₃)	Fisher
Lime (calcium hydroxide) (Ca(OH) ₂)	Continental Lime
Sodium bicarbonate (NaHCO ₃)	Aldrich
Sodium carbonate (Na ₂ CO ₃)	BDH Chemicals
Portland cement mix	Lafarge
DISAL™	Handy Chemicals
DAXAD™ 19LKN	Hampshire Chemicals

*Preparatory Examples:**Example 1: Solvent Deasphalting of Bitumen Upgrading Residues*

856 g of CANMET hydrocracking residue (a 64% conversion hydrocracking residue from PetroCanada) was mixed with 1712 g of hexane ($d=0.66$) in a vessel.

- 5 The mixture was heated at 66.5°C with considerable kneading with a metal rod for 30 min. During this time, evaporated hexane was replaced. After 30 min, the mixture was allowed to cool. A hard layer developed at the bottom of the vessel and the supernatant liquid was decanted off. The hard layer was treated with 500 ml of fresh hexane as before, and the liquid decanted off after 30 min. A residue
10 weighing 393 g remained which was heated in a vacuum oven to a constant weight of 364.3 g. This final SDA residue (CANMET SDA residue) contained 17.6% of material insoluble in sulfonation solvents.

- Similar solvent deasphalting processes were performed on Husky catalytic hydrocracking residue and Syncrude fluid coking recycle to produce Husky SDA
15 residue and Syncrude SDA residue, respectively.

Example 2: Sulfonation of CANMET SDA residue with oleum

- Oleum (212 g containing 78.6 g SO_3) made from H_2SO_4 and SO_3 was charged to a 500 ml 3-necked reaction flask fitted with an air driven stirrer and a thermometer. Powdered mortar ground CANMET SDA residue (12.6 g) was
20 added to the vigorously stirred oleum using an addition funnel fitted with an auger feed arrangement over a 27-minute period. A cold water bath maintained temperature below 30°C . The reaction mixture was stirred for a total of 60 min.

- The reaction mixture was poured into 550 ml of water in increments so that the temperature did not exceed 40°C . The resulting aqueous mixture was
25 centrifuged to obtain a lightly colored first liquid and 215.65 g of a first sludge. The first sludge was separated from the lightly colored liquid and then the first sludge was dispersed in water to a total volume of about 400 ml.

The dispersion was treated with 550 ml of 10% NaOH resulting in a pH of 8.753. The treated dispersion was centrifuged to obtain about 955 ml of a very dark second liquid and 73.82 g of a second sludge. The second sludge was separated from the very dark liquid and treated with 25 ml of 10% NaOH to form
5 150 ml of a third liquid with pH of 12.87. In total, 70 g of NaOH was used for neutralization.

The first, second and third liquids were combined and centrifuged to obtain a supernatant and an insoluble solid. The dried insoluble solid weighed 1.86 g, implying that a minimum of 10.74 g of the original 12.6 g of CANMET SDA residue
10 was sulfonated (sulfonated SDA residue being generally soluble in aqueous medium). This example verifies that it is possible to sulfonate an SDA residue without the use of organic solvent.

Example 3: Sulfonation of Husky SDA residue with oleum

Oleum (176.6 g containing 64.5 g SO_3) made from H_2SO_4 and SO_3 was
15 charged to a 500 ml 3-necked reaction flask fitted with an air driven stirrer and a thermometer. Ground Husky SDA residue (16.92 g) was added to the vigorously stirred oleum using an addition funnel fitted with an auger feed arrangement over a 1 h 21 min period. A cold water bath maintained temperature below 30°C.

The reaction mixture was poured into 550 ml of water in increments so that
20 the temperature did not exceed 40°C. The resulting 850 ml of aqueous mixture was centrifuged to obtain about 750 ml of a dark but transparent liquid and about 175 g of a sludge that was difficult to remove from the centrifuge cups. The sludge was separated from the liquid and then the sludge was dispersed in water to a total volume of about 400 ml.

25 Solid NaOH (9.43 g) was added to the 400 ml of water dispersion and a pH of 1.134 was obtained when the sodium hydroxide fully dissolved. CaCO_3 (20.07 g) was then added slowly with stirring. Considerable foaming was observed. The pH was 1.134. The dispersion was allowed to stand overnight. The next day, a gel had formed and 100 ml of water was added to liquefy the mixture. The pH was

6.002. Another 0.98 g of CaCO_3 was added and the pH was 6.566. Then, 15 ml of a 10% NaOH solution was added bringing the pH to 11.318. Another 2 ml of 10% NaOH was added to bring the pH to 11.988. The mixture was centrifuged to obtain 555 ml of solution. Evaporation of a 50 ml aliquot of the solution yielded 3.0 g of dry solid, which indicated that a total of 33.3 g of dry solid can be obtained from the 555 ml of solution. The solid is sulfonated SDA residue.

Table 2 provides a comparison of the composition of the Husky SDA residue feed stock and the sulfonated Husky SDA residue of Example 3.

Table 2

Component	Husky SDA residue	Sulfonated Husky SDA residue
Carbon	85.74%	26.52%
Hydrogen	6.87%	2.62%
Nitrogen	1.45%	0.43%
Sulfur	4.12%	9.12%

Example 4: Sulfonation of CANMET SDA residue with SO_3 in methylene chloride

4A: CANMET SDA residue (14 g) was dissolved in methylene chloride (50 ml). Sulfur trioxide (SO_3) (46 g) was dissolved in methylene chloride (46 ml). The two solutions were simultaneously fed into a reactor charged with 250 ml methylene chloride and fitted with a rotor-stator mixer for continuously subdividing and dispersing the feeds and reaction products in the reaction mixture. Solid reaction products were separated from the liquid by centrifugation and dispersed in water. The aqueous mixture was treated with NaOH (3.5 g) and lime (24.5 g) achieving a pH of 11.258 to precipitate the sulfates and produce a solution of sulfonated CANMET SDA residue. The mixture was centrifuged to remove gypsum. The solution of sulfonated CANMET SDA residue could be used directly as a water requirement reducing agent, or the solution could be evaporated to obtain 24.5 g of a solid product.

4B: The process of Example 4A was performed except that the solution of sulfur trioxide was fed stepwise to the solution of CANMET SDA residue.

4C: The process of Example 4A was performed except that the solution of sulfur trioxide was fed stepwise to the solution of CANMET SDA residue, and
5 the amount of SO₃ was 200 wt% more than the amount of CANMET SDA residue.

Table 3 provides a comparison of the composition of the CANMET SDA residue feed stock and the sulfonated CANMET SDA residue of Example 4B.

Table 3

Component	CANMET SDA residue	Sulfonated CANMET SDA residue
Moisture	0.48%	12.72%
Carbon	85.33%	31.20%
Hydrogen	5.24%	1.72%
Nitrogen	1.57%	0.49%
Sulfur	4.98%	12.30%

10 *Example 5: Sulfonation of Husky SDA residue with SO₃ in organic solvent*

5A: A 100 ml solution containing 14.96 g of Husky SDA residue in methylene chloride were fed simultaneously with a 50 ml solution containing 45 g of sulfur trioxide (SO₃) in methylene chloride into a reactor containing 250 ml methylene chloride. The mixture was mixed with a rotor-stator mixer and the
15 reactor was cooled with a bath at 14°C. Feeding was completed in 67 min and after a further 10 min the mixer was stopped. There was some solid product deposited on the reactor walls and the mixer surface. The mixture was centrifuged and 210 ml of clear liquid was obtained. The solids were dispersed in water and 600 ml of aqueous acidic product was obtained. NaOH (3.5 g) and lime (29.7 g)
20 were added to obtain a pH of 12.266. This mixture was centrifuged and the liquid obtained was evaporated to yield a solid product, which was dried to a constant

weight of 33.1 g in a vacuum oven. The solid product had low solubility in water and the addition of NaOH had little effect.

The solid product (29.5 g) was treated with 300 ml of water and the resulting mixture had a pH of 8.016, perhaps due to absorbed CO₂. NaHCO₃ (4.0 g) was added and the pH was 6.567. Then, 1.8 g of Na₂CO₃ was added to achieve a pH of 9.986. After centrifugation, the liquid was evaporated to give solid sulfonated Husky SDA residue and the solid dried to a constant weight of 26.9 g.

5B: A 50 ml solution containing 12 g of Husky SDA residue in tetrachlorethylene was simultaneously fed with 10 ml of solution containing 10 g of sulfur trioxide (SO₃) in tetrachlorethylene to a reactor containing 130 ml of tetrachloroethylene and 5 g of SO₃ over a period of 38 min. The reactor was cooled with a bath with initial temperature of -5°C and final temperature of -9°C. The reaction mixture was mixed with a rotor-stator mixer. Then, another 20 ml of solution containing 20 g of SO₃ was fed to the reaction mixture over period of 20 min and mixing continued for another 20 min after that.

The reaction mixture was centrifuged to separate solvent (tetrachloroethylene) and product sludge. The sludge was treated with 225 ml of water, and when centrifuged more tetrachlorethylene was separated and some sludge was obtained. The sludge was dried and the dried sludge weighed 2.34 g. The aqueous product mix was treated with 4.0 g of NaOH and 25.0 g of lime to produce a mixture with pH of 12.029. The mixture was centrifuged to remove precipitated gypsum.

The resulting supernatant solution was treated further with 5.2 g of NaHCO₃ and 0.64 g of NaOH to achieve a pH of 8.29, and then centrifuged to isolate a precipitate that was produced. The precipitate when dry weighed 3.4 g.

The precipitated gypsum was extracted with 200 ml of aqueous solution containing 6.0 g of Na₂CO₃ and 8.4 g of extract was obtained.

The combined products were found to contain considerable amounts of poorly water soluble components and therefore were treated with another 3.2 g NaHCO₃ and 0.4 g of NaOH to a pH of 9.361. Centrifugation produced 4.4 g of precipitate when dry and 487 ml of product solution. A 50 ml aliquot when evaporated gave 3.35 g of product. Thus, total yield is calculated to be 32.63 g. This product was very water soluble.

Table 4 provides a comparison of the composition of the Husky SDA residue feed stock and the sulfonated Husky SDA residue of Example 5A.

Table 4

Component	Husky SDA residue	Sulfonated Husky SDA residue (5A)
Carbon	84.40%	35.61%
Hydrogen	7.20%	2.03%
Nitrogen	1.40%	0.56%
Sulfur	4.76%	14.09%

Example 6: Sulfonation of Syncrude SDA residue with SO₃ in methylene chloride

Syncrude SDA residue was sulfonated under conditions similar to those of Example 5A to produce a sulfonated Syncrude SDA residue. Table 5 provides a comparison of the composition of the Syncrude SDA residue feed stock and the sulfonated Syncrude SDA residue of Example 6.

Table 5

Component	Syncrude SDA residue	Sulfonated Syncrude SDA residue
Carbon	82.52%	34.26%
Hydrogen	7.22%	2.17%
Nitrogen	0.92%	0.47%
Sulfur	6.13%	14.59%

Example 7: Sulfonation of CANMET SDA residue with SO₃ in tetrachloroethylene

A 17 ml solution containing 5.0 g of CANMET SDA residue in tetrachloroethylene and a 20 ml solution containing 15 g of SO₃ in tetrachloroethylene were fed simultaneously into a glass reactor equipped with a low gap rotor-stator mixer. The reactor was cooled with a water bath at 8°C and feeding was completed in 16 min. There were some deposits on the reactor walls and mixer. The reaction mixture was centrifuged and the solids were dispersed in 100 ml of water. The aqueous mixture was centrifuged (a small amount of sludge was obtained). The solution was made basic with NaOH and lime to remove sulfates as gypsum. The solution was evaporated and the solid sulfonated CANMET SDA residue obtained was dried to a constant weight of 8.5 g. A similar run involving stepwise SO₃ feed gave the same results.

Example 8 – Comparative: Sulfonation of CANMET hydrocracking residue

A sulfonated hydrocracking residue from US 5,584,920 was prepared for comparative purposes. Sulfonation was carried out under conditions similar to those of Example 4A. 15 g of CANMET hydrocracking residue and 45 g of SO₃ were used. 27.1 g of sulfonated CANMET hydrocracking residue were obtained. Table 6 provides a comparison of the composition of CANMET hydrocracking residue feed stock and sulfonated CANMET hydrocracking residue of Example 8.

Table 6

Component	CANMET hydrocracking residue	sulfonated CANMET hydrocracking residue
Carbon	76.45%	35.32%
Hydrogen	8.05%	2.75%
Nitrogen	1.04%	0.40%
Sulfur	4.74%	14.80%

Use of Sulfonated SDA Residues:

The use of sulfonated SDA residues as water requirement reducing admixtures in cement-based mixtures was evaluated on the basis of air entrainment, mortar flow, compressive strength and conduction calorimetry.

5 *Example 9: Air Entrainment Testing*

For air entrainment, the densities of mixtures containing mortar were determined to assess the extent of air entrainment. Denser admixtures have less entrained air. Mortar mixtures were mixed and packed into a standard steel cup using a standard procedure. Mixing was done according to an ASTM standard mix design (ASTM C305-99e1 "Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency", ASTM International, herein incorporated by reference). The standard cup had a volume of 180 ml, and was filled in three layers. A first layer was placed by tapping the cup on its bottom. Second and third layers were tamped in place by tamping each layer fifteen times. Density was determined by weighing the cup and dividing by the known volume. The mixing and packing procedure were the same in all cases. The mortars contained sand (ASTM 20-30 mesh, 67.9 wt%), Portland cement (22.6 wt%), water (9.4 wt%) and a water requirement reducing admixture (0.1 wt%), and differed only in the type of water requirement reducing admixture used. Table 7 provides the results of the air entrainment assessment.

Table 7

Example	Water requirement reducing admixture	Density (g/cm ³)
C1	DISAL™	2.14
8	sulfonated CANMET hydrocracking residue	1.97
4A	sulfonated CANMET SDA residue	2.08
4B	sulfonated CANMET SDA residue	2.14
5A	sulfonated Husky SDA residue	2.15
6	sulfonated Syncrude SDA residue	2.07
7	Sulfonated CANMET SDA residue	2.17

DISAL™ is a commercial superplasticizer for cement-based mixtures and contains naphthalene sulphonates sodium salts. Example 8 is a water requirement reducing agent made in accordance with US 5,584,920. Examples 4A, 4B, 5A, 6 and 7 are examples of the present invention. It is evident from Table 5 7 that sulfonated SDA residues of the present invention provide for less entrained air in a cement-based mixture than the sulfonated residues disclosed in US 5,584,920. Further, sulfonated SDA residues of the present invention can be as effective or more effective than commercially available products.

Example 10: Mortar Flow Testing

10 Mortar flow tests measure the workability of a mortar mixture. Mortar mixtures that are more workable at a given water content will require less water to be able to work. To test mortar flow, a standard procedure for mortar mixing was used for each mortar composition tested. The mortar was packed using a standard procedure into a stainless steel cylindrical form having a diameter of 4.2 15 cm and a height of 5 cm. The form was removed to leave a cylindrical wet briquette on a platform. The platform was dropped through 33.3 cm and the average diameter of the flattened briquette was determined by measuring the longest and shortest diameters of the flattened briquette and then taking the average. The average diameter is a measure of workability, with larger average 20 diameters indicating greater workability. The mortars contained beach sand (finer than 50 mesh, 53.5 wt%), Portland cement (32.2 wt%), water (14.1 wt%) and a water requirement reducing admixture (0.2 wt%), and differed only in the type of water requirement reducing admixture used. Table 8 provides results.

Table 8

Example	Water requirement reducing admixture	Average diameter (cm)
C1	DISAL™	8.6
5A	sulfonated Husky SDA residue	10.5
6	sulfonated Syncrude SDA residue	11.5
7	sulfonated CANMET SDA residue	9.3

It is evident from Table 8 that the water requirement reducing admixtures of the present invention provide superior workability than a commercially available product.

Example 11: ASTM Testing

5 Mortar samples were mixed according to ASTM standard mix practice (ASTM C305-99e1 "Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency", ASTM International, herein incorporated by reference), using an ASTM standard mix design for mortar (ASTM C109 "Standard Test Method for Compressive Strength of Hydraulic Cement
10 Mortars (Using 2-in. or [50mm] Cube Specimens)", ASTM International).

Tests in accordance with ASTM specifications were conducted on the prepared mortar samples, the samples comprising various water requirement reducing admixtures. Specifically, the following tests were performed.

Flow of mortar: Flow was conducted in accordance with ASTM C109 using
15 50 mm cube specimens in conjunction with the specifications set out in ASTM C230. (ASTM C109-99 "Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or [50 mm] Cube Specimens)", ASTM International, herein incorporated by reference). (ASTM C230-98 "Standard Specification for Flow Table for Use in Tests of Hydraulic Cement", ASTM
20 International, herein incorporated by reference),

Air entrainment: Air entrainment was measured through wet density and air content in accordance with ASTM C185 (ASTM C185-99, "Standard Test Method for Air Content of Hydraulic Cement Mortar", ASTM International, herein incorporated by reference). Since the sand in the mortar composition was not
25 washed, some additional air entrainment may affect the accuracy of the air content values.

Compressive strength: Compressive strength was conducted in accordance with ASTM C109 using 50 mm cube specimens. (ASTM C109-99

“Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or [50 mm] Cube Specimens)”, ASTM International, herein incorporated by reference).

Table 9 provides the compositions of the mortars tested and the test results
5 obtained therefor.

Table 9

	<u>Control</u>	<u>Ex. C2</u>	<u>Ex. 5B</u>	<u>Ex. 3'</u>	<u>Ex. 3''</u>
<i>Composition mixed as per ASTM C305:</i>					
cement (g)	600	600	600	600	600
s/c weight ratio	2.75	2.75	2.75	2.75	2.75
w/c weight ratio	0.4	0.4	0.4	0.4	0.4
admixture (wt%)	0.0	0.5	0.5	0.5	1.0
<i>Flow test as per ASTM C109 in conjunction with ASTM C230:</i>					
15 min	19	84	83	81	113
75 min		77	70	76	90
<i>Air entrainment test as per ASTM C185:</i>					
wet density (g/cc)	2.24	2.18	2.24	2.21	2.14
air content (%)	7.7	9.9	7.7	8.8	11.7
dry density (g/cc)	2.18	2.11	2.18	2.17	2.12
<i>Compressive strength test as per ASTM C109:</i>					
compressive strength (psi)	2933	5050	5058	4400	4392
time (hrs)	26	26	26	22	22

In Table 9, s/c weight ratio is the ratio of sand to cement, w/c ratio is the ratio of water to cement and admixture is the amount of water requirement reducing
10 admixture expressed as weight percent based on weight of the cement. The sand was standard ASTM 20-30 mesh sand as specified in ASTM C778 (C778-02 Standard Specification for Standard Sand) and the cement was Lafarge brand

Portland cement. The admixture in Ex. C2 is a commercial water requirement reducing admixture called DAXAD™ 19LKN.

Based on wet density, water reducing admixtures of the present invention can provide for less entrained air in a cement-based mixture than a commercially available admixture. Further, admixtures of the present invention can provide for comparable entrained air than a control without any admixture.

Based on the flow tests, it is evident that water requirement reducing admixtures of the present invention provides for better workability of a cement-based mixture than a control without any admixture. Further, admixtures of the present invention can provide for comparable or better workability than a commercially available admixture.

Based on the compressive strength, it is evident that water requirement reducing admixtures of the present invention provides for better compressive strength of a cement-based mixture than a control without any admixture. Further, admixtures of the present invention can provide for compressive strength comparable to a commercially available admixture.

Example 12: Conduction Calorimetry

Another indicator of water reducing requirement effectiveness is conduction calorimetry, which measures exothermicity vs. time to give an indication of cement hydration. Conduction calorimetry experiments were conducted using a Thermonics Tam Air Cement Calorimeter system. The system was maintained at $24 \pm 0.1^\circ\text{C}$ and configured with a ± 60 mW signal range. The reference cells were loaded with a heat capacity mass equivalent weight of 5 g of cement with a water to cement ratio of 0.4. The system was set to acquire data every two minutes for the duration of the test. Glass amphiboles specifically designed for the calorimeter chamber with a crimp top were used for each specimen. The dry powder fractions for each mix design were weighed and recorded and placed into the amphibole. (Model dry mix weight was 5 g of binding agents OPC). Samples were dry mixed to a homogeneous blend and stored at 23°C until needed. Deionized water was

preconditioned to 23°C to minimize thermal shock effects. To each specimen, 2.5 ml of water was added using a micropipette (for 0.4 w/c ratio). Data acquisition was initiated after the water was added but before the dry powder was mixed. Mixing time usually took between 4 and 8 minutes for all samples depending on the stiffness of the mix. Once mixed the samples were capped a threaded hook was attached and the samples were lowered into the conduction calorimeter chamber. The chamber cells were capped and the time of initial installation and the time of specimen equilibration were noted.

Fig. 1 provides the results of the conduction calorimetry testing for the mortar samples listed in Table 10. Samples listed in Table 10 were prepared as per ASTM C305 as described above in Example 11.

Table 10

sample	cement (g)	w/c weight ratio	admixture (wt%)
Control	5	0.4	0.0
C2	5	0.4	0.5
C3	5	0.4	1.0
5B'	5	0.4	0.5
5B''	5	0.4	1.0
3'	5	0.4	0.5
3''	5	0.4	1.0

In Table 10, w/c ratio is the ratio of water to cement and admixture is the amount of water requirement reducing admixture expressed as weight percent based on the weight of the cement. The cement was Portland cement. The admixture used in samples C2 and C3 was DAXAD™ 19LKN. The admixture used in samples 5B' and 5B'' was the sulfonated solvent deasphalting residue of Example 5B. The admixture used in samples 3' and 3'' was the sulfonated solvent deasphalting residue of Example 3.

It is evident from Fig. 1 that there is less retardation with the water reducing requirement admixtures of the present invention (samples 5B', 5B'', 3' and 3'') than with the existing market leading superplasticizer, DAXAD™ 19LKN (samples C2 and C3).

5 From the foregoing, it will be seen that this invention is one well adapted to attain all the ends and objects hereinabove set forth together with other advantages which are obvious and which are inherent to the structure. It will be understood that certain features and sub-combinations are of utility and may be employed without reference to other features and sub-combinations. This is
10 contemplated by and is within the scope of the claims. Since many possible embodiments may be made of the invention without departing from the scope thereof, it is to be understood that all matter herein set forth or shown in the drawing is to be interpreted as illustrative and not in a limiting sense.

Claims:

1. Sulfonated solvent deasphalting residue of a solvent deasphalted bitumen upgrading residue.
2. Sulfonated solvent deasphalting residue as claimed in claim 1, wherein the
5 bitumen upgrading residue is a hydrocracking residue or a coker product.
3. Sulfonated solvent deasphalting residue as claimed in claim 1 or 2 having a weight average molecular weight of 600 g/mol or greater.
4. Sulfonated solvent deasphalting residue as claimed in claim 1 or 2 having a weight average molecular weight of 1000 g/mol or greater.
- 10 5. Sulfonated solvent deasphalting residue as claimed in any one of claims 1 to 4, wherein the solvent deasphalted bitumen upgrading residue is produced from a bitumen upgrading residue, and the solvent deasphalted bitumen upgrading residue has a lower content of alkyl groups than the bitumen upgrading residue.
6. Sulfonated solvent deasphalting residue as claimed in any one of claims 1
15 to 5 comprising 15-40 wt% carbon.
7. Sulfonated solvent deasphalting residue as claimed in any one of claims 1 to 6 comprising 1-4 wt% hydrogen.
8. Sulfonated solvent deasphalting residue as claimed in any one of claims 1 to 7 comprising 5-20 wt% sulfur.
- 20 9. Use of one or more sulfonated solvent deasphalting residues as defined in any one of claims 1 to 8 as a dispersant in an aqueous dispersion of solids.
10. Use as claimed in claim 9, wherein the aqueous dispersion of solids comprises a cement-based mixture.
11. Use as claimed in claim 10, wherein the cement-based mixture is mortar,
25 concrete or cement.

12. Use as claimed in any one of claims 9 to 11, wherein the one or more sulfonated solvent deasphalting residues acts as a water requirement reducing admixture in the aqueous dispersion of solids.

13. Use as claimed in any one of claims 9 to 12, wherein the aqueous dispersion of solids further comprises a pozzolanic materials to supplement or replace cementitious materials, an accelerator for reducing set time, a set retarder for delaying set time, an air-entrainer for freeze-thaw resistance, a corrosion inhibitor, an expansive admixture for minimizing shrinkage, a shrinkage reducing admixture, a water repelling admixture, or a mixture thereof.

14. Process for preparing a sulfonated solvent deasphalting residue, the process comprising providing a solvent deasphalting residue and contacting the solvent deasphalting residue with a sulfonating agent to produce the sulfonated solvent deasphalting residue.

15. Process as claimed in claim 14, further comprising neutralizing the sulfonated solvent deasphalting residue with a base.

16. Process as claimed in claim 15, wherein the base comprises NaOH.

17. Process as claimed in claim 15, wherein the base comprises NaOH, $\text{Ca}(\text{OH})_2$, CaCO_3 , or mixtures thereof.

18. Process as claimed in any one of claims 14 to 17, further comprising adding calcium hydroxide to precipitate excess sulfates as calcium sulfates.

19. Process as claimed in any one of claims 14 to 17, further comprising adding calcium carbonate to precipitate excess sulfates as calcium sulfates.

20. Process as claimed in claim 18 or 19, further comprising adding a soluble salt with a counter-anion that produces an insoluble calcium salt to remove excess calcium.

21. Process as claimed in claim 20, wherein the soluble salt comprises a soluble bicarbonate.

22. Process as claimed in claim 20, wherein the soluble salt comprises sodium bicarbonate.
23. Process as claimed in any one of claims 14 to 16, further comprising separating excess sulfates with a membrane.
- 5 24. Process as claimed in any one of claims 14 to 23, wherein the sulfonating agent comprises oleum or sulfur trioxide.
25. Process as claimed in any one of claims 14 to 24, wherein the sulfonating agent and the solvent deasphalting residue are reacted in a weight ratio of no less than 0.5 parts sulfonating agent to 1 part solvent deasphalting upgrading residue.
- 10 26. Process of claim 25, wherein the weight ratio is greater than or equal to 1:1 sulfonating agent to solvent deasphalting residue.
27. Process as claimed in any one of claims 14 to 26, wherein the solvent deasphalting residue is prepared by extracting a bitumen upgrading residue with a C₃-C₂₀ alkane.
- 15 28. Process as claimed in any one of claims 14 to 26, wherein the solvent deasphalting residue is prepared by extracting a bitumen upgrading residue with a C₃-C₈ alkane.
29. Process as claimed in any one of claims 14 to 26, wherein the solvent deasphalting residue is prepared by extracting a bitumen upgrading residue with
20 hexane.
30. Process as claimed in any one of claims 27 to 29, wherein the bitumen upgrading residue is a hydrocracking residue or a coker product.
31. Process as claimed in any one of claims 27 to 30, wherein the solvent deasphalting residue has a lower content of alkyl groups than the bitumen
25 upgrading residue.

32. Process as claimed in any one of claims 14 to 31, wherein the solvent deasphalting residue has a weight average molecular weight of 200 g/mol or greater.
33. Process as claimed in any one of claims 14 to 31, wherein the solvent
5 deasphalting residue has a weight average molecular weight of 600 g/mol or greater.
34. Process as claimed in any one of claims 14 to 33, wherein the solvent deasphalting residue comprises 75-90 wt% carbon.
35. Process as claimed in any one of claims 14 to 34, wherein the solvent
10 deasphalting residue comprises 5-10 wt% hydrogen.
36. Process as claimed in any one of claims 14 to 35, wherein the solvent deasphalting residue comprises 4-7 wt% sulfur.
37. Process as claimed in any one of claims 14 to 36, wherein the solvent deasphalting residue comprises asphaltenes.

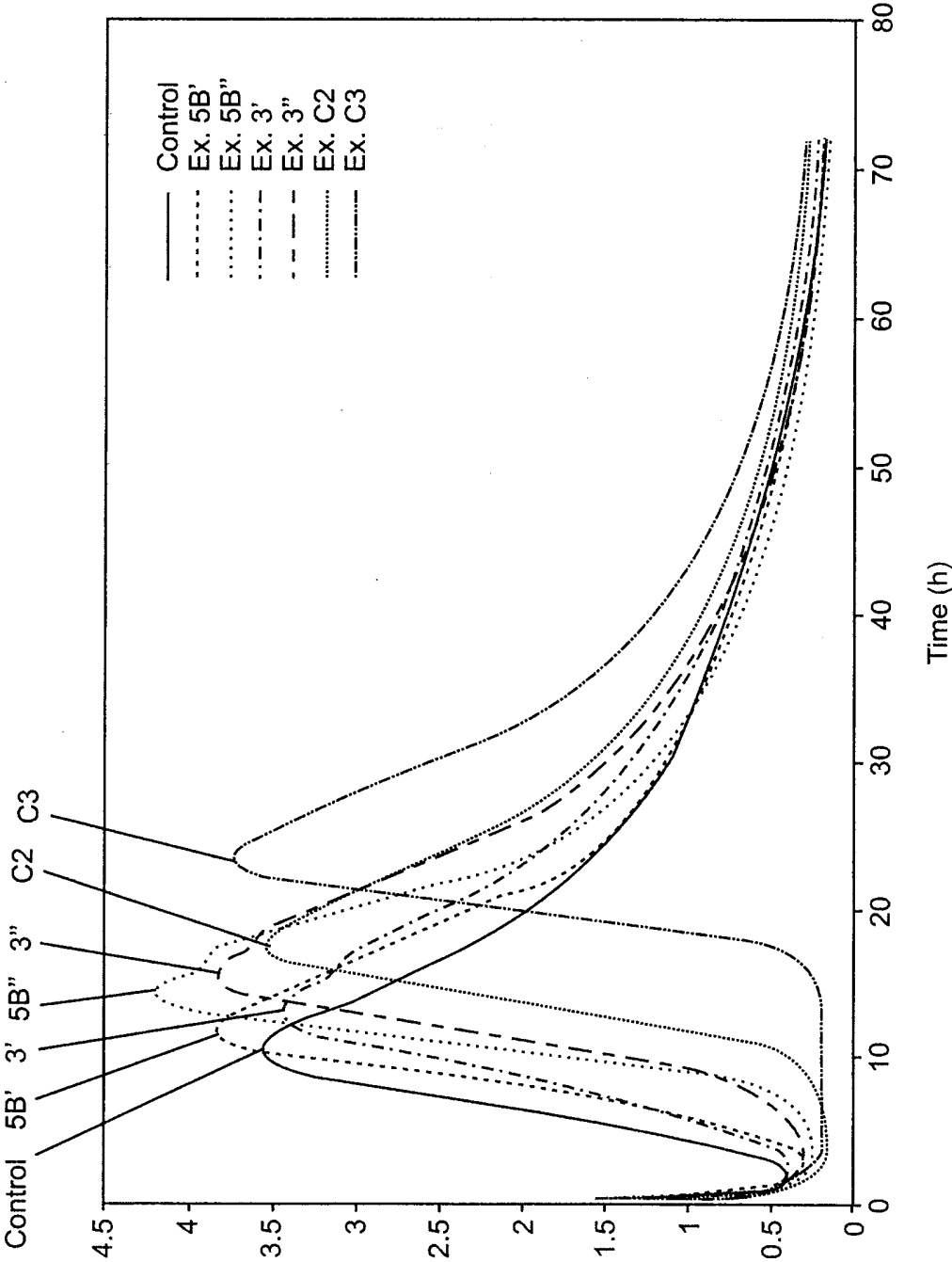


FIG. 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2006/000412

A. CLASSIFICATION OF SUBJECT MATTER IPC: C08L 95/00 (2006.01) , C10C 3/02 (2006.01) , C04B 40/06 (2006.01) , C04B 24/36 (2006.01) , C04B 24/16 (2006.01) , B01F 17/08 (2006.01) According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C08L 95/00, C10C 3/02, C04B 40/06, C04B 24/36, C04B 24/16, B01F 17/08 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used) Canadian Patent Database, Delphion, Qpat, USPTO, Espacenet		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3,970,690 (SUZUKI, S. et al.) 20-07-1976 col. 1 line 57 - col 2, line 12; col. 3 line 18 - col. 4, line 59; Example 3	1-37
X Y	US 5,322,556 (PREVEDELLO, A. et al.) 21-06-1994 col. 1, lines 37-63; col. 2, lines 24-43, 56-64; col. 3, lines 3-51; Examples; and Claims 1-20	1-17, 23-37 18-22
Y	US 5,584,920 (SAWATZKY, P et al.) 17-12-1996 Examples	14-24
☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents :	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family	
"A" document defining the general state of the art which is not considered to be of particular relevance		
"E" earlier application or patent but published on or after the international filing date		
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)		
"O" document referring to an oral disclosure, use, exhibition or other means		
"P" document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search	Date of mailing of the international search report	
28 April 2006 (28-04-2006)	6 July 2006 (06-07-2006)	
Name and mailing address of the ISA/CA Canadian Intellectual Property Office Place du Portage I, C114 - 1st Floor, Box PCT 50 Victoria Street Gatineau, Quebec K1A 0C9 Facsimile No.: 001(819)953-2476	Authorized officer Owen Terreau (819) 934-6370	

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2006/000412

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of the first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons :

1. ☐ Claim Nos. :

because they relate to subject matter not required to be searched by this Authority, namely :

2. ☒ Claim Nos. : 14 (part)

because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically :

Claim 14 defines a process that uses any solvent deasphalted residue; however, as stated at page 2, lines 10-11, the problem to be solved is to find a use for the insoluble portion of the extraction of bitumen-upgrading residue. The search was, therefore, limited to the product and process using the bitumen-upgrading residue only.

3. ☐ Claim Nos. :

because they are dependant claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows :

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claim Nos. :

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim Nos. :

Remark on Protest ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/CA2006/000412

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
US3970690	20-07-1976	NONE	
US5322556	21-06-1994	AU630529 B2 CA2032838 A1 CN1027899C C DE69007776D D1 EP0450201 A1 IT1237807 B JP4250839 A PL288408 A1 SU1834886 A3 ZA9010010 A	29-10-1992 22-06-1991 15-03-1995 05-05-1994 09-10-1991 17-06-1993 07-09-1992 09-09-1991 15-08-1993 30-10-1991
US5584920	17-12-1996	CA2173284 A1	21-10-1996