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(54) Title: A SOLID COMPOSITION FOR SUGAR PURIFICATION

(57) Abstract: A solid composition for removing color impurities in sugar liquor or syrup and a method of using said solid composition, in which said solid composition comprises at least a quaternary ammonium compound and a phosphoric compound.

A solid composition for sugar purification

Description

[0001] This application claims priority to PCT International Patent Application No. PCT/CN2016/083428 filed on May 26, 2016, the whole content of this application being incorporated herein by reference for all purposes.

Technical Field

[0002] The present invention relates to a solid composition for sugar purification. The solid composition can remove colour impurities in a sugar liquor or syrup. Said solid composition comprises a quaternary ammonium compound and a phosphoric compound.

Background Art

[0003] Fine sugars are normally obtained by purification of raw sugars or sugar juices. For example, raw sugars can be obtained from sugar juices by the processes of clarification, evaporation to a thick sugar syrup, and crystallization. Then the crystallized product can be dissolved in water so as to obtain sugar liquors. Subsequently, the sugar liquors can be further purified and processed for obtaining fine sugars having an acceptable standard of purity. Alternatively, sugar syrups, which are obtained from sugar juices, can be subject to the purification process without the step of crystallization of the raw sugars.

[0004] The whiteness of fine sugars is one important sugar quality criteria. One aim of purification of the sugar liquor or syrup is to reduce the colour impurities, such that the purified sugar product has desired whiteness. Various methods for reducing the colour impurities during the sugar purification process are known in the art. One known method is phosphatation process which is aimed to produce calcium phosphate floc using phosphoric compound and lime, followed by a flocculation step by adding a polymer as flocculant. One important modification to the phosphatation process is the application of colour precipitants, such as certain quaternary ammonium compounds. Quaternary ammonium compounds, which are cationic in nature, can improve the precipitation of

anionic high molecular weight colour impurities, which can be more readily removed as flotation scum.

[0005] Conventionally, the quaternary ammonium compound and the phosphoric compound are added to sugar containing mixtures in separate streams. For example, in US Patent No. 3,698,951, there is disclosed a method for removing colour impurities in sugar liquors by adding a quaternary ammonium compound, followed by addition of phosphoric acid. The separate addition of the reagents is laborious and such method requires high carpex costs, energy and maintenance costs as well. The quaternary ammonium compound is usually diluted in water before its addition to the sugar liquor or syrup. However, the quaternary ammonium compound solution tends to have relatively high viscosity, which affect the efficiency of the addition and may sometimes cause blockage of the equipment. In order to solve this problem, high dilution factors are required so as to bring the viscosity of the solution of the quaternary ammonium compound to a sufficiently low level. This will waste water and costs.

Summary of Invention

[0006] It has been found that the above mentioned problems can be solved by the present invention.

[0007] In a first aspect of the present invention, there is provided a solid composition, notably a solid composition for removing colour impurities in a sugar liquor or syrup, comprising at least a quaternary ammonium compound and a phosphoric compound; wherein the weight ratio of the quaternary ammonium compound to the phosphoric compound is in the range of 1:1 to 1:5.

[0008] Preferably, the weight ratio of the quaternary ammonium compound to the phosphate compound is in the range of 1:1 to 1:3.

[0009] Notably, the quaternary ammonium compound has the general formula of :

$$[N^{+}(R_1)(R_2)(R_3)(R_4)]_yX^{-} \quad (I)$$

wherein :

R_1, R_2, R_3, and R_4, which may be same or different, represent a saturated or unsaturated, straight or branched aliphatic group having from 1 to 30 carbon atoms, or an aromatic group;

X is an anion;

y is the valence of X.

[0010] Preferably, the quaternary ammonium compound has the general formula :

$$[N^+(R_5)_2(R_6)(R_7)]_yX^- \quad \text{(II)}$$

wherein :

R_5 is an alkyl or hydroxyalkyl group containing from 8 to 22 carbon atoms;

R_6 is a alkyl or hydroxyalkyl group containing from 1 to 4 carbon atoms;

R_7 is R_5 or R_6;

X is an anion;

y is the valence of X.

[0011] The quaternary ammonium compound may have the general formula :

$$[N^+((CH_2)_n\text{-}T\text{-}R_8)_m(R_9)_{4-m}]_yX^- \quad \text{(III)}$$

wherein :

R_8 is independently selected from C_1-C_{24} alkyl or hydroxyalkyl group;

R_9 is independently selected from C_1-C_4 alkyl or hydroxylalkyl group;

T is $-C(=O)-O-$, $-O-C(=O)-$, $-NR_{10}-C(=O)-$ or $-(C=O)-NR_{10}-$, wherein R_{10} is hydrogen, a C_1-C_6 alkyl or a C_1-C_6 hydroxyalkyl group;

n is an integer from 0 to 5;

m is selected from 1, 2 and 3;

X is an anion;

y is the valence of X.

[0012] The quaternary ammonium compound may have the general formula of :

$$[N^+(R_{11})(R_{12})(R_{13})((CH_2)_z\text{-Ph})]_yX^- \quad \text{(V)}$$

wherein :

R_{11} and R_{12}, which may be the same or different, represent a straight or branched alkyl or hydroxyalkyl group having from 1 to 24 carbon atoms;

R_{13} is a straight or branched alkyl or hydroxyalkyl group having from 1 to 8 carbon atoms;

z=0 or an integer of 1 to 3;

Ph represents phenyl group;

X is an anion;

y is the valence of X.

[0013] Preferably, the quaternary ammonium compound is selected from the group consisting of C_{14}-C_{18} alkyl dimethyl ammonium compound, di stearyl dimethyl ammonium compound, di palmityl dimethyl compound, di hexadecyl dimethyl ammonium compound, di octadecyl dimethyl ammonium compound, di oleyl dimethyl ammonium compound, di hydrogenated rapeseed alkyl dimethyl ammonium compound, and a mixture thereof.

[0014] Preferably, the phosphoric compound is phosphoric acid.

[0015] In a second aspect of the present invention, there is provided a method for reducing colour impurities in a sugar liquor or syrup by adding a quaternary ammonium compound and a phosphoric compound to the sugar liquor or syrup; wherein the weight ratio of the quaternary ammonium compound to the phosphoric compound is in the range of 1:1 to 1:5.

[0016] Notably, there is provided a method for reducing colour impurities in a sugar liquor or syrup, comprising the steps of :

(1) providing an aqueous solution or dispersion of the solid composition according to the first aspect of the present invention; and

(2) adding said aqueous solution or dispersion in the sugar liquor or syrup.

[0017] Preferably, the method further comprises the steps of :

(a) adding of a lime-based compound and a flocculating agent in the sugar liquor or syrup, so as to form a flocculant precipitate of the colour impurities;

(b) separating the flocculant precipitate from the sugar liquor or syrup.

[0018] Preferably, the flocculating agent is a polyacrylamide.

[0019] Preferably, the quaternary ammonium compound is present in an amount of from 100 to 500 ppm based on the weight of solid sugar in the sugar liquor or syrup.

[0020] In a third aspect of the present invention, there is provided a use of the solid composition according to the first aspect of the present invention for reducing colour impurities in a sugar liquor or syrup.

[0021] In a forth aspect of the present invention, there is provided a method for preparing a solid composition comprising a quaternary ammonium compound and a phosphoric compound; wherein the method comprises a step of mixing the quaternary ammonium compound and the phosphoric compound, the weight ratio of the quaternary ammonium compound to the phosphoric compound is in the range of 1:1 to 1:5.

Detailed Description

[0022] Throughout the description, including the claims, the term "comprising one" or "comprising a" should be understood as being synonymous with the term "comprising at least one", unless otherwise specified, and "between" should be understood as being inclusive of the limits.

[0023] It should be noted that in specifying any range of concentration, weight ratio or amount, any particular upper concentration, weight ratio or amount can be associated with any particular lower concentration, weight ratio or amount.

[0024] As used herein, the term "alkyl" means a saturated hydrocarbon radical, which may be straight, branched or cyclic, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl, t-butyl, pentyl, n-hexyl, cyclohexyl.

[0025] As used herein, the term "hydroxyalkyl" means an alkyl radical, which is substituted with a hydroxyl groups, such as hydroxymethyl, hydroxyethyl, hydroxypropyl, and hydroxydecyl.

[0026] As used herein, the term "aryl" means a monovalent unsaturated hydrocarbon radical containing one or more six-membered carbon rings in which the unsaturation may be represented by three conjugated double bonds, which may be substituted one or more of carbons of the ring with hydroxy, alkyl, alkenyl, halo, haloalkyl, or amino, such as, for example, phenoxy, phenyl, methylphenyl, dimethylphenyl, trimethylphenyl, chlorophenyl, trichloromethylphenyl, aminophenyl.

[0027] As used herein, the term "aralkyl" means an alkyl group substituted with one or more aryl groups, such as, for example, phenylmethyl, phenylethyl, triphenylmethyl.

[0028] The present invention provides a solid composition, notably a solid composition for reducing colour impurities in a sugar liquor or syrup, comprising at least a quaternary ammonium compound and a phosphoric compound; wherein the weight ratio of the quaternary ammonium compound to the phosphoric compound is in the range of 1:1 to 1:5. The colour impurities in the sugar liquor or syrup notably include plant pigments, melanoidins, caramels and alkaline degradation products of fructose. The solid composition has good storage stability and can provide excellent colour removal efficiency.

[0029] The term "solid composition", as used herein, refers a composition in the form of a solid such as a powder, a particle, an agglomerate, a flake, a granule, a pellet, a tablet, a brick, a paste, a block such as a molded block, a unit dose, or another solid form known to those of skill in the art. The term "solid" refers to the state of the composition under the expected conditions of storage and use of the composition. In general, it is expected that the composition will remain in solid form at ambient temperature (approximately 25°C). When referring to a paste, it is meant that the solid composition will not flow perceptibly and will substantially retain its shape under moderate stress or pressure or mere gravity, as for example, the shape of a mold when removed from the mold, the shape of an article as formed upon extrusion from an extruder, and the like.

[0030] The term "quaternary ammonium compound" (also referred to as "quat"), as used herein, means a compound containing at least one quaternized nitrogen wherein the nitrogen atom is attached to four organic groups. The quat may comprise one or more quaternized nitrogen atoms. Preferably, the quat comprises only one quaternized nitrogen atom.

[0031] The term "sugar liquor or syrup", as used herein, means any liquor or syrup containing a sugar or a melted raw sugar. Typically, the sugar is derived from a plant source, such as, a sugar cane, a sugar beet and a corn. "Raw sugar" means a sugar which has been minimally processed and which contains soluble and insoluble impurities. The raw sugar can be obtained from sugar juices by the processes of clarification, evaporation to a thick sugar syrup, and crystallization. Then the crystallized product can

be dissolved in water so as to obtain the sugar liquors, which is also called "melter liquor". Alternatively, sugar syrups, which are obtained from sugar juices, can be used as the feedstock for the sugar refining process.

[0032] According to the present invention, the quat may have the general formula of :

$$[N^+(R_1)(R_2)(R_3)(R_4)]_yX^- \quad (I)$$

wherein :

R_1, R_2, R_3, and R_4, which may be same or different, represents a saturated or unsaturated, straight or branched aliphatic group having from 1 to 30 carbon atoms, or an aromatic group, such as aryl or aralkyl group; X is an anion, for example halide, such as Cl or Br, sulphate, alkyl sulphate, nitrate or acetate, preferably, X is chloride or methylsulfate; y is the valence of X.

[0033] The aliphatic group as defined in general formula (I) may comprise hetero atoms such as oxygen, nitrogen, sulphur and halogens. Optionally, the aliphatic group comprises at least an ester or amide function.

[0034] Advantageously, the quat is an alkyl quat which has the general formula :

$$[N^+(R_5)_2(R_6)(R_7)]_yX^- \quad (II)$$

wherein :

R_5 is an alkyl or hydroxyalkyl group containing from 8 to 22 carbon atoms, such as C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$, $C_{18}H_{37}$, preferably, R_5 contains from 12 to 20 carbon atoms;

R_6 is an alkyl or hydroxyalkyl group containing from 1 to 4 carbon atoms, such as methyl, ethyl and propyl group, preferably R_6 is methyl;

R_7 is R_5 or R_6;

X is an anion, for example halide, such as Cl or Br, sulphate, alkyl sulphate, nitrate or acetate, preferably, X is chloride or methylsulfate; y is the valence of X.

[0035] Notably, the quat according to general formula (II) is a dialkyl dimethyl quat. Examples of the quat of general formula (II) include C_{14}-C_{18} alkyl dimethyl ammonium compound (such as DHT21 sold by the Solvay Company), di tallow alkyl dimethyl ammonium compound, di stearyl dimethyl ammonium compound, di palmityl dimethyl compound, di

hexadecyl dimethyl ammonium compound, di octadecyl dimethyl ammonium compound, di oleyl dimethyl ammonium compound, di hydrogenated rapeseed alkyl dimethyl ammonium compound.

[0036] Advantageously, the quat has the general formula :

$$[N^+((CH_2)_n\text{-}T\text{-}R_8)_m(R_9)_{4-m}]_yX^- \quad \text{(III)}$$

wherein :

R_8 is independently selected from C_1-C_{24} alkyl or hydroxyalkyl group;

R_9 is independently selected from C_1-C_4 alkyl or hydroxylalkyl group;

T is $-C(=O)-O-$, $-O-C(=O)-$, $-NR_{10}-C(=O)-$ or $-(C=O)-NR_{10}-$, wherein R_{10} is hydrogen, a C_1-C_6 alkyl or a C_1-C_6 hydroxyalkyl group;

n is an integer from 0 to 5;

m is selected from 1, 2 and 3;

X is an anion, for example halide, such as Cl or Br, sulphate, alkyl sulphate, nitrate or acetate, preferably, X is chloride or methylsulfate;

y is the valence of X.

[0037] Preferably, m as defined in general formula (III) is 2. Accordingly, the quat may have the general formula :

$$[N^+((CH_2)_n\text{-}T\text{-}R_8)_2(R_9)_2]_yX^- \quad \text{(IV)}$$

R_8, R_9, T, n, X and y are as defined in general formula (III).

[0038] Examples of the quat of general formula (III) include :

TET : Di(tallowcarboxyethyl)hydroxyethyl methyl ammonium methylsulfate,

TEO : Di(oleocarboxyethyl)hydroxyethyl methyl ammonium methylsulfate,

TES : Distearyl hydroxyethyl methyl ammonium methylsulfate,

TEHT : Di(hydrogenated tallow-carboxyethyl)hydroxyethyl methyl ammonium methylsulfate,

TEP : Di(palmiticcarboxyethyl)hydroxyethyl methyl ammonium methylsulfate,

DEEDMAC : Dimethylbis[2-[(1-oxooctadecyl)oxy]ethyl]ammonium chloride.

[0039] Advantageously, the quat has the general formula of :

$$[N^+(R_{11})(R_{12})(R_{13})((CH_2)_z\text{-}Ph)]_yX^- \quad \text{(V)}$$

wherein :

R_{11} and R_{12}, which may be the same or different, represents a straight or branched alkyl or hydroxyalkyl group having from 1 to 24 carbon atoms;

preferably from 8 to 24 carbon atoms;

R_{13} is a straight or branched alkyl or hydroxyalkyl group having from 1 to 8 carbon atoms, preferably from 1 to 3 carbon atoms;

z=0 or an integer of 1 to 3, preferably z=1;

Ph represents phenyl group, the phenyl group may have at least one substituent selected from the group consisting of halide, nitrite, and sulphate on any available position;

X is an anion, for example halide, such as Cl or Br, sulphate, alkyl sulphate, nitrate or acetate, preferably, X is chloride or methylsulfate;

y is the valence of X.

[0040] Examples of the quats of general formula (V) include di stearyl methyl benzyl ammonium compound, di tallow alky methyl benzyl ammonium compound, di palmityl methyl benzyl compound, di hexadecyl methyl benzyl ammonium compound, di octadecyl methyl benzyl ammonium compound.

[0041] It is appreciated that the solid composition may comprise a single quat or a mixture of more than one quats.

[0042] According to the present invention, the phosphoric compound may be phosphoric acid or a phosphate compound. Suitable phosphate compounds include, but not limited to tripolyphosphates, prophosphates, hexametaphophates, trisodium phosphates, sodium phosphate monobasic, calcium phosphate monobasic, ammonium phosphate monobasic, sodium phosphate dibasic, ammonium phosphate dibasic or any water-soluble phosphate salt which will not substantially decrease the pH of the sugar syrup or sugar liquor is expected to be within the purview of this invention. Preferably, the phosphoric compound is phosphoric acid.

[0043] The solid composition may further comprise water and an organic solvent, such as ethanol and isopropanol.

[0044] The solid composition may further comprise a polycationic polymer. Suitable polycationic polymers include copolymer of di-allyl dimethyl ammonium chloride (DADMAC) and acrylic amide, copolymer of DADMAC and sodium acrylate, copolymer of DADMAC, acrylic amide and sodium acrylate, copolymer of dimethylamine-epichlorohydrin.

[0045] The solid composition may also comprise oxidant which can be used in sugar purification. Suitable oxidants include hydrogen peroxide and hypochloride.

[0046] According to the present invention, the weight ratio of the quat to the phosphoric compound which are comprised in the solid composition is in the range of 1:1 to 1:5 (including: 1:1, 1:1.1, 1:1.2, 1:1.3, 1:1.4, 1:1.5, 1:1.6, 1:1.8, 1:2, 1:2.2, 1:2.4, 1:2.6, 1:2.8, 1:3, 1:4, 1:5 etc., and all values and subranges between stated values as if explicitly written out). Preferably, said weight ratio is in the range of 1:1 to 1:3, more preferably in the range of 1:1.2 to 1:3. In the context of the present invention, the weight ratio is calculated based on the weight of the active ingredients.

[0047] The solid composition may be prepared by blending the quat component and the phosphoric compound component by any mixing means well known to a person skilled in the art. Accordingly, the present invention also provides a method for preparing a solid composition comprising a quaternary ammonium compound and a phosphoric compound; wherein the method comprises a step of mixing the quaternary ammonium compound and the phosphoric compound, the weight ratio of the quaternary ammonium compound to the phosphoric compound is in the range of 1:1 to 1:5. Typically, the quat is melt by heating it to a temperature above its melting point, such as about 65^{o}C, then the phosphoric compound can be added to the quat with agitation, preferably with heating. Subsequently, the mixture may be cooled to ambient temperature for solidifying the composition.

[0048] In another aspect, the present invention provides a method for reducing colour impurities in a sugar liquor or syrup by adding a quaternary ammonium compound and a phosphoric compound to the sugar liquor or syrup; wherein the weight ratio of the quaternary ammonium compound to the phosphoric compound is in the range of 1:1 to 1:5. The quaternary ammonium compound and the phosphoric compound may be added to the sugar liquor or syrup at the same time or premixed and added as a blend.

[0049] The present invention also provides a method for reducing colour impurities in a sugar liquor or syrup by using the solid composition described herein. Notably, the method comprises the steps of :

(1) providing an aqueous solution or dispersion of the solid composition; and

(2) adding said solution or dispersion in the sugar liquor or syrup.

[0050] The solid composition may be dissolved or dispersed in water, optionally with organic solvents. Preferably, the concentration of the quat in such solution or dispersion is from 5 wt% to 30 wt%, more preferably from 10 wt% to 20 wt%.

[0051] The solution or dispersion that contains the quat and the phosphoric compound may be added in the sugar liquor or syrup in a reaction tank with metering pump and agitation apparatus, which brings the quat into contact with the colour impurities. Notably, the reaction is conducted at a temperature of 70-90℃, preferably 80-85℃. The precipitate formed in this reaction is initially very finely divided and can hardly be observed with the naked eye; but its presence can be revealed by measurement of the optical properties of the liquor, for example by measuring the optical density at 420 nm, using a spectrophotometer. In accordance to one example embodiment of the present invention, such fine precipitate can be removed by filtration, using a filter medium having sufficiently small porosity.

[0052] One advantage of the present invention is that it allows the quat and the phosphoric compound being conveniently added to the sugar liquor or syrup in a single stream, which can save time and costs. Also, the viscosity of a diluted aqueous solution of the solid composition is lower compared to a solution containing quat alone at the same quat concentration. This is particularly advantageous as lower viscosity of the dilution aqueous solution allows rapid and sufficient mixing of the quat with the sugar liquor or syrup, which can enhance the efficiency of the reaction between the quat and the colour impurities. In addition, the melting point of the solid composition is lower than that of a quat solid, energy can thus

be saved by using the solid composition when melting the colour precipitate due to lower temperature and shorter heating time required.

[0053] The effective dose amount of the solid composition can be readily determined by a person skilled in the art. Generally, the dose amount of the solid composition is from about 200 to about 2000 ppm based on the weight of the solid sugar in the sugar liquor or syrup. Preferably, the dose amount of the solid composition is from about 400 to about 1000 ppm based on the weight of the solid sugar in the sugar liquor or syrup.

[0054] According to the present invention, the method may further comprise the steps of :

(a) adding a lime-based compound and a flocculating agent in the sugar liquor or syrup, so as to form a flocculant precipitate of the colour impurities;

(b) separating the flocculant precipitate from the sugar liquor or syrup.

[0055] Notably, the flocculant precipitate is calcium phosphate.

[0056] The term "lime-based compound" used herein refers to calcium-containing compound which can be used to neutralize the solution acidity and form precipitating insoluble calcium phosphates in the sugar liquors or syrups with the phosphoric compounds. Suitable lime-based compounds include, but not limited to, calcium hydroxide, either as slurry with water (milk of lime) and lime succrate. The lime-based compound may be added to the sugar liquor or syrup in a sufficient amount to raise the pH of the sugar liquor or syrup to be between 6 and 8, preferably between 6.8 and 7.2.

[0057] A flocculating agent may be added to the sugar liquor or syrup to increase the size of precipitate scum comprising most of calcium phosphate coagulum and other colour impurities precipitated by incorporating with the quat.

[0058] Preferably, the flocculating agent is an anionic polyeletrolyte, such as polyacrylate, polyacrylamide, preferably polyacrylamide. The polyacrylamide may be comprised in an amount of about 5 to about 30 ppm based on the weight of the solid sugar in the sugar liquor or syrup. Preferably, the polyacrylamide is present in an amount of about 10 to

about 25 ppm based on the weight of the solid sugar in the sugar liquor or syrup.

[0059] The polyacrylamide used in the present invention preferably has an average Molecular Weight of from 12,000,000 to 30,000,000 Daltons. More preferably, the polyacrylamide has an average Molecular Weight of 22,000,000 Daltons.

[0060] After the flocculation, the flocculant precipitate containing the colour impurities, which may be in the form of floating scums, can be removed from the sugar liquor or syrup by a physical separation method including flotation such as air-flotation, filtration and the like. A preferred separation method for the present invention is the air-flotation method, for which there is an additional step of micro aeration before the step of adding the flocculating agent. The micro aeration may take place to produce an aerated sugar liquor or syrup. This step can either perform in a reaction tank with a stirring device or using an air compressor. The air trapped scums to float in the sugar liquor or syrup can be then removed from the liquor surface by a skimming device, such as a scrapper.

[0061] Generally, by using the method of the present invention, the colour value of the sugar product can be reduced to 15-100 ICUMSA units, more typically, 20-50 ICUMSA units.

[0062] The present invention will now be described with reference to a number of specific examples, which should not be considered as limiting the scope of the claimed invention.

[0063] Should the disclosure of any patents, patent applications, and publications which are incorporated herein by reference conflict with the description of the present application to the extent that it may render a term unclear, the present description shall take precedence.

Examples

[0064] **Materials**

Di-alkyl quat : DHT21; C_{14}-C_{18} alkyldimethyl ammonium chloride (CAS No. 68002-59-5); from the Solvay Company

Mono-alkyl quat : octadecyl trimethyl ammonium chloride (CAS No. 112-

03-8); from the Solvay Company

Benzyl quat : di C_{14}-C_{18} alkyl methyl benzyl ammonium chloride (CAS No. 61789-73-9); from the Solvay Company

Phosphoric acid : 85 wt%

[0065] **Colour removal performance tests**

[0066] Sample preparation

Solid blends were prepared by mixing DHT21 (from the Solvay Company) and phosphoric acid , wherein the weight ratios of the DHT21 to the phosphoric acid in such samples were shown in Table 1 below. The solid blends were melt at 60°C and subsequently diluted in hot water to obtain solutions with a concentration of DHT21 being 10 wt% (active). Raw sugars, obtained from sugar cane juice by simple lime treatment, were dissolved in hot water to obtain a sugar liquor of 60-65 Brix. The sugar liquor had a sugar value of 500-1500 ICUMSA units.

[0067] Phosphatation treatment

The sugar liquor was heated to 80-85°C, subsequently, the diluted solution of the blend was added in the sugar liquor and stirred for 15 mins. The dose amount of quat was 300 ppm based on the weight of the solid sugar in the sugar liquor. Then, lime succrate was added in the mixture, with stirring, to bring the pH value of the mixture to 6.9-7.0.

[0068] Flotation

Subsequently, the sugar liquor was transferred to a separatory funnel and a PAM solution (0.1 wt%) was added in the sugar liquor (the dose amount of PAM was 15-20 ppm based on the solid sugar content). The sugar liquor was shaken and the separatory funnel was immerged in boiling water bath for 10 mins. The precipitate containing the colour impurities floated up to the top of the sugar liquor. 40 ml of the clear sugar liquor were collected from the bottom of the funnel for colour value tests.

[0069] Colour value test

The collected sugar liquor was diluted in water (final concentration of the sugar was 35-40 Brix). The pH value of the solution was adjusted to 7.0 by using diluted HCl or NaOH solution. Subsequently, the solution was

filtered with a filter paper (porous size 0.45 μm) and the absorption of the solution was detected at 420 nm with UV/Vis spectrometer.

[0070] The colour value (COL) was calculated according to the formula :

COL (ICUSMA or IU420) = $\frac{A420}{B \times L \times \rho} \times 10^5$

where :

A420 is expressed as absorbance of the sugar liquor at 420 nm wave length;

B is the brix of the sugar liquor at 25℃ (detection of brix of the sugar liquor is performed with Abbe-Refractometer, unit is °Bx);

L is the length of the cuvette;

ρ is the density of the sugar liquor.

[0071] The colour removal rate was calculated according to the formula :

Colour removal rate = ($COL_{raw\ liquor} - COL_{flotation}$) /$COL_{raw\ liquor}$ * 100%

[0072] The colour removal rate results were shown in table 1 below :

Table 1

Samples	DHT21/H_3PO_4 (w/w)	Colour removal rate (%)
Example 1	1:1	51.8
Example 2	1:1.5	55.1
Example 3	1:2	54.8
Example 4	1:3	55.3
Comparative Example 1	1:0.5	44.5
Comparative Example 2	1:0.8	45.7

[0073] Another set of experiments were conducted according to the methods described above except that DHT21 in the solid blends was replaced by a benzyl quat, di C_{14}-C_{18} alkyl methyl benzyl ammonium chloride (obtained from the Solvay Company).

Table 2

Samples	Benzyl quat/H_3PO_4 (w/w)	Colour removal rate (%)
Example 5	1:1	57.6
Example 6	1:1.5	58.9
Example 7	1:2	59.2
Example 8	1:3	59.5
Comparative Example 3	1:0.5	50.1
Comparative Example 4	1:0.8	52.7

[0074] As shown in Tables 1 and 2, the colour removal efficiency of the solid composition was affected by the weight ratio of the quat to the phosphoric compound. The solid compositions are more effective in reducing the colour impurities when the weight ratio is no less than 1:1.

[0075] **Stability tests**

[0076] A solid blend containing DHT21 and phosphoric acid were prepared as described above. The solid blend was incubated in an oven at 54°C for four weeks. The contents of DHT21 and phosphoric acid were titrated before and after the incubation, respectively. Titration of the phosphoric acid was conducted, using NaOH, and phenolphthalein as the colour indicator. The procedure of such titration method is well known by a person skilled in the art. Titration of DHT21 was conducted according to the methods described in Chinese National Standard GB/T 5174-2004. Results were shown in Table 3 below :

Table 3

	DHT21 content (%)	H_3PO_4 content (%)
0 weeks	49.5	35.7
4 weeks	49.9	36.1

[0077] Results showed that the solid composition according to the present invention can maintain the stability of its components after incubation at 50°C for up to 4 weeks. There was a slight decrease in the content of DHT21, which should be due to evaporation of organic solvents.

[0078] **Viscosity tests**

[0079] Solid DHT21 or solid blends of DHT21 and phosphoric acid were dissolved in water with the various DHT21 concentrations as shown in Table 4 below. Then the viscosity of the solutions was measured by using a Brookfield LVT viscometer at 100 rpm shearing speed (spindle #S2). The measurement was done at ambient temperature, 40°C and 60°C, respectively. The unit of the viscosity is cP.S. Results are shown in Table 4 below :

Table 4

DHT21 concentration	Samples	Ambient temperature	40°C	60°C
2 wt%	DHT21	212	170	76.4
	Blend	50	13.6	11.2
6 wt%	DHT21	7150	2840	4440
	Blend	2420	149	74.8
10 wt%	DHT21	Solid	5300	2280
	Blend	Solid	137.6	368
15 wt%	DHT21	Solid	9000	6700
	Blend	Solid	1260	462

[0080] Results showed that the solution comprising the quat and phosphoric acid exhibited markedly lower viscocity compared to those comprising the quat alone (quat contents were kept to be the same).

[0081] **Colour removal performance tests of different quat compounds**

[0082] Solid blends were prepared according to the procedure as described above and according to the formulations in Table 5 below. Either di-alkyl quat (DHT21) or mono-alkyl quat (FENTACARE® 1831 70) was used. The colour removal performance was evaluated as described above. Results are shown in Table 5 below :

Table 5

Samples	Formulation	Colour removal rate (%)
Example 9	Di-alkyl quat/H_3PO_4, 1:1 (w/w)	51.8
Example 10	Di-alkyl quat/H_3PO_4, 1:2 (w/w)	54.8
Comparative Example 5	Mono-alkyl quat/H_3PO_4, 1:1 (w/w)	45.8
Comparative Example 6	Mono-alkyl quat/H_3PO_4, 1:2 (w/w)	52.6

[0083] Results showed that the di-alkyl quat, when formulated in solid blend with the phosphoric acid, led to higher colour removal efficiency compared to mono-alkyl quat.

[0084] **Flotation rate tests**

[0085] Solid blends were prepared according to the procedure as described above and according to the formulations in Table 6 below. Either di-alkyl quat (DHT21) or mono-alkyl quat was used. The weight ratio of the quat compound and the phosphoric acid in the solid blends was 1:1 (w/w).

[0086] The solid blends were melt at 60°C and subsequently diluted in hot water to obtain solutions with a concentration of quat being 10 wt% (active). Raw sugars, obtained from sugar cane juice by simple lime treatment, were dissolved in hot water to obtain a sugar liquor of 60-65 Brix. The sugar liquor had a sugar value of 500-1500 ICUMSA units.

[0087] The sugar liquor was subject to phosphatation treatment as described above. Subsequently, the sugar liquor was transferred to a separatory funnel and a PAM solution (0.1 wt%) was added in the sugar liquor (the dose amount of PAM was 15-20 ppm based on the solid sugar content). The sugar liquor was shaken and the separatory funnel was immerged in boiling water bath for 10 mins. The precipitate containing the colour impurities floated up to the top of the sugar liquor. Floatation rate was

determined at different time points after the separatory funnel was immerged in the boiling water bath. For the determination of the floatation rate, the results are estimated by naked eye examination and the floatation rate is expressed by dividing the amount of flocculent participates floated to the top surface of the sugar liquor by total amount of flocculent participates occurring in the sugar liquor. Results are shown in Table 6 below.

Table 6

Samples	**Di-alkyl quat/H_3PO_4**	**Mono alkyl quat/H_3PO_4**
Flotation rate		
5 mins	95%	85%
10 mins	100%	95%

[0088] it is highly desirable that the flocculant precipitate containing the colour impurities, once occurs, can float up rapidly and separate from the clear sugar liquor. This is particularly important in the industry scale sugar clarification process as a faster floatation rate can lead to higher efficiency of the process. Results showed that the di-alkyl quat, when formulated in the solid blend, led to faster flotation rate compared to mono-alkyl quat.

Claims

1. A solid composition comprising at least a quaternary ammonium compound and a phosphoric compound; wherein the weight ratio of the quaternary ammonium compound to the phosphoric compound is in the range of 1:1 to 1:5.
2. The solid composition according to claim 1, wherein the weight ratio of the quaternary ammonium compound to the phosphate compound is in the range of 1:1 to 1:3.
3. The solid composition according to claim 1 or 2, wherein the quaternary ammonium compound has the general formula of :

   $[N^+(R_1)(R_2)(R_3)(R_4)]_yX^-$ (I)

   wherein :

   R_1, R_2, R_3, and R_4, which may be same or different, represent a saturated or unsaturated, straight or branched aliphatic group having from 1 to 30 carbon atoms, or an aromatic group;

   X is an anion;

   y is the valence of X.
4. The solid composition according to any one of claims 1 to 3, wherein the quaternary ammonium compound has the general formula :

   $[N^+(R_5)_2(R_6)(R_7)]_yX^-$ (II)

   wherein :

   R_5 is an alkyl or hydroxyalkyl group containing from 8 to 22 carbon atoms;

   R_6 is a alkyl or hydroxyalkyl group containing from 1 to 4 carbon atoms;

   R_7 is R_5 or R_6;

   X is an anion;

   y is the valence of X.
5. The solid composition according to any one of claims 1 to 3, wherein the quaternary ammonium compound has the general formula :

   $[N^+((CH_2)_n\text{-}T\text{-}R_8)_m(R_9)_{4-m}]_yX^-$ (III)

   wherein :

   R_8 is independently selected from C_1-C_{24} alkyl or hydroxyalkyl group;

   R_9 is independently selected from C_1-C_4 alkyl or hydroxylalkyl group;

T is $-C(=O)-O-$, $-O-C(=O)-$, $-NR_{10}-C(=O)-$ or $-(C=O)-NR_{10}-$, wherein R_{10} is hydrogen, a C_1-C_6 alkyl or a C_1-C_6 hydroxyalkyl group;

n is an integer from 0 to 5;

m is selected from 1, 2 and 3;

X is an anion;

y is the valence of X.

6. The solid composition according to any one of claims 1 to 3, wherein the quaternary ammonium compound has the general formula of :

$$[N^+(R_{11})(R_{12})(R_{13})((CH_2)_z\text{-}Ph)]_yX^- \quad (V)$$

wherein :

R_{11} and R_{12}, which may be the same or different, represent a straight or branched alkyl or hydroxyalkyl group having from 1 to 24 carbon atoms;

R_{13} is a straight or branched alkyl or hydroxyalkyl group having from 1 to 8 carbon atoms;

z=0 or an integer of 1 to 3;

Ph represents phenyl group;

X is an anion;

y is the valence of X.

7. The solid composition according to any one of claims 1 to 4, wherein the quaternary ammonium compound is selected from the group consisting of C_{14}-C_{18} alkyl dimethyl ammonium compound, di stearyl dimethyl ammonium compound, di palmityl dimethyl compound, di hexadecyl dimethyl ammonium compound, di octadecyl dimethyl ammonium compound, di oleyl dimethyl ammonium compound, di hydrogenated rapeseed alkyl dimethyl ammonium compound, and a mixture thereof.
8. The solid composition according to any one of claims 1 to 7, wherein the phosphoric compound is phosphoric acid.
9. A method for reducing colour impurities in a sugar liquor or syrup by adding a quaternary ammonium compound and a phosphoric compound to the sugar liquor or syrup; wherein the weight ratio of the quaternary ammonium compound to the phosphoric compound is in the range of 1:1 to 1:5.
10. A method for reducing colour impurities in a sugar liquor or syrup, comprising the steps of :

(1) providing an aqueous solution or dispersion of the solid composition according to any one of claims 1 to 8; and

(2) adding said aqueous solution or dispersion in the sugar liquor or syrup.

11. The method according to claim 9 or 10, wherein the method further comprises the steps of :

(a) adding of a lime-based compound and a flocculating agent in the sugar liquor or syrup, so as to form a flocculant precipitate of the colour impurities;

(b) separating the flocculant precipitate from the sugar liquor or syrup.

12. The method according to claim 10 or 11, wherein the flocculating agent is a polyacrylamide.

13. The method according to any one of claims 9 to 12, wherein the quaternary ammonium compound is present in an amount of from 100 to 500 ppm based on the weight of solid sugar in the sugar liquor or syrup.

14. Use of the solid composition according to any one of claims 1 to 8 for reducing colour impurities in a sugar liquor or syrup.

15. A method for preparing a solid composition comprising a quaternary ammonium compound and a phosphoric compound; wherein the method comprises a step of mixing the quaternary ammonium compound and the phosphoric compound, the weight ratio of the quaternary ammonium compound to the phosphoric compound is in the range of 1:1 to 1:5.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2017/085456

A. CLASSIFICATION OF SUBJECT MATTER

C13B 20/14(2011.01)i

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)

C13B

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

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

CPRSABS;CJFD;CNTXT;CNABS;DWPI:ammonium,sugar,quaternary,phosphoric acid

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 101812546 A (UNIV GUANGXI) 25 August 2010 (2010-08-25) claims 1-5	1-2, 9, 15
Y	CN 101812546 A (UNIV GUANGXI) 25 August 2010 (2010-08-25) claims 1-5	3-8, 10-14
Y	US 3698951 A (TATE & LYLE LTD) 17 October 1972 (1972-10-17) claims 1-12, description column 3, lines 21-40	3-8, 10-14

☐ Further documents are listed in the continuation of Box C.

☑ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
16 August 2017	**24 August 2017**

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
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Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
CN 101812546 A	25 August 2010	CN 101812546 B	28 March 2012
US 3698951 A	17 October 1972	IT 1036010 B	30 October 1979
		DE 1792654 A1	08 June 1972
		DE 1792654 C3	13 March 1980
		GB 1224990 A	10 March 1971
		DE 1792654 B2	12 July 1979
		FR 1582468 A	26 September 1969