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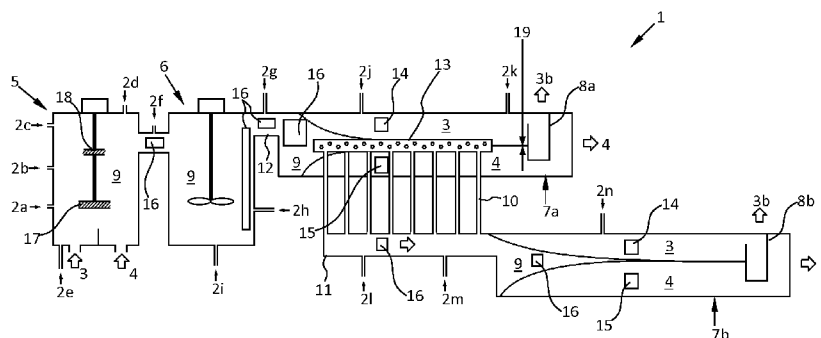
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## ANTIOXIDANTS FOR USE IN SOLVENT EXTRACTION SYSTEMS

**CROSS-REFERENCE TO RELATED APPLICATIONS**

This application is an international PCT Application which claims the benefit of U.S. Provisional Patent Application No. 61/736,238, filed 12 December 2012.

**FIELD OF THE INVENTION**

This invention relates to equipment and processes for improving solvent extraction circuits, and more particularly to systems and methods for reducing wax buildup and/or crud formation in mixer settlers and related SX/EW devices.

**BACKGROUND OF THE INVENTION**

*Ahrens, et al. JACS 2001, 123, 9164-9165* suggests that hindered phenols may be suitable antioxidants. *Frei, et al. PNAS 1990, 87, 4879-4883* suggests that ubiquinol (e.g., derivatives such as *Ubiquinol-9* and *Ubiquinol-10*) may possess antioxidant properties. *Pieri, et al. Life Sciences 1994, 55, PL271-PL276* further suggests that melatonin is an antioxidant. Moreover, *Slobodan, et al. JACS 1999, 121, 9677-9681* suggests curcumin may exhibit antioxidation properties. According to *Buettner, G. R. Archives BioChem. BioPhys. 1993, 300, 535-543*, vitamin E and tocopherols may be considered antioxidants. Lastly, retinol can be

considered an antioxidant, according to *Tesoriere, et al. Archives Biochem. BioPhys.* 1997, 343, 13-18.

Antioxidants are typically used in polyolefin processing (e.g., those produced by BASF). Pipelines carrying the polyolefins use seeding wax crystals to prevent buildup of waxes within the pipe. Hydrocarbon solvents, such as those used in hydrometallurgical solvent extraction systems, degrade by auto-oxidation in the presence of dissolved oxygen. Attack by oxygen is a free radical chain reaction which requires only very low activation energy. Degradation is enhanced by heat, shear and the presence of radical initiators such as humics (major components of crud), iron salts, manganese, and cobalt. Exposure of the solvent to UV radiation, as through exposure to sunlight, can dramatically increase free radical generation and eventually lead to wax and crud formation. This may degrade UV stabilizers which might already be present in the manufactured solvents (e.g., benzophenone). It is anticipated by the inventors of the present invention that the addition of one or more soluble antioxidants into the organic phase of a solvent extraction system/process will provide thermal stability and scavenge free radicals – thus, increasing lixiviant lifetime and preventing wax formation which is a known precursor to crud formation.

FIG. 1 schematically illustrates a traditional mixer settler device 900. The mixer settler device 900 may comprise a primary mixer 905, an auxiliary mixer 906, and a settling tank 907. An organic phase 903 and an aqueous phase 904 enter the primary mixer 905, where the two may be mixed, thereby forming an emulsion 909. The residence time of the emulsion 909 may be extended via one or more auxiliary mixing devices 906. Once mass transfer between the organic 903 and aqueous 904 phases is complete, the emulsion 909 may be moved to a settling

tank 907, where the two immiscible liquids separate away from each other (with the lighter organic phase 903 on top). A weir 908 may remove the organic 903 from the tank 907, and the rest of the aqueous phase 904 may be collected from lower portions of the tank 907 and removed.

Problems that currently exist with conventional mixer settlers include difficulties with coalescence. In some cases, droplet size may be too small to coalesce, and/or portions of the organic phase 903 may become trapped or “entrained” within portions of the aqueous phase 904, and vice-versa. In such cases, the emulsion phase 909 may not go away fully (zone 901). Moreover, setting rates may be very slow. Typically, the total flow rates through a mixer settler 900 are governed by the fastest times it takes for the two immiscible liquids 903, 904 to separate. Additionally, solvents within the organic phase 903 are under constant exposure to oxidizing conditions (e.g., high shear in the mixers 905, 906). Moreover, radical initiators such as oxygen and acid commonly found in solvent extraction circuits will quickly consume any antioxidants which may have already been pre-loaded into the solvents from the manufacturer.

There is currently no known prior literature which suggests adding or otherwise using supplemental free radical scavengers or anti-oxidants within SX circuits, nor is there any known prior literature from extractant manufacturers or suppliers which recommends continued monitoring of antioxidant levels within the organic phase 903 and adding antioxidants as said levels drop as does the present invention.

## OBJECTS OF THE INVENTION

It is, therefore, an object of the present invention to speed up the solvent extraction process.

It is also an object of the present invention to reduce wax buildup in and around equipment found in solvent extraction processes, including the organic phase.

It is also an object of the present invention to reduce crud formation in and around equipment found in solvent extraction processes, including the organic phase.

It is a further object of the present invention to increase the lifetime of lixiviant (e.g., oxime) in and around equipment found in solvent extraction processes.

These and other objects of the present invention will be apparent from the drawings and description herein. Although every object of the invention is believed to be attained by at least one embodiment of the invention, there is not necessarily any one embodiment of the invention that achieves all of the objects of the invention.

## SUMMARY OF THE INVENTION

A method of solvent extraction is disclosed. The method generally comprises the steps of: providing an organic solution; providing an organic-soluble antioxidant; and, dissolving the antioxidant in the organic solution, thereby reducing crud formation. In some embodiments, the organic-soluble antioxidant may comprise one or more of the following: a phenol or hindered phenol, ubiquinol (e.g., Ubiquinol-9 and/or Ubiquinol-10), melatonin, curcumin, vitamin E,

and/or retinol (i.e., vitamin A1). The antioxidant may be biologically derived. In some instances, blends of multiple antioxidants may be provided throughout portions of the solvent extraction circuit (e.g., a mixer settler tank). The blends of antioxidants may comprise mixtures of Tetrakis [methylene (3,5-di-tert-butyl-4-hydroxyhydrocinnamate)] methane and Tris (2,4-di-tert-butylphenyl) phosphite. Blends of antioxidants may also comprise mixtures of thiodiethylene bis (3,5-di-tert-butyl-4-hydroxycinnamate) and disteryl-beta,beta'-thiodipropionate. In some embodiments, the method may comprise a step of monitoring antioxidant levels within the solvent extraction system in order to verify whether or not antioxidant levels are adequate. Additional antioxidant or blends of antioxidants may be added according to the monitoring.

A solvent extraction circuit for the reduced formation of crud is also disclosed. The circuit generally comprises at least one mixer, a first settler; and delivery means for providing an organic-soluble antioxidant to one or more portions of the at least one mixer and/or the first settler. In some embodiments, the circuit may comprise an emulsion zone removal means for speeding up flow rates in the first settler. In some instances, at least one second settler may be operatively connected to the emulsion zone removal means to process the removed emulsion separately and differently than the first settler. A majority of the emulsion zone may, for example, be sucked from, pumped from, or otherwise removed from the first settler and subsequently transferred to the second settler. Flow rates within the second settler may be less than, equal to, or greater than the first settler. In some instances, target depth skimming apparatus and methods such as the ones described in co-pending application PCT/US2011/066391 (filed on 21 December 2011 and published on 28 June 2012 as WO 2012/088228) may be advantageously utilized to remove portions of an emulsion.

### BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a schematic representation of a typical mixer settler in an SX/EW circuit;

FIG. 2 shows a modified mixer settler in accordance with some embodiments of the invention;

FIGS. 3-17 show chemical compositions and components thereof which may be used as antioxidants within a solvent extraction circuit according to some embodiments; and,

FIG. 18 shows a solvent extraction method according to certain embodiments.

### DETAILED DESCRIPTION OF THE INVENTION

The following description of the non-limiting embodiments shown in the drawings is merely exemplary in nature and is in no way intended to limit the inventions disclosed herein, their applications, or uses.

Turning now to FIG. 2, a solvent extraction circuit may comprise a mixer settler 1 having a primary mixer 5, an auxiliary mixer 6, and a first settler 7a. An organic phase 3 and an aqueous phase 4 may enter the primary mixer 5, where the two are mixed, thereby forming an emulsion 9. In some instances, one or more impellers 17, 18, of different diameters, widths, spacings, and/or configurations (e.g., such as axial or radial-type impeller configurations) may be advantageously utilized. The residence time of the emulsion 9 may be extended via the auxiliary mixer 6 (which may have a different impeller arrangement than the primary mixer 5). Once

mass transfer between the organic 3 and aqueous 4 phases is complete, the emulsion 9 may be moved to the first settler 7a, where the two immiscible liquids separate away from each other (with the lighter organic phase 3 on top of the heavier aqueous phase 4). A first weir 8a removes the organic 3 from the first settler 7a, and the rest of the aqueous phase 4 is collected from lower portions of the first settler 7a and is subsequently removed.

To alleviate the aforementioned problems that currently exist with conventional mixer settlers, means 13 for removing portions of the emulsion zone 9 may be provided. The means 13, may comprise, for instance, a number of perforated pipes extending lengthwise along the first settler 7a at middle portions thereof, between the organic 3 and aqueous 4 layers. In some non-limiting embodiments, as shown, the means 13 for removing portions of the emulsion zone 9 may convey the emulsion 9 to the inlet 11 of a second settler 7b, via a number of delivery channels 10. Flow rates through the second settler 7b may be different (e.g., slower) than the flow rates in the first settler 7a. In this respect, the first settler 7a may be able to handle much higher flow rates, somewhat independently of the ability for the immiscible liquids 3, 4 in the emulsion zone 9 to separate out quickly. Moreover, the emulsion zone 9 may be nearly eliminated in the first settler 7a, or at least reduced to much smaller thicknesses 19 than those emulsion zones 901 exhibited by prior art solutions. A second weir 8b may remove the organic 3 from the second settler 7b, and the rest of the aqueous phase 4 is collected from lower portions of the second settler 7b and then subsequently removed.

In the first 7a and/or second 7b settler, different coalescing media 14, 15, 16 may be placed in different portions of the settler. For instance, a first coalescing media 14 having first coalescing properties and being formed of a first material and structure may be placed in areas located within the organic phase 3 so as to remove small entrained amounts of aqueous solution

4. Similarly, a second coalescing media 15 having second coalescing properties and being formed of a second material and structure may be placed in areas located within the aqueous phase 4 so as to remove small entrained amounts of organic solution 3 within. Additionally, a third coalescing media 16 having third coalescing properties and being formed of a third material and structure may be placed in areas located within the emulsion 9. The third coalescing media may be optimized to quickly separate a majority of the two immiscible phases 3, 4. Each of the structures may have different porosities, charges, hydrophobicity, sizes, materials, material combinations, or the like. In some instances, the third coalescing media 16 may be provided to other portions of the mixer settler device 1 which are upstream from the settler(s) 7a, 7b. For instance, one or more of the mixers 5, 6, may comprise third coalescing media 16, and the inlets 11, 12, of each settler 7a, 7b may also comprise coalescing media 16.

Means 2a-m for introducing an antioxidant to the organic phase 3 may be provided at any single location or multiple locations on the mixer settler device 1. For example, means 2a may be provided at lower sidewall portions of the primary mixer 5; means 2b may be provided at middle sidewall portions of the primary mixer 5; and/or means 2c may be provided at upper sidewall portions of the primary mixer 5. Means 2d for delivery of the antioxidant may also be provided at upper portions of the primary mixer 5, and/or may enter the primary mixer 5 from a lower portion of the mixer 5 – e.g., adjacent the organic influent 3. Connection piping between the primary mixer 5 and the auxiliary mixer 6 may further comprise means 2f for introducing one or more antioxidants or antioxidant blends. Likewise, inlets 11, 12 of the first 7a and second 7b settlers may comprise means for antioxidant delivery 2g, 2l, 2m. Moreover, means 2j, 2k, 2n for delivering antioxidant to the organic phase 3 within the settler portion 7a, 7b may be utilized. Means 2a-m for antioxidant delivery may comprise one or more valves, nozzles, spargers, hoses,

feed hoppers, screw feeds, or pipes connected at any portions of the mixer settler 1 which are within, surrounded by, or adjacent to the organic phase 3 – including weirs 8a, 8b. In some embodiments, means 2a-m for antioxidant delivery may be incorporated within portions of coalescing media 14, 15, 16, for instance, by providing one or more valves, nozzles, spargers, hoses, feed hoppers, screw feeds, or pipes which are configured to deliver an antioxidant to the organic phase 3 which are operatively coupled to coalescing media 14, 15, 16. While the preferred mechanism used to provide said means for antioxidant delivery is contemplated to be a nozzle which is operatively coupled to a control valve; said means 2a-m may simply alternatively comprise an operator manually-dumping specified amounts of antioxidant into one or more portions of the mixer and/or settlers 7a, 7b via a bucket or hopper. Lastly, lower and side portions of the auxiliary mixer 6 may comprise inlets 2i, 2h for the addition of antioxidants to the emulsion 9. In an alternative embodiment, the solvent and/or the diluent in the organic phase 3 may be formulated with one or more antioxidants or antioxidant blends as a step separate from or prior to entering the solvent extraction process.

The types of antioxidants delivered to the organic phase 3 may comprise single antioxidants, or antioxidant blends and may include, without limitation, phenols, hindered phenols, ubiquinols (e.g., Ubiquinol-9 and/or Ubiquinol-10), melatonin, curcumin, glutathione, vitamin C which has been derivitized to make it oil soluble, vitamin E, and/or retinol (i.e., vitamin A1). The antioxidants used may or may not be biologically derived. In some instances, blends of antioxidants may include mixtures of Tetrakis [methylene (3,5-di-tert-butyl-4-hydroxyhydrocinnamate)] methane and Tris (2,4-di-tert-butylphenyl) phosphite. One example of this is IRGANOX® B-225, which is a 50%-50%/wt. mixture of Tetrakis and Tris. Alternatively, blends of antioxidants may include mixtures of thiodiethylene bis (3,5-di-tert-

butyl-4-hydroxycinnamate) and disteryl-beta,beta'-thiodipropionate. One example of this might be BNX® 1225, which is a 50%-50%/wt. mixture of the same. FIGS. 1-17 show exemplary, non-limiting examples of antioxidants (and/or components of antioxidant blends) which may be utilized. The stabilizers recited in US 5,711,767 and US 5,024,775 for the prevention of oxidative degradation of gasoline and petroleum distillates are also incorporated herein as non-limiting examples of suitable molecules which may be used as antioxidants for purposes of this invention. It will be understood by those skilled in the art that additive packages normally found in petroleum fuels may not be present at all, or may not be present in high enough concentrations to enable the present invention.

It is highly preferable that the antioxidants remain upstream from electrowinning circuits and other equipment downstream of solvent extraction circuits. This will reduce potential upset to the electrowinning process, cathode quality, and damage to the electrowinning equipment. Therefore, in some instances (while not shown), one or more filtration systems or separation steps may be used or performed in order to ensure that all antioxidants have been removed from the organic 3 and/or aqueous phases 4 prior to subsequent processing and recovery.

It is envisaged that approximately 0.01ppm to roughly about 1000 ppm of antioxidant may be added to the organic 3 in any convenient manner to see beneficial levels of crud formation reduction. Preferably, between about 1 and 50 ppm may be used. In some particular embodiments, single-digit parts per million (ppm) ranges may be practiced. In other non-limiting exemplary embodiments, approximately 10-30 ppm of antioxidant may be added to the organic phase 3, for example, 25 ppm of antioxidant.

It should be known that the particular features, processes, and benefits which are shown and described herein in detail are purely exemplary in nature and should not limit the scope of the invention. For example, while the shown embodiments exhibit common commercially-available antioxidants, which require no modification, it should be understood that additional functional groups may be added to molecules to form more unique antioxidants (e.g., antioxidant molecules without a CAS number). Moreover, combinations and selective blends of one or more custom or off-the-shelf antioxidants may be used. In some instances, phenolic antioxidant blends like BNX® brand antioxidant and thermal stabilizer blends may be used. One particular non-limiting example may include BNX® 1225, which is a 50%-50% mixture of BNX® 1010 (*Tetrakis [Methylene-3 (3',5'-di-tert-butyl-4-hydroxyphenyl) propionate] methane*,  $C_{73}H_{100}O_{12}$ , CAS #6683-19-8) and Benefos® 1680 (*Tris (2, 4- di-tert-butylphenyl) phosphate*,  $C_{42}H_{63}O_3P$ , CAS #31570-04-4). Other non-limiting phenolic antioxidant blends may include INGRANOX® brand antioxidant blends, which might include one or more parts of Irganox® 1010, Irgafos® 168, Irganox® 1035, and Disteryl thiodipropionate (e.g., Irganox® B-225 and Irganox® B-835 blends).

Secondary antioxidants such as organophosphorus compounds and/or thiosynergists such as esters of 3,3-thiodipropionic acid (frequently referred to as hydroperoxide decomposers) may also be utilized in combination with the above-described primary antioxidant additives according to certain aspects of the invention, in order to provide synergistic stabilization effects. In use, the secondary antioxidants may operate by decomposing hydroperoxides into non-radical, non-reactive, and thermally-stable products. The hydroperoxide decomposers may generally prevent the split of hydroperoxides into extremely reactive alkoxy and hydroxy radicals. Trivalent phosphorus compounds may be added to the organic, since phosphites and phosphonites (e.g.,

having the structures shown in FIG. 17) are sensitive to water and can hydrolyze, forming an acidic, hydrolysis-resistant species. Hydroquinone antioxidants (synthetic) and other similar natural antioxidants (ferulic acid) thereof may also be advantageously utilized as antioxidants where described herein.

Although the invention has been described in terms of particular embodiments and applications, one of ordinary skill in the art, in light of this teaching, can generate additional embodiments and modifications without departing from the spirit of or exceeding the scope of the claimed invention. For example, the means 13 for removing emulsion phase from the first settler 7a may comprise horizontally-arranged perforated pipe as shown, or the means may alternatively be provided by one or more elongated horizontal slits, one or more transversely extending perforated tubes extending across the width of the first settler 7a, or other conceivable means of removing the middle emulsion phase 9 from the first settler 7a and settling it separately in a second settler 7b. While not shown, the means 13 for removing the emulsion 9 may also comprise means 2a-m for delivering antioxidant. Moreover, while the means 2a-m for delivering antioxidant to the organic phase 3 is shown in combination with a mixer settler device, it may be placed at one or more convenient locations within other types of solvent extraction circuits/flowsheets. For example, the means 2a-m may be provided in conjunction with a column reactor or a continuous countercurrent leach reactor/extractor to deliver one or more antioxidants or antioxidant blends to the organic phase 3. Lastly, each means 2a-m for delivering antioxidant to the organic phase 3 may disperse a different type, blend, amount, or concentration of antioxidant to the organic phase at different locations throughout the mixer settler device 1. Accordingly, it is to be understood that the drawings and descriptions herein are

proffered by way of example to facilitate comprehension of the invention and should not be construed to limit the scope thereof.

## CLAIMS

What is claimed is:

1. A method of solvent extraction comprising the steps of:
  - (a) providing an organic solution;
  - (b) providing an organic-soluble antioxidant; and,
  - (c) dissolving the antioxidant in the organic solution, thereby reducing crud formation.
2. The method of claim 1, wherein the organic-soluble antioxidant comprises a phenol.
3. The method of claim 2, wherein the phenol is a hindered phenol.
4. The method of claim 1, wherein the organic-soluble antioxidant comprises ubiquinol.
5. The method of claim 1, wherein the ubiquinol comprises Ubiquinol-9 and/or Ubiquinol-10.
6. The method of claim 1, wherein the organic-soluble antioxidant comprises melatonin.
7. The method of claim 1, wherein the organic-soluble antioxidant comprises curcumin.
8. The method of claim 1, wherein the organic-soluble antioxidant comprises vitamin E and/or tocopherols.
9. The method of claim 1, wherein the organic-soluble antioxidant comprises retinol.

10. The method of claim 1, wherein the organic-soluble antioxidant comprises is biologically-derived.
11. The method of claim 1, wherein the organic-soluble antioxidant comprises a blend of antioxidants.
12. The method of claim 11, wherein the blend of antioxidants comprises a mixture of Tetrakis [methylene (3,5-di-tert-butyl-4-hydroxyhydrocinnamate)] methane and Tris (2,4-di-tert-butylphenyl) phosphite.
13. The method of claim 11, wherein the blend of antioxidants comprises a mixture of thiodiethylene bis (3,5-di-tert-butyl-4-hydroxycinnamate) and disteryl-beta,beta'-thiodipropionate.
14. The method of claim 1, further comprising the step of monitoring levels of the organic-soluble antioxidant within the organic solution, in order to verify whether or not antioxidant levels are adequate within the organic solution.
15. The method of claim 14, further comprising the step of adding additional organic-soluble antioxidant to the organic solution if the step of monitoring levels reveals that antioxidant levels within the organic solution are not adequate.
16. A solvent extraction circuit [1] for the reduced formation of crud comprising:
- (a) at least one mixer [5, 6];
  - (b) a first settler [7a]; and,

(c) delivery means [2a-2m] for providing an organic-soluble antioxidant to one or more portions of the at least one mixer [5, 6] and/or the first settler [7a].

17. The solvent extraction circuit [1] of claim 16 further comprising emulsion zone removal means [10, 13], for speeding up flow rates in the first settler [7a].

18. The solvent extraction circuit of claim 17, wherein at least one second settler [7b] is operatively connected to the emulsion zone removal means [10, 13].

19. The solvent extraction circuit of claim 18, wherein a majority of the emulsion zone [9] is sucked from, pumped from, or otherwise removed from the first settler [7a] and subsequently transferred to said second settler [7b].

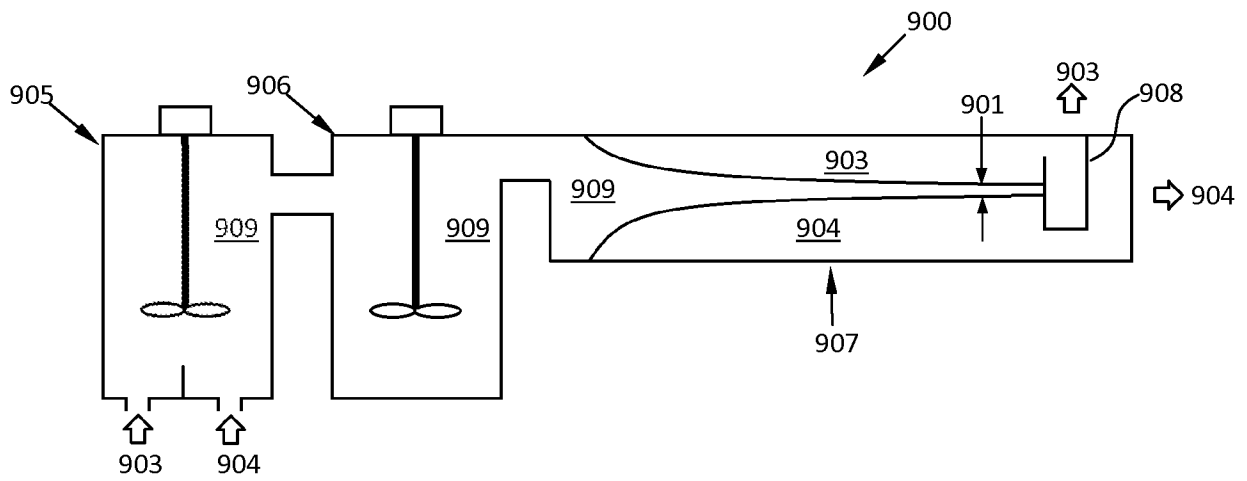


FIG. 1  
(PRIOR ART)

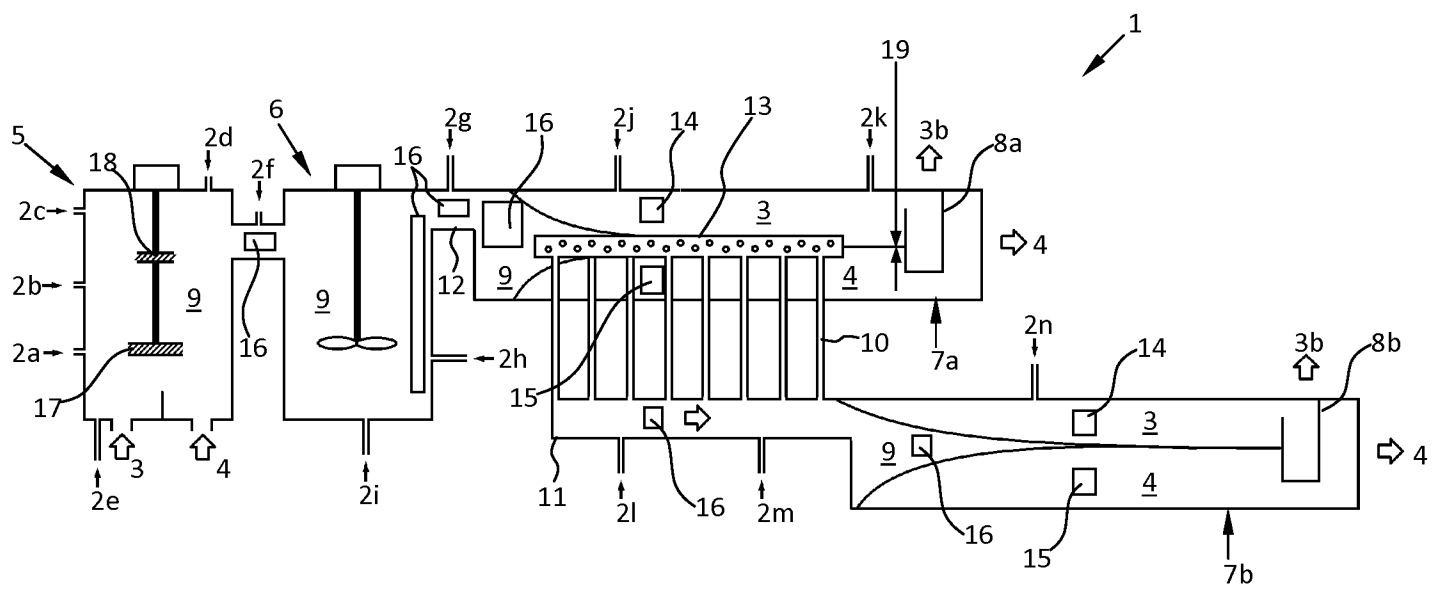


FIG. 2

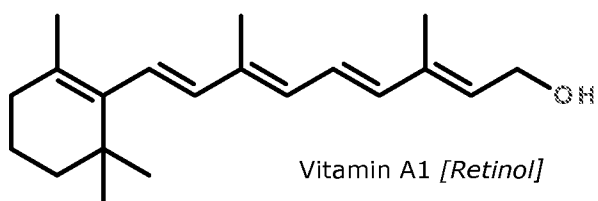


FIG. 3

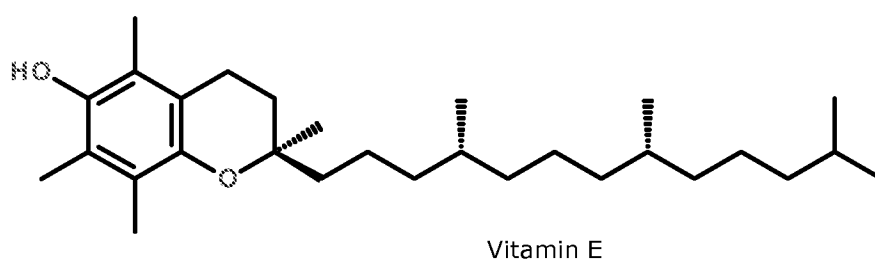


FIG. 4

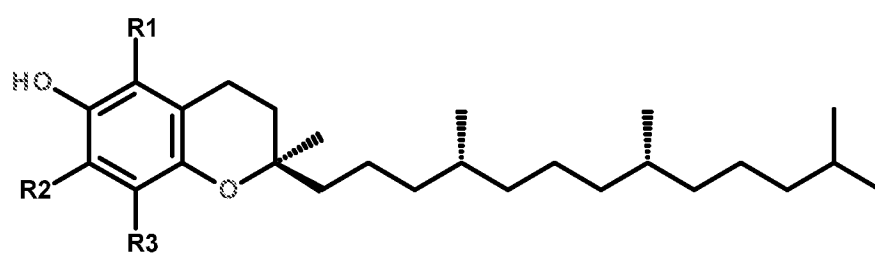


FIG. 5

Tocopherols (where R1, R2 and R3 are a combination of H and CH<sub>3</sub> groups) - derivatives of Vitamin E

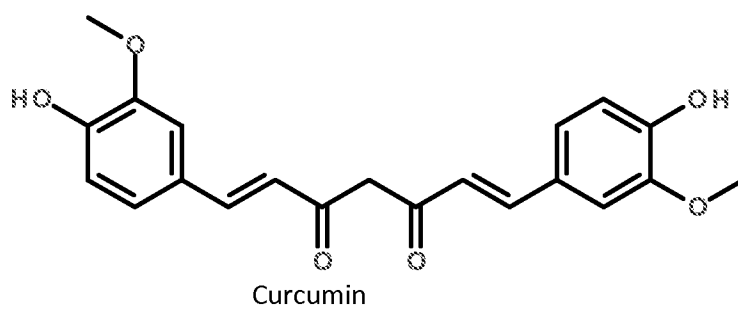
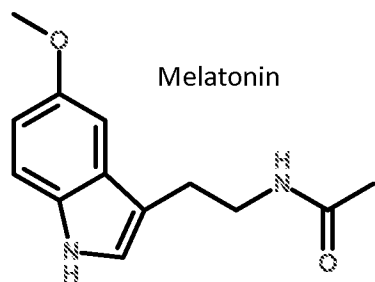


FIG. 6



Melatonin

FIG. 7

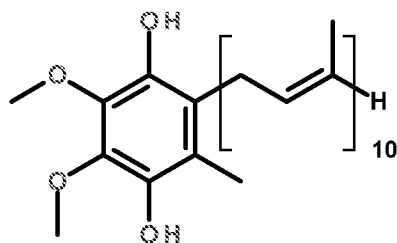
Ubiquinol-10 [CoEnzyme Q<sub>10</sub>]

FIG. 8

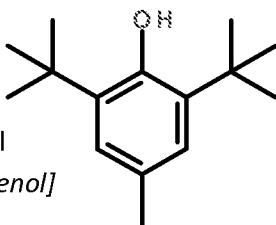
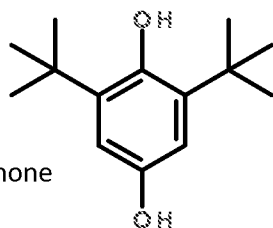
2,6-di-tert-butyl-*p*-cresol  
[2,6-di-*t*-butyl-4-methyl phenol]

FIG. 9



2,6-di-tert-butyl hydroquinone

FIG. 10

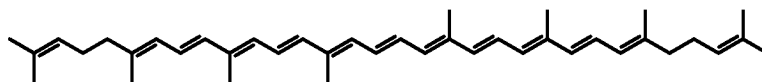


FIG. 11

Lycopene [6*E*,8*E*,10*E*,12*E*,14*E*,16*E*,18*E*,20*E*,22*E*,24*E*,26*E*]- 2,6,10,14,19,23,27,31-Octamethyldotriaconta-2,6,8,10,12,14,16,18,20,22,24,26,30-tridecaene]

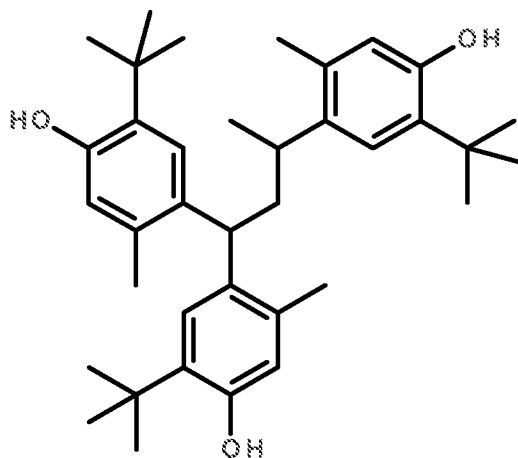


FIG.12

1,1,3-tris(2-methyl-4-hydroxyl-5-*tert*butylphenyl) butane

FIG. 13

Irganox® 1010

[Tetrakis (methylene (3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate) methane]

BNX® 1010

[Tetrakis [Methylene-3 (3',5'-di-*tert*-butyl-4-hydroxyphenyl) propionate] methane]

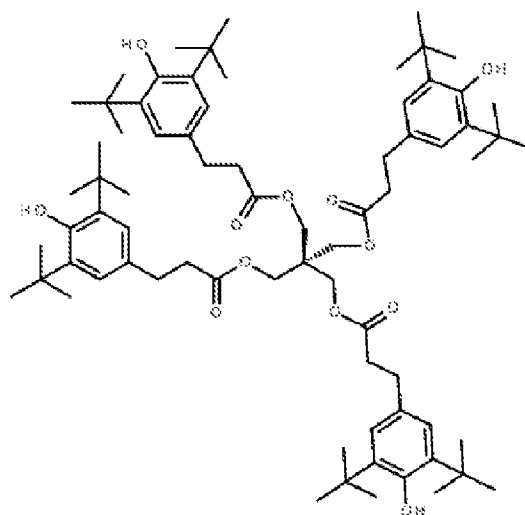


FIG. 14

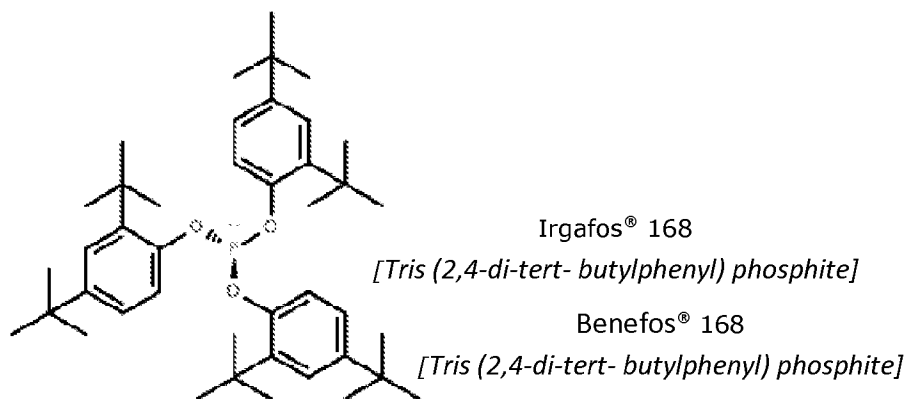


FIG. 15

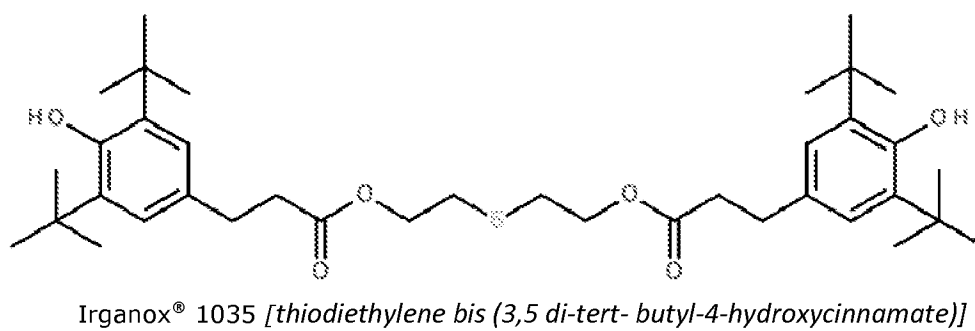


FIG. 16

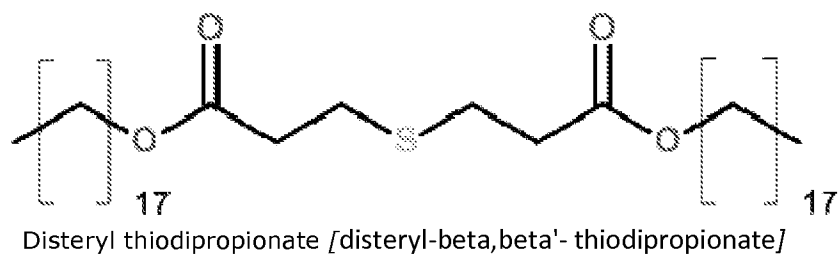
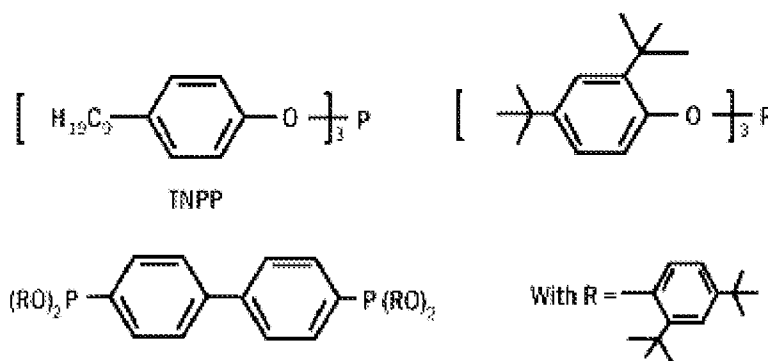


FIG. 17



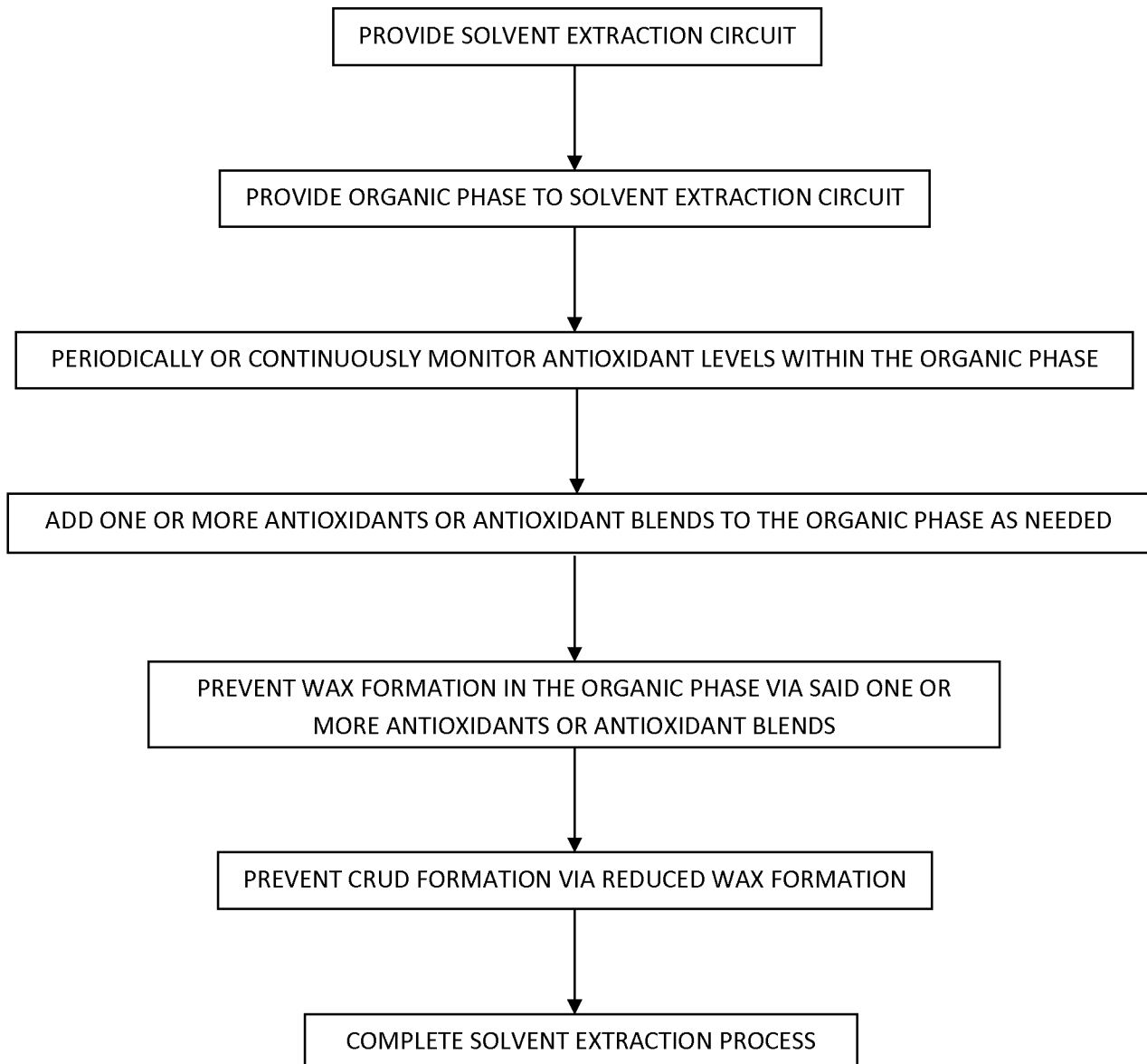


FIG. 18

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US13/73859

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B01D 11/00, 11/04, 17/025 (2014.01)

USPC - 210/294, 600, 634

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)

IPC(8): B01D 11/00, 11/04, 17/025 (2014.01)

USPC: 210/294, 600, 634

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)

MicroPatent (US-G, US-A, EP-A, EP-B, WO, JP-bib, DE-C,B, DE-A, DE-T, DE-U, GB-A, FR-A); Google Scholar; IP.com; ProQuest;  
KEYWORDS: solvent extraction, solution, antioxidant, ubiquinol, melatonin, curcumin, vitamin E, tocopherol, retinol, reduce, minimize, crud, wax, transfer, pump, second, settler, emulsion, removal, measure, monitor

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                              | Relevant to claim No. |
|-----------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| Y         | WO 93/25645 A1 (MOFFAT, CF et al.) 23 December 1993; page 3, paragraph 3; page 8, paragraph 1; page 10, paragraph 1                                                                             | 1-19                  |
| Y         | US 6,013,304 A (TODD, GN) 11 January 2000; figure 1; column 4, lines 53-59; column 5, lines 22-32; column 6, lines 12-49; column 11, lines 32-61; column 12, lines 1-35; column 26, lines 29-35 | 1-15                  |
| Y         | US 8,241,681 B2 (HERRMANN, M et al.) 14 August 2012; column 5, lines 20-26; column 10, lines 39-65; column 11, lines 1-4                                                                        | 4-5, 9                |
| Y         | WO 2011/072264 A2 (RICHARDS, G) 16 June 2011; paragraphs [0086], [00104]                                                                                                                        | 6, 13                 |
| Y         | WO 2011/090685 A1 (HAN, SJ et al.) 28 July 2011; paragraphs [0034], [0045]                                                                                                                      | 12-13                 |
| Y         | US 7,328,809 B2 (GIGAS, B et al.) 12 February 2008; figures 1-2; column 2, lines 40-46; column 4, lines 3-5; column 5, lines 11-37                                                              | 16-19                 |
| Y         | US 4,218,311 A (NEWRICK, GM) 19 August 1980; figure 1; column 1, lines 21-46; column 2, lines 22-55                                                                                             | 17-19                 |
| Y         | US 3,867,511 A (CHIANG, PT et al.) 18 February 1975; figure 3; column 5, lines 39-68                                                                                                            | 19                    |

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

\* 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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"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

"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

"&amp;"

document member of the same patent family

Date of the actual completion of the international search

11 March 2014 (11.03.2014)

Date of mailing of the international search report

27 MAR 2014

Name and mailing address of the ISA/US

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