

(51) International Patent Classification:
B08B 3/08 (2006.01)(21) International Application Number:
PCT/US2012/022722(22) International Filing Date:
26 January 2012 (26.01.2012)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/437,585 28 January 2011 (28.01.2011) US(71) Applicant (for all designated States except US): **EMERY OLEOCHEMICALS LLC** [US/US]; 4900 Este Avenue, Cincinnati, OH 45232 (US).(72) Inventor: **WALKER, Thomas, Chad**; 1513 Shirepeak Way, Independence, KY 41051 (US).(74) Agents: **CAREY, James, P.** et al.; Wood, Herron & Evans, LLP, 2700 Carew Tower, 441 Vine Street, Cincinnati, OH 54202-2917 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished upon receipt of that report (Rule 48.2(g))

(54) Title: CLEANING COMPOSITIONS AND METHOD OF USING THE SAME

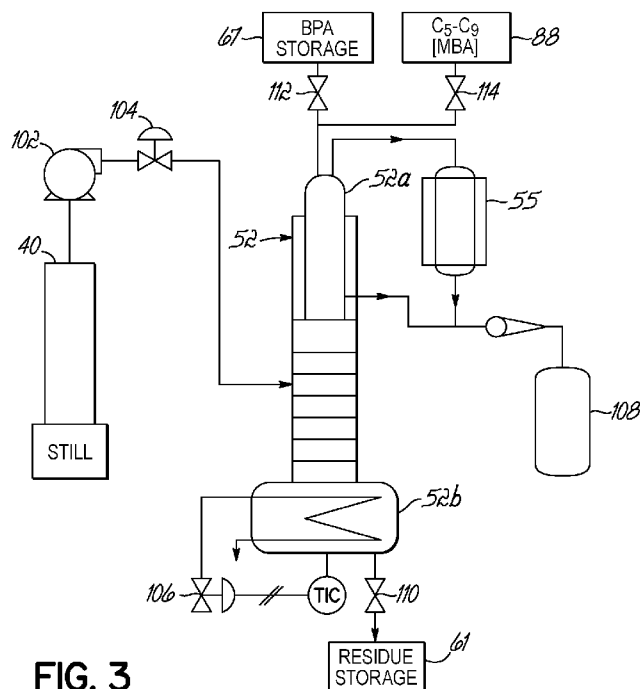


FIG. 3

(57) Abstract: A process for cleaning an apparatus includes contacting the interior surface of the apparatus with cleaning compositions. The cleaning compositions include carboxylic acids derived from the ozonolysis of unsaturated compounds having between 6 to 24 carbons, where the ozonide formed by the ozonolysis undergoes an oxidative cleavage to form a mixture of monocarboxylic acids and dicarboxylic acids.

CLEANING COMPOSITIONS AND METHOD OF USING THE SAME

FIELD OF THE INVENTION

[0001] The present invention relates to cleaning compositions, and processes of using the same, which are primarily intended for cleaning apparatus utilized in the oxidative ozonolysis of unsaturated compounds.

BACKGROUND OF THE INVENTION

[0002] Commercial production of azelaic acid and pelargonic acid has been realized via an oxidative cleavage of an alkenyl ($-C=C-$) unit in oleic acid. For example, azelaic acid has been prepared from oleic acid by oxidation with chromium sulfate, as disclosed in U.S. Patent No. 2,450,858. However, because stoichiometric use of chromium reagents is undesirable, a more efficient approach utilizing ozone has been developed, as disclosed and described in U.S. Patent Nos. 2,813,113; 5,801,275; 5,883,269; and 5,973,173.

[0003] The basic process will be best understood by referring to the description in the accompanying FIG. 1, which is a diagrammatic flow chart indicating the pieces of equipment used and their relationship in the ozonolysis process. Referring to FIG. 1, oleic acid is supplied to a feed tank 10 and then to an ozone absorber 13, wherein the oleic acid is flowed counter-current to a continuous flow of a gaseous mixture comprising oxygen/ozone gas introduced to the ozone absorber 13. The ozone absorber 13 is cooled or refrigerated to substantially control the temperature of the reaction occurring therein.

[0004] The ozone absorber 13 receives ozonized oxygen-containing gas by a continuous closed system through which the gas mixture circulates. Thus, a given quantity of oxygen may be used and reused multiple times and the system need be bled and fed with make up oxygen only to a small extent to maintain the oxygen content at a predetermined high level by replacing oxygen consumed after a portion has been converted to ozone. The

circulating oxygen system comprises an oxygen supply 16 that leads to a dehydrator 19. From the dehydrator 19, the gas mixture is transferred to an ozone generator 22, which converts a portion of the oxygen to ozone by using electricity. From the ozone generator 22, the ozonized gaseous mixture passes into the ozone absorber 13 in which substantially all of its ozone content is absorbed by the oleic acid as further explained below. During the residence time of the oleic acid ozonide-containing mixture in the ozone absorber 13, the mixture may increase in viscosity. If desired, the viscosity of the mixture may be reduced by introducing compatible diluents, such as pelargonic acid, as discussed further below.

[0005] Upon exiting the ozone absorber 13, the gas mixture, now substantially devoid of ozone, passes to an electrostatic precipitator 25, which removes any fine mist organic matter that may have been picked up in the ozone absorber 13. The purified gas mixture then passes from the electrostatic precipitator 25 through a compression pump 28 to a cooler 31 and then returns to the dehydrator 19, in which substantially all moisture is removed from the gas mixture. Between the cooler 31 and the dehydrator 19, oxygen-containing gas, which may be obtained from or bled from the system through an ozone generating system valve 34, may be supplied to the ozonide decomposing system reactor 37.

[0006] The aforementioned absorption of ozone by oleic acid forms oleic acid ozonides, which are transferred to the ozonide decomposing system reactor 37 and treated with oxygen bled from the ozone generating system valve 34. The ozonide decomposing system reactor 37 may be any type device which is adapted to provide substantial interfacial contact between a liquid and a gas and which may be cooled to moderate the temperature of the reaction. The oxygen bled from the ozone generating system is fed into the bottom of the ozonide decomposing system reactor 37 and is agitated with the liquid in each tank by means of mechanical agitators which are not shown.

[0007] While only one integral ozonide decomposing system reactor 37 is shown in the drawing, it is to be understood that the reactor 37 may comprise distinct regions configured for independent temperature, independent pressure control, or both. Alternatively, any number of reactors may be used depending upon the size of the reactors, the rate of the flow of the ozonides and their decomposition products, and the efficiency of the agitation in effecting contact between the oxygen gas and the liquid being treated. Further, alternative embodiments having more than one reactor may be connected in a series configuration, a parallel configuration, or both.

[0008] Temperature control is an important operating parameter for the ozonide decomposing system reactor 37. More specifically, the incoming stream of ozonides must be heated to reach a suitable reaction temperature at which the ozonide moiety may efficiently undergo oxidative decomposition upon exposure to one or more catalysts to preferentially form an aldehyde and a carboxylic acid. The ozonide decomposition catalysts may include Brønsted–Lowry acids, Brønsted–Lowry bases, Lewis acids, Lewis bases, metals, or salts and soaps thereof. Exemplary ozonide decomposition catalysts may include at least in part, Na, K, B, Sn, Zn, Pt, Pd, Rh, Ag, Mn, Cu, Ni, titania/silica or titania/P₂O₅ composites, and combinations thereof. The catalyst can be introduced into the process in the form of a soluble material or in the form of a solid or supported catalyst.

[0009] After reaching a suitable reaction temperature, further oxidation of the aldehyde functional group to an acid functional group may occur at a rate sufficient to generate heat, which may in turn contribute to elevating the temperature of the incoming stream of ozonides. However, cooling water may need to be supplied in order to prevent the temperature from rising above a predetermined level. As such, the temperature is controlled in order to be suitable for efficient oxidation to convert the ozonides to mixed oxidation products. In FIG. 1, the heating and cooling apparatus are not shown.

[0010] From the ozonide decomposing system reactor 37, the mixed oxidation products pass to a first distillation unit 40 wherein pelargonic acid and other carboxylic acids are distilled from the mixed oxidation products to form a first distillate and a first residue of the mixed oxidation products. The first distillate, which contains pelargonic acid, is converted to a liquid in a first condenser 43 and then is delivered to a crude pelargonic acid storage tank 46. However, some of the crude pelargonic acid may be used to dilute the oleic acid reactant and the oleic acid ozonides in the absorber 13 if desired. Thus, pelargonic acid, which may be crude or further purified, may be added to the ozone absorber 13 in order to reduce the viscosity of the ozonides in the absorber 13. The amount of recycled pelargonic acid supplied to the absorber 13 may be controlled with a valve 49.

[0011] It should be noted that other viscosity reducers and diluents may be used. The diluents can be known materials which do not readily react with ozone and which are compatible with the ozonides or the reaction products, or can be a portion of the reaction product. Such diluents include, but are not limited to, saturated short chain acids such as acetic acid, butanoic acid, caproic acid, heptanoic acid, caprylic acid, pelargonic acid, and capric acid; esters such as ethyl acetate and butyl acetate; and alkanes such as hexane, octane, and decane. However, the use of pelargonic acid is recommended because, as an end product of the process, it does not interfere with the operation of the circulating oxygen system and requires no separate distillation. In other words, since pelargonic acid is one of the end products of the process, it is a suitable diluent.

[0012] The first residue of the mixed oxidation products, now stripped of a substantial portion of the available pelargonic acid, are next conveyed to an azelaic acid distillation unit 52 in which a portion of the first residue of the mixed oxidation products is distilled to form a second distillate, which includes azelaic acid, and a second residue of the mixed oxidation products. The second distillate is condensed by passage through an azelaic acid distillate

condenser 55 to form a crude azelaic acid, which is transferred to a crude azelaic acid storage tank 58. The second residue of the mixed oxidation products or pitch that remains after distilling away the second distillate is removed from the azelaic acid distillation unit 52 through a drain and stored in container 61. The second residue of the mixed oxidation products may still contain some amount of azelaic acid, so further processing, if desired, can occur to recover a portion thereof.

[0013] The crude azelaic acid condensate may also contain a wide variety of monocarboxylic acids of undetermined identity, with the majority being C6 to C18 monocarboxylic acids. These monocarboxylic acids usually comprise 15 to 20% of the crude azelaic acid condensate. The next step in the process is to purify the crude azelaic acid.

[0014] From the crude azelaic acid storage tank 58, the crude azelaic acid is transferred to extractor 64 where the crude azelaic acid is extracted with hot water (e.g., about 175°F, about 80°C to about 210°F, about 99°C) to form a hot aqueous solution of azelaic acid, or in some instances, the aqueous extraction is performed in combination with a solvent that is not miscible with water. The by-product acids that do not dissolve in the hot aqueous azelaic acid solution are decanted from the extractor 64 to a by-product acid (BPA) storage vessel 67. Meanwhile, the hot aqueous azelaic acid solution is transferred to an evaporator 70 in which water is removed therefrom. Next, azelaic acid in molten form is fed from the evaporator 70 to a flaker 73 where the temperature is reduced to below the melting point, and then solid flakes of azelaic acid are conveyed to an azelaic acid storage bin 76.

[0015] While the process and apparatus described above provide azelaic and pelargonic acids from oleic acid, deficiencies exist with respect to personnel safety, system efficiencies and equipment longevity. One such deficiency or limitation of the prior art procedure and apparatus is the detrimental build up of substances on the internal components of the azelaic acid distillation unit 52 during the distillation of the mixed oxidation products

stripped of pelargonic acid. During the azelaic acid distillation step, the primary purpose is the removal of azelaic acid from the first residue of mixed oxidation products mixture. However, this mixture may also contain oxidation catalyst byproducts that have carried over from the ozonide decomposing system reactor 37. These oxidation catalyst byproducts, including manganese salts, tend to plate out onto surfaces of heating components within the azelaic acid distillation unit 52 thereby leaving a catalyst-derived deposit on the surface. This catalyst-derived deposit may also include polymers of the various organic molecules being distilled, which can be formed on the hot surfaces of the heating components. The catalyst-derived deposit acts as a thermal insulator and thereby lowers the overall heat transfer capacity of the heating component. As such, periodic cleaning is necessary.

[0016] The prior art cleaning methods have required taking the azelaic acid distillation unit 52 off-line and opening up the azelaic acid distillation unit 52 to remove the heating component, which was then cleaned by physical methods such as water or steam blasting, chemical treatments, scraping, or combinations thereof. These invasive cleaning methods require extended periods of down time wherein the azelaic acid distillation unit 52 is off-line. Further, these prior art cleaning methods also require many man-hours of labor physically disassemble, clean, and reassemble the azelaic acid distillation unit 52 and its heating components, with increased risks of injury to personnel. As such, new and/or improved cleaning methods are needed.

SUMMARY OF THE INVENTION

[0017] According to an embodiment of the invention, a process of cleaning an apparatus is provided, the process comprising: i) maintaining a temperature of the apparatus between 250°F (120°C) to about 500°F (260°C); ii) contacting a quantity of a mixture comprising C6 to C18 monocarboxylic acids with at least a portion of an internal surface of the apparatus having a catalyst-derived deposit thereon and derived from at least one

oxidation catalyst; iii) maintaining the mixture comprising C6 to C18 monocarboxylic acids in the apparatus for a time sufficient to thereby affect separation of at least a portion of the catalyst-derived deposit from the internal surface of the apparatus to form a material comprising the mixture comprising C6 to C18 monocarboxylic acids and the at least a portion of the catalyst-derived deposit; iv) removing the material comprising the mixture comprising C6 to C18 monocarboxylic acids and the at least a portion of the catalyst-derived deposit from the apparatus; and v) contacting a quantity of a mixture comprising C2 to C12 monocarboxylic acids with at least a portion of the internal surface of the apparatus. The mixture comprising C6 to C18 monocarboxylic acids and the mixture comprising C2 to C12 monocarboxylic acids are derived from a method comprising a) ozonizing a mixture comprising an ethylenically unsaturated compound having between 6 to 24 carbons with an ozone-containing gas to form a plurality of ozonization products; b) cleaving the plurality of ozonization products under oxidative conditions in the presence of the at least one oxidation catalyst to form mixed oxidation products; c) isolating the mixture comprising C6 to C18 monocarboxylic acids that are derived from the mixed oxidation products; and d) isolating the mixture comprising C2 to C12 monocarboxylic acids that are derived from the mixed oxidation products.

[0018] According to another embodiment of the invention, a process for producing a carboxylic acid mixture comprising a saturated mono carboxylic acid and a saturated dicarboxylic acid is provide, the process comprising the steps of a) generating an ozone gas in an ozone generator; b) contacting the ozone gas with an unsaturated carboxylic acid feed comprising an unsaturated carboxylic acid in an absorber to obtain an ozonide; c) contacting the ozonide with an oxygen gas and at least one catalyst in a reactor to obtain the carboxylic acid mixture; and d) purifying the carboxylic acid mixture by distilling at least a portion of

the carboxylic acid mixture in a distillation unit, wherein the reactor or the distillation unit has been cleaned by the a process according to any of the claims 1 to 7.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019] The accompanying drawings, which are incorporated in and constitute a part of this specification, illustrate embodiments of the invention and, together with the general description of the invention given above, and the detailed description given below, serve to describe the invention.

[0020] FIG. 1 is a schematic representation of an oleic acid ozonolysis plant (under the prior art).

[0021] FIG. 2 is a schematic representation of a system for forming a cleaning composition from crude pelargonic acid according to one embodiment of the present invention.

[0022] FIG. 3 is a schematic representation of a distillation unit system according to an embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0023] According to embodiments of the present invention, cleaning compositions and their method of use are provided. The compositions comprise a mixture of carboxylic acids derived from a method of ozonizing ethylenically unsaturated compounds. Suitable ethylenically unsaturated compounds are not particularly limited by their source and may include any number of carbon atoms, such as between 6 to 24 carbon atoms. The ethylenically unsaturated compounds may include between 12 to 20 carbon atoms. For example, the ethylenically unsaturated compounds may have 18 carbon atoms. Further, the ethylenically unsaturated compounds may include additional functional groups, such as carboxylic acids. The ethylenically unsaturated compounds may be derived from animal or plant sources. Accordingly, the ethylenically unsaturated compounds include fatty acids,

including those obtained from palm oil or tallow. In one example, the ethylenically unsaturated compounds include oleic acid.

[0024] The mixture of carboxylic acids obtained from ozonizing ethylenically unsaturated compounds may include C2 to C18 monocarboxylic acids. For example, the mixture of carboxylic acids may include C2 to C16, C5 to C9, or C6 to C18 monocarboxylic acids. Similarly, the mixture of carboxylic acids obtained from ozonizing ethylenically unsaturated compounds may include C2 to C18 dicarboxylic acids.

[0025] The cleaning compositions may be obtained by a method of first ozonizing a mixture of one or more ethylenically unsaturated compounds having between 6 to 24 carbons with an ozone-containing gas to form a plurality of ozonization products. The plurality of ozonization products is cleaved under oxidative conditions in the presence of a suitable catalyst to form a mixture of oxidatively-cleaved ozonization products. The mixture of oxidatively-cleaved ozonization products, herein after referred to as "mixed oxidation products," may include a variety of carboxylic acids, including an amount of dicarboxylic acid. According to one aspect of embodiments of the present invention, cleaning compositions, which are useful in the processes described herein, may be subsequently isolated from the mixed oxidation products. For example, isolating a mixture comprising C2 to C12 monocarboxylic acids that are derived from the mixed oxidation products may be achieved by performing a first distillation, where the mixed oxidation products is distilled under a first set of distillation conditions to provide a first distillate and a first residue of the mixed oxidation products; and performing a second distillation, where the first distillate is distilled under a second set of distillation conditions to provide the mixture comprising C2 to C12 monocarboxylic acids. Optionally, the isolating of the mixture comprising C2 to C12 monocarboxylic acids may also include removing at least one water soluble dicarboxylic acid impurity by washing the mixture comprising C2 to C12 monocarboxylic acids with water.

[0026] Thus, according to one embodiment, a first cleaning composition may be isolated from mixed oxidation products derived from the ozonolysis of oleic acid. In this embodiment, the oleic acid-derived mixture of mixed oxidation products includes substantial quantities of pelargonic and azelaic acid, along with other carboxylic acids. A first distillation step may be performed under a first set of distillation conditions, such as at a temperature of about 425°F to about 475°F (about 218°C to about 246°C) and at a pressure of about 25 torr to about 50 torr to provide a first distillate. For example, the first distillation may be performed at 440°F and 23 torr.

[0027] The first distillate includes pelargonic acid, along with many other volatile carboxylic acid compound impurities, such as monocarboxylic acids having C2 to C16 chain lengths. Other impurities include dicarboxylic acids, such as succinic acid, glutaric acid and the like. This first distillate may be stored in a crude pelargonic acid storage tank 46. According to another embodiment of the present invention, a first residue of the mixed oxidation products or the undistilled fraction may be further processed to yield a second cleaning composition, as discussed further below.

[0028] If desired, the first distillate may be transferred from storage tank 46 to an extractor 79 and washed with water to remove water-soluble impurities, such as short-chain dibasic acids (e.g., succinic acid) prior to performing a second distillation, as shown in FIG. 2. The washing step may be performed on the first distillate under various extraction conditions in extractor 79, such as at a temperature of about 150°F to about 212°F (about 65°C to about 100°C) and at about atmospheric pressure to provide a washed first distillate, which may be substantially free of short chain dibasic acids. For example, the extraction may be performed at 170°F at atmospheric pressure. Although not shown, the washed extract may be dried prior to the second distillation step.

[0029] The second distillation step may be performed on the first distillate or the washed first distillate. Accordingly, the first distillate or the washed distillate is transferred to a second distillation unit 82, as shown in FIG. 2. The second distillation step may be performed under a second set of distillation conditions, such as at a temperature of about 310°F to about 370°F (about 154°C to about 188°C) and at a pressure of about 10 torr to about 30 torr to provide a second distillate comprising C2 to C12 monocarboxylic acids. For example, the second distillation may be performed at 340°F and 20 torr. Under these second distillation conditions, a second distillate is formed and includes C2-C12 monocarboxylic acids. The second distillate is condensed by passage through a second distillate condenser and transferred to storage container 88. This second distillate may be used as a cleaning composition of the present invention and will be referred hereinafter as "MBA."

[0030] According to an embodiment, MBA may primarily include C5 to C9 monocarboxylic acids. For example, a typical monocarboxylic acid profile of MBA may include greater than about 75 wt% of C5 to C9 monocarboxylic acids, based on the total weight of the MBA composition. Accordingly, one exemplary MBA composition includes: C5 monocarboxylic acid, e.g., valeric acid (about 2 wt% to about 4 wt%); C6 monocarboxylic acid, e.g., caproic acid (about 24 wt% to about 28 wt%); C7 monocarboxylic acid, e.g., enanthic acid (about 28 wt % to about 32 wt%); C8 monocarboxylic acid, e.g., caprylic acid (about 11 wt% to about 13 wt%); and C9 monocarboxylic acid, e.g., pelargonic acid (about 26 wt% to about 29 wt%), wherein the wt% is based on a total weight of the MBA. According to another embodiment, MBA comprises greater than about 90 wt% of monocarboxylic acids of C9 or less.

[0031] MBA, which is comprised of shorter chain acids and thus more relatively more acidic than longer chain acids, more aggressively attacks the catalyst-derived deposits

on the internal surface of the equipment such as the azelaic acid still 52. But being more volatile than the longer chain acids, is generally used at a relatively lower temperature.

[0032] The undistilled portion or residue of the first distillate may be further processed to provide a purified pelargonic acid. The residue of the first distillate in the second distillation unit 82 may be transferred to a pelargonic acid distillation unit 91. The pelargonic acid distillation step may be performed under suitable distillation conditions, such as at a temperature of about 300°F to about 360°F (about 149°C to about 182°C) and at a pressure of about 1 torr to about 20 torr to provide the purified pelargonic acid. For example, the pelargonic acid distillation may be performed at 330°F and 5 torr. The pelargonic acid distillation vapors can be condensed by passage through a pelargonic acid distillate vapor condenser 94 and transferred to a pelargonic acid storage tank 97. The undistilled portion or residue may be transferred out of the pelargonic acid distillation unit 91 to a storage tank 100.

[0033] The undistilled fraction of the mixed oxidation products from the ozonolysis of oleic acid may be further processed to yield a second cleaning composition. The mixed oxidation products, substantially stripped of the available pelargonic acid, may be transferred to an azelaic acid distillation unit 52 in which azelaic acid, along with the carboxylic acids having similar boiling point properties, are distilled to form a crude azelaic acid distillate vapor. The crude azelaic acid distillate vapor can be condensed by passage through an azelaic acid distillate condenser 55 to form a crude azelaic acid condensate, which is transferred to a crude azelaic acid storage tank 58. The non-volatile pitch or residue that remains after distilling away the volatile acids is removed from the azelaic acid distillation unit 52 through a drain 110 and can be transferred to a storage container 61.

[0034] The crude azelaic acid condensate also contains a wide variety of monocarboxylic acids of undetermined identity, with the majority being C6 to C18 monocarboxylic acids. These monocarboxylic acids usually comprise 15 to 20% of the crude

azelaic acid condensate. Referring to Fig. 1, from the crude azelaic acid storage tank 58, the crude azelaic acid condensate is transferred to a first extractor 64 where the azelaic acid is mixed with hot water (e.g., 210°F, 99°C), where a portion of the C6 to C18 monocarboxylic acids does not dissolve in the water and may be separated therefrom. The portion of the C6 to C18 monobasic acids that do not dissolve in hot water are removed from aqueous solution of azelaic acid in the extractor 64 and transferred to the by-product acid storage 67. This separation of the C6 to C18 monocarboxylic acids from the aqueous soluble constituents may be facilitated by using an organic solvent, which in one embodiment has a boiling point of about 100°C or greater. With or without using an organic solvent, the mixture comprising C6 to C18 monocarboxylic acids may be used as a cleaning composition of the present invention and will be referred hereinafter as "BPA."

[0035] The BPA, which is comprised of relatively longer chain acids and thus less acidic than shorter chain acids, such as those in MBA, less aggressively attacks the catalyst-derived deposits. But being more volatile than MBA, is generally used at a relatively higher temperature.

[0036] According to an embodiment, BPA may primarily include C6 to C18 monocarboxylic acids. For example, a typical carboxylic acid profile of BPA may include greater than about 50 wt% of C6 to C18 monocarboxylic acids, based on the total weight of the BPA composition. Accordingly, one exemplary BPA composition includes: C9 monobasic acid, e.g., pelargonic acid (about 14 wt% to about 18wt%); C12 monobasic acid, e.g., lauric acid (about 1 wt% to about 2 wt%); C14 monobasic acid, e.g., myristic acid (about 15 wt% to about 20 wt%); C16 monobasic acid, e.g., palmitic acid (about 28 wt% to about 36 wt%); and C18 monobasic acid, e.g., stearic acid (about 5 wt% to about 7 wt%), and may further include C9 dibasic acid, e.g., azelaic acid (about 3 wt% to about 5 wt%); C11 dibasic

acid, e.g., undecandioic acid (about 5 wt% to about 7 wt%); and C12 dibasic acid, e.g., dodecandioic acid (about 3 wt% to about 4 wt%).

[0037] An exemplary cleaning procedure for a distillation apparatus according to an embodiment of the present invention may be understood with reference to FIG. 3. From a fully running oleic acid ozonolysis system, first isolate the azelaic acid distillation unit 52 from the first distillation unit 40 by turning off a feed pump 102 and closing a feed pump valve 104. The azelaic acid distillation unit 52 has a top section 52A and a reboiler 52B. Turn off a heat source for the azelaic acid distillation unit 52 by closing a steam valve 106 and isolate the azelaic acid distillation unit 52 from its downstream distillate receiver 108. Partly drain the azelaic acid distillation unit 52 by opening drain valve 110. Slowly add BPA to the azelaic acid distillation unit 52 by opening a valve 112 between the BPA storage 67 and the top 52A of the azelaic acid distillation unit 52. The BPA is added until all the residue in the reboiler 52A is displaced with the BPA and only BPA remains in the reboiler.

[0038] The rate of the addition of the BPA to the azelaic acid distillation unit 52 is controlled to minimize flashing of the liquid BPA to vapor. For example, if the azelaic acid distillation unit 52 is under vacuum of about 20 torr, the BPA will flash until the azelaic acid distillation unit 52 is less than 300°F. With the heat off the azelaic acid distillation unit 52, the residue receiver will fill more quickly than usual. Pump it empty as necessary. It is important to keep the BPA and the catalyst-derived deposit mixture moving out of the still. When sufficient BPA has been added to the reboiler to displace all the residual contents of the azelaic acid distillation unit 52, the contents of the reboiler 52B is transferred to storage. It is during this step of the process that a substantial quantity of the catalyst-derived deposits are liberated from the internal surface of the azelaic acid distillation unit and thereby entrained in the BPA mixture.

[0039] Subsequent to the BPA treatment, MBA is added to the azelaic acid distillation unit 52 by opening a valve 114 between the MBA storage 88 and the top 52A of the azelaic acid distillation unit 52. A sufficient quantity of MBA is added to the azelaic acid distillation unit to fill the reboiler 52B. The MBA is maintained in the azelaic acid reboiler 52B for approximately 15 minutes, and then the MBA, which also contains a portion of any remaining catalyst-derived deposit left over from the BPA treatment, is removed from the azelaic acid reboiler 52B to storage. After removing the BPA and catalyst-derived deposit mixture, the azelaic acid distillation unit 52 may be restarted.

[0040] Thus, the combination of a treating an apparatus such as the azelaic acid distillation unit 52 with sequential treatments of cleaning compositions substantially removes the catalyst-derived deposits from the internal surface of the unit 52 without unduly impacting a continuous processing in an ozonolysis plant and without requiring personnel to physically or mechanically remove the catalyst-derived residue.

[0041] The methods and cleaning compositions described herein may be useful to clean apparatus used in the processing of the mixed oxidation products derived from the ozonization of ethylenically unsaturated compounds, which includes but is not limited to ethylenically unsaturated carboxylic acids. As mentioned above, the methods and cleaning compositions are particularly suited for use with an ozonolysis system that breaks down oleic acid into pelargonic acid and azelaic acid. However, the methods and cleaning compositions may be useful for cleaning apparatus used in processing oxidation products derived from the ozonolysis of other unsaturated compounds. The unsaturated compounds may generally have between 6 and 30 carbon atoms, for example between 8 and 24 carbon atoms, and one or more unsaturated carbon to carbon bonds. The monobasic and/or dibasic acid products that result from the ozonolysis reaction are determined by the location of the one or more unsaturated carbon to carbon bonds in the unsaturated acid. The unsaturated acids may be

isolated from come from biological sources, such as plants, animals, or microorganisms.

Alternatively, the unsaturated acids may be isolated from petroleum sources and synthetic sources. Exemplary mono unsaturated acids and their respective potential oxidation products are included in the Table below.

Carbons	Exemplary Unsaturated Fatty Acid	Exemplary Monobasic Product	Exemplary Dibasic Product
10	Obtusilic acid	Caproic acid	Succinic acid
10	Caproleic acid	Formic acid	Azelaic acid
11	Undecenoic acid	Formic acid	Sebacic acid
12	Lauric acid	Propionic acid	Azelaic acid
14	Myristoleic acid	Valeric acid	Azelaic acid
16	Palmitoleic acid	Heptanoic acid	Azelaic acid
18	Petroselinic acid	Lauric acid	Adipic acid
18	Oleic acid	Pelargonic acid	Azelaic acid
18	Vaccenic acid	Heptanoic acid	Hendecanedioic acid
18	Octadecenoic acid	Caproic acid	Dodecanedioic acid
20	Gadoleic acid	Undecanoic acid	Azelaic acid
22	Cetoleic acid	Undecanoic acid	Hendecanedioic acid
22	Erucic acid	Pelargonic acid	Brassylic acid
24	Selacholeic acid	Pelargonic acid	Pentadecanedioic acid
26	Hexacosenoic acid	Pelargonic acid	Heptadecanedioic acid
30	Tricosenoic acid	Pelargonic acid	Heneicosanedioic acid

[0042] While the table above includes monounsaturated acids, it is understood that polyunsaturated acids or polyols could be utilized as well. The resulting monobasic acids and dibasic acids, and their respective derivatives, may be used for a number of different purposes such as in the preparation of lubricant base stocks, plasticizers, lacquers, herbicides, skin treatments, textile coning oils, flotation agents for mineral refining, fragrances, catalyst scavengers, corrosion inhibitors, metal cleaners, polymerization initiators, lithium complex greases, epoxy flexibilizers, thermosetting unsaturated polyester resins, polyamide hot melts, urethane elastomers, and elastomeric fibers, wire coatings and molding resins.

[0043] While the present invention has been illustrated by the description of one or more embodiments thereof, and while the embodiments have been described in considerable detail, they are not intended to restrict or in any way limit the scope of the appended claims to

such detail. Additional advantages and modifications will readily appear to those skilled in the art. The invention in its broader aspects is therefore not limited to the specific details, representative product and/or method and examples shown and described. The various features of exemplary embodiments described herein may be used in any combination. Accordingly, departures may be made from such details without departing from the scope of the general inventive concept.

What is claimed is:

1. A process of cleaning an apparatus, comprising:
 - i) maintaining a temperature of the apparatus between 250°F (120°C) to about 500°F (260°C);
 - ii) contacting a quantity of a mixture comprising C6 to C18 monocarboxylic acids with at least a portion of an internal surface of the apparatus having a catalyst-derived deposit thereon and derived from at least one oxidation catalyst;
 - iii) maintaining the mixture comprising C6 to C18 monocarboxylic acids in the apparatus for a time sufficient to thereby affect separation of at least a portion of the catalyst-derived deposit from the internal surface of the apparatus to form a material comprising the mixture comprising C6 to C18 monocarboxylic acids and the at least a portion of the catalyst-derived deposit;
 - iv) removing the material comprising the mixture comprising C6 to C18 monocarboxylic acids and the at least a portion of the catalyst-derived deposit from the apparatus; and
 - v) contacting a quantity of a mixture comprising C2 to C12 monocarboxylic acids with at least a portion of the internal surface of the apparatus.
2. The process of claim 1, wherein the mixture comprising C6 to C18 monocarboxylic acids and the mixture comprising C2 to C12 monocarboxylic acids are derived from a method comprising:
 - a) ozonizing a mixture comprising an ethylenically unsaturated compound having between 6 to 24 carbons with an ozone-containing gas to form a plurality of ozonization products;

b) cleaving the plurality of ozonization products under oxidative conditions in the presence of at least one oxidation catalyst to form mixed oxidation products;

c) isolating the mixture comprising C6 to C18 monocarboxylic acids that are derived from the mixed oxidation products; and

d) isolating the mixture comprising C2 to C12 monocarboxylic acids that are derived from the mixed oxidation products.

3. The process according to claim 2, wherein the ethylenically unsaturated compound is derived from plant or animal sources.

4. The process according to any of the claims 2 to 3, wherein the ethylenically unsaturated compound is an unsaturated fatty acid.

5. The process according to any of the claims 2 to 4, wherein the ethylenically unsaturated acid is derived from palm oil or tallow.

6. The process according to any of the claims 2 to 5, wherein the ethylenically unsaturated acid is oleic acid.

7. The process according to any of the claims 1 to 6, wherein the isolating the mixture comprising C2 to C12 monocarboxylic acids comprises:

1) performing a first distillation, wherein the mixed oxidation products are distilled under a first set of distillation conditions to provide a first distillate and a first residue of the mixed oxidation products; and

2) performing a second distillation, wherein the first distillate is distilled under a second set of distillation conditions to provide the mixture comprising C2 to C12 monocarboxylic acids.

8. The process according to any of the claims 1 to 6, wherein the isolating the mixture comprising C6 to C18 monocarboxylic acids comprises:

1) performing a first distillation, wherein the mixed oxidation products are distilled under a first set of distillation conditions to provide a first distillate and a first residue of the mixed oxidation products;

2) performing a third distillation, wherein the first residue of the mixed oxidation products is distilled under a third set of distillation conditions to provide the mixture comprising C6 to C18 monocarboxylic acids.

9. A process for producing a carboxylic acid mixture comprising a saturated monocarboxylic acid and a saturated dicarboxylic acid, comprising the steps of

a) generating an ozone gas in an ozone generator;

b) contacting the ozone gas with an unsaturated carboxylic acid feed

comprising an unsaturated carboxylic acid in an absorber to obtain an ozonide;

c) contacting the ozonide with an oxygen gas and at least one catalyst in a reactor to obtain the carboxylic acid mixture; and

d) purifying the carboxylic acid mixture by distilling at least a portion of the carboxylic acid mixture in a distillation unit,

wherein the reactor or the distillation unit has been cleaned by the a process according to any of the claims 1 to 8.

10. The process of claim 9, wherein the saturated mono carboxylic acid is pelargonic acid, or wherein the saturated dicarboxylic acid is azelaic acid.
11. A chemical derivative of a carboxylic acid obtained from the carboxylic acid produced by a process according to any of the claims 9 to 10.

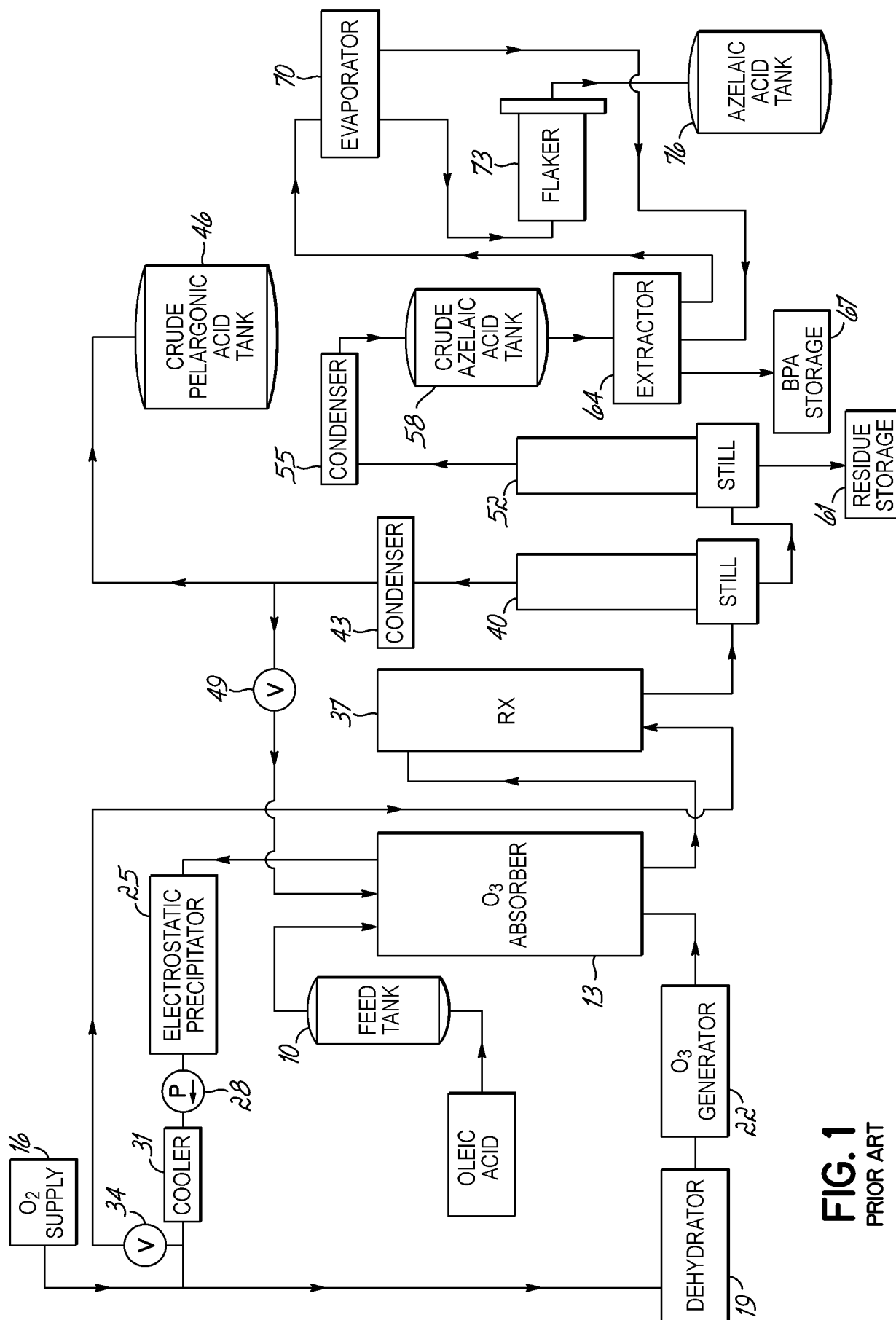


FIG. 1
PRIOR ART

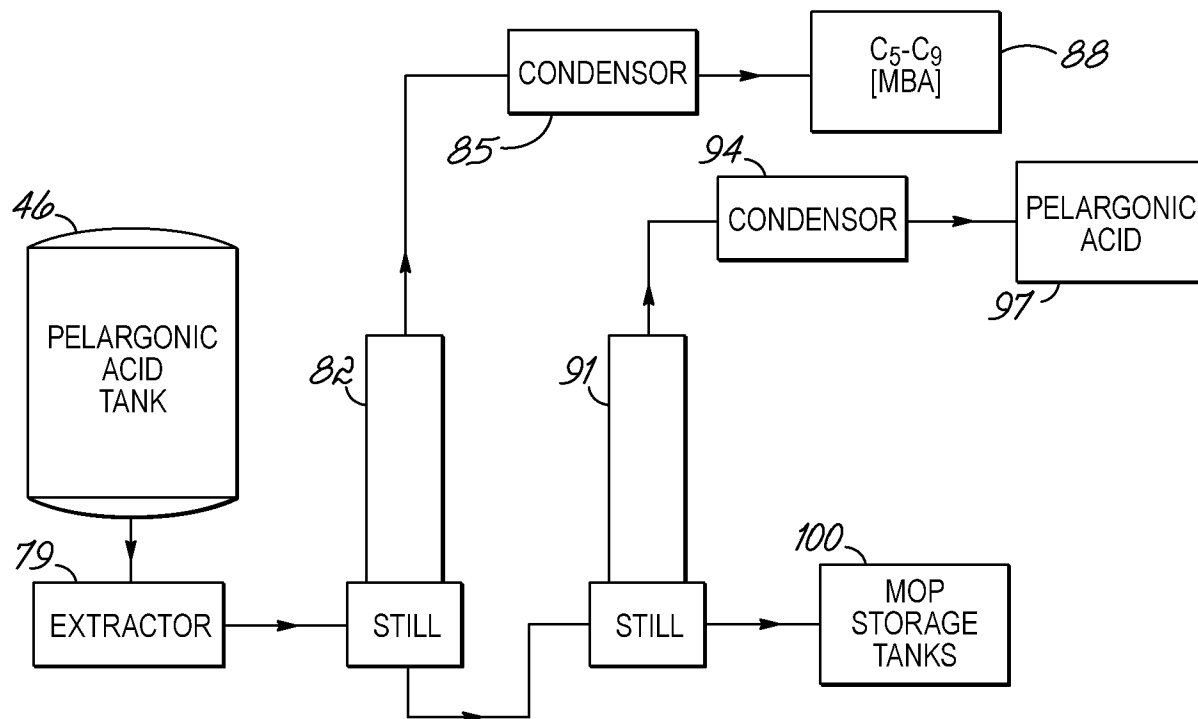


FIG. 2

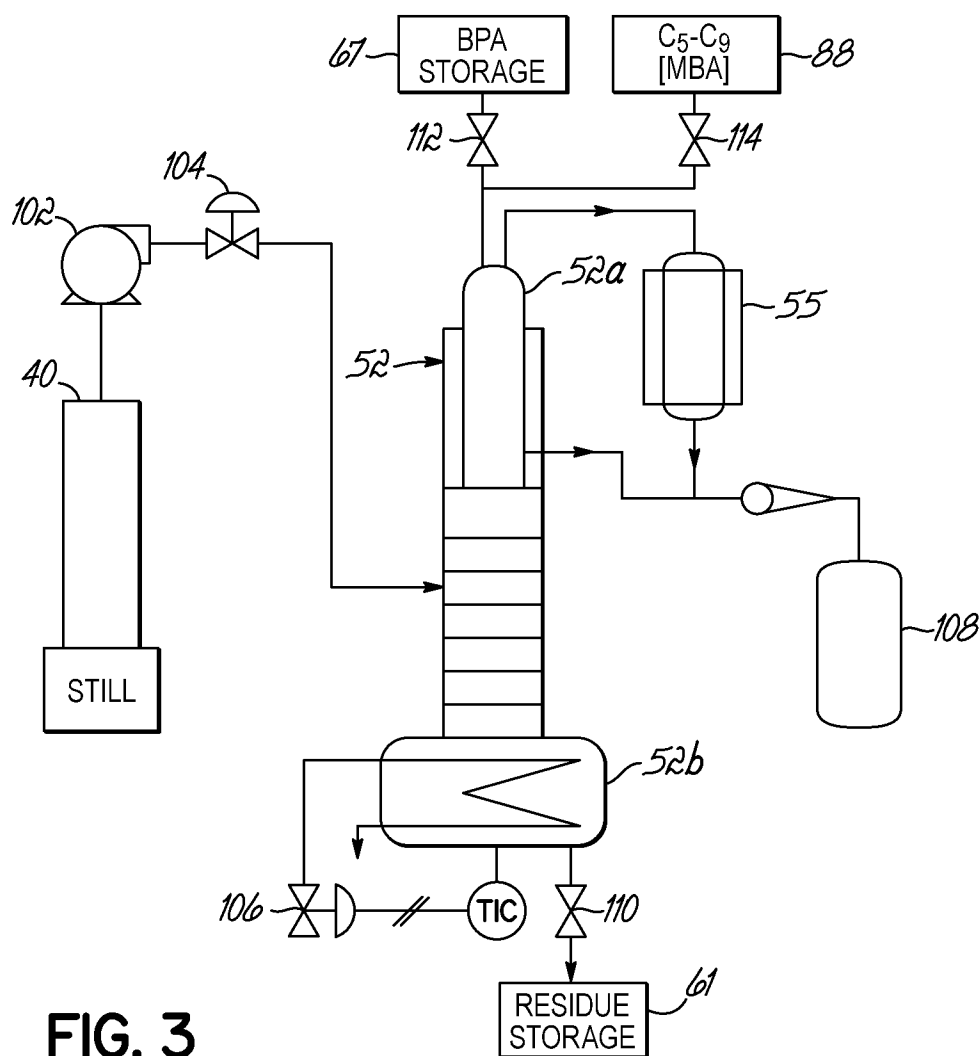


FIG. 3