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(54) **Title:** METHOD FOR QUENCHING PEROXYCARBOXYLIC ACID RUNAWAY REACTIONS

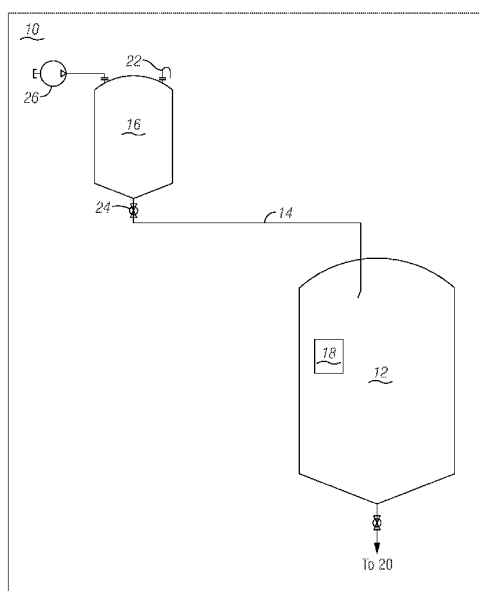


FIG. 1

(57) **Abstract:** Systems for quenching peroxydicarboxylic acid and peroxide chemistry runaway reactions provide safe and efficacious systems to prevent uncontrolled runaway reactions, such as decomposition reactions, of peroxydicarboxylic acid and peroxide chemistry compositions are disclosed. The systems provide prompt detection and dispensing of a stabilizer into a tank or other storage vessel containing a peroxide composition, peroxydicarboxylic acid composition or a peroxydicarboxylic acid-forming composition to stop a runaway reaction. Methods for quenching peroxide and peroxydicarboxylic acid runaway reactions are also disclosed.



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**TITLE: METHOD FOR QUENCHING PEROXYCARBOXYLIC ACID
RUNAWAY REACTIONS**

CROSS-REFERENCE TO RELATED APPLICATION

5 This application claims priority under 35 U.S.C. § 119 to Provisional Application U.S. Serial No. 63/002,434, filed on March 31, 2020, which is herein incorporated by reference in its entirety including without limitation, the specification, claims, and abstract, as well as any figures, tables, or examples thereof.

10 **FIELD OF THE INVENTION**

The invention relates to systems for quenching peroxycarboxylic acid and peroxide chemistry runaway reactions to provide safe and efficacious systems to prevent uncontrolled runaway reactions, such as decomposition reactions, of peroxycarboxylic acid and peroxide chemistry compositions. The systems provide prompt detection and
15 dispensing of a stabilizer into a tank or other storage vessel containing a peroxide composition, peroxycarboxylic acid composition or a peroxycarboxylic acid-forming composition to stop a runaway reaction. Methods for quenching peroxide and peroxycarboxylic acid runaway reactions are also provided.

20 **BACKGROUND OF THE INVENTION**

Peroxycarboxylic acids have emerged as effective alternatives for cleaning, sanitizing, and disinfecting in various applications. In addition to performance benefits available from the peroxycarboxylic acids, a significant benefit is the safety of decomposition products being the corresponding carboxylic acid, hydrogen peroxide and
25 water. Peroxycarboxylic acids can be provided in equilibrium or non-equilibrium compositions, prepared, and shipped ready for use, or generated onsite for applications of use. In applications where a peroxycarboxylic acid is formed, stored and/or transported there are safety precautions employed for the compositions. When peroxycarboxylic acids are stored in large quantities it is a particular challenge for the volume to shed
30 decomposition heat in comparison to smaller quantities.

In some instances, contaminants, such as trace levels of materials such as alkalis, halides, organics, or transitional metals can cause decomposition reactions and result in an

uncontrolled runaway reaction leading to a boil out of the contents. Most often iron or other metal contaminants are the cause. This can present a safety hazard as the reaction can produce large quantities of gas in a short time capable of boiling out the contents, with the potential to explode, releasing two phase gas and liquid flow of acidic, corrosive, and oxidizing materials from the storage vessel.

Due to the spontaneous decomposition tendency of peroxy-carboxylic acids it is common to stabilize the composition by the addition of various chemicals, such as 1-Hydroxyethylidene-1,1-diphosphonic acid (HEDP) or Dipicolinic acid (DPA). However, only small quantities can be utilized in light of both practical and regulatory limits for these stabilizers, which are often included in the low range of about 10,000ppm and 500ppm, respectively. While these levels generally suffice for protection against nominal contamination levels, they are easily overwhelmed by contaminants that enter the formulae either via raw materials or poor plant/customer hygiene. They are also more easily overwhelmed in large volume containers such as 1000L totes.

Various systems for the production and use of peroxy-carboxylic acid solutions have utilized acids, such as sulfuric acid, acetic acid, citric acid, or nitric acid, to prevent peroxy-carboxylic acid degradation within nonequilibrium composition to lower the pH and potentially quench a reaction. *See* US 2018/0042231. However, there are concerns with using many of these acids to slow the decomposition of a peracid as many of these are reactive with peracids and will produce exothermic decomposition.

These methods and systems can further include the use of stabilizers or chelating agents to bind contaminants or substances that otherwise would react with the peroxy-carboxylic acid and/or hydrogen peroxide oxidizers. Stabilizers are most often used in equilibrium compositions to stabilize and prevent degradation of the peroxy-carboxylic acid. *See also* US 2020/0323205. The use of stabilizers has also been recognized to provide value in complexing metal ion agents at temperatures in excess of 35°C; however, WO 95/022816 teach it is preferred for aqueous bleaching composition comprising an organic peroxyacid to be produced at a temperature below 30°C or in the alternative if reactions are above 35°C they should be carried out in the absence of the metal ion complexing agents.

However, no sufficient solutions have been provided for runaway reactions by the prior art. Instead, there has been an emphasis on monitoring pressure and/or temperature of

reactions to form peroxy-carboxylic acids. For example, in US 2020/0323205, the use of pressure and/or temperature detects the potential for a runaway reaction. For example, the pressure monitoring could be accomplished by use of a differential pressure sensor within a feedback control loop, wherein a pressure reading exceeding a set point would cause a safety release valve and/or rupture disk to be employed or venting to occur. As a further example, it is disclosed that temperature can be monitored through use of temperature probes placed upstream and down-stream of the reaction, and if the downstream temperature is higher than the upstream temperature then this can trigger a safety shut off of the heater and pumps. Moreover, US 2020/0323205 utilizes heated reactions and cooling is taught as the method for quenching undesired reactions.

It is therefore an object of this disclosure to provide systems for quenching the earliest stages of an uncontrolled runaway decomposition reaction to interrupt and stop the reaction from taking place.

It is a further object of this disclosure to provide systems for quenching runaway decomposition reactions that are applicable for use in storage tanks and/or vessels and/or transport tanks and/or vessels.

It is a further object of the disclosure to provide systems for detecting the earliest stages of an uncontrolled runaway decomposition reaction.

It is another object of this disclosure to provide methods for quenching runaway decomposition reactions, including methods that allow continued use of the peroxy-carboxylic acid composition.

Other objects, aspects and advantages of this invention will be apparent to one skilled in the art in view of the following disclosure, the drawings, and the appended claims.

SUMMARY OF THE INVENTION

In accordance with the background described herein, the described and other problems associated with the storage and production of peroxy-carboxylic acid compositions are solved by a system and method for quenching peroxy-carboxylic acid runaway reactions, in particular the quenching of industrial peroxy-carboxylic acid auto catalyzed runaway reactions.

In embodiments, a system for quenching peroxide or peroxy-carboxylic acid runaway reactions comprising: a first tank storing a peroxide composition, peroxy-carboxylic acid composition or a peroxy-carboxylic acid-forming composition; a second tank storing a stabilizer; at least one temperature probe housed in the first tank; a
5 dispense module that dispenses the stabilizer from the first tank into the second tank; and a programmable controller for controlling the operation of the system to quench the runaway reactions in response to determining that the temperature measured by the temperature probe has reached (i) a first predetermined temperature, (ii) a predetermined increase in rate of temperature increase as a function of time, or (iii) a change in
10 temperature of greater than about 25°F (13.8°C) over ambient temperature. Various embodiments of the system are disclosed herein.

In embodiments, methods of quenching a runaway reaction of a peroxide or peroxy-carboxylic acid composition comprise: detecting (i) an increase in temperature or (ii) a predetermined increase in rate of temperature increase as a function of time, in a first
15 tank, wherein the first tank contains a peroxide composition, a peroxy-carboxylic acid composition or mixing a peroxy-carboxylic acid-forming composition; dispensing a stabilizer into the first tank, wherein the stabilizer is housed in a second tank; and quenching the runaway reaction. Various embodiments of the methods are disclosed herein.

20 While multiple embodiments are disclosed, still other embodiments will become apparent to those skilled in the art from the following detailed description, which shows and describes illustrative embodiments. Accordingly, the drawings and detailed description are to be regarded as illustrative in nature and not restrictive.

25 **BRIEF DESCRIPTION OF THE DRAWINGS**

FIGS. 1-2 illustrate schematic views of systems for quenching runaway reactions, according to some aspects of the present disclosure.

FIG. 3 depicts a flow chart of a method of controlling the system of FIGS. 1-2, said method to be carried out, at least in part, by a programmable controller.

30 FIG. 4 shows a heat histogram measuring boil out reactions of lab scale iron-induced runaway decomposition tests of a peroxyacetic acid composition of several

samples, including samples with added water or stabilizer to quench the reaction as described in Example 1.

FIGS. 5-6 illustrate schematic views of systems for quenching runaway reactions in additional types of storage and/or transport vessels, according to some aspects of the present disclosure.

FIG. 7 is a graph showing temperature measurements of a lab scale iron-induced runaway decomposition reaction and the use of two different stabilizers to quench as described in Example 3.

FIG. 8 is a heat histogram measuring boil out reactions of lab scale iron-induced runaway decomposition tests of a more concentrated peroxyacetic acid composition of several samples, including samples with added stabilizers to quench the reaction as described in Example 4.

FIG. 9 is a graph showing temperature measurements and the positive second derivative (acceleration) of change in $dTemp/dTime$ as described in Example 5.

Various embodiments of the present invention will be described in detail with reference to the drawings, wherein like reference numerals represent like parts throughout the several views. Reference to various embodiments does not limit the scope of the invention. Figures represented herein are not limitations to the various embodiments according to the invention and are presented for exemplary illustration of the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The embodiments are not limited to particular systems and methods for quenching runaway decomposition reactions, which can vary and are understood by skilled artisans. It has been surprisingly found that the systems and methods described herein for quenching runaway reactions are able to quench the reaction at the earliest stages and in some embodiments are able to use the peroxy-carboxylic acid that was quenched with the stabilizer(s) providing a benefit of not having to discard the peroxy-carboxylic acid composition.

It is further to be understood that all terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting in any manner or scope. For example, as used in this specification and the appended claims, the singular forms "a," "an" and "the" can include plural referents unless the content clearly indicates

otherwise. Further, all units, prefixes, and symbols may be denoted in its SI accepted form. Numeric ranges recited within the specification are inclusive of the numbers within the defined range. Throughout this disclosure, various aspects are presented in a range format. It should be understood that the description in range format is merely for
5 convenience and brevity and should not be construed as an inflexible limitation on the scope of the invention. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range (e.g. 1 to 5 includes 1, 1.5, 2, 2.75, 3, 3.80, 4, and 5).

So that the present invention may be more readily understood, certain terms are
10 first defined. Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which embodiments of the invention pertain. Many methods and materials similar, modified, or equivalent to those described herein can be used in the practice of the embodiments without undue experimentation, but the preferred materials and methods are described
15 herein. In describing and claiming the embodiments, the following terminology will be used in accordance with the definitions set out below.

The term "about," as used herein, refers to variation in the numerical quantity that can occur, for example, through typical measuring and liquid handling procedures used for making concentrates or use solutions in the real world; through inadvertent error in these
20 procedures; through differences in the manufacture, source, or purity of the ingredients used to make the compositions or carry out the methods; and the like. The term "about" also encompasses amounts that differ due to different equilibrium conditions for a composition resulting from a particular initial mixture. Whether or not modified by the term "about", the claims include equivalents to the quantities.

The term "weight percent," "wt-%," "percent by weight," "% by weight," and variations thereof, as used herein, refer to the concentration of a substance as the weight of that substance divided by the total weight of the composition and multiplied by 100. It is understood that, as used here, "percent," "%," and the like are intended to be synonymous with "weight percent," "wt-%," etc.
25

The methods and systems may comprise, consist essentially of, or consist of the components and ingredients as well as other ingredients described herein. As used herein, "consisting essentially of" means that the methods and systems may include additional
30

steps, components, or ingredients, but only if the additional steps, components, or ingredients do not materially alter the basic and novel characteristics of the claimed methods and compositions.

In communications and computing, a computer readable medium is a medium
5 capable of storing data in a format readable by a mechanical device. The term “non-transitory” is used herein to refer to computer readable media (“CRM”) that store data for short periods or in the presence of power such as a memory device.

One or more embodiments described herein can be implemented using
programmatic modules, engines, or components. A programmatic module, engine, or
10 component can include a program, a sub-routine, a portion of a program, or a software component or a hardware component capable of performing one or more stated tasks or functions. A module or component can exist on a hardware component independently of other modules or components. Alternatively, a module or component can be a shared element or process of other modules, programs, or machines.

Systems for Quenching Peroxycarboxylic Acid Runaway Reactions

Exemplary systems **10** for quenching peroxycarboxylic acid runaway reactions are shown in FIGS. 1-2 and include a first tank **12** storing a peroxide composition, peroxycarboxylic acid composition or a peroxycarboxylic acid-forming composition comprising a peroxide source, a carboxylic acid, and optionally catalysts and/or acidulants,
20 a second tank **16** fluidly connected to, and in one embodiment positioned upstream from, the first tank **12** by way of a fluid connection **14**, said second tank **16** storing a stabilizer, at least one temperature probe **18** housed in the first tank, a dispense module **24** that dispenses the stabilizer from the second tank into the first tank, a fluid collector, outlet, valve, fluid connection, or other suitable means **20** for outputting fluid from the first tank
25 **12**, and a programmable controller **30** (illustrated in FIG. 3) for controlling the operation of the system **10**.

The first tank **12** for storing a peroxide composition, peroxycarboxylic acid composition or a peroxycarboxylic acid-forming composition is any type of tank, vessel, drum, cylinder, container, receptacle, bin, or the like. Storage tanks, and more particularly
30 reservoirs, chambers, compartments, and/or cavities located therein, are commonly employed for holding volumes of peroxycarboxylic acid compositions for storage and/or shipment. Similarly, precursor chemicals and/or peroxycarboxylic acid-forming

compositions can be held in separate reservoirs, chambers, compartments, and/or cavities of the same tank, or in more tanks, such as at a point of manufacturing and/or in situ generation of chemistry. The first tank **12** can be any shape, size, and material suitable for storing the peroxy-carboxylic acid without introducing contaminants or substances known to react with the peroxy-carboxylic acids. In some embodiments, the first tank **12** is a bulk storage tank, container, tote and/or drum. As referred to herein, bulk also includes intermediate sized bulk storage tanks, containers, totes and/or drums, such as sizes of at least about 250 gallons, 300 gallons, or larger.

The fluid connection **14** between the first tank **12** and the second tank **14** can be direct or indirect and can, by way of example, comprise a line, pipe, conduit, tube, port, opening, passage, and/or other suitable means of connection.

The second tank **16** for storing a stabilizer(s) for quenching the decomposition reactions is any type of tank, vessel, drum, cylinder, container, receptacle, bin, or the like. The second tank **16** can be any shape, size, and material suitable for storing the stabilizer(s) without introducing contaminants or substances known to react with peroxy-carboxylic acids.

At least one temperature probe **18** is housed within the first tank **12** to monitor the temperature of the peroxide composition, peroxy-carboxylic acid composition or peroxy-carboxylic acid-forming composition stored in the first tank **12**. In some embodiments, a plurality of temperature probes are located within the first tank (such as shown in FIG. 2 where more than one probe is depicted). In embodiments, at least two, three, four, five, six, or more temperature probes are located within the first tank **12**. The number of temperature probes **18** will vary based upon the shape and size of the first tank **12**. It is preferred to have a plurality of temperature probes **18** across all regions of the tank to measure for the earliest indications of changes in temperature of the peroxide composition, peroxy-carboxylic acid composition or a peroxy-carboxylic acid-forming composition.

Temperature probe(s) **18** can include any suitable type of thermal sensor / monitor for measuring temperature. For example, the thermal sensor / monitor can comprise transducer(s); thermistor(s); thermocouple(s); thermometer(s), such as infrared (“IR”) guns; and/or the like. Temperature probes **18** can be coated with a compatible material that does not introduce contaminants into the system **10**. Exemplary materials can include, for

example, stainless steel (*e.g.* 316L stainless), alloys, such as nickel, molybdenum, chromium (*e.g.* Hasteloy C) and/or polymers such as fluoropolymers of tetrafluoroethylene (*e.g.* polytetrafluoroethylene (PTFE)), or the like.

Optionally, and by way of non-limiting examples, the means **20** for outputting fluid
5 from the first tank **12** can be: (a) used to dose to an application of use, (b) put into a container for spraying, (c) for further processing, and/or the like; a vent **22**, exhaust, opening, pressure release mechanism, or other suitable safety feature can be in the second tank **16**, as shown in FIG. 1; the dispense module **24** can comprise or work in tandem with one or more of the following computer driven components: actuators, flow controls, flow
10 meters, valves, and/or other suitable aspects of the system **10**; and/or a pump **26** or series of pumps can be configured to pump the stabilizer into and/or from the second tank **26**.

The programmable controller **30** can comprise a microprocessor, a microcontroller, an arithmetic logic unit (“ALU”), a central processing unit (“CPU”), and/or some other programmable computing device which serves as the electronic circuitry that carries out
15 the instructions of computer programs. The programmable controller **30** performs the basic arithmetic, logic, controlling, and input/output (“I/O”) operations specified by the instructions. The programmable controller **30** can be included in a tablet, telephone, handheld device, laptop, user display, display, and/or other suitable computing devices which allow for input and output of electronic functions.

20 In other words, the controller **30** is configured, via logic circuits, memory, operating systems, compilers, and/or other electrical arrangements or programmatic modules, to control the system **10**. For example, and with reference to FIG. 3, the controller **30** continuously monitors for and thus is able to detect (illustrated in FIG. 3 as detect step **32**) when the temperature probe(s) **18** reaches (i) a first predetermined
25 temperature, (ii) a predetermined increase in rate of temperature increase as a function of time, or (iii) a change in temperature of greater than about at least 25°F (13.8°C) above ambient temperature. If such a scenario exists, the controller **30** can then instruct the dispense module **24** to dispense (illustrated in FIG. 3 as dispense step **34**) the stabilizer from the second tank **16** into the first tank **12** and thereby quench, interrupt, or stop
30 (illustrated in FIG. 2 as quench step **34**) runaway reactions from taking place and/or progressing.

By way of example only, the controller **30** can control the operation of the system for quenching the runaway reactions by sensing and recording of data, opening/closing of valves in the system, activating pumps and/or other actuators within the system **10**, and timing of the operations, together with providing associated warnings, safety checks and historical data.

It should be appreciated that the controller may be any type or make of controller **30** known to those skilled in the art. Beneficially, the controller **30** is programmable such that it is programmed according to a user's location, preferred end use application, and/or environment where the peroxide or peroxy-carboxylic acid compositions are stored and/or where a peroxy-carboxylic acid-forming composition is generated and/or stored prior to use. In some embodiments, the user's location can be determined through geotagging, or automatically determining location through the use of a global positioning system ("GPS") receiver. In such embodiments, it is recognized that a programmable controller **30** is in communication, potentially wired, wireless, or a combination thereof, with the temperature probes **18** in the first tank **12** to detect either an increase in temperature within the first tank **12** and/or the reaching of a first (and/or second or more) predetermined temperature or detecting a predetermined increase in rate of temperature increase as a function of time. It is also to be appreciated that the controller **30** is in communication, potentially wired, wireless, or a combination thereof, with the dispense module **24**, actuators, flow controls, flow meters, valves, and/or other aspects of the system **10** to control the operation of the system **10** and to quench the runaway reactions which are detected according to the changes in temperature measured by the temperature probes.

The controller **30** can be communicatively connected to one or more display devices or modules with various status indicators, such as light emitting diodes ("LEDs"). To interface with the user, the one or more display devices, modules, or even the controller **30** itself will preferably include a graphical user interface ("GUI"). However, it is also to be appreciated other various user interfaces ("UI") can be used, such as those with audio communications means (*e.g.* speakers, microphones, headphones, etc.), typical computer input/output means (*e.g.* computer mice, keyboards, touchscreens, etc.), and/or mechanical input/output means (*e.g.* knobs, dials, switches, buttons, etc.). For example, status indicators can indicate the current operation of a peroxy-carboxylic acid reaction to generate a peroxy-carboxylic acid composition. As a further example, the status indicators

can indicate a current temperature (or average temperature of the zones) of the first tank, or other status of the system (*e.g.* status of the quenching reaction itself). It should be appreciated that the status indicators may be used for any other purpose related to operating characteristics of the system.

5 In some embodiments the GUI is used to input commands into the controller **30** and to provide a computer-assisted means through which operators can set up and deploy the quenching system into operation in an intended environment. In some embodiments, the GUI and the status indicators provide operators with functionality to monitor operation of the tanks for storage and/or generation of the peroxide or peroxy-carboxylic acid
10 compositions by displaying information relating to the temperature (or other measurements, *e.g.* pressure) that are monitored by the controller. In still other embodiments, the GUI is used only to alert an operator of the temperature (or other measurements, *e.g.* pressure) that are monitored by the controller, and the subsequent steps for quenching of the runaway reaction are fully automated and do not require further
15 operator authorization to ensure the reaction is timely quenched.

 In further embodiments, systems **10** for quenching peroxy-carboxylic acid runaway reactions (*e.g.* FIGS. 5-6) can be provided in a manner that does not include the temperature probes **18** and/or programmable controller **30**. In such embodiments, there can be a tank **12** storing a peroxide composition, peroxy-carboxylic acid composition or a
20 peroxy-carboxylic acid-forming composition comprising a peroxide source, a carboxylic acid, and optionally catalysts and/or acidulants, and a vessel **16** fluidly connected to or disposed or housed within the tank **12**. In an embodiment the fluid connection can be a vessel disposed within or adjacent to the tank **12**, such that the vessel **16** storing the stabilizer, could for example be coated in a substance (*e.g.* wax or wax-like substance) that
25 melts and/or disintegrates to dose the stabilizer into the tank **12** upon a sufficient elevation of temperature within the tank **12**.

 Such an embodiment, without the temperature probe(s) and/or any automated dispense module allows for the dosing of the stabilizer from the second tank into the first tank. In the FIGS. 5-6, the tank **12** is a storage and/or transport container, *e.g.* tote (FIG. 5),
30 drum (FIG. 6), or the like, and the vessel **16** containing the stabilizer is connected to a tube or probe **15** that is in contact with the peroxide composition, peroxy-carboxylic acid composition or peroxy-carboxylic acid-forming composition. The probe **15** and the vessel

16 storing the stabilizer may be affixed to a lid or other opening 17 for the tank 12. Such embodiments depicted in FIGS. 5-6 ensure that when the tank 12 is closed and there is the potential for a runaway reaction that would cause an increase in temperature in the tank 12, the vessel 16 storing the stabilizer will melt and/or disintegrate and thereby dose the stabilizer into the tank 12. As one skilled in the art will appreciate, the particular material that makes up the vessel 16 storing the stabilizer is design to melt and/or disintegrate upon a sufficient elevation of temperature within the tank to indicate the initiation of a potential runaway reaction, namely a temperature of 45°C, 50°C, 55°C, or 50°-55°C.

The material is inert and compatible with the peroxide composition, peroxy-carboxylic acid composition or peroxy-carboxylic acid-forming composition. This temperature would melt the inert material that makes up at least a portion of the vessel 16. As one can envision from the description herein, either the entirety of the vessel 16 or a portion of the vessel is made of the material that will melt or disintegrate upon the elevated temperature within the tank 12. In some embodiments the vessel 16 could be made of plastic tubing that is compatible with the peroxide composition, peroxy-carboxylic acid composition or peroxy-carboxylic acid-forming composition (*e.g.* PVC), and the plastic tubing is capped inside one or both ends (*i.e.* a plug) with a wax or peroxy species compatible plastic. The size of the vessel 16 will depend on the size of the tank 12 as it is sized to hold sufficient stabilizer to quench a reaction in the particular tank 12 (*i.e.* tote or drum). In an exemplary, non-limiting embodiment a vessel large enough to contain approximately 2 kg of the stabilizer DPA could be housed within a 1000 kg tote (the tank 12).

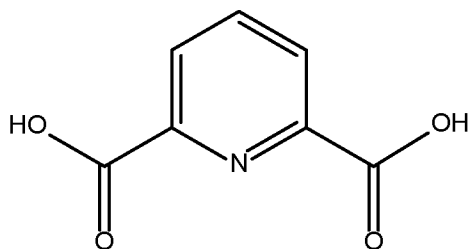
Additional embodiments (not depicted) without the temperature probe(s) and/or any automated dispense module can include encapsulated stabilizer in fluid connection (*e.g.* contained within the tank 12) with the peroxide composition, peroxy-carboxylic acid composition or peroxy-carboxylic acid-forming composition housed within the tank 12. The encapsulating material that prevents contact of the stabilizer with the peroxy species maintains the separation until an increase in temperature, namely a temperature reaching 45°C 50°C, 55°C, or 50°-55°C. The encapsulating material is also compatible with the peroxide composition, peroxy-carboxylic acid composition or peroxy-carboxylic acid-forming composition. This temperature would melt the material that encapsulates the stabilizer.

Stabilizers

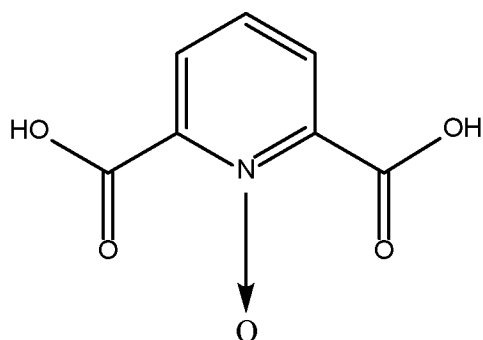
The system and methods described provide a stabilizer to the peroxide composition, peroxy-carboxylic acid composition, or peroxy-carboxylic acid-forming composition to quench (*i.e.* stop) a runaway decomposition reaction. Beneficially, the stabilizer(s) can be added by the system and methods during the early stages of an uncontrolled runaway decomposition reaction in order to quench or interrupt and stop the reaction from taking place. In some embodiments more than one stabilizer can be added by the system.

In an embodiment, the stabilizer is a phosphoric acid (H_3PO_4) or salt thereof, pyrophosphoric acid or salt thereof, phosphonic acid or salt thereof, or a pyridine carboxylic acid, a salt thereof or derivative thereof. An exemplary stabilizer is 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP) or a salt thereof. Further exemplary stabilizers include aminotrimethylene phosphonic acid, ethylene diamine tetramethylene phosphonic acid, hexamethylene diamine tetramethylene phosphonic acid, diethylene triamine tetramethylene phosphonic acid.

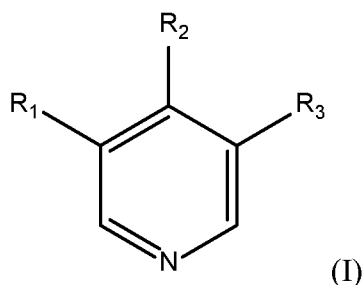
In an embodiment, the stabilizer is a pyridine carboxylic acid, a salt thereof or derivative thereof. Exemplary stabilizers include 2,6-pyridine (mono or di) carboxylic acids, including 2,6-pyridinedicarboxylic acid (DPA). The 2,6-pyridinedicarboxylic acid has the following structure:



In a further aspect, the 2,6-pyridine (mono or di) carboxylic acids can include 2,6-pyridine (mono or di) carboxylic acid oxides, shown below as the 2,6-pyridinedicarboxylic acid oxide having the following structure:

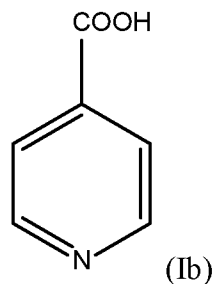
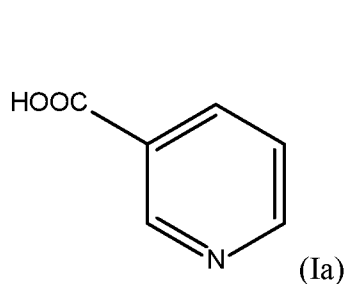


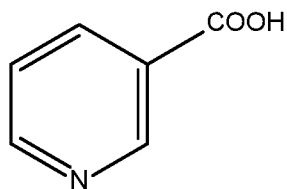
Additional pyridine carboxylic acid derivatives include 3-pyridinecarboxylic acid (niacin, nicotinic acid, Vitamin B3), 4-pyridinecarboxylic acid (isonicotinic acid), 5-pyridinecarboxylic acid, 3,4-pyridinedicarboxylic acid, 3,5-pyridinedicarboxylic acid (dinicotinic acid), 4,5-pyridinedicarboxylic acid, 3,4,5-pyridinetricarboxylic acid, oxides thereof, and/or salts. The pyridine carboxylic acids, salts thereof, or derivatives thereof can have the following structure:



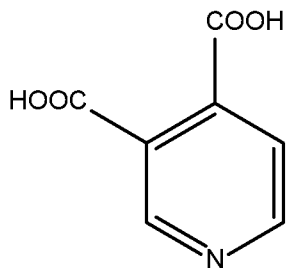
10

wherein R_1 , R_2 and R_3 are independently COOH or H, or a salt thereof. Exemplary structures include the following:

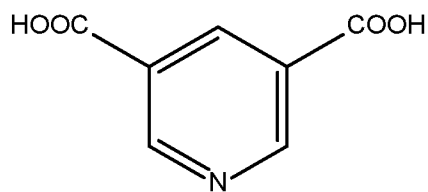




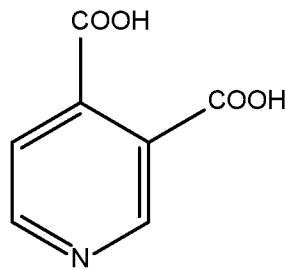
(Ic)



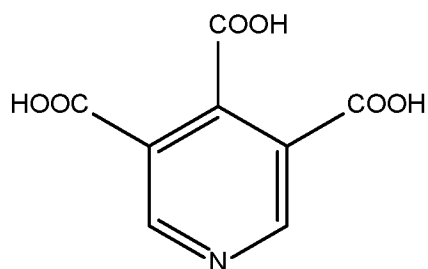
(Id)



(Ie)



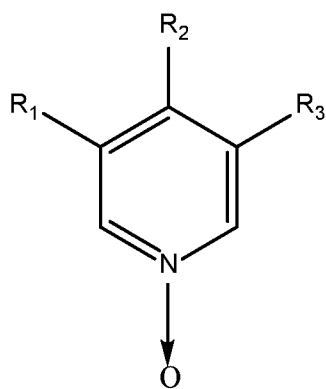
(If)



(Ig)

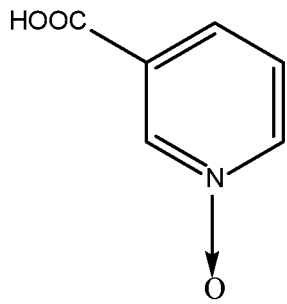
5

In a further aspect, the pyridine carboxylic acids can include pyridine carboxylic acid oxides having the following structure:

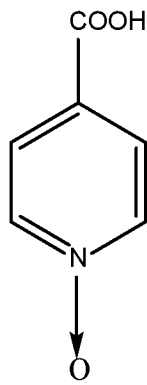


(II)

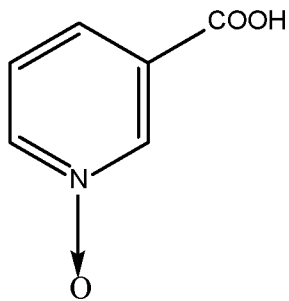
10 wherein R₁, R₂ and R₃ are independently COOH or H, or a salt thereof. Exemplary structures include the following:



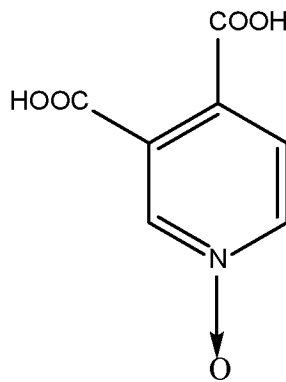
(IIa)



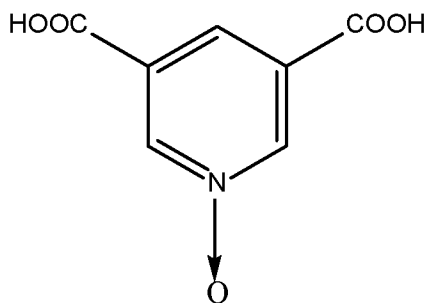
(IIb)



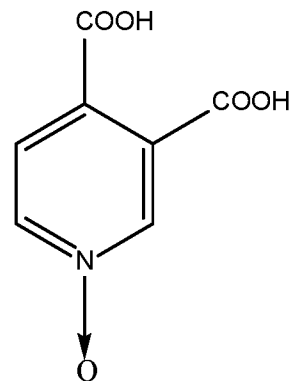
(IIc)



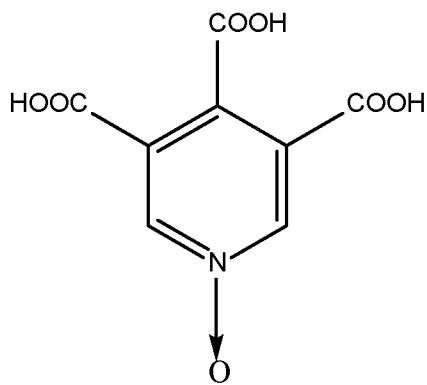
(IIId)



(IIe)



(IIf)



(IIg)

In an embodiment, a combination of stabilizers is employed. In an exemplary embodiment, a combination of 1-hydroxyethylidene-1,1-diphosphonic acid or a salt thereof and 2,6-pyridinedicarboxylic acid is employed as the stabilizers.

In an embodiment, the stabilizer(s) can be provided as a liquid or a free-flowing solid. In an embodiment, the stabilizer(s) can be provided as a solid, such as a solid block, that would first require dissolution before being dispensed into the first tank housing the peroxide composition, peroxydicarboxylic acid composition, or peroxydicarboxylic acid-forming composition to quench a runaway decomposition reaction.

Without being limited to a particular mechanism of action the use of the stabilizers to quench a decomposition reaction, such as that caused by iron or other contaminants, overcomes the kinetics of the reaction. One skilled in the art would expect for a stabilizer, such as a phosphoric acid or salt thereof, to bind to the contaminant (*e.g.* iron) in a stoichiometric manner and not exponential in its ability to quench the decomposition reactions as the stabilizer should bind catalytically ~~due to the finite number of sites to bind~~ and quench the decomposition reaction. However, the stabilizers are shown to be able to quench (*i.e.* stop) the reaction and therefore provide more than preventative action. Instead the stabilizers provide kinetically exponential effects in stopping the runaway decomposition reactions.

As a further benefit, the stabilizer can remain in the peroxy species containing composition (*e.g.* peroxydicarboxylic acid composition) after the quenching reaction as they are compatible with the compositions. This is a further benefit to being able to salvage and use the compositions following the methods of quenching a runaway reaction, as suggested by the optional (hollow arrow) salvage step **38** in FIG. 2.

Peroxy Species

The system and methods described provide the stabilizer into a peroxy species, which can include a peroxide composition, a peroxy-carboxylic acid composition or peroxy-carboxylic acid-forming composition to quench a runaway decomposition reaction.

5 In embodiments, a single peroxy species is employed, as such reaction is likely to occur in a storage tank or vessel containing the peroxy species. However, in some embodiments more than one peroxy species can be employed, such as a mixed peroxy-carboxylic acid composition. As used herein, the terms “mixed” or “mixture” when used relating to the peroxy species can include any combination thereof. However, in
10 certain embodiments a mixed peroxy-carboxylic acid composition is employed and includes more than one peroxy-carboxylic acid.

According to the invention, a peroxy-carboxylic acid (*i.e.* peracid) is included. As used herein, the term “peracid” may also be referred to as a “per-carboxylic acid,” “peroxy-carboxylic acid” or “peroxyacid.” Sulfoperoxy-carboxylic acids, sulfonated
15 peracids and sulfonated peroxy-carboxylic acids are also included within the terms “peroxy-carboxylic acid” and “peracid” as used herein. The terms “sulfoperoxy-carboxylic acid,” “sulfonated peracid,” or “sulfonated peroxy-carboxylic acid” refers to the peroxy-carboxylic acid form of a sulfonated carboxylic acid, such as those disclosed in U.S. Patent No. 8,344,026, 8,809,392 and 9,359,295, each of which are incorporated herein by
20 reference in their entirety. As one of skilled in the art appreciates, a peracid refers to an acid having the hydrogen of the hydroxyl group in carboxylic acid replaced by a hydroxy group. A peroxy-carboxylic acid includes any compound of the formula $R-(COOOH)_n$ in which R can be hydrogen, alkyl, alkenyl, alkyne, acyclic, alicyclic group, aryl, heteroaryl, or heterocyclic group, and n is 1, 2, or 3, and named by prefixing the parent acid with
25 peroxy. Preferably R includes hydrogen, alkyl, or alkenyl.

Exemplary peroxy-carboxylic acids include varying lengths of peroxy-carboxylic acids (*e.g.* C1-22) and they can be prepared from any known method of reaction, whether producing equilibrium or non-equilibrium peroxy-carboxylic acid compositions. As an example, an acid-catalyzed equilibrium reaction between a carboxylic acid and hydrogen
30 peroxide can provide a peroxy-carboxylic acid composition. Alternatively, an auto-oxidation of aldehydes or reaction of hydrogen peroxide with an acid chloride, acid anhydride, carboxylic acid anhydride, sodium alcoholate or alkyl and aryl esters can

provide a peroxy-carboxylic acid composition. Still further, non-equilibrium reactions can be used such as those disclosed in U.S. Patent Nos. 8,846,107 and 8,877,254, which are incorporated herein by reference in their entirety.

In some embodiments, a peroxy-carboxylic acid includes at least one water-soluble
5 peroxy-carboxylic acid in which R includes alkyl of 1-22 carbon atoms. For example, in one embodiment, a peroxy-carboxylic acid includes peroxyacetic acid. In another embodiment, a peroxy-carboxylic acid has R that is an alkyl of 1-22 carbon atoms substituted with a hydroxyl group or other polar substituent such that the substituent improves the water solubility. Methods of preparing peroxyacetic acid are known to those
10 of skill in the art including those disclosed in U.S. Pat. No. 2,833,813, which is herein incorporated herein by reference in its entirety.

As referred to herein a peroxy-carboxylic acid-forming composition can include a peroxy-carboxylic acid composition that includes a peroxide source and a carboxylic acid (or a precursor). Optionally, the peroxy-carboxylic acid composition could include
15 stabilizers, acid catalysts, acidulants, surfactants, hydrotropes, solvents, defoaming agents as well as tracing compounds for analytical monitoring.

Various commercial formulations of peroxy-carboxylic acids are available, including for example peroxyacetic acid (approximately 15%) available as EnviroSan (Ecolab, Inc., St. Paul MN). Most commercial peroxy-carboxylic acids solutions state a
20 specific peroxy-carboxylic acid concentration without reference to the other chemical components in a use solution. However, it should be understood that commercial products, such as peroxyacetic acid, will also contain the corresponding carboxylic acid (e.g. acetic acid), hydrogen peroxide and water.

In an embodiment, any suitable C1-C22 peroxy-carboxylic acid can be used. In
25 some embodiments, the C1-C22 peroxy-carboxylic acid is a C2-C20 peroxy-carboxylic acid. In other embodiments, the C1-C22 peroxy-carboxylic acid is a C1, C2, C3, C4, C5, C6, C7, C8, C9, C10, C11, C12, C13, C14, C15, C16, C17, C18, C19, C20, C21, or C22 carboxylic acid. In an embodiment employing a peroxy-carboxylic acid the composition can have any ratio of hydrogen peroxide to peroxy-carboxylic acid. In some embodiments, the ratio of
30 hydrogen peroxide to peroxy-carboxylic acid is from about 0:10 to about 10:0, or from about 0.5:10 to about 10:0.5.

Indicators for Delivery of Stabilizer

In some embodiments, the stabilizer can be combined with a dye. Preferred dyes include inert dyes to provide a visual indicator of the activation of the stabilizer and the methods described herein. This would beneficially provide a visual indicator of the dosing
5 or release of the stabilizer into a vessel containing the peroxide composition, peroxy-carboxylic acid composition or peroxy-carboxylic acid-forming composition. This embodiment is particularly beneficial in tanks (*e.g.* storage and/or transport vessels) that may not have the temperature probes to detect a runaway reaction. This embodiment is further beneficial in tanks that are made of materials (*e.g.* natural HDPE or other material)
10 that you can see into the tank as opposed to a dark colored tank.

Methods

Methods for quenching an uncontrolled runaway decomposition reaction to interrupt and stop the reaction from taking place are provided. The methods employing the systems beneficially stop the reaction at very early stages to minimize any danger to the
15 system and/or users, such as those handling storage tanks and/or vessels and/or transport tanks and/or vessels containing the peroxide composition, a peroxy-carboxylic acid composition or peroxy-carboxylic acid-forming composition. The methods also beneficially allow continued use of the peroxide composition, a peroxy-carboxylic acid composition or peroxy-carboxylic acid-forming composition.

The methods of quenching a runaway reaction of a peroxide composition or a peroxy-carboxylic acid composition include a first step of detecting an increase in temperature or an increase in the rate of increase in temperature. In an embodiment, there is detected in the first tank an increase in temperature of at least 25°F (13.8°C) above ambient temperature or a first predetermined temperature by a temperature probe housed in
25 a first tank, wherein the first tank contains a peroxide composition, a peroxy-carboxylic acid composition or a peroxy-carboxylic acid-forming composition. In an embodiment, there is detected in the first tank a predetermined increase in rate of temperature increase as a function of time, wherein the first tank contains a peroxide composition, a peroxy-carboxylic acid composition or a peroxy-carboxylic acid-forming composition. The
30 increase in rate of temperature increase is a positive change in the rate of temperature increase as a function of time (also understood as a positive second derivative or temperature per unit time). One skilled in the art will ascertain that an increase in the

magnitude of the change in temperature as a function of time is an approach that protects the system from false positives in the detection step. For example, if the probe(s) in the first tank have a warm raw material transferred into it, a simple threshold criteria for a first predetermined temperature could trigger a quench that is not required as there is no runaway reaction. Instead, the dTemp/dTime values should be getting smaller and only an actual runaway reaction can cause increases in the dTemp/dTime values and therefore trigger the quenching as described herein.

The measurement of changes in temperature of the tank housing the peroxy species described herein is achieved by the temperature probe(s) housed within the tanks. The measurements of changes in temperature can be a single measurement of any one temperature probe or an average of a plurality of temperature probes, based on the programmable controller for the system.

In some embodiments, a change in temperature of at least 25°F (13.8°C) above ambient temperature is a measurement according to the system of the initiation of a runaway reaction. In some embodiments, a first predetermined temperature of 104°F (40°C), 45°C, 50°C or 55°C is a measurement according to the system of the initiation of a runaway reaction. As one skilled in the art will ascertain from the disclosure herein, the programmable controller can also allow a user to program at number of additional predetermined temperatures to measure according to the system to initiate the methods of quenching a runaway reaction. In an embodiment, the temperature measurements by the temperature probes indicate the temperature of the peroxy species housed in the first tank is approaching or has exceeded the self-accelerating decomposition temperature (SADT) value or is approaching an increase in temperature that would exceed the SADT.

Upon the measurement of the change in temperature of at least 25°F (13.8°C) above ambient temperature or the measurement of the first (or any additional) predetermined temperatures, the system dispenses the stabilizer into the first tank wherein the temperature probes indicated a runaway reaction has begun. The stabilizer is housed in a second tank and is dispense into the first tank to quench the runaway reaction. Beneficially, these measurements of change in temperature and/or predetermined temperatures initiate the dispensing of the stabilizer to the first tank at the very early stages of an uncontrolled runaway decomposition reaction in order to quench and stop the dangerous reaction from taking place. As the rate of temperature change in a runaway

reaction will increase over time (*i.e.* accelerates), the early or initial detection of the increase in temperature beneficially allows the early detection of the runaway reaction.

In embodiments, the stabilizer is added to a first tank by any dosing, such as pumping the stabilizer from a second tank or otherwise adding a source of the stabilizer to
5 the first tank. In an embodiment, the stabilizer could be loaded into a tube or other means that can be dosed, injected, or otherwise added to the first tank. For example, a loaded tube containing the stabilizer could be injected after fitting the tube into an opening (*e.g.* fitted on a thread opening). Any suitable way of adding the stabilizer into the first tank is embodied by the described systems and methods.

10 In alternative embodiments, the dosing of the stabilizer is not measured by a change in temperature. Instead, the increase in temperature within a tank or vessel will cause the dispensing of the stabilizer through the melting or disintegrating of a vessel housing the stabilizer (and optionally a dye). Upon reaching a predetermined temperature (*e.g.* 40°C, 50°C, or 55°C) that causes at least a portion of the vessel housing the stabilizer to melt
15 and/or disintegrate, the stabilizer is in contact with the peroxy species to quench the reaction. In this embodiment the dosing of the stabilizer is quick as the vessel housing the stabilizer is already submerged in the tank housing the chemistry undoing the exothermic reaction.

In embodiments, the stabilizer is added to the first tank within about 5 seconds, 10
20 seconds, or about 15 seconds (or any predetermined amount of time by the programmable controller) of the detected temperature changes or predetermined temperature(s) by the system.

In embodiments, the stabilizer is a phosphoric acid or salt thereof, pyrophosphoric acid or salt thereof, phosphonic acid or salt thereof, or a pyridine carboxylic acid, a salt
25 thereof or derivative thereof. In some embodiments, the stabilizer comprises 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP) or a salt thereof and/or 2,6-pyridinedicarboxylic acid. In embodiments, the stabilizer is a liquid, solid, or a powder. In embodiments, the stabilizer is dosed at a rate of at least about 2 wt-% based on the weight of the composition in the first tank, namely the peroxide composition, peroxy-carboxylic acid composition or peroxy-carboxylic acid-forming composition. In other embodiments,
30 the stabilizer is dosed at any suitable concentration. In some embodiments, the stabilizer is dosed at a rate of at least about 2 wt-%, about 2 wt-% to about 10 wt-%, about 2.5 wt-% to

about 10 wt-%, or about 2.5 wt-% to about 5 wt-%, based on the weight of the composition in the first tank.

In some embodiments, a dye or visual indicator is also included with the stabilizer to provide a visual indicator of the activation of the stabilizer and the methods described
5 herein. This beneficially provides a visual indicator of the dosing or release of the stabilizer into a vessel containing the peroxide composition, peroxydicarboxylic acid composition or peroxydicarboxylic acid-forming composition.

In embodiments, the quenching of the peroxide composition, a peroxydicarboxylic acid composition or peroxydicarboxylic acid-forming composition beneficially do not
10 consume the peroxy species. Unlike a decomposition reaction where the peroxy species is consumed, the quenching stops this process and the peroxy species remain intact in the compositions. This allows for the salvaging or continued use of the compositions and/or safe disposal of the compositions as opposed to conventional need to discard a consumed chemistry following a runaway decomposition reaction. In an embodiment, from about
15 80% to about 95% of the peroxy species in the treated peroxide composition, peroxydicarboxylic acid composition and/or peroxydicarboxylic acid-forming composition are retained and able to be used in the desired application of use. In an embodiment, at least about 80%, 85%, 90%, 95%, or greater of the peroxy species in the treated peroxide composition, peroxydicarboxylic acid composition and/or peroxydicarboxylic acid-forming
20 composition are retained and able to be used in the desired application of use.

EXAMPLES

Embodiments of the present invention are further defined in the following non-limiting Examples. It should be understood that these Examples, while indicating certain
25 embodiments of the invention, are given by way of illustration only. From the above discussion and these Examples, one skilled in the art can ascertain the essential characteristics of this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the embodiments of the invention to adapt it to various usages and conditions. Thus, various modifications of the embodiments of the
30 invention, in addition to those shown and described herein, will be apparent to those skilled in the art from the foregoing description. Such modifications are also intended to fall within the scope of the appended claims.

EXAMPLE 1

A lab scale runaway reaction test was conducted to assess ability of a stabilizer to quench the reaction. The test was conducted inside insulated Dewar flasks in order to conserve all the heat energy to the runaway reaction modeling a real event. The Dewar flasks do not have constriction, instead they have an open throat for venting. A commercially available peroxyacetic acid composition (peracetic acid 5 wt-%; acetic acid 5-10 wt-%; hydrogen peroxide 10-30 wt-%; remaining water) was used with iron to trigger a decomposition reaction as would occur with iron contaminants in a peroxide or peroxy-carboxylic acid composition. The evaluated conditions are shown in Table 1. The 6 grams ferric chloride hexahydrate and ferric chloride anhydrous salt were added to 200g of the peracetic acid/hydrogen peroxide composition in a 500mL cylindrical Dewar flask and the temperature in the flasks were monitored over time. The ferric ions are a known antagonist for peroxide compounds as are chloride ions and both are likely responsible for the exothermic decomposition reaction that builds to an eventual literal boiling hot decomposition of both the peracetic acid and the hydrogen peroxide.

A limitation of the laboratory assessments described herein is that the iron chloride is an effective contaminant to initiate rapid and aggressive boil out in the peroxy-carboxylic acid composition, however the chloride ion may actually interfere with the stabilizer used to quench the runaway reaction. The HEDP stabilizer for example is intended for metals and not chloride. However, the testing in the field or non-laboratory reactions overcome this limitation of the laboratory examples as they do not experience such exaggerated contamination conditions such as those described herein.

25 TABLE 1

	Mass, g	Mass, g	Mass, g	ppm	Mass of Peracid, g	Quench		
Sampl e	FeCl ₃ , 45%	FeCl ₃ , 100%	Total FeCl ₃	Total FeCl ₃ in peracid	Per- oxyacetic Acid	Stabilizer	Mass, g	wt% ratio Stabil izer
A	6	0.5	3.2	16000	200	none	0	NA
B	6	0.25	2.95	14750	200	none	0	NA
C	Rxn abandoned				200	none	0	NA

D	6	0.5	3.2	16000	200	HEDP (60%)	20	10 wt%
E	6	0.5	3.2	16000	200	DI-H ₂ O	20	10 wt%
F	6	0.5	3.2	16000	200	HEDP (60%)	10	5 wt%
G	6	0.5	3.2	16000	200	HEDP (60%)	5	2.5 wt%
G2	6	0.5	3.2	16000	200	HEDP (60%)	5	2.5 wt%

Samples A and B were not treated with any stabilizer and demonstrate the runaway negative Controls. Sample C was discarded. Samples D, F, G, and G2 had the stabilizer HEDP added to the peroxyacetic acid composition. Sample E was run with equivalent water (to the stabilizer) as a positive Control; also confirming that the quench of the HEDP stabilizer Samples were not due to heat sink or simple dilution of the peroxyacetic acid composition with water.

The results are shown in FIG. 4, illustrating samples D, F, G, and G2 dosed with the HEDP stabilizer were able to quench the decomposition reaction. The x-axis of the figure shows the time of the measurements, and the y-axis shows the temperature in degrees Fahrenheit. Samples A and B show a runaway reaction, the temperatures quickly boil out to 200°F where the chemistry boils off as a result of the contaminants decomposing the peroxycarboxylic acid composition and steam comes off the system which is a result of the oxygen liberated in the decomposition reaction and the consumption of the peroxygen species (here the peroxyacetic acid), leaving hot water in the flask. This reaction in the laboratory is an accelerated decomposition reaction to show a fast contamination and runaway over minutes instead of hours to days as would take place in larger volumes and less significant contamination.

The 2.5% relative mass (G samples) partially quenched but continued to climb. Both 5% and 10% (F and D respectively) performed well in that the reaction was quenched (or stated another way the exotherm was truncated) and no further increase in temperature was observed, confirming the quench of the runaway reaction. The data shows that the temperature in the flasks cools down relatively slowly which is a result of the shape of the flask container itself holding the peroxycarboxylic acid composition as well as the exaggerated contamination conditions.

This set of laboratory experiments shows that as little as a 2.5% ratio of quench solution in the form of HEDP (60% aq.) was capable of completely arresting the exothermic reaction. To demonstrate if this was simply a heat quenching effect, the HEDP solution was substituted by as much as 10% room temperature deionized water (E sample) which showed very slight effect on the progress of the eventual runaway (*i.e.* a slightly less steep curve to the boil out). As is stated in literature quenching these types of runaway reactions by simple thermal means may require as much as 400% relative water quenches. Since there are commercial interests in as large as 30,000-gallon tanks of peracids (*e.g.* peracetic acid solutions) it is imperative that the quench be as potent as possible. In some aspects this would be on the order of about 2.5% to about 10% of the target vessel.

EXAMPLE 2

A large-scale quench test was also completed. Approximately 100,000 pounds of a peroxyacetic acid composition stored in approximately 37 storage totes, wherein each tote had a volume of 1000L or around 330 gallons (*i.e.* standard Intermediate Bulk Containers (IBC)), that became contaminated with zinc were tested to confirm ability of the stabilizer HEDP to control a runaway decomposition reaction underway, as assessed by off gassing and self-heating of the peroxyacetic acid composition in the totes. The self-heating was a warm to hot increase in temperatures of the storage totes.

The tote that housed the composition with the runaway reaction had a temperature of at least 99.9°C and the remainder of the heat energy was used to convert water to steam. The remaining totes were not able to obtain a temperature reading. They were warm to the touch and various qualitative assessments were made. For example, the material was visibly off gassing, and the totes were reported to have been bulging (*i.e.* exceeding the vent capacity) and there was a slight amount of vapor escaping.

HEDP stabilizer was delivered on site and added to each tote to provide a 10% target dosing of HEDP. Approximately 7% of the total volume of each tote of the HEDP was dosed / added to the contaminated product. Onsite assessment confirmed the HEDP was able to quench the reaction, stopped the off gassing, and allowed the containers to cool enough for them to be transported safely for disposal.

EXAMPLE 3

Additional laboratory testing was conducted to evaluate an additional stabilizer. For practical purposes, the lab induced runaway described in this Example and Example 1 were scaled to cause complete destruction of the chemistries within 5-60 minutes, but these relatively high levels of contamination are generally in great excess to the contamination levels necessary to cause the runaways in large vessels, in some instances by a factor of 100-1000 higher. Forensic analysis of a 1000L tote which ran away over a period of several days boiling out and spilling out its contents, it was found that only about 1ppm copper along with sub ppm levels of several transition metals were all that was necessary to contaminate the chemistry and induce the runaway reaction. This demonstrates that a lower wt-% ratio of stabilizer to the chemistry would be effective to quench a reaction.

FIG. 7 shows testing over a period of 600 minutes comparing HEDP to DPA. The testing with only 0.6 wt% HEDP stabilizer (9g of 60% HEDP added to 900g of the 20% peracid) failed to quench the runaway (as evidenced by the continued climb after returning the flask to the 48°C oven). This is shown in FIG. 7 when the HEDP was dosed just after 500 minutes the exotherm was quenched, until the heating was resumed and the curve then continues to produce the exotherm and exhibit a slow runaway reaction. In contrast, the 0.1 wt% dipicolinic acid stabilizer (0.9 grams DPA added to 900g of the 20% peracid) quenched it for at least 100 minutes (as evidenced by the isothermal condition and the slope decreasing to zero showing complete arrest sustained for 100 minutes (shown as 600 minutes in the graph)).

EXAMPLE 4

In various applications it is desired to provide a combination of stabilizers to quench a reaction, such as both HEDP and DPA. In field applications of use a combination of stabilizers is preferred including a range of about 1:3 to 3:1, and preferably a 1:1 combination (or 50/50 mixture). As the dipicolinic acid is a powder of only several percent solubility in water in order to maximize solubility a mixture of the sodium or potassium salts of HEDP and dipicolinic acid is a preferred embodiment. Testing was conducted using the stabilizer IV shown in Table 2 and according to the conditions of Table 3.

TABLE 2

Stabilizer components	I	II	III	IV
DPA (100%)	100			9
HEDP (60%)		100	17	9
NaOH (100%)			9	8
Water			74	84
Physical form	Solid	Liquid	Liquid	Liquid

Table 2 shows additional blends of stabilizer components that can be employed as described herein. The examples of stabilizers that could be provided as solids or liquids show exemplary single stabilizer formulations to dose to a runaway reaction as well as combination stabilizers. In some exemplary embodiments, the NaOH is added to neutralize the acidic HEDP protons and DPA protons. Conversion of the acids to the sodium salts via NaOH, provides enhanced water solubility especially for the combination of the two agents which have been previously shown to act synergistically towards stabilizing peracids.

TABLE 3

Sample	Mass, g	Mass, g	ppm	Mass of Peracid, g	Quench		
	FeCl ₃ *6H ₂ O	Total FeCl ₃ ,	Total FeCl ₃ in peracid	Peroxyacetic Acid (25% peracid/12% H ₂ O ₂)	Stabilizer	Mass, g	wt% ratio Stabilizer
A	0.5	0.3	3000	100	IV	10	10 wt%
B	0.5	0.3	3000	100	IV	20	20 wt%
C	0.5	0.3	3000	100	IV	20	20 wt%
D	0.5	0.3	3000	100	IV	40	40 wt%

Additional testing following the methods of Example 1 were conducted using a more concentrated peracid composition. In Example 1 a 5% peroxyacetic acid composition was evaluated and, in this testing, a 25% peroxyacetic acid composition with 11% hydrogen peroxide equilibrium mixture was evaluated. This condition represents a more potent chemistry for potential of a runaway reaction. In this reaction the preferred 50/50

blend of stabilizers was not as successful as the first example with the more dilute peroxyacid composition. This can be seen in FIG. 8 where the inflection in the curves around 50°C when the stabilizers were added to quench the reactions, but they continued boiling off the chemistry at ~100°C (at least of A-D in FIG. 8). The addition of the stabilizers show a significant slowing down of the reaction.

However, as mentioned in Example 1, this is not indicative of non-laboratory or actual use of the chemistries where there is not such excessive contamination of the systems and there is a much longer timeline (*e.g.* 2-3 days as opposed to minutes/hours) of the runaway reactions. The multiple evaluations confirm that the use of the systems and methods described herein are more readily quenched in the field than in the accelerated and exaggerated laboratory conditions using the much higher contaminant levels to induce the runaway reactions on a smaller scale (*i.e.* flask).

EXAMPLE 5

A runaway reaction was observed to analyze the rate of temperature increase during the runaway reaction as measured in Table 4 and depicted in FIG. 9.

TABLE 4

dTemp/dTime (rate of temp climb)					
Time (min)	Temp (°C)	(°C/20min)	(°C/hour)	(°C/2hour)	(°C/3hour)
20	49.4	0.4			
40	49.9	0.5			
60	50.2	0.3	1.2		
80	50.6	0.4			
100	51	0.4			
120	51.4	0.4	1.2	2.4	
140	51.7	0.3			
160	52.1	0.4			
180	52.4	0.3	1		3.4
200	52.9	0.5			
220	53.2	0.3			
240	53.6	0.4	1.2	2.2	
260	54.1	0.5			
280	54.4	0.3			
300	54.9	0.5	1.3		
320	55.3	0.4			

340	55.7	0.4			
360	56.2	0.5	1.3	2.6	3.8
380	56.6	0.4			
400	57	0.4			
420	57.5	0.5	1.3		
440	58	0.5			
460	58.5	0.5			
480	59	0.5	1.5	2.8	

In some embodiments, a change in $dTemp/dTime$ measured in regular intervals (*i.e.* 20 minutes), can be monitored or processed, such as described in Example 3 with successive 20-minute intervals showing an increased rate value in order to trigger a quenching process. Since early intervention is critical, measuring $dTemp/dTime$ is an efficient way to process data in an objective manner. As one skilled in the art could ascertain from the disclosure herein, a mildly contaminated system could have single measurements that could be interpreted as false indications of a runaway reaction. As shown with this data by the time 3 successive rate increases are measured the system is excessively hot and may not be quenchable. In this case if rate increases are measured in larger intervals such as 1 hour, 2 hour or 3 hours it allows some overcoming of the natural noise in the data, but not until one uses the 2-hour intervals are 3 successive rate increases found and by this time the system temperature is a 60°C.

Therefore, this study shows that an effective and efficient approach is to use all of the temp vs time data points to define a 2nd order polynomial or higher and assuming over 98% correlation a second derivative can be calculated, and one arrives at a very objective (*i.e.* yes or no) determination of a runaway reaction. If the second derivative is positive, there is a runaway reaction and requires quenching. Beneficially there is no need to lose critical hours before the intervention is triggered. A final safeguard is to use a simple maximum system temperature that can be predetermined, such as 60°C.

It is to be understood that while the invention has been described in conjunction with the detailed description thereof, the foregoing description is intended to illustrate, and not limit the scope of the invention, which is defined by the scope of the appended claims. Other embodiments, advantages, and modifications are within the scope of the following

claims. In addition, the contents of all patent publications discussed supra are incorporated in their entirety by this reference.

The features disclosed in the foregoing description, or the following claims, or the accompanying drawings, expressed in their specific forms or in terms of a means for
5 performing the disclosed function, or a method or process for attaining the disclosed result, as appropriate, may, separately, or in any combination of such features, be utilized for realizing the invention in diverse forms thereof.

What is claimed is:

1. A system for quenching peroxide or peroxy-carboxylic acid runaway reactions comprising:
 - 5 (a) a first tank storing a peroxide composition, peroxy-carboxylic acid composition or a peroxy-carboxylic acid-forming composition; and either (b) or (c)-(f),
 - (b) a vessel storing a stabilizer within the first tank, wherein the vessel is at least partially made of a material that will melt at a predetermined temperature, and wherein the predetermined temperature is indicative of a runaway reaction in need of the
 - 10 stabilizer to quench the reaction;
 - (c) a second tank storing a stabilizer;
 - (d) at least one temperature probe housed in the first tank;
 - (e) a dispense module that dispenses the stabilizer from the first tank into the second tank; and
 - 15 (f) a programmable controller for controlling the operation of the system to quench the runaway reactions in response to determining that the temperature measured by the temperature probe has reached (i) a first predetermined temperature, (ii) a predetermined increase in rate of temperature increase as a function of time, or (iii) a change in temperature of greater than about 25°F (13.8°C) over ambient
 - 20 temperature.
2. The system of claim 1, comprising more than one temperature probes in the first tank.
3. The system of any one of claims 1-2, wherein the temperature probe(s) are coated with
- 25 a material that does not introduce contaminants into the system.
4. The system of any one of claims 1-3, further comprising a pump configured to pump the stabilizer into the first tank.
- 30 5. The system of any one of claims 1-4, wherein the stabilizer is phosphoric acid or salt thereof, pyrophosphoric acid or salt thereof, phosphonic acid or salt thereof, a pyridine carboxylic acid or a salt or derivative thereof, or combinations thereof.

6. The system of claim 5, wherein the stabilizer comprises 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP) or a salt thereof.
- 5 7. The system of claim 5, wherein the stabilizer comprises 2,6-pyridinedicarboxylic acid.
8. The system of any one of claims 1-7, wherein the first tank is a bulk storage tank, container, tote and/or drum of a peroxy-carboxylic acid composition.
- 10 9. A method of quenching a runaway reaction of a peroxide or peroxy-carboxylic acid composition comprising:
detecting (i) an increase in temperature or (ii) a predetermined increase in rate of
temperature increase as a function of time, in a first tank, wherein the first tank
contains a peroxide composition, a peroxy-carboxylic acid composition or mixing a
15 peroxy-carboxylic acid-forming composition;
dispensing a stabilizer into the first tank, wherein the stabilizer is housed in either a second
tank or a vessel within the first tank; and
quenching the runaway reaction,
wherein the increase in temperature is at least about 25°F (13.8°C) above ambient
20 temperature or a first predetermined temperature by a temperature probe housed in
a first tank, or
wherein the increase in temperature to the predetermined temperature melts at least a
portion of the vessel housing the stabilizer to dispense the stabilizer into the tank.
- 25 10. The method of claim 9, wherein the first predetermined temperature is greater than
45°C.
11. The method of any one of claims 9-10, wherein the stabilizer is added within about 15
seconds of the temperature probe measuring the change in temperature indicating a
30 runaway reaction or the melting of the vessel (or portion thereof) housing the stabilizer.
12. The method of any one of claims 9-11, wherein the stabilizer is phosphoric acid or salt

thereof, pyrophosphoric acid or salt thereof, phosphonic acid or salt thereof, a pyridine carboxylic acid or a salt or derivative thereof, or combinations thereof.

13. The method of claim 12, wherein the stabilizer comprises 1-hydroxyethylidene-1,1-
5 diphosphonic acid (HEDP) or a salt thereof.

14. The method of claim 12, wherein the stabilizer comprises 2,6-pyridinedicarboxylic acid.

10 15. The method of any one of claims 9-14, wherein the stabilizer further includes an alkali metal hydroxide to neutralize protons of the stabilizers.

16. The method of any one of claims 9-15, wherein the stabilizer is a liquid, solid, or a powder.

15

17. The method of any one of claims 9-16, wherein the stabilizer is dosed at a rate of at least about 2 wt-% based on the weight of the peroxy-carboxylic acid composition or peroxy-carboxylic acid-forming composition in the tank.

20 18. The method of claim 17, wherein the stabilizer is dosed at a rate of about 2.5 wt-% to about 10 wt-% based on the weight of the peroxy-carboxylic acid composition or peroxy-carboxylic acid-forming composition in the tank.

25 19. The method of any one of claims 9-18, wherein the peroxy-carboxylic acid composition or peroxy-carboxylic acid-forming composition is salvaged after the quenching with the stabilizer and can be reused instead of disposed.

30

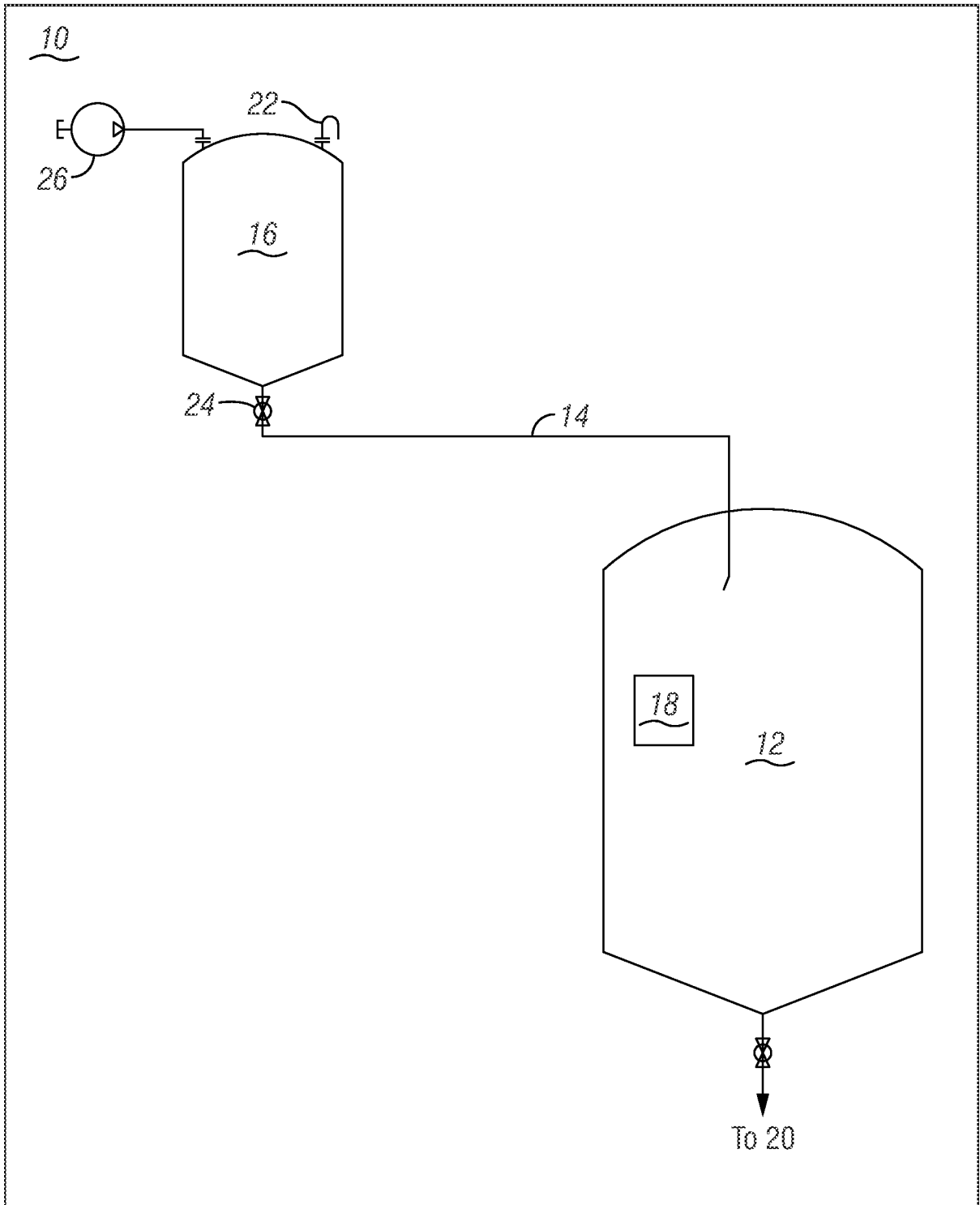


FIG. 1

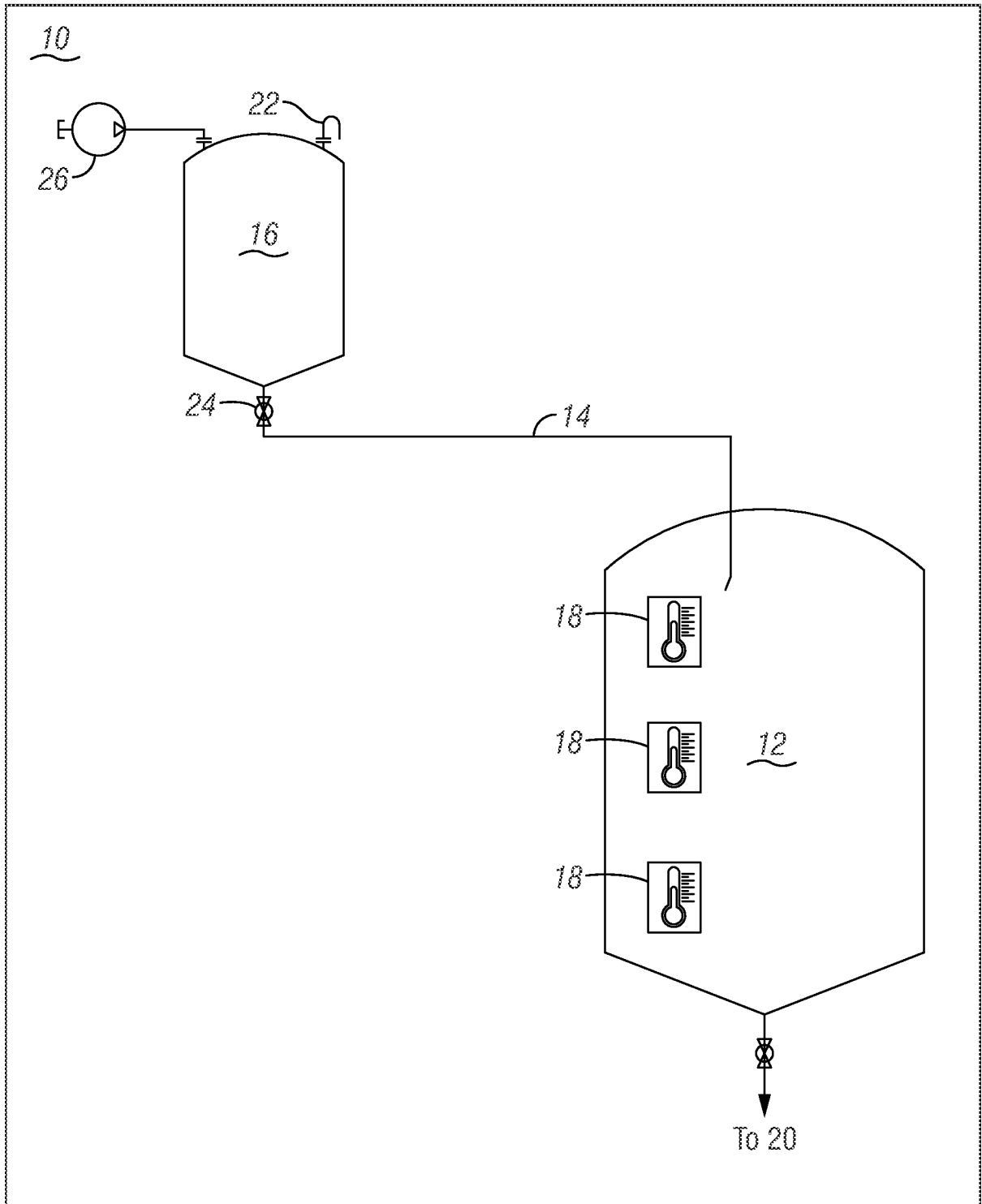


FIG. 2

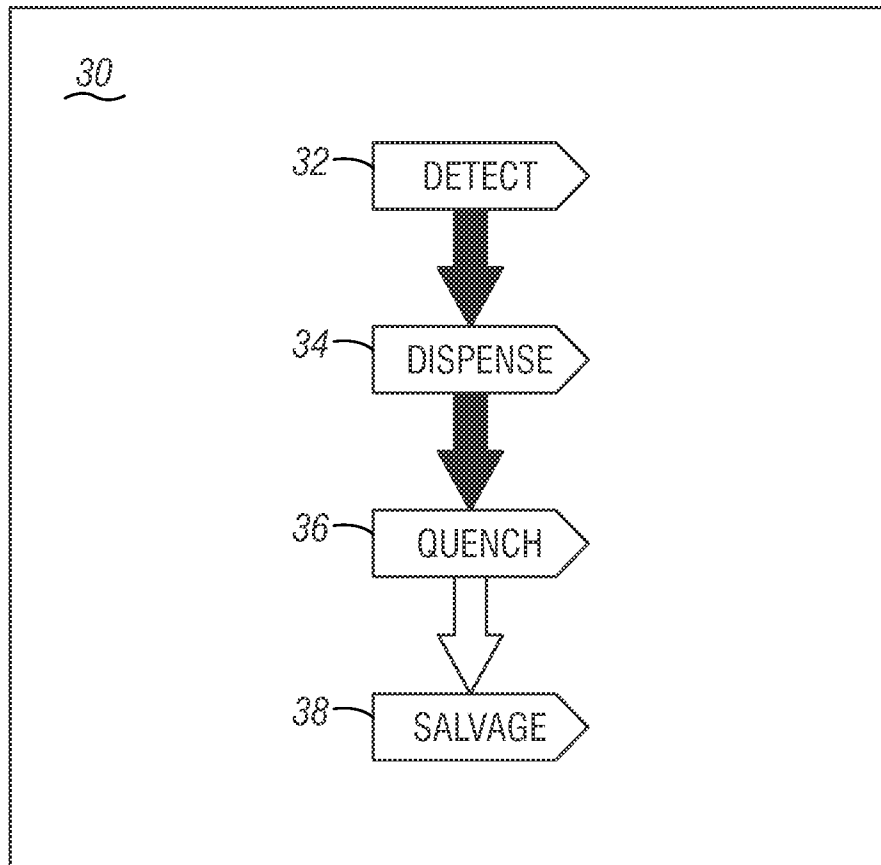


FIG. 3

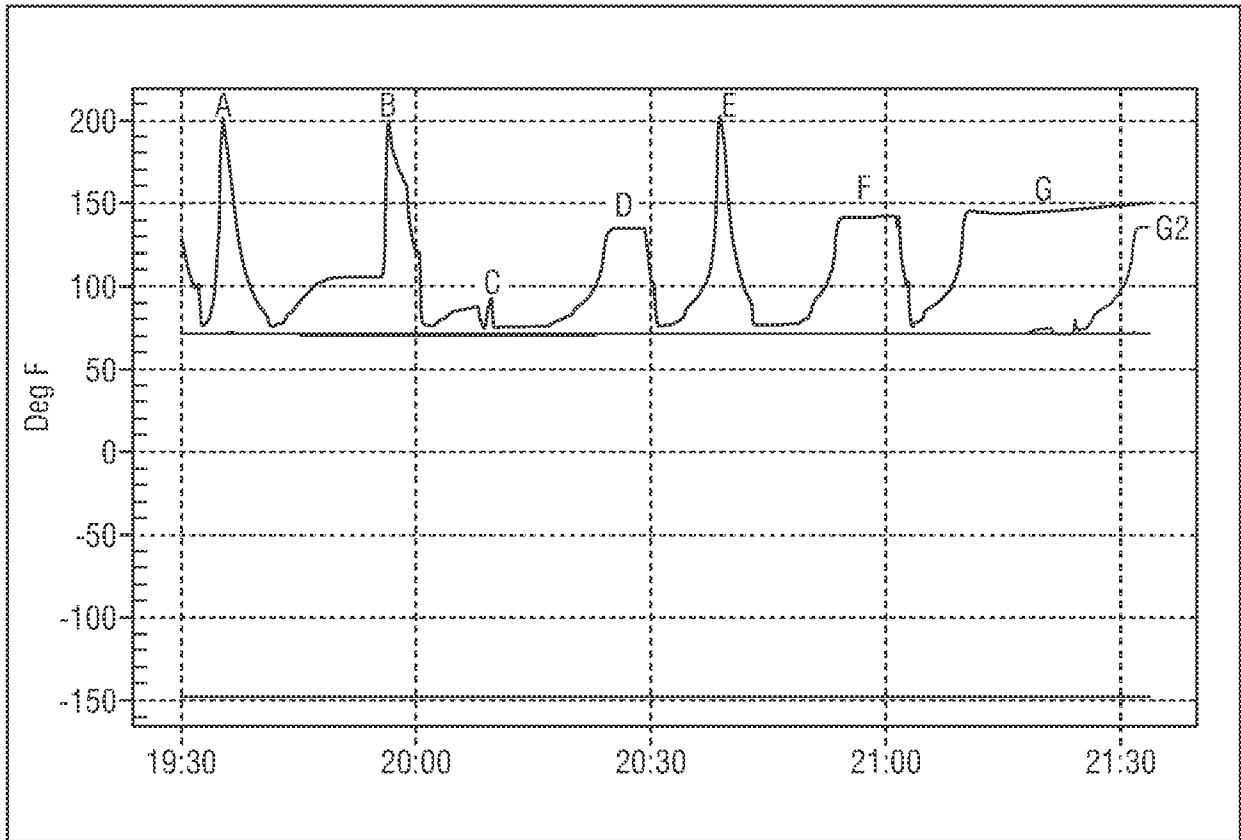


FIG. 4

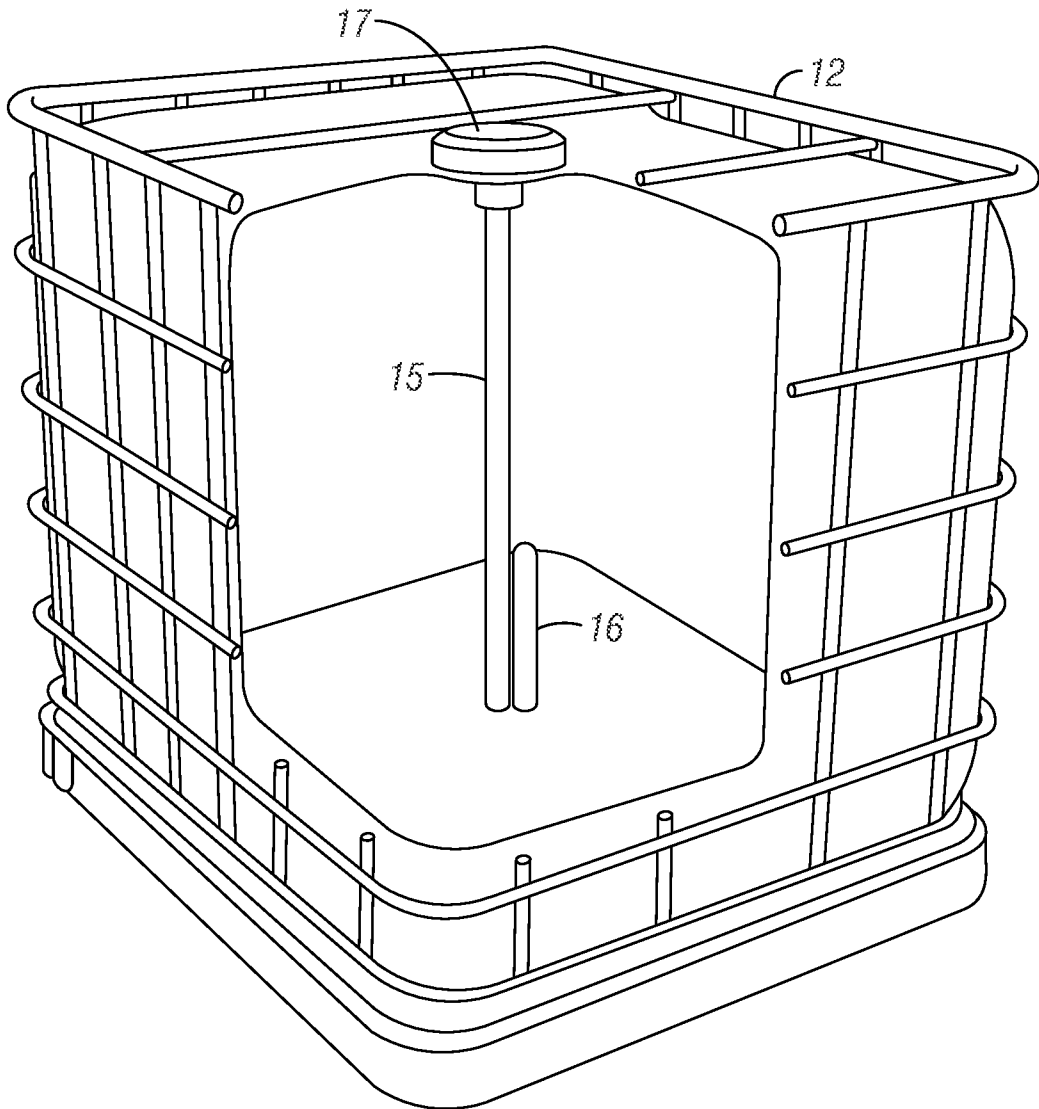


FIG. 5

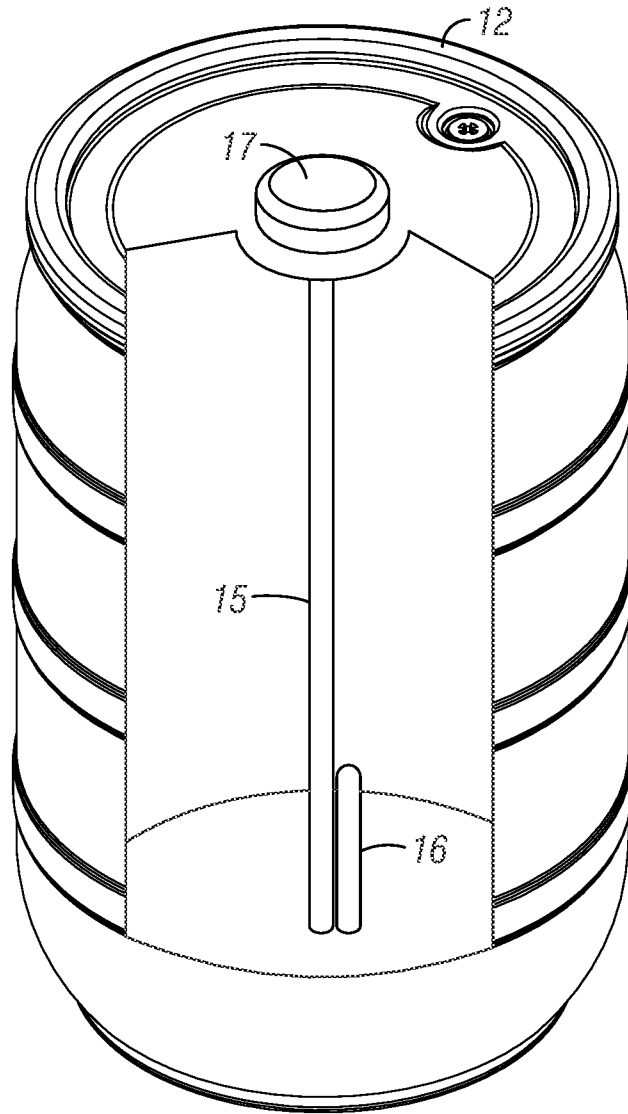


FIG. 6

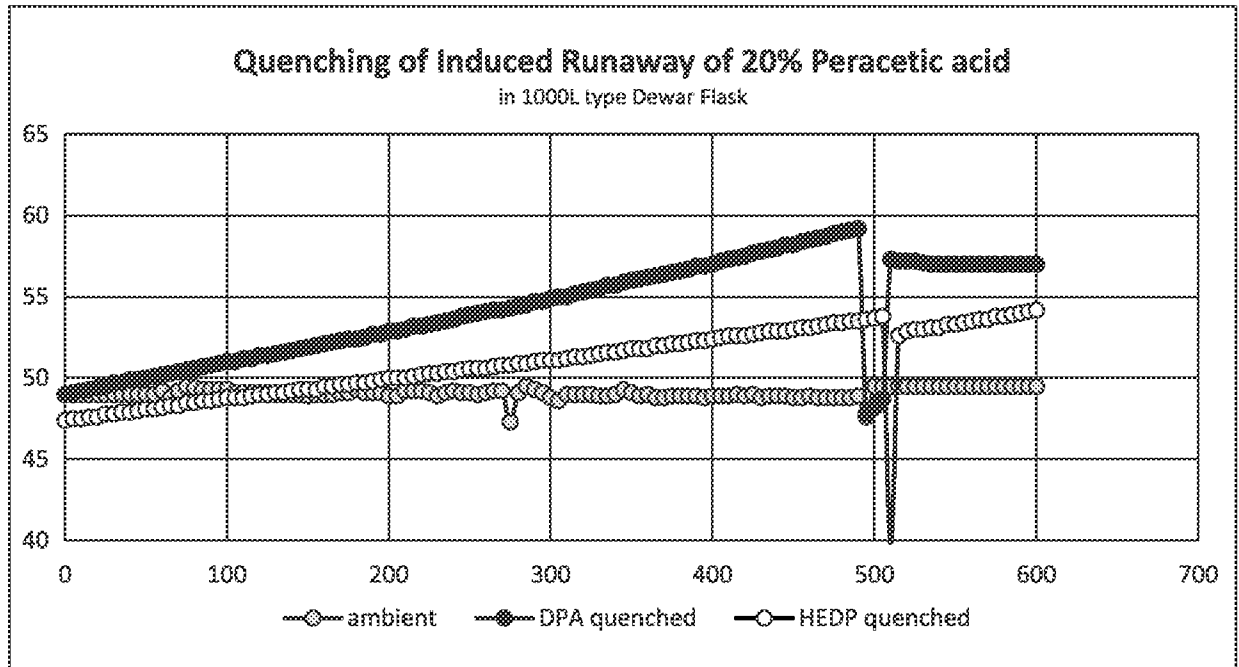


FIG. 7

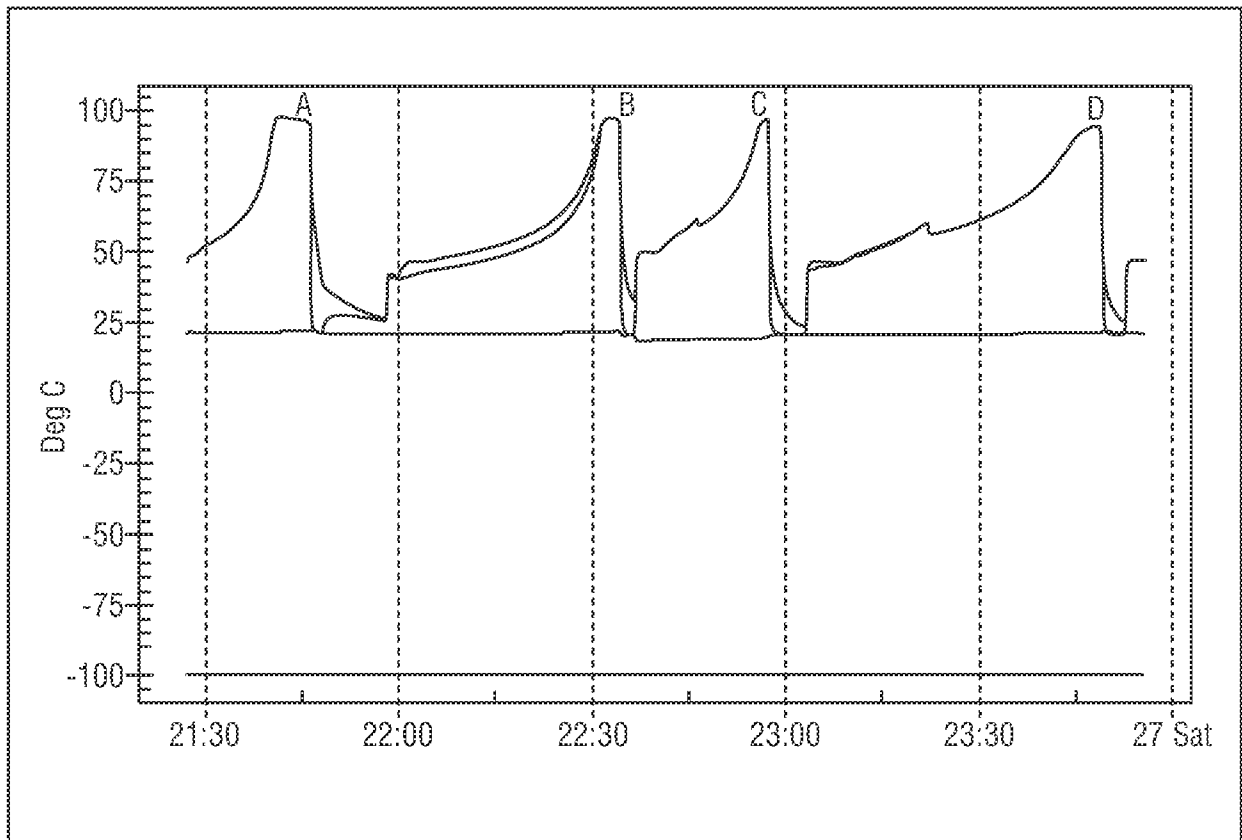


FIG. 8

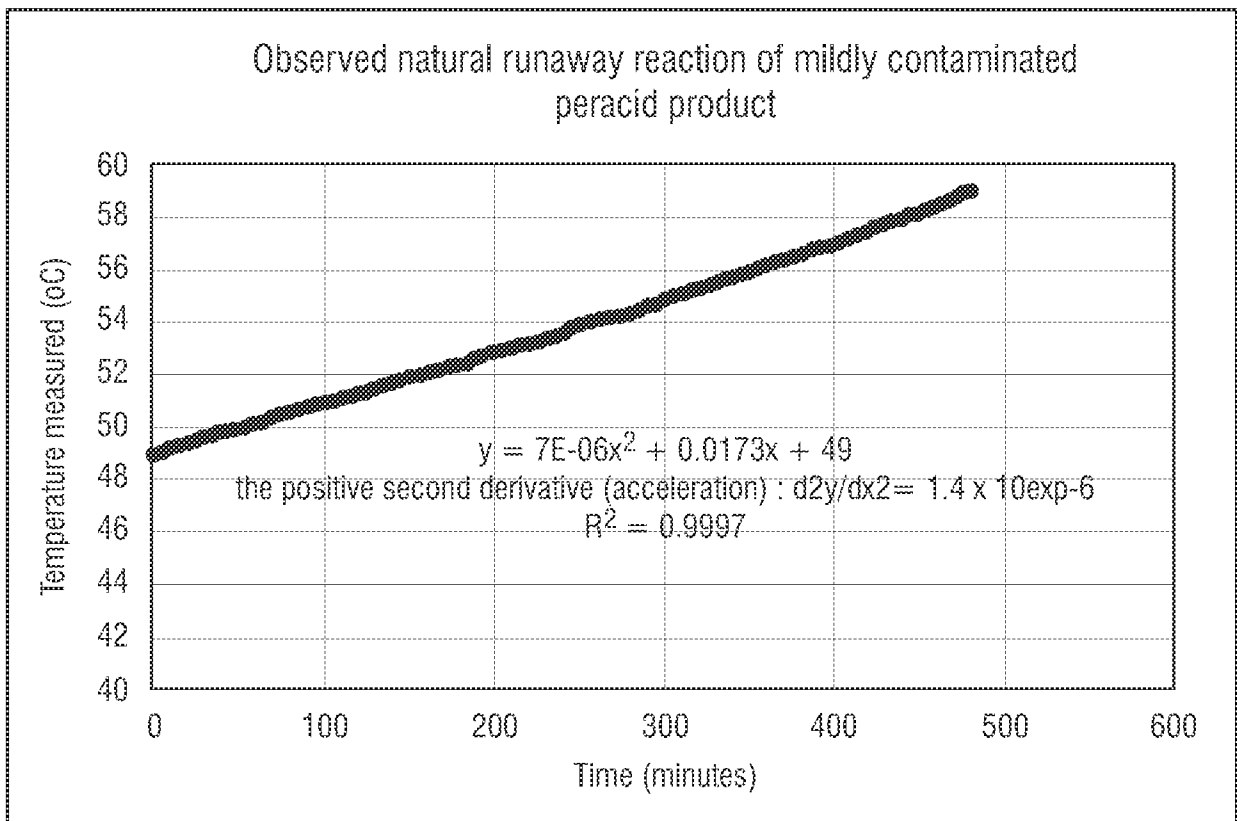


FIG. 9

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2021/025030

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C407/00 C07C409/26
ADD.
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)
C07C
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)
EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2014/256811 A1 (LI JUNZHONG [US] ET AL) 11 September 2014 (2014-09-11) paragraph [0042]; examples 1-4 -----	1-19
A	WO 94/20600 A1 (UNILEVER PLC [GB]; UNILEVER NV [NL]) 15 September 1994 (1994-09-15) page 3, lines 1-9; examples 1-6 -----	1-19

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
- "E" earlier application or patent but published on or after the international filing date
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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

- "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
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- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search 30 June 2021	Date of mailing of the international search report 08/07/2021
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Matés Valdivielso, J

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2021/025030

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