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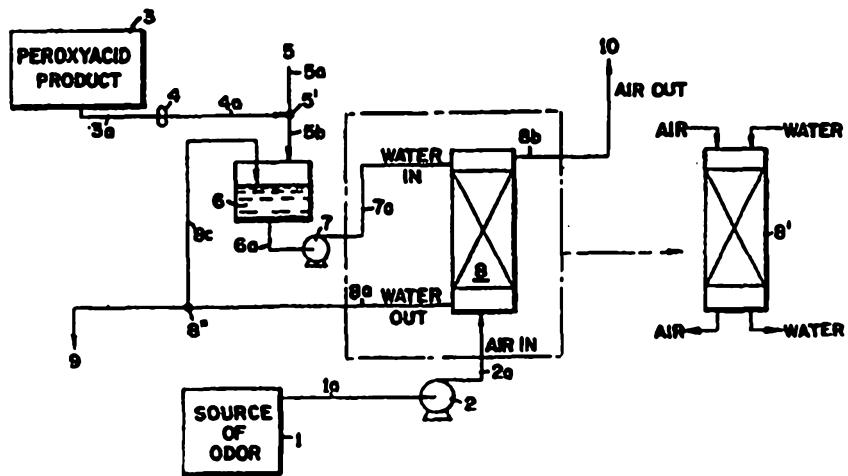
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(54) Title: PEROXYACID COMPOUND USE IN ODOR REDUCTION



(57) Abstract

Disclosed is a process for the treatment of a plant fluid effluent containing odor compounds including an alkyl mercaptan or an alkyl thiol, an amine compound, ammonia, hydrogen sulfide and mixtures thereof by contacting the plant effluent in either a counterflow or cocurrent flow process. In the process, the effluent is contacted with an aqueous solution comprising a peracid compound and optionally an essential oil. When contacted with the peracid, odor compounds in the effluent are oxidized and converted from the gaseous phase into a chemically modified highly aqueous soluble phase in the aqueous treatment. In this way, odor removal from the gas is preferred and odor compounds are efficiently transferred into the aqueous treatment solution. The use of such a process produces a significant improvement in odor quality index as measured by a conventional process using an expert panel when compared to conventional treatment methods.

PEROXYACID COMPOUND USE IN ODOR REDUCTION

Field of the Invention

The invention relates to the use of peroxyacid compounds in odor reduction.

5 The invention relates to removing odor compounds from the atmosphere or from volumes of gas arising from the processing of organic materials. The processing can occur in large processing plants or in small loci such as kitchens or doctors offices. More specifically, the invention relates to an odor reduction process using liquid/atmospheric or liquid/liquid processing to treat gaseous or other effluent

10 containing odor compounds. The odor can comprise organic and inorganic compounds including organic sulfur compounds, organic nitrogen compounds, organic oxo-compounds, ammonia, hydrogen sulfide, etc. and mixtures thereof.

Background of the Invention

15 Industrial plants, agricultural installations, hospitals, kitchens, etc. that handle large quantities of organic material such as hog farms, dairy farms, chicken farms, meat packing plants, animal rendering plants, composting plants, paper mills, sewage treatment plants and other similar installations can generate large quantities of odors that typically exit the facility in an odor contaminated atmospheric effluent

20 flume or other effluents. Such an effluent can contain a large variety of odoriferous or odor causing inorganic and organic chemicals or molecules including organic sulfides or organic thiols (mercaptans), monoamines, diamines, triamines, ammonia, alcohols, formaldehyde, acetaldehyde, carboxylic acids, skatole, carbon disulfide and hydrogen sulfide and other odor forming oxidizable compounds. An atmospheric effluent having one or more of such compounds can have a strong odor and can be highly objectionable within the plant to plant personnel and outside the plant to plant neighbors.

25 An odor is a gas phase emission that produces an olfactory stimulus. The odor thresholds of many chemicals that act as odor compositions common throughout the chemical process industries include, for example, ethyl sulfide having an odor threshold in the atmosphere of 0.25 parts per billion (ppb), hydrogen sulfide with an odor threshold of 0.4 ppb, dimethyl sulfide with an odor threshold of 1.0



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ppb, ethyl mercaptan with an odor threshold of 1.0 ppb, methyl mercaptan with an odor threshold of 1.1 ppb. With a low threshold a small amount of these and similar odors common in plant effluent are serious olfactory problems. Such odors result from processing large quantities of organic materials and are generated by the action 5 of micro-organisms in any biologically active system on a source of organic material producing the odors. There are many other odor producing chemicals possible, however, as shown in this representative, non-inclusive list:

1. Sulfur compounds

10	Hydrogen Sulfide	Thiophene
	Carbonyl Sulfide	Isobutyl Mercaptan
	Methyl Mercaptan	Diethyl Sulfide
	Ethyl Mercaptan	n-Butyl Mercaptan
	Dimethyl Sulfide	Dimethyl Disulfide
15	Carbon Disulfide	3-Methylthiophene
	Isopropyl Mercaptan	Tetrahydrothiophene
	tert-Butyl Mercaptan	2, 5-Dimethylthiophene
	n-Propyl Mercaptan	2-Ethylthiophene
	Ethyl Methyl Sulfide	Diethyl Disulfide

20

2. Organic nitrogen compounds

25	Primary amines
	secondary amines
	tertiary amines
	pyridines
	amides
	ammonia

3. Organic oxygen compounds (oxo-hydrocarbon compounds)

30	primary alcohols
	carboxylic acids
	aldehydes
	ketone compounds
	phenolics

35

Attempts have been made to reduce the production of the odor compounds and to reduce the release of the odor compounds from plants. Robinson, "Develop a Nose for Odor Control", Chemical Engineering News, October 1993 contains a generic disclosure of odor problems and conventional odor control using aqueous

treatment compositions including H_2O_2 , $FeCl_3$, $KMnO_4$, $NaOH$ and others. Careful control over the organic materials within the plant and reduction of microbial populations within the plant have been attempted to reduce the generation of the odor compounds in the plant atmosphere. Attempts to scrub the odor compounds from the plant atmosphere have been made using a variety of simple absorptive and oxidizing scrubbing materials. Fragrance chemicals that simply mask the offensive odors have been tried. Sodium hydroxide ($NaOH$), activated carbon are useful absorptives. Oxidizing materials such as ozone (O_3), chlorine dioxide (ClO_2), sodium hypochlorite ($NaClO$) and others have been attempted. Some degree of success has been achieved using these oxidative materials to remove organic odor molecules from atmospheric effluents. While chlorine dioxide has had some success, chlorine dioxide is highly toxic, difficult to handle and must be generated on site. Such difficulties lead to substantial resistance to its use. Further hydrogen peroxide is also known for odor control. Hydrogen peroxide by itself is not effective against a broad range of odor constituents without additional treatment materials. However, the application of oxidative technologies including ozone, hydrogen peroxide, chlorine dioxide and other oxidants have had some limited success.

The use of peroxyacid materials in microbiological methods are also known. For example, Grosse-Bowing et al., U.S. Patent Nos. 4,051,058 and 4,051,059 disclose peracetic containing antimicrobial compositions. Stas et al., U.S. Patent Nos. 4,443,342 and 4,595,577 disclose the treatment of waste water and waste gases containing dialkyldisulfides by metal catalytic oxidation of these compounds by means of a peroxide compound in an aqueous medium. Lokkesmoe, U.S. Patent No. 5,409,713 teaches peracetic materials as microorganism sanitizers or growth inhibitors in aqueous transport systems typically containing produce and large amounts of challenged soil load.

Fraser, in "Peroxygens in environmental protection", Effluent and Water Treatment Journal, June 1986 disclose that hydrogen peroxide (H_2O_2) can be used to reduce odor. Fraser only discusses microbial control with peracetic acid and does not correlate odor control to peroxyacid treatment or concentration. Littlejohn et al., "Removal of NO_x and SO_2 from Flue Gas by Peracid Solutions", Ind. Eng. Chem.



Res. Vol. 29, No. 7, pp. 1420-1424 (1990) disclose peroxyacids in removing nitric oxides and sulfur dioxide from coal fire derived flue gas.

Peracetic acid, neat and in aqueous solutions containing peracetic acid has a strong pungent oxidizing odour resembling but stronger than acetic acid. Such materials have not been seriously considered as odour reducing materials because of the nature of its odour. The concern being that in any treatment process using a significant amount of peracetic acid, the resulting treated effluent would inherently obtain the pungent odour of the peracetic acid. Further, peracetic acid solution inherently contain large amounts of acetic acid (HOAc).

Brief Discussion of the Invention

The invention involves a process for removing odour compounds from an atmospheric plant fluid effluent. In the process of the invention, the plant atmosphere or other effluent is contacted with an aqueous treatment solution containing a controlled amount of peroxyacid. Sufficient peracid is used to control odour but not contribute a peroxy acid or acid smell to the treated effluent. The process is typically conducted in a batch or continuous treatment mechanism such as a falling film contactor, a wet scrubber or venturi mechanism. A fluid effluent includes both a liquid and a gaseous effluent.

The invention also involves an improved process for removing odour compounds from an atmospheric plant fluid effluent. In the process of the invention, the plant atmosphere or other effluent is contacted with an atomized, fogged or otherwise finely divided spray of aqueous treatment solution containing a controlled amount of a peroxyacid. Sufficient peroxy acid is used to control odour but not contribute a peroxy acid smell to the treated effluent. The process is typically conducted outside the venturi restriction zone or tower packing chamber, and may be conducted alone or along with other peroxyacid treatments. In a preferred embodiment, however, the process of the invention is viewed as a pretreatment useful alongside other treatment processes.

Thus, in a first embodiment, the invention provides a process for removing an odour from an atmospheric effluent, the process comprising:

(a) contacting an atmospheric effluent comprising an odour component with an aqueous peroxyacid treatment composition, forming an oxidized odour component and dissolving the oxidized odour component in the aqueous treatment composition to form an aqueous treatment composition containing the oxidized odour and an effluent with reduced odour;

(b) removing at least a portion of the aqueous treatment composition containing the oxidized odour; and



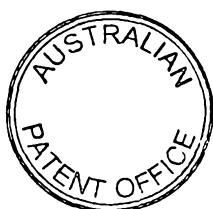
(c) returning the effluent with reduced odour to the atmosphere;
wherein the aqueous peroxyacid treatment composition comprises peroxyacetic acid.

In a preferred form, the process comprises contacting an atmosphere effluent comprising an odour component with a finely divided aqueous peroxy acid treatment composition, forming an oxidized odour component and dissolving the oxidized odour component in the aqueous treatment composition; wherein the finely divided aqueous peroxy acid treatment composition has an average droplet size of 25 to 500 μm .

Thus, in another embodiment, the invention provides a pre-treatment or post-treatment process for removing an odour from an atmospheric effluent, the process comprising contacting an atmospheric effluent comprising an odour component with a finely divided aqueous peroxy acid treatment composition, forming an oxidized odour component and dissolving the oxidized odour component in the aqueous treatment composition to form a treated effluent and returning the treated effluent to another treatment step or to the atmosphere; wherein the finely divided aqueous peroxy acid treatment composition has an average droplet size of 25 to 500 μm ; and wherein the aqueous peroxy acid treatment composition comprises peroxyacetic acid.

The invention is also found in a process for removing an odour from an atmospheric effluent. In this process, the atmospheric effluent comprising an odour component is contacted with an aqueous peroxyacid treatment composition to form an oxidized odour component. The oxidized odour component is dissolved in the aqueous treatment composition to form an aqueous treatment composition containing the oxidized odour and an effluent with reduced odour. At least a portion of the aqueous treatment composition containing the oxidized odour is removed. This process is followed by a subsequent process in which the atmospheric effluent comprising an odour component is contacted with a finely divided aqueous peroxy acid treatment composition, thereby forming an oxidized odour component which is then dissolved in the aqueous treatment composition to form an aqueous treatment composition containing the oxidized odour. At least a portion of the aqueous treatment composition containing the oxidized odour is removed, and the effluent with reduced odour is returned to the atmosphere.

In a further embodiment, the invention involves a pre-treatment or post-treatment process for removing an odour from an atmosphere effluent, the process comprising contacting an atmosphere effluent comprising an odour component with a finely divided aqueous peroxy acid treatment composition comprising at least about 100 ppm of peroxyacetic acid, at least about 100 ppm of hydrogen peroxide and at least about 20 ppm of acetic acid,



forming an oxidized odour component and dissolving the oxidized odour component in the aqueous treatment composition; wherein the finely divided aqueous peroxy acid treatment composition has an average droplet size of 25 to 500 μm ; and wherein the aqueous peroxy acid treatment composition comprises peroxyacetic acid.

5 In another form, the invention involves a process for removing odour compounds from an atmospheric plant fluid effluent. In the process of the invention, the plant atmosphere or other effluent is contacted with an aqueous treatment solution containing a controlled amount of a peroxyacid and one or more fragrant essential oils. Sufficient peroxyacid is used to control odour but not contribute a peroxyacid or acid smell to the treated effluent. The process is typically
10 conducted in a batch or continuous treatment mechanism such as a falling film contactor, a wet scrubber or venturi mechanism. A fluid effluent includes both a liquid and a gaseous effluent.

Thus, in a still further embodiment, the invention provides a process for removing an odour from an atmospheric effluent, the process comprising:

15 (a) contacting an atmospheric effluent comprising an odour component with an aqueous peroxyacid treatment composition and one or more essential oils, forming an oxidized odour

component and dissolving the oxidized odour component in the aqueous treatment composition to form an aqueous treatment composition containing the oxidized odour and an effluent with reduced odour;

20 (b) removing at least a portion of the aqueous treatment composition containing the oxidized odour; and

(c) returning the effluent with reduced odour to the atmosphere; wherein the aqueous peroxyacid treatment composition comprises peroxyacetic acid.

Surprisingly, the peroxyacid is not destroyed by the essential oils at a rate that interferes with oxidative odour reduction. In contrast, chlorine or chlorine dioxide as used in the prior art are incapable of surviving contact with essential oils as they rapidly lose their oxidizing capacity. Using a combination of a peroxyacid and an essential oil, surprisingly, allows the essential oil to behave as both a masking agent and an odour chemical reactant that augments the oxidative capacity of the peroxyacid; especially towards sulfur containing malodorous compounds.

Accordingly, the invention can be found in a process for removing an odour from an atmosphere effluent, the process comprising contacting an atmosphere effluent comprising an odour component with an aqueous peroxyacid treatment composition and one or more essential oils, forming an oxidized odour component



and dissolving the oxidized odor component or an odor component in the aqueous treatment composition to form a used treatment; and removing at least a portion of the used treatment.

5

Brief Discussion of the Drawings

Figure 1a shows a block diagram of an odor reduction scheme as previously described, including a source of oxidant, a source of odor and effluent, a cocurrent scrubber apparatus or a counter current scrubber apparatus, the aqueous treatment and the resulting waste aqueous stream.

10

Figure 1b shows in greater detail a small portion of figure 1a, showing how the fogging pretreatment of the invention can be incorporated into the greater odor reduction scheme seen in figure 1a.

Figure 2a shows a venturi used as a means to contact the odor laden atmosphere or liquid effluent with the aqueous peroxyacid composition.

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Figure 2b shows in greater detail a small portion of figure 2a, showing how the fogging pretreatment of the invention can be incorporated into the greater odor reduction scheme seen in figure 2a.

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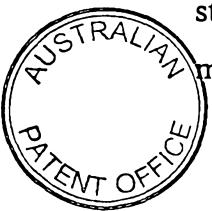
Figure 3 is a graphical comparison of the oxidant survival rate in the invention treatment method of using peroxyacids co-injected with essential oils versus previously used oxidative systems.

Detailed Discussion of the Invention

In the treatment of gaseous effluent, when a gaseous atmospheric effluent gas phase contacts the finely divided aqueous treatment phase, oxidizable odor molecules from the gas phase react with the oxidizing peracetic acid material in the aqueous treatment, are chemically converted into freely soluble compounds and is scrubbed from the gas phase. Specifically, the gas molecules contact a liquid droplet, the odor causing compounds transfer from the gas phase into the liquid phase and are then reacted with the peracetic acid to form water soluble, low volatile compounds. Other soluble components of the gas phase simply are solubilized in the acidic aqueous phase. The resulting atmospheric effluent has a substantially reduced concentration of odor compound or composition and has a less objectionable odor.

level. For the purpose of this application, the term "active oxygen", active species" and "active ingredients" are substantially synonymous and refer to the total concentration of peroxide, peroxyacid or other available oxidizing species in a treatment that can oxidize the odor molecules or components. The term "atmosphere effluent" relates to any gaseous stream emanating from an industrial plant, agricultural facility, hospital, institutional kitchen, doctors office, household kitchen, etc. processing organic materials that result in the release of odor molecules into the atmosphere effluent. The atmosphere effluent can contain a large variety of odoriferous or odor causing chemicals or molecules including oxo-hydrocarbons, 5 organo sulfides or organic thiols (mercaptans), monoamines, diamines, triamines, ammonia, alcohols, phenolics, formaldehyde, acetaldehyde, skatole, carbon disulfide and hydrogen sulfide and other odor forming oxidizable organic compounds. Such 10 atmosphere effluent typically is released in a flume that moves with the atmosphere and slowly mixes into the atmosphere, becomes diluted and dispersed 15 into the environment. Further, not only does the peroxyacid (such as peracetic acid) material result in the oxidation of odor components into freely soluble materials that remain in the aqueous phase, we have found that the use of such an acidic material results in the absorption of organic bases such as ammonia and amines resulting in the effective scrubbing of these compounds from the atmospheric effluent material. 20 In large part the process is designed to favor the mass transfer of odor compounds into the aqueous treatment.

The process of the invention uses absorption, more specifically a gas/liquid absorption, a liquid/liquid absorption or solid particulate/liquid absorption, during and after an oxidative reaction to separate odor components from a fluid effluent. 25 Both odor and particulate materials can be absorbed by the oxidizing liquid stream. In the process, absorption is driven by the solubility of the odor compounds, and oxidized odor materials, in the aqueous phase. At the same time, a chemical reaction between an aqueous stream and a gas stream results in washing or scrubbing oxidized odor compounds or compositions from the effluent with the liquid 30 composition. As a result of the chemical reaction between the odor molecules in the stream and the treatment liquid, one or more of the oxidized constituents of the gas mixture will preferentially dissolve in the liquid and can thus be efficiently removed.



In treatment of gaseous odor, the gas constituent reacts with the oxidant to form a highly water soluble material which forms a physical solution in the liquid and is removed from the gas stream.

Such a gas absorption is preferably carried out in a device where intimate contact between a gas phase and a finely divided liquid phase or a finely divided gas phase and a liquid phase is obtained. Such devices, including sparged and agitated vessels and the various types of tray towers, can contact a gas phase with a liquid and can disperse the gas phase into bubbles or foams. Tray towers are typically the most important of these since countercurrent multistage contact and other contacting can be obtained. The gas can be contacted in the form of a finely divided or small bubble into a bulk liquid in a sparged vessel (bubble column). Finely divided gas or atmospheric bubbles can be dispersed into a mechanically agitated vessel in which the liquid contents are agitated to ensure close contact with the finely divided bubbles and the liquid. Multistage absorption can be obtained using multistage tray towers using a variety of towers, baffles, barriers, downspouts and other mechanical means to ensure close contact between the gas phase and the liquid phase. Venturi scrubbers can be used along with wetted-wall towers, spray towers and spray chambers, packed towers, and any other countercurrent or cocurrent apparatus that can ensure close contact between the atmospheric or odor containing gas phase and the liquid treatment. The process can be run either continuous or in semibatch or batch mode. During the process, the accumulated treatment composition containing a substantial quantity of the odor compounds and the oxidized odor compounds are removed from the process equipment and directed to typically on-site treatment or municipal sewage treatment plants. In smaller applications, or liquid/liquid applications a venturi system is preferred while in larger applications, a countercurrent scrubber towers can be preferred.

In a countercurrent column, the oxidative treatment solution is fed in the top of the absorber and the effluent or gas mixture enters from the bottom. The odor components of the gas reacts with and dissolves in the liquid treatment composition. The aqueous treatment composition containing the oxidized odor generating substances is removed from the bottom of the column. Conversely, in a cocurrent column both streams enter the column at one end and depart at the opposite end. In

either case, the resulting treatment solution containing the scrubbed materials is then treated in an industrial, agricultural or municipal waste water treatment facility.

The vertical absorber may be a packed column operating either countercurrently or cocurrently, plate column operating either countercurrently or 5 cocurrently, a falling film contactor or a simple spray absorption column operating cocurrently. Preferred packed columns can be shell filled with packing material designed to disperse the liquid and bring the liquid in finely divided form in close contact with the rising effluent stream. Packed columns offer simple and cheap construction and are preferred for complex or corrosive gases because packed 10 columns can be made from ceramics or other non reactive packings. In plate towers, liquid flows from plate to plate in a cascade fashion while the effluent gas bubbles through the flowing liquid within each plate through a multitude of dispersing means or through the cascade of liquid as in a shower deck tray. These absorbers are used where tall columns are required. The fundamental physical principles underlying the 15 absorption of the odor molecules from the plant atmosphere effluent in a gas absorption reaction mode relates to the solubility of the reaction product between the peroxyacid (preferably peracetic acid) oxidant liquid phase and the gas molecules. The rate of mass transfer is high (odor removal is efficient) because the reaction 20 product, between the odor molecules and the organic peracid oxidant, comprises molecules such as sulfate, alcohol, aldehyde, carboxylic acid and salts, ammonium ion (NH_4^+), protonated amines and other similar species which are highly soluble in water solutions particularly at acid pH. Since these oxidized and other non-oxidized materials are highly soluble in the aqueous treatment solutions, mass transfer principles tend to favor the dissolution of such materials in the aqueous treatment 25 composition and result in highly efficient odor molecule scrubbing. The treatment compositions of the invention are adapted for use in commonly available scrubber systems. Such systems can be obtained from a variety of manufacturers including EST Corp., D.R. Technology, Inc., PEPCO and VIATEC. In smaller applications, a venturi contactor may be preferred.

30 The invention is also concerned with a process whereby a finely divided or fogged peroxy acid composition is used to augment an odor reduction process. It has been found that a fogged peroxy acid composition is highly effective at odor

reduction. Preferred average droplet size ranges from 25 to 500 μm (10^{-6}m) in diameter, with a more preferred size range of 30 to 100 μm and a most preferred range of 30 to 60 μm . By contrast, conventional treatments utilize spray droplets which range from 1000 to 100,000 μm . Without being limited by theory, it is
5 believed that the augmented effectiveness is due to the vastly greater droplet surface area, which results in a greatly expanded level of contact surface between the peroxy acid droplets and the odor causing compounds. This makes it possible to greatly reduce the volume of aqueous peroxy acid solution used. While treatments utilizing larger droplets use an aqueous flow rate of about 9 to 100 gallons per minute (35 to
10 380 liters per minute), the use of smaller droplets permit effective odor control at use flow rates of about 0.1 to 3 gallons per minute (0.4 to 11 liters per minute).

There are a number of different ways to form the droplets of the desired size. Most atomizers can be categorized into one of three common categories: pressure nozzles, two-fluid nozzles and rotary devices. These devices are available
15 commercially from Spraying Systems Company. The degree of atomization is determined by the fluid and or gas pressure along with the spray head bore size and design. The specified droplet size can be determined from commercial correlation charts which are available from suppliers. Preferably, an air injected atomizing nozzle is used. This type produces a much smaller droplet size in the range of 20 to
20 40 μm .

The process described above is preferably used as a pretreatment, alongside additional peroxy acid composition treatments. These additional treatments are preferably carried out in a device where intimate contact between a gas phase and a finely divided liquid phase or a finely divided gas phase and a liquid phase is
25 obtained. Such devices, including sparged and agitated vessels and the various types of tray towers, can contact a gas phase with a liquid and can disperse the gas phase into bubbles or foams. Tray towers are typically the most important of these since countercurrent multistage contact and other contacting can be obtained. The gas can be contacted in the form of a finely divided or small bubble into a bulk liquid in a sparged vessel (bubble column). Finely divided gas or atmospheric bubbles can be dispersed into a mechanically agitated vessel in which the liquid contents are
30 agitated to ensure close contact with the finely divided bubbles and the liquid.

Multistage absorption can be obtained using multistage tray towers using a variety of towers, baffles, barriers, downspouts and other mechanical means to ensure close contact between the gas phase and the liquid phase. Venturi scrubbers can be used along with wetted-wall towers, spray towers and spray chambers, packed towers, 5 and any other countercurrent or cocurrent apparatus that can ensure close contact between the atmospheric or odor containing gas phase and the liquid treatment. The process can be run either continuous or in semibatch or batch mode. During the process, the accumulated treatment composition containing a substantial quantity of the odor compounds and the oxidized odor compounds are removed from the 10 process equipment and directed to typically on-site treatment or municipal sewage treatment plants. In smaller applications, or liquid/liquid applications a venturi system is preferred while in larger applications, a countercurrent scrubber towers can be preferred.

The aqueous treatment compositions of the invention can be introduced into 15 the wet scrubber in the form of a simple aqueous stream, an agitated stream, or a spray having an effective concentration of a peroxyacid treatment composition. The treatment compositions of the invention comprise a peroxyacid, preferably peracetic acid having the formula $\text{CH}_3\text{CO}_3\text{H}$. The peracetic acid is an unstable composition that is typically made by the direct acid catalyzed equilibrium oxidation reaction 20 between 5 to 98 wt % hydrogen peroxide in contact with the liquid carboxylic acid, typically acetic acid or by auto-oxidation of aldehydes, acid chlorides, carboxylic anhydrides with hydrogen peroxide or other peroxy oxidizing compositions.

In treating liquid effluents, a batch or continuous treatment can be used. In 25 batchwise treatment the effluent can be treated in large stirred tanks. In continuous treatment, the effluent can be treated by a continuous stream of peracid that can be added in a pumped or metered treatment. One common metering scheme is to add the treatment using a venturi. In a venturi the passage of the effluent past a venturi causes the treatment to be drawn into the effluent. The ratio of addition can be controlled by a selected venturi or metering means.

30 Preferably, the process of the invention uses a combination of peracetic acid, hydrogen peroxide and acetic acid. The compositions of the invention contain water, peracetic acid, hydrogen peroxide and acetic acid across a relatively broad

range of concentrations. Peracetic acid is a freely water soluble liquid having a pungent, acrid odor resembling acetic acid, but with a strong oxidizing character. The compositions useful in the process of the invention also comprise a proportion of hydrogen peroxide. Hydrogen peroxide in combination with the peroxyacid, 5 preferably peracetic acid, provides a surprising level of successful odor scrubbing capacity when compared to conventional scrubbers. Hydrogen peroxide apparently provides an effervescent action in the treatment composition that tends to help in providing finely divided aqueous treatment particles that improve oxidation by the peroxyacid and absorption through small particles with large surface area. The 10 concentration of hydrogen peroxide is adjusted with respect to the concentration of acetic acid and water to ensure that the treatment composition contains preferably greater than about 1 ppm, preferably about 1 to 1000 ppm of residual or active peracetic acid in the treatment composition for highly efficient odor molecule scrubbing. The concentration of the active ingredients in the treatment composition 15 can be adjusted using make-up amounts of the concentrate material delivered to the continuously flowing aqueous stream during processing.

The compositions useful in the process of the invention may also comprise any number of functional and non-functional adjuvants. Specifically, these 20 compositions may comprise stabilizing agents, wetting agents, as well as pigments or dyes among other constituents. Stabilizing agents may be added to the composition of the invention to stabilize the peroxyacid and hydrogen peroxide to prevent the premature decomposition of the oxidizing material within the 25 composition of the invention. Chelating agents or sequestrants are generally useful in the compositions of the invention in the form of alkyl diamine polyacetic acid-type chelating agents such as EDTA, acrylic and polyacrylic acid-type agents, phosphonic acid, and phosphonate-type chelating agents among others. Preferred sequestrants include phosphonic acid and phosphonic acid salts including 1-hydroxyethylidene-1,1-diphosphonic acid, amino[tri(methylenephosphonic acid)] and other phosphonate based sequestering agents. Also useful in the compositions 30 of the invention are surfactant, wetting or defoaming agents. Wetting agents function to increase the surface area and reduce particle size of the particulate aqueous treatment composition. Such wetting agents are known within the art to



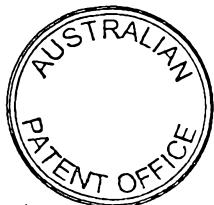
raise the surface activity of the composition of the invention. Preferred wetting agents are low foaming nonionic surfactants which may be used comprising ethylene oxide moieties, propylene oxide moieties as well as a mixture thereof and EO-PO heteric or block compositions. Defoaming agents comprising silica, silicones, 5 aliphatic acids or esters, alcohols, sulfates, sulfonates, amines, amides, nonionic materials and others can be helpful in defoaming the mixture during processing. The treatment compositions may contain a number of other constituents selected by the operator to enhance the properties of the materials.

10 The treatment compositions can comprise concentrate materials that fall within the following generic formula:

Treatment Concentrate

Ingredient	Useful Wt%	Working Wt%	Preferred W%
Peracetic Acid	1-40	2-30	4-20
Hydrogen Peroxide	1-50	3-40	5-30
Acetic Acid	1-90	3-60	5-40
Sequestrant	0.1-10	0.1-5	0.5-2
Water	Balance	Balance	Balance

15 The above compositions comprise concentrate materials that can be metered into an aqueous stream directed to the scrubber apparatus. Such a concentrate can be metered into an aqueous stream in an amount forming a residual concentration containing about 1 to 500 ppm peracetic acid, 1 to 3,000 ppm hydrogen peroxide, 1 to 600 ppm of acetic acid and other active components, preferably about 1 to 50 ppm 20 peracetic acid, 1 to 500 ppm hydrogen peroxide, 1 to 300 ppm of acetic acid and other active components. As a general guideline, the following table sets forth working ranges of active ingredients in the treatment composition after dilution in the aqueous stream within the wet scrubber. Significantly larger concentrations can add an objectionable odor of the treatment materials into the air stream.



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Residual or Active Concentrations in the Treatment

Treatment Constituent	Useful (ppm)	Working (ppm)	Preferred (ppm)
Peracetic Acid	1-500	1-100	1-50
Hydrogen Peroxide	1-3,000	1-1,000	1-500
Acetic Acid	1-600	1-400	1-300
Sequestrant	0.01-50	0.01-25	0.01-10
Water	Balance	Balance	Balance

These concentrations are determined using the following formulas:

5

$$\text{Dosed Concentration} = \frac{\text{grams of active ingredient added}}{\text{grams of liquid solution}}$$

$$\text{Residual Concentration} = \frac{\text{grams of active ingredient detected by analysis after reaction}}{\text{grams of liquid solution}}$$

10

These compositions comprise concentrate materials that can also be atomized into a scrubber apparatus. Since the odor is being treated with a low-flow, high surface area fog, the peroxy acid concentration of the treatment is typically higher than traditional water treatments using low surface area misting solutions. Such a concentrate can form a dosed concentration containing about 1 to 30,000 ppm peroxy acid, 1 to 30,000 ppm hydrogen peroxide, 1 to 5000 ppm of carboxylic acid and other active components, preferably about 100 to 5000 ppm peroxyacetic acid, 100 to 5000 ppm hydrogen peroxide, 20 to 300 ppm of acetic acid and other active components. As a general guideline, the following table sets forth working ranges of active ingredients in the fog treatment composition.

15

20

Dosed Concentrations

Treatment Constituent	Useful (ppm)	Working (ppm)	Preferred (ppm)
Peroxy acid	1-30,000	50-10,000	100-5,000
Hydrogen Peroxide	1-30,000	50-10,000	100-5,000
Carboxylic Acid	1-5,000	10-500	20-300
Sequestrant	0.01-50	0.01-25	0.01-10
Water	Balance	Balance	Balance

Another way to view composition ranges is to use ratios between various critical components. The first important ratio is that between the peroxy acid and 5 the carboxylic acid. The aqueous peroxy acid fog treatment composition comprises less than 4 parts by weight, preferably less than 2.5 parts by weight, of peroxy acid per each part of carboxylic acid.

The second important ratio is that between hydrogen peroxide and the peroxy acid. The aqueous peroxy acid fog treatment composition comprises less than 5 10 parts by weight of hydrogen peroxide per each part of peroxy acid, preferably less than 2 parts by weight of hydrogen peroxide per each part of peroxy acid.

Because active oxygen can come from more than one source, it is also important to consider the total active oxygen content. The aqueous peroxy acid fog treatment composition comprises a dosed peroxy acid and hydrogen peroxide 15 concentration resulting in an active oxygen concentration of less than about 20,000 parts by weight of active oxygen per one million parts of the treatment, preferably less than about 5,000 parts by weight of active oxygen per one million parts of the treatment and more preferably less than about 2,000 parts by weight of active oxygen per one million parts of the treatment.

20 A particularly aqueous peroxy acid fog treatment composition comprises 1 to 90 weight percent (wt %) of acetic acid, 1 to 50 wt % of hydrogen peroxide, a sequestrant, and 1 to 40 wt % of peroxyacetic acid.

Traditionally, in removing odor compositions from an effluent stream, a 25 continuous stream of the treatment composition is directed to the top of a scrubber column. The treatment composition flows counter-currently through the column to scrub odor compositions from the effluent gas. It is possible, however, to accomplish this using co-current flow if using a packed column or spray chamber. The spray chamber would utilize a high-flow (4 to 380 liters per minute), low-



surface area spray mist (1000-100,000 μm diameter droplets) to effect sufficient mass transfer of the odor compounds to the aqueous phase. The dosed peroxy acid concentration would typically be about 30 to 200 ppm in the spray. To maintain an effective concentration of the peroxyacetic acid in the treatment composition, a 5 make up amount of the concentrate must be either continually or intermittently added to the continuous stream to maintain at least about 1 ppm of residual peroxyacetic acid, preferably at least about 2 and preferably at least 25 ppm of residual peroxyacetic acid during operations. In the current invention, a high surface area, concentrated peroxy acid fog (dosed peroxy acid is about 100 to 50,000 ppm 10 (parts by weight of active peroxy acid per one million parts of solution), with a droplet size which ranges from 25 to 500 μm) is atomized in a pre-chamber or duct either before or after a conventional spray system. The atomized fog flow rate is only about one-tenth to one-fiftieth that found in conventional spray treatments. In this situation, the flow rate of the atomized fog is such that 28 liters of atmospheric 15 effluent is contacted with about 0.01 to 0.18 liters of aqueous treatment solution. Thus, even though a high concentration of peroxy acid is utilized, the low flow rate allows for an enhanced economic treatment process over a conventional malodor reduction process.

The compositions may also contain one or more essential oils, which are 20 generally defined as distillable odoriferous products of plant origin. While the principle components are mono- to tetra-unsaturated olefin terpenes, essential oils may also contain benzenoid and aliphatic compounds as well. Terpenes are unsaturated hydrocarbons which are based on the isoprene unit of alternating double bonds. Terpenes of use in the invention include citral, camphor, α and β -pinene, 25 terpineol, limonene, α and β -terpinene, α and β -phellandrene, cedrene, geraniol, linalool, neral and abietic acid. Especially preferred terpenes include citral, camphor, α and β -pinene, terpineol and limonene. Preferred essential oils can also include such aldehydes as benzaldehyde and cinnamaldehyde.



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The treatment compositions can comprise concentrate materials that fall within the following generic formula:

Treatment Concentrate 1

Ingredient	Useful Wt%	Working Wt%	Preferred W%
Peroxyacid	1-40	2-30	4-20
Hydrogen Peroxide	1-50	3-40	5-30
Carboxylic Acid	1-90	3-60	5-40
Sequestrant	0.1-10	0.1-5	0.5-2
Water	Balance	Balance	Balance

5

Treatment Concentrate 2

Ingredient	Useful Wt%	Working Wt%	Preferred W%
Essential Oil	10-100	50-100	80-95
Mineral Spirits	0-80	0-20	0-15
Surfactants	0-20	0-10	0-5

The above compositions, co-injected with essential oils, comprise

10 concentrate materials that can be metered into an aqueous stream directed to the scrubber apparatus. An oxidative concentrate such as treatment concentrate 1 can be metered into an aqueous stream along with separately added essential oils (such as treatment concentrate 2) in an amount forming a residual concentration containing about 1 to 1000 ppm peroxyacid, 1 to 2,000 ppm hydrogen peroxide, 1 to 600 ppm of carboxylic acid (e.g. acetic acid) and other active components, about 1 to 10,000 ppm of essential oil, preferably about 30 to 150 ppm peroxyacid, 1 to 500 ppm hydrogen peroxide, 1 to 300 ppm of carboxylic acid and other active components and 10 to 500 ppm of essential oil. As a general guideline, the following table sets forth working ranges of active ingredients in the treatment composition after dilution

15 in the aqueous stream within the wet scrubber.

20



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Residual or Active Concentrations

Treatment Constituent	Useful (ppm)	Working (ppm)	Preferred (ppm)
Peroxyacid	1-1,000	5-300	30-150
Hydrogen Peroxide	1-2,000	1-1,000	1-500
Carboxylic Acid	1-600	1-400	1-300
Sequestrant	0.01-50	0.01-25	0.01-10
Essential Oil	1-10,000	5-1,000	10-500
Water	Balance	Balance	Balance

During operations, in removing odor compositions from an effluent stream, a
5 continuous stream of the treatment composition is directed to the top of a scrubber column. The treatment composition flows counter-currently through the column to scrub odor compositions from the effluent gas. It is possible, however, to accomplish this using co-current flow if using a packed column or spray chamber. To maintain an effective concentration of the peracetic acid in the treatment
10 composition, a make up amount of the concentrate must be either continually or intermittently added to the continuous stream to maintain at least about 1 ppm of residual peracetic acid, preferably at least about 2 and preferably at least 25 ppm of residual peracetic acid during operations.

Exemplary peracetic acid formulas (equilibrium mixtures).

15

Ingredient	Wt%
Acetic Acid	32.0
Hydrogen Peroxide	11.1
Sequestrant	1.5
Water	41.0
Peracetic Acid	15.0

Ingredient	Wt%
Acetic Acid	6.5
Hydrogen Peroxide	26.6
Sequestrant	1.0
Peracetic Acid	4.7
Water	61.6

Ingredient	Wt%
Acetic Acid	30.0
Hydrogen Peroxide	7.0
Sequestrant	1.0
Peroxyacetic Acid	5.0
Peroctanoic Acid	0.5
Hydrotrope (coupling agent)	5.0
Octanoic Acid	3.0
Water	balance

5

Ingredient	Wt%
Acetic Acid	46.0
Hydrogen Peroxide	4.0
Sequestrant	1.0
POAA (Peroxyacetic acid)	12.0
POOA (Peroxyoctanoic acid)	2.0
Octanoic Acid	8.2
Water	26.5

During operations to maintain the concentrations of the peracetic acid mentioned above, the exemplary peracetic acid formulations are typically added as 10 make-up to the treatment streams at rates of about 100 to 2000 ppm of the peracetic acid formulations in the aqueous stream typically flowing as make-up water at the rate of about 1 to 10,000 L-min⁻¹. The use of make-up solution directed to the continuously flowing treatment stream is a preferred means to introduce the peracetic acid material into the scrubber or venturi apparatus.

15

Process Parameters

In the odor reduction treatment process of the invention, an aqueous solution is passed in a continuous stream through the scrubber apparatus. In typical

applications, the aqueous treatment composition passes through the scrubber at a rate of about 1 to 10,000 L-min⁻¹, depending upon the size of the scrubber. Typically, the scrubber is a vertical wet scrubber having interior packing. The aqueous solution passes through the column packing in a finely divided form comprising streams, 5 droplets, etc. through the column packing. The rate of solution flow is adjusted depending upon the size of the scrubber, the volumetric flow rate of gas, and the soil level of the gas.

The aqueous treatment material is added to the continuously flowing aqueous stream in make-up water. The aqueous peroxyacid material, preferably peracetic acid, is typically added in a concentrate at a dosed concentration of about 10 to 1000 10 ppm, preferably about 10 to 300 ppm of peracetic acid to make-up water added to the aqueous stream at a rate of about 1 to 500 liters per hour. The effective residual concentration of peroxyacid preferably peracetic acid in the aqueous stream is maintained between 1 and 500 ppm peracetic acid, preferably about 1 to 100 ppm 15 peracetic acid, most preferably about 1 to 50 ppm peracetic acid. The effective concentration of essential oils, if used, is maintained at a concentration of 1 to 10,000 ppm, preferably 10 to 500 ppm.

The atmospheric effluent from the plant atmosphere is passed through the scrubber at a rate of about 100 to 3 million liters of atmosphere effluent per minute 20 (atmos. L-min⁻¹). Preferably, the aqueous treatment material has a flow rate such that 28 liters of atmospheric effluent is contacted with about 0.01 to 10 liters of aqueous treatment solution. The temperature of the scrubber is maintained at ambient temperatures, however, somewhat elevated temperatures can enhance the oxidation and dissolution of the gas in the liquid stream. The wet scrubber can be 25 operated continually at such ratios to efficiently remove odor compounds from the atmospheric stream. The odor compounds and oxidized odor compounds remain solubilized in the aqueous phase. After the odor reduction process is used for some period, the odor compounds are removed with a portion of the aqueous stream that can be removed from the scrubber continually. Such a proportion of the aqueous 30 stream can comprise about 1 to 500 liters of the aqueous stream per hour (L-hr⁻¹). Alternatively, the aqueous stream can be removed batchwise or in its entirety periodically, e.g. every 4, 6, 12 or 24 hours, bi-weekly, weekly, etc. The process can



compounds within the gaseous phase 2a. The tower operates countercurrently, meaning that the aqueous stream 7a enters at the top and exits the bottom while the air stream 2a enters the bottom and exits at the top. The air stream 8b exiting the top



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of the tower flows to an optional stack 10. The aqueous stream 8a exiting the bottom of the tower flows to diverter valve 8'', which recycles a portion of the aqueous flow back to the holding tank 6 while diverting the remainder as waste stream 9. Alternatively, the contacting column 8' can also operate cocurrently.

5 Figure 1b shows the peroxy acid pretreatment process of the invention. Odor laden airflow 14 is seen passing through air inlet 2. Compressor 11 is used along with atomizer 13 to provide a fogged peroxy acid pretreatment into the airflow 14. Also seen is a peroxy acid pretreatment solution source 12.

10 Figure 2a shows generally a venturi system 20 that can be used to contact odor laden air with the peroxy acid treatment. This installation can be used in smaller locations such as hog barns, effluent lagoons, etc. In Fig.2, odor laden fluid, air or liquid, 21 enters the venturi 20 through air inlet 35. The fluid 21 enters the restricted area 22, in the venturi 20, that produces an area of increased speed and reduced pressure. In the restricted area 22 the odor laden fluid 21a is contacted with the spray 23 from a source of peroxy acid treatment 24. The treated fluid 21b with reduced odor exits the venturi 20 at vent or air exit 31. The treatment solution 24 is directed to the venturi 20 restricted area 22 using pump 25. Make-up water results from water source 28. Make up peroxy acid (peroxyacetic acid) is provided by source 26 and metering pump 27. Over flow or excess treatment solution is drawn 15 off by overflow means 29 to a sewage treatment zone 30. The fluid 21 can be forced into the venturi 20 or can be drawn from the venturi 20 from the vent 31.

20

25 Figure 2b shows a portion of figure 2a, demonstrating how the peroxy acid pretreatment of the invention can be incorporated into the greater odor reduction scheme outlined in figure 2a. Specifically, the odor laden inflow 21 is seen passing through the air inlet 35. A compressor 32 and a peroxy acid solution source 33 are used to provide an atomized pretreatment spray via atomizer 34. The pretreated air then passes along to receive additional treatment as seen in figure 2a.

30 Figure 3 is a graphical comparison of the oxidant survival rate in the invention treatment method of using peroxyacids co-injected with essential oils versus previously used oxidative systems. As seen in the figure, upon spiking an essential oil (pine oil) into a conventional treatment system such as chlorine or chlorine dioxide, the loss of oxidant is rapid; with essentially complete elimination

within about five to ten minutes. This rapid oxidant loss would negate the use of simultaneous essential oil addition. In contrast, the peroxyacid rate of decay is much lower with a small residual remaining even after one hour. This demonstrates the unexpected synergistic effect resulting from the combination of the peroxyacids with
5 the essential oils.

Working Examples

The following examples are intended to illustrate but not limit the invention.

10

Example 1

Exhaust air from a blood drying operation in a rendering plant is directed first into a venturi and then into a packed column scrubber at an air flow rate of 15,000 cubic feet per minute (cfm), or 425 cubic meters per minute. Water which was treated with a 4.5% POAA (peracetic acid), 27% H_2O_2 solution is pumped into
15 the venturi and through the tower countercurrently to the air flow. Plastic contacting rings are used in the tower to maximize the surface area of contact between the aqueous and gaseous phases. The recirculation rate of liquid through the column is approximately 200 gallons per minute (gpm), or 760 liters per minute. The makeup water feed rate into the venturi and the scrubber is 10 gpm (38 liters per minute).
20 Approximately 1100 ppm (vol/vol) of the 4.5% peracetic acid solution (POAA) is fed into the makeup water to the venturi and the tower. The specific gravity of the POAA product is 1.12 gm/cm³. Therefore, the dosed active peracetic acid concentration is $(1.12)(1150)(0.045) = 58$ ppm wt/wt peracetic acid. The residual POAA concentration by thiosulfate/KI/starch titration ranges from 15-20 ppm.
25 Results of this treatment increased the rate of odor removal from the scrubber as compared to using two previous products per the following table:



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Test	Odor Evaluation	Air Treatment Score	Cleanliness of Scrubber Interior
1	Chlorine gas combined with sodium hydroxide	1.0	1.0
2	Organic acid and octylphenol ethoxylate (surfactant) and sulfosuccinate (surfactant)	1.0	1.0
3	Peracetic acid solution	3.5	4.0

As shown the prior art treatments (tests 1 and 2) yielded relatively low scores from the odor and cleaning panel. The use of the compositions and methods of the invention (test 3) gives surprisingly improved odor and cleanliness evaluations. The treatment with peracetic acid (POAA) gave the best odor removal and also kept the scrubber interior the cleanest of all three treatments. The Air treatment score is based on the rating of the treatment's effectiveness on a scale of 1-5. A score of 1 means that virtually no difference in olfactory response occurred (i.e., no odor reduction). A score of 5 indicates complete removal of the odor from the air stream. The Cleanliness indicates the amount of slime and deposits on surfaces of the scrubber and packing. A score of 1 indicates visible, thick deposits after running the scrubber for several days. A score of 5 indicates complete removal of deposit and slime layers from the interior surfaces and maintenance of a deposit-free surface over time.

Example 2

The water used in the venturi and packed tower system described in Example 1 was treated with various of ratios of peroxyacetic acid (POAA) and hydrogen peroxide (H_2O_2). The active ingredients in the concentrated products used for this testing were as follows:

Formula	% POAA	% H ₂ O ₂	% Acetic Acid (AA)	SG
1	4.5	27	6.5	1.12
2	15.0	11.0	31.4	1.11
3	0.0	35.0	0.0	1.13
4	4.7	6.9	24.0	1.08

All formulas contained 1.5% DEQUEST[®]2010 (1-hydroxyethylidene-1,1-diphosphonic acid, HEDP), with the balance being water.

5 In this system, the venturi and tower were used in series, with the gases first contacting the venturi, and then passing through the packed tower before being ejected from the plant stack to the atmosphere. The odorous gases being treated were exhaust gases from a blood dryer.

The effect of each type of treatment on Odor Intensity was studied by taking
10 10 liter samples in Tedlar bags of the exhaust gas just prior to the venturi (inlet) and immediately after the tower scrubber (outlet). The inlet and outlet samples were taken simultaneously in order provide the best representation of odor changes in the scrubber system. These bags were then submitted to a trained odor panel on the same day as sampling and tested for Odor Intensity (Int), which is defined as the
15 offensive intensity of the odor as compared to standard solutions of n-butanol, and is reported as ppm n-butanol equivalent. The Odor Intensity tests were run according to ASTM Standard Practice E544-75/88. Duplicate samples were taken for all tests.

Reductions in the Odor Intensity indicate removal of odorous compounds from the air stream. If the percentage (%) reduction is negative, then the intensity of
20 the odor actually increases due to the treatment in the scrubber. If the percentage (%) is positive, then the intensity of the odor actually is reduced due to the treatment in the scrubber. The following table gives results of Intensity tests for various formulas of POAA and H₂O₂ described in the above table diluted to various dosed concentrations (ppm) of active ingredients, as shown below. The treatments of the
25 invention reduce the odor intensity by at least about 5 %, preferably by 35 %, most preferably by 50 %.

Percent Reductions in Odor Intensity					
Formula	POAA	AO	AA	H ₂ O ₂	% Reduction Intensity
1	80	240	116	480	-33
2	267	147	560	195	9
2	80	45	168	59	47
3	0	240	0	512	-120
4	80	74	415	117	58
1	40	120	58	240	-81

All concentrations are in dosed ppm active species. AA represents the concentration
 5 of acetic acid. AO (Active Oxygen) represents the total oxidizing potential of the product and is calculated by multiplying the active oxygen contributed by POAA (21% AO) by the level of POAA in the system, and then adding this to the active oxygen contributed by H₂O₂ (47% AO) times the level of H₂O₂ in the system. For example 80 ppm POAA times 0.21 plus 480 ppm H₂O₂ times 0.47 equals 240 ppm
 10 total active oxygen (AO) in the first row of the table. The POAA contains 21% AO, as calculated by the ratio of molecular weights for oxygen (16) and POAA (76). H₂O₂ has 47% AO, calculated by the ratio of molecular weights for oxygen (16) and H₂O₂ (34). The above data shows that higher levels of POAA will reduce the intensity of the odor, but higher levels of H₂O₂ will actually increase the odor
 15 intensity (i.e.) a negative percent Reduction Intensity indicates an unfavorable rise in the intensity of the odor. This phenomenon is more clearly seen if the data are presented in the following manner.

The following table shows percent reductions in odor intensity (as n-butanol) as a function of peroxy acetic acid and hydrogen peroxide concentrations in scrubber
 20 water. Negative results indicate increased odor.

Hydrogen Peroxide concentration in Scrubber Water (ppm)

		59	117	195	240	480	512
Peroxy	0						-120%
acetic							
acid in	40				-81%		
scrubber							
water	80	47%	58%			-33%	
(ppm)							
	267		9%				

The above figure shows that for given dosed concentrations of POAA, there

5 is significant odor intensity reduction only if the corresponding dosed H₂O₂ concentration is not too high. H₂O₂ used at higher concentrations will give significant increases in odor intensity, which is not desirable. This behavior is unexpected, since both POAA and H₂O₂ are oxidizing agents. The effect is most noticeable when only H₂O₂ is used to treat the scrubber water. In this case, the

10 intensity increased by 120%. An overwhelmingly strong amine/ammonia odor was also noticed in the scrubber water when H₂O₂ alone was used.

Example 3

The water used in the venturi and packed tower system described in Example

15 1 was treated with a variety of ratios of peroxyacetic acid (POAA) and hydrogen peroxide (H₂O₂) as described in Example 2.

The effect of each type of treatment on Odor Detection Threshold reduction was studied by taking 10 liter samples in Tedlar bags of the exhaust gas just prior to the venturi (inlet) and immediately after the tower scrubber (outlet). These bags

20 were then submitted to a trained odor panel on the same day as sampling and tested for Odor Detection Threshold (DT), which is defined as the number of dilutions of the sample required to make the odor emission barely detectable. The DT tests were run according to ASTM Standard Practice E679-91. Duplicate samples were taken for all tests.

Reductions in the DT dilution ratio indicate removal of odorous compounds from the air stream. The following table gives results of DT tests for various formulas of POAA and H₂O₂.

POAA	AO	AA	H ₂ O ₂	% Red DT
80	240	116	480	38
267	147	560	195	8
80	45	168	59	42
0	240	0	512	37
80	74	415	117	7
40	120	58	240	14

5

All concentrations are in dosed ppm active species. AA represents the concentration of acetic acid. AO (Active Oxygen) represents the total oxidizing potential of the product and is calculated by multiplying the active oxygen contributed by POAA 10 (21% AO) by the level of POAA in the system, and then adding this to the active oxygen contributed by H₂O₂ (47% AO) times the level of H₂O₂ in the system. For example 80 ppm POAA times 0.21 plus 480 ppm H₂O₂ times 0.47 equals 240 ppm total active oxygen (AO) in the first row of the table. THE POAA contains 21% AO, as calculated by the ratio of molecular weights for oxygen (16) and POAA (76). 15 H₂O₂ has 47% AO, calculated by the ratio of molecular weights for oxygen (16) and H₂O₂ (34).

The above data shows that significant reductions in odor thresholds occur at high levels of either POAA or H₂O₂. Focusing on formulas with POAA (since odor intensity increases with H₂O₂ only formulas), the data can be shown as follows:

20

Acetic acid concentration is scrubber water (ppm)

		58	116	168	415	560
Peroxy acid	40	14				
Conc. in	80		38	42	7	
Scrubber	267					8
Water (ppm)						

This data shows that for POAA formulas, the level of POAA and AA (acetic acid) are important. The best reductions in odor threshold are achieved when dosed POAA concentrations are above 40 ppm while maintaining dosed acetic acid levels below about 300 ppm.

5

Example 4

One liter gas samples were taken from the blood dryer scrubber system described in Examples 2 and 3 submitted for Gas Chromatography (GC) analysis in order to determine what types of odor molecules were present, and to what extent the odor molecules were removed by various treatments of POAA and H_2O_2 . Samples 10 were again taken simultaneously just prior to the venturi (inlet) and after the tower (outlet).

Twenty sulfur compounds were analyzed, including: hydrogen sulfide, carbonyl sulfide ($C=S$), methyl mercaptan, ethyl mercaptan, dimethyl sulfide, carbon disulfide, isopropyl mercaptan, n-butyl mercaptan, n-propyl mercaptan, ethyl methyl sulfide, thiophene, isobutyl mercaptan, diethyl sulfide, n-butyl mercaptan, dimethyl disulfide, 3-methylthioprene, tetrahydrothioprene, 2,5-dimethylthioprene, 2-ethylthioprene, diethyl disulfide.

Most of the compounds were below the detection limit of the instruments, except for hydrogen sulfide and methyl mercaptan in some of the tests. Results for 20 percent reduction of hydrogen sulfide (H_2S) from inlet to outlet for various ratios of POAA and H_2O_2 are shown in the following table:

25

**Percent Reduction of Hydrogen Sulfide
For Various Ratios of POAA and H_2O_2**

POAA Dosed (ppm)	H_2O_2 Dosed (ppm)	Percent Reduction H_2S
0	512	52
80	59	61
80	117	63
267	195	69



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These results show that, although all treatments reduced H₂S levels, the greatest reduction came from high levels of POAA.

Results for percent reduction of methyl mercaptan from inlet to outlet are shown below:

5

**Percent Reduction of Methyl Mercaptan
For Various Ratios of POAA and H₂O₂**

POAA Dosed (ppm)	H ₂ O ₂ Dosed (ppm)	Percent Reduction Methyl Mercaptan (CH ₃ SH)
0	512	0
40	240	46
80	480	28
80	117	36
267	195	23

10 The results show that formulas with POAA will reduce methyl mercaptan concentrations in the gas stream. However, H₂O₂ alone provides no reduction for this molecule. In the above two tables, not all tested ratios of H₂O₂ and POAA are shown, since for some the tests, the results were below the detection limit of the instruments.

15

Example 5

For the system described in Example 2, samples of the venturi and packed tower scrubber water were also taken, and the odor strength emanating from each water sample was scored on a scale from one to five. Five being the most offensive, and one being the least offensive odor. The results for each of the formulas tested 20 are shown below. In these tests, the venturi and the packed tower samples gave equal odor strength scores for all treatments.

Odor Strength of Scrubber Water for Various Treatments					
Formula	POAA	AO	AA	H_2O_2	All concentrations are active dosed species (ppm)
					Water Odor Score
1	80	240	116	480	3
2	267	147	560	195	1
2	80	45	168	59	2
3	0	240	0	512	5
4	80	74	415	117	3
1	40	120	58	240	4

Low odor strength scores for the scrubber water are achieved with higher levels of POAA. Conversely, higher H_2O_2 levels gave stronger odors in the scrubber water.

Example 6

The application method of using micron-sized (25 to 500 μm) peroxy acid fogs was compared to liquid peroxy acid treatments. In this example, hydrogen sulfide levels were monitored during the hydrolyzing of chicken feathers. This process generates a continuous low-level background of hydrogen sulfide followed by high level bursts when the feathers are transferred from the oven to the dryer. The reduction of this high-level odor in intensity and the rate at which it occurs is critical to emission regulations. In the table, experiment 1 is the method previously described while experiments 2 and 3 pertain to the current method. Level 1 refers to a peroxyacetic acid dosed level of 500 ppm while level 2 refers to a peroxyacetic acid dosed level of 2,500 ppm.

	Treatment Method	H ₂ S Level five minutes after malodor release ^a	Time to return to pre-release level of H ₂ S
1	conventional spray (1,000 to 10,000 µm)	48 ppm	15 minutes
2	sub-millimeter atomized fog spray, level 1 peroxy acid (25 to 500 µm)	14 ppm	5 minutes
3	sub-millimeter atomized fog spray, level 2 peroxy acid (25 to 500 µm)	7 ppm	4 minutes

a) From an industrial Feather Scrubber releasing bursts of malodorous hydrogen sulfide.

5 The test results show a significant improvement both in residual malodor after five minutes and in the speed in which the malodors are removed.

Example 7

10 The table demonstrates the composite odor reduction from the new peroxy acid application method, as measured by olfactory evaluation from grab samples. Odor samples were taken via air pump and collected in Tedlar sampling bags. The samples were evaluated by an olfactory panel, and all scores were averaged. The results are tabulated on a scale of 1 to 10, wherein 10 indicates most malodorous.

	Treatment Method	Odor Ranking
1	conventional spray (1,000 to 10,000 µm)	6.2
2	atomized fog spray, level 1 peroxy acid (25 to 500 µm)	5.0
3	atomized fog spray, level 2 peroxy acid (25 to 500 µm)	4.6

15 a) An odor panel of 6 members; samples were taken five minutes after the malodor was introduced into the air stream.

The data demonstrates the added advantage of the current peroxy acid fogging method over the previous treatment method. A comparison of experiment 1 with experiment 3 shows a reduction of 1.6 units; whereas a reduction of 0.5 units is deemed significant.

Example 8

The table compares a conventional spray treatment to the fogging method. The conventional spray treatment uses a venturi/packed tower system with dosed internal sprays of 5,000 to 40,000 μm droplet sized peroxyacetic acid at 30 to 100 ppm peroxy acid while the invention method uses 40 to 100 μm sized droplets of 1000 to 15,000 ppm dosed peroxy acid. The total spray flow in the conventional system was about 40 gallons per minute (150 liters per minute) while the improved fogging method had a spray rate of only about 1.6 gallons per minute (6 liters per minute).

10

Odor Evaluation¹

	Treatment Condition	Peroxy acid Concentration (ppm)	Total Peroxy acid Use (liters per day)	Odor Rating (1-10, 10=best) "Non-Condensable Odor Intensity" ²
1	Peroxyacetic Acid Conventional Spray ³	30	45	3
2	Peroxyacetic Acid Conventional Spray ³	100	150	5
3	Peroxyacetic Acid Atomized Fog ⁴	1,000	5	5
4	Peroxyacetic Acid Atomized Fog ⁴	15,000	83	8

1) Odor rating from an industrial rendering plant olfactory analysis of relative intensities and detection thresholds.

2) Odor intensity as measured by the rendering facility as "sharpness" of the malodors from the treated stack. Usually defined in the industry as the site perimeter level of "non-condensables, cooker smell and sulfides."

3) Peroxyacetic conventional spray using low surface area, large droplet sized sprays in a packed tower.

4) Fogging atomizer using high surface area, small droplet, low solution-flow fogs in open ductwork.

15

As seen in Example 6 and Example 7, this example demonstrates the improved art of using a high-concentration, low-flow, high-surface area peroxy acid fog for control of non-condensable odors. These non-condensables are easily recognizable in the rendering industry and are characterized by a bitter/burnt/decay odor profile. The data demonstrates the improvement on odor control with less peroxy acid consumption using the current method over the prior art. In all these



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examples the resulting data shows more than an additive or linear result from the improved inventive technology.

Example 9

5 As seen in figure 3, upon spiking an essential oil (pine oil) into a conventional treatment system such as chlorine or chlorine dioxide, the loss of oxidant is rapid; with essentially complete elimination within about five to ten minutes. This rapid oxidant loss would negate the simultaneous use of essential oils. In contrast, the peroxyacid rate of decay is much lower with a small residual 10 remaining even after one hour.

15 This improvement in the art is unexpected since the apparent ability of the peroxyacids to eliminate malodors should couple its ability to also oxidize the essential oils and thereby render both inactive. In other words, mutual destruction. This is the effect found in the other systems. The comparative data is also seen below:

Time (minutes)	POAA (Relative Rate)	Chlorine dioxide (Relative Rate)	Chlorine (Relative Rate)
0	90	130	150
0.5	77	90	110
1	73	30	70
2	70	5	30
5	68	0	5
10	63	0	0
20	55	0	0
45	38	0	0
60	8	0	0

Example 10

The objective of this example was to compare the use of peroxyacids alone with the improved and synergistic method of co-injecting peroxyacids and essential oils for odor elimination. The table compares the results of using synergistic blends 5 of peroxyacids and essential oils (experiments 5-7) versus control treatments of using either alone (experiments 1-4).

	Peroxyacid Treatment Condition	Peroxyacid Concentration (ppm)		Pine Oil ¹ Concentration (ppm)		Tower ² Odor Rating (1-10, 10=best)	
		Cooker	Raw	Cooker	Raw	Cooker	Raw
Control Studies							
1	peroxyacetic acid	60	90	0	0	5.0	6.0
2	peroxyacetic acid	120	90	0	0	5.0	5.0
3	pine oil ¹	0	0	62	62	2.5	3.0
4	pine oil ¹	0	0	125	125	3.0	3.0
Examples							
5	peroxyacetic acid + pine oil ¹	120	90	125	125	7.9 (45 min.) ³	8.9 (45 min.) ³
6	peroxyacetic acid + pine oil ¹	60	90	62	62	8.0 (50 min.) ³	8.5 (45 min.) ³
7	peroxyacetic acid + pine oil ¹	50	105	4	4	8.0 (7 min.) ³	8.0 (45 min.) ³

1) Pine oil from a mix of pine terpenes and mineral spirits.

2) Odor Rating from olfactory analysis subjective scale of relative intensity.

3) Time duration of treated synergistic effect.

10

15

The above data shows that synergistic blends of peroxyacids and essential oils are noticeably more effective than either tested alone. Experiment 7 shows that even a minor amount of essential oil has a beneficial effect. The use of peroxyacid alone does little to eliminate malodors while the use of pine oil alone is a poor masking agent. Thus, it was found that when using peroxyacids alone a musty-bitter smell remains after treatment of a carcass cooker scrubber, and a sewery-pine smell is achieved if pine oil is used alone. However, if both odor treatment components are co-added, an extremely low intensity pine smell is found with no

musty/sewery/bitter components to it; i.e., the addition of both the essential oil and peroxyacid creates an almost “no smell” situation with a hint of the essential oil.

Example 11

5 This example demonstrates the use of mixed essential oils for enhanced odor controls using peroxyacids in an industrial rendering plant cooker scrubber.

Odor Evaluation¹

				Odor Rating (1-10, 10 = best)	
	Treatment Condition	Peroxyacid Concentration (ppm)	Essential Oil Concentration (ppm)	Relative Malodor Intensity ²	Relative Odor Detection ³
Control Studies					
1	Peroxyacetic Acid	30	0	3	2
2	Peroxyacetic Acid	100	0	5	5
3	α -Pinene/ Benzaldehyde ⁴	0	20	1	1
4	α -Pinene/ Benzaldehyde ⁴	0	50	3	2
5	α -Pinene/ trans- cinnamaldehyde ⁵	0	50	4	3
Examples					
6	Peroxyacetic Acid + α -Pinene/ Benzaldehyde	30	20	6	7
7	Peroxyacetic Acid + α -Pinene/ Benzaldehyde	50	20	8	8
8	Peroxyacetic Acid + α -Pinene/ Benzaldehyde ⁴	100	50	9	8
9	Peroxyacetic Acid + α -Pinene/trans- cinnamaldehyde ⁵	100	50	9	9

1) Odor rating from an industrial rendering plant olfactory analysis of relative intensities and detection thresholds.

2) Odor intensity as measured by the rendering facility as "sharpness" of the malodors from the treated stack. Usually defined in the industry as the site perimeter level of "non-condensables, cooker smell and sulfides."

5 3) Odor detection as measured by the rendering facility as the "level" of total odor; i.e., treatment chemicals plus malodors.

4) A 70/30 wt/wt ratio of α -pinene/benzaldehyde essential oil mixture.

5) A 70/30 wt/wt ratio of α -pinene/trans-cinnamaldehyde essential oil mixture

10 The above specification, example and data provide a clear basis for understanding the operation of the compositions and methods of the invention.

While the invention can be embodied in a variety of specific examples and processes, the invention resides in the claims hereinafter appended.

The claims defining the invention are as follows:

1. A process for removing an odour from an atmospheric effluent, the process comprising:

5 (a) contacting an atmospheric effluent comprising an odour component with an aqueous peroxyacid treatment composition, forming an oxidized odour component and dissolving the oxidized odour component in the aqueous treatment composition to form an aqueous treatment composition containing the oxidized odour and an effluent with reduced odour;

(b) removing at least a portion of the aqueous treatment composition containing the oxidized odour; and

10 (c) returning the effluent with reduced odour to the atmosphere;

wherein the aqueous peroxyacid treatment composition comprises peroxyacetic acid.

2. The process of claim 1 wherein the odour is removed as measured by an odour threshold score which is reduced by 20% or more.

3. The process of claim 1 or claim 2 wherein in a wet scrubber tower, the atmospheric effluent is a gaseous stream passing vertically against a countercurrent flow of finely divided particulates or thin streams of the aqueous peroxyacid treatment composition.

4. The process of any one of claims 1-3 wherein the aqueous peroxyacid treatment composition comprises a residual acetic acid concentration of less than about 600 parts by weight per one million parts of the treatment.

5. The process of claim 3 wherein the aqueous treatment composition comprises a concentrate that comprises 1 to 90 weight percent (wt%) of acetic acid, 1 to 50 wt% of hydrogen peroxide, a sequestrant, and 1 to 40 wt% of peroxyacetic acid.

6. The process of any one of claims 1-5 wherein 28 liters of atmospheric effluent is contacted with about 0.01 to 10 liters of aqueous treatment solution.

7. The process of claim 1 wherein, in a vertical scrubber column, the atmospheric effluent is a gaseous stream passing vertically with a cocurrent flow of finely divided particulates or thin streams of the aqueous peroxyacid treatment composition.

8. A pre-treatment or post-treatment process for removing an odour from an atmospheric effluent, the process comprising contacting an atmospheric effluent comprising an odour component with a finely divided aqueous peroxy acid treatment composition, forming an oxidized odour component and dissolving the oxidized odour component in the aqueous treatment composition to form a treated effluent and returning the treated effluent to another treatment step or to the atmosphere;



wherein the finely divided aqueous peroxy acid treatment composition has an average droplet size of 25 to 500 μm ; and wherein the aqueous peroxy acid treatment composition comprises peroxyacetic acid.

9. The process of claim 8 wherein the finely divided aqueous peroxy acid treatment composition comprises a dosed peroxy acid concentration of less than about 30,000 parts by weight per one million parts of the treatment.

10. The process of claim 8 wherein the finely divided aqueous peroxy acid treatment composition comprises a concentrate that comprises 1 to 90 wt% of acetic acid, 1 to 50 wt% of hydrogen peroxide, a sequestrant, and 1 to 40 wt% of peroxyacetic acid.

11. The process of any one of claims 8-10 wherein 28 liters of atmospheric effluent is contacted with one 0.01 to 0.18 liters of aqueous treatment solution.

12. A process for removing an odour from an atmospheric effluent, the process comprising:

a process for removing an odour as claimed in any one of claims 1-7; and subsequently:

15 (a) contacting an atmospheric effluent comprising an odour component with a finely divided aqueous peroxy acid treatment composition, forming an oxidized odour component and dissolving the oxidized odour component in the aqueous treatment composition to form an aqueous treatment composition containing the oxidized odour;

20 (b) removing at least a portion of the aqueous treatment composition containing the oxidized odour; and

(c) returning the effluent with reduced odour to the atmosphere.

13. A pre-treatment or post-treatment for removing an odour from an atmosphere effluent, the process comprising contacting an atmosphere effluent comprising an odour component with a finely divided aqueous peroxy acid treatment composition comprising at least about 100 ppm of peroxyacetic acid, at least about 100 ppm of hydrogen peroxide and at least about 20 ppm of acetic acid, forming an oxidized odour component and dissolving the oxidized odour component in the aqueous treatment composition; wherein the finely divided aqueous peroxy acid treatment composition has an average droplet size of 25 to 500 μm ; and

25 wherein the aqueous peroxy acid treatment composition comprises peroxyacetic acid.

14. A process for removing an odour from an atmospheric effluent, the process comprising:

(a) contacting an atmospheric effluent comprising an odour component with an aqueous peroxyacid treatment composition and one or more essential oils, forming an oxidized odour component and dissolving the oxidized odour component in the aqueous treatment composition to



form an aqueous treatment composition containing the oxidized odour and an effluent with reduced odour;

(b) removing at least a portion of the aqueous treatment composition containing the oxidized odour; and

5 (c) returning the effluent with reduced odour to the atmosphere;

wherein the aqueous peroxyacid treatment composition comprises peroxyacetic acid.

15. The process of claim 14 wherein the essential oil is a terpene.

16. The process of claim 15 wherein the terpene is selected from the group consisting of citral, camphor, α and β -pinene, terpineol, limonene, α and β -terpinene, α and β -phellandrene, 10 cedrene, geraniol, linalool, neral and abietic acid.

17. The process of claim 15 wherein the terpene is selected from the group consisting of mono-, di-, tri- and tetra unsaturated olefin terpenes.

18. The process of claim 15 wherein the terpene is selected from the group consisting of citral, camphor, α and β -pinene, terpineol and limonene.

19. The process of claim 14 wherein the essential oil is an aldehyde.

20. The process of claim 19 wherein the aldehyde is selected from the group consisting of benzaldehyde and cinnamaldehyde.

21. The process of any one of claims 14-20 wherein the aqueous treatment composition comprises a concentrate that comprises 1 to 90 wt% of acetic acid, 1 to 50 wt% of hydrogen peroxide, a sequestrant, and 1 to 40 wt% of peroxyacetic acid.

22. A process for removing an odour from an atmospheric effluent, substantially as hereinbefore described with reference to any one of the examples.

23. A process for removing an odour from an atmospheric effluent, substantially as hereinbefore described with reference to Figure 1b or Figure 2.

25. An atmospheric effluent from which an odour has been removed by a process according to any one of claims 1-23.

Dated 16 April, 2002

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FIG. 1A

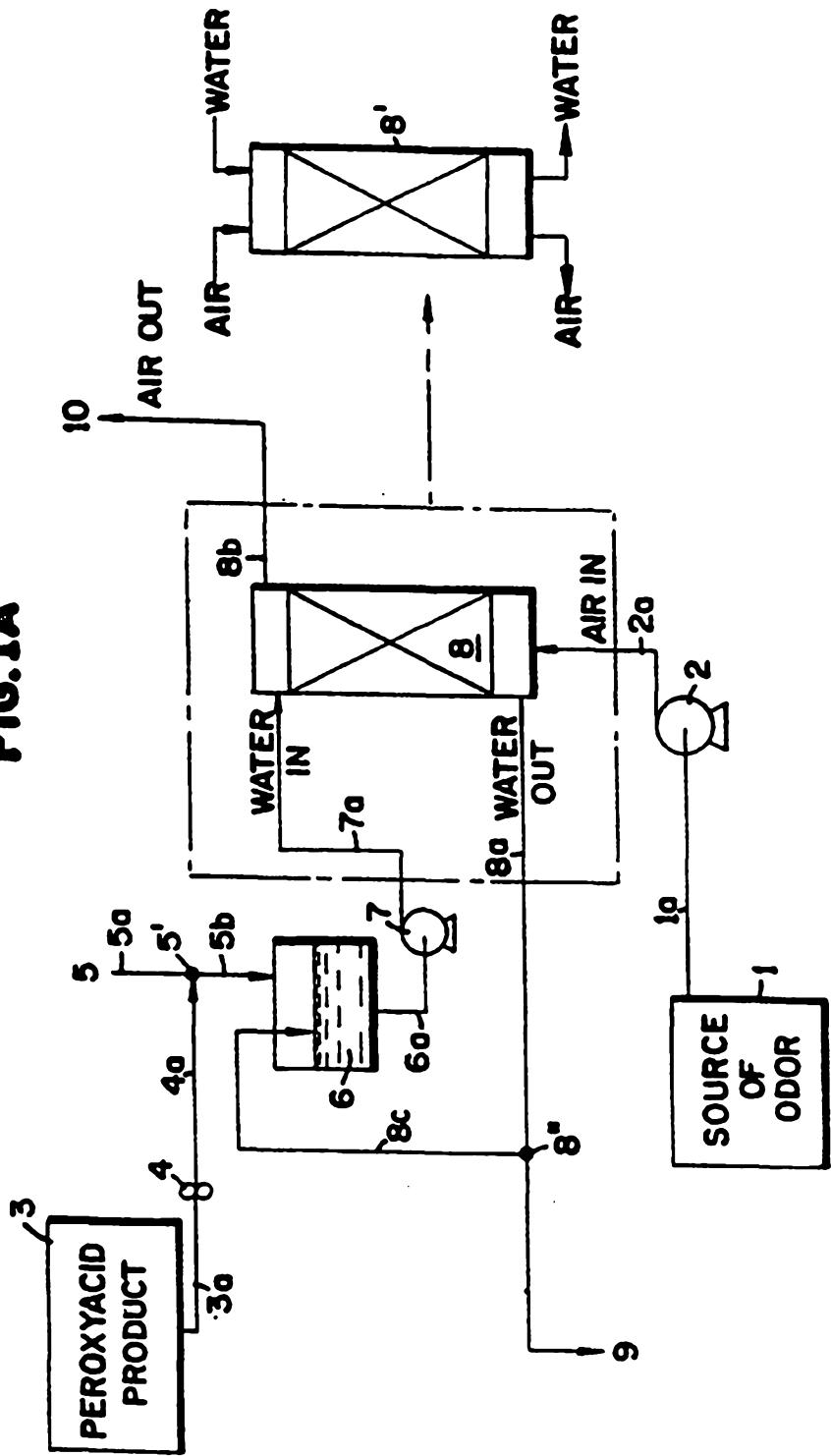


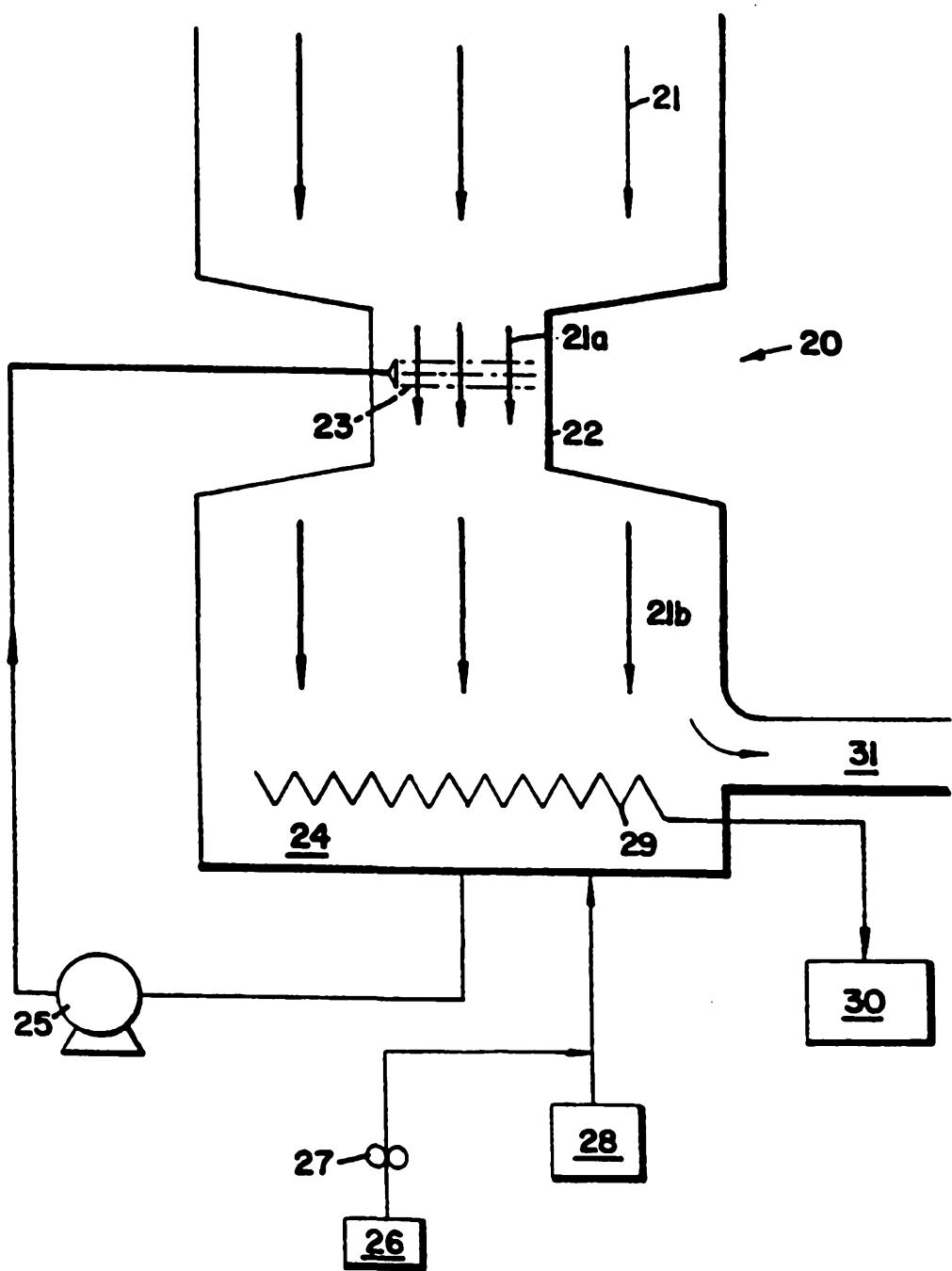
FIG. 2A

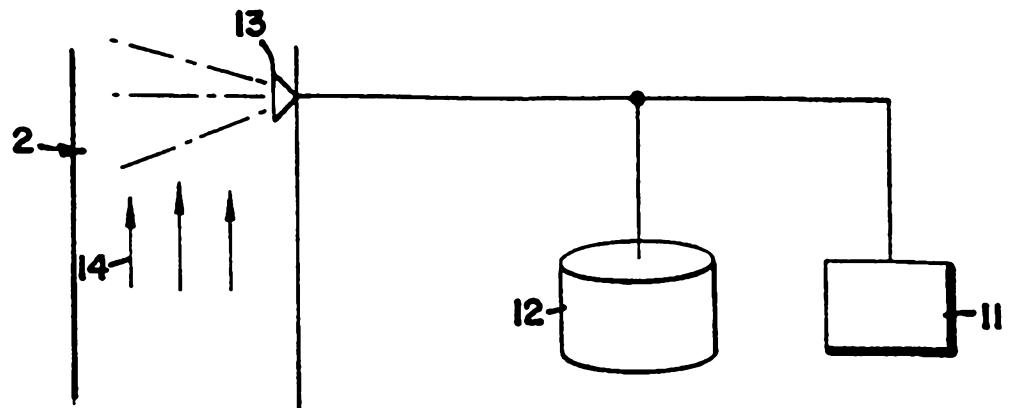
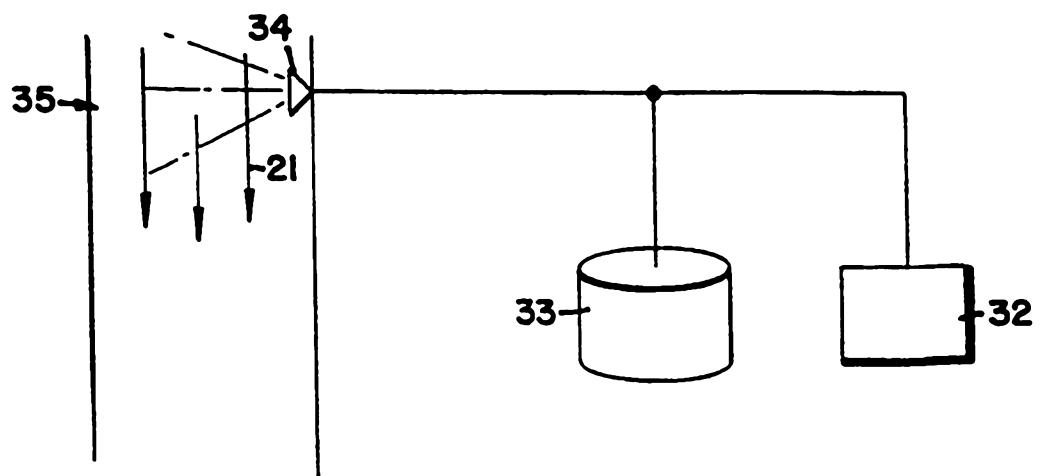
FIG. 1B**FIG. 2B**

Figure 3
Oxidant Reduction Rate
after essential oil spike

