

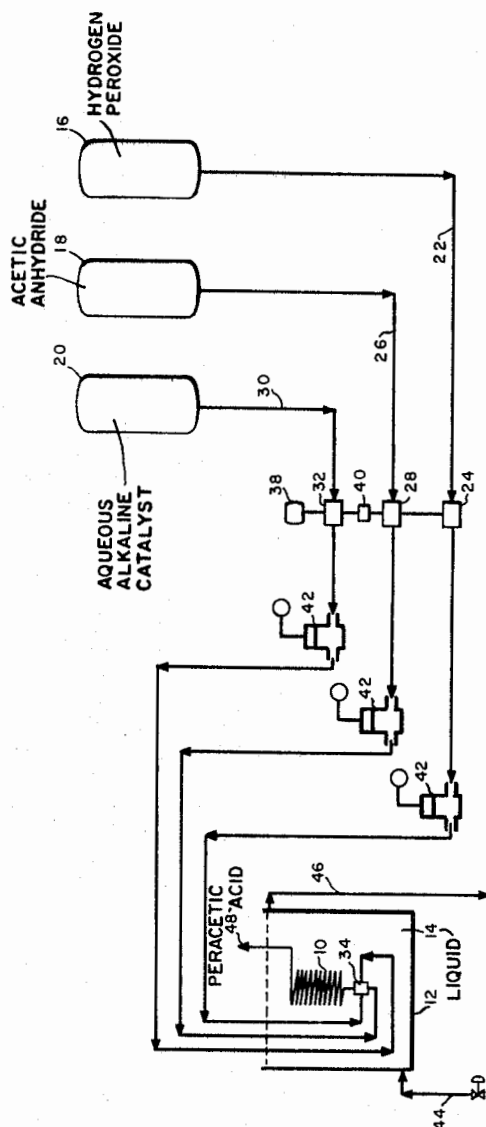
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MANUFACTURE OF PERACETIC ACID

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1

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## MANUFACTURE OF PERACETIC ACID

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## ABSTRACT OF THE DISCLOSURE

A method for the production of an aqueous peracetic acid solution by the reaction of hydrogen peroxide with acetic anhydride in the presence of an alkaline catalyst comprising continuously introducing the reactants into a tubular reaction zone at a rate to produce a turbulent flow designated by a Reynolds number of 5,000 to 30,000 and a residence time in the reaction zone of 30 seconds to 5 minutes at a temperature of 80° to 140° F.

This invention relates to the manufacture of dilute, aqueous peracetic acid solutions having a neutral to acid pH, and particularly to a method and apparatus for manufacturing such peracetic acid solutions which operate efficiently and without hazard.

Aqueous peracetic acid at a concentration of on the order of 0.5 to 7% by weight is known to be a very effective bleaching agent for fibers such as cellulosic, polyamide, rayon, regenerated cellulose and linen fibers, as well as other fibers useful in the pulp, paper and textile fields. This peracid is particularly useful because it is effective at neutral to slightly acid pH; accordingly, it is not necessary, as it is with most prior bleaching methods, to employ highly alkaline conditions in pretreatments and/or bleaching. Avoidance of alkaline conditions is important because alkalinity causes undesired changes in fiber properties.

Furthermore, peracetic acid has the advantage in bleaching that it is suitable for bleaching fibers which contain vat- or naphthol-dyes; prior bleaching methods frequently caused variations in hue or fastness, so that a restricted number of dyestuffs were suitable heretofore for dyeing articles to be bleached. Another advantage of the peracetic acid bleach is that it does not develop highly toxic fumes and it is not destructive of materials of construction, particularly stainless steels. Peracetic acid is also useful in chemical applications, bactericidal and sanitizing applications and other uses calling for a dilute peracid having a neutral to acid pH.

In view of these advantages, noted particularly for bleaching, workers for many years have attempted to produce dilute peracetic acid in commercial quantities. Typically, Reichert et al. in their U.S. Patent 2,377,038, issued in 1945, taught a method for making dilute peracetic acid solutions (preferably alkaline) useful in textile bleaching and other operations. Their patent pointed up the fact that bleaching solutions of peracids must be relatively dilute and that the common methods of producing peracetic acid, for example reaction of high concentration hydrogen peroxide and acetic acid or acetic anhydride in the presence of sulfuric acid or other acid catalysts, are not suitable for peracid bleach solution preparation since they are not susceptible to use in bleacheries which do not have the equipment necessary for handling high concentration peroxygen chemicals.

However, despite the work of Reichert et al. and others, and despite the desirability of bleaching with peracetic acid because of its noted advantages, peracetic acid has not become generally accepted commercially for this use.

2

The reason for this failure of peracetic acid to find widespread application in bleaching is not apparent from a consideration of material published on the subject, but is very real. Commercial trials in this country and abroad in the last few years were abandoned when bleaching ranges employing peracetic acid in several mills quite unexpectedly encountered explosions. Once again, peracetic acid failed to materialize as a generally useful commercial bleaching chemical.

It therefore is an object of this invention to provide a method and apparatus for producing continuously for direct use, dilute peracetic acid having a neutral to acid pH.

It is a further object to provide such peracetic acid efficiently, and particularly by means which avoids the hazardous conditions heretofore encountered in the production of dilute peracetic acid by prior methods.

It has now been found that prior, batch methods of producing dilute peracetic acid solutions employing alkaline catalysts for reaction of relatively dilute hydrogen peroxide with acetic anhydride provide unduly large amounts of the explosive reaction intermediate diacetyl peroxide for unduly long times, both because of the large amount of peracid solution which is produced and stored in batch operations and because of the large amount of diacetyl peroxide provided in the overall reaction and the long time required for conversion of it to the desired product in the batch process. The process of this invention avoids maintaining large amounts of diacetyl peroxide in the peracid-forming reaction mix and in the product, both because in this process the diacetyl peroxide is consumed essentially instantaneously, and because the process operates continuously so that no bulk storage of peracid is necessary.

The herein process involves continuously introducing into a tubular reaction zone at a temperature of about 80° to 140° F., and preferably about 110° to 130° F., and under an even pressure and at a rate to provide a turbulent flow of reactants expressed as a Reynolds number value of about 5,000 to 30,000, the following reactants in the following amounts: (a) an aqueous hydrogen peroxide source to provide in the reaction mixture an active oxygen concentration of 0.8 to 12.0 volumes, (b) acetic anhydride in an amount to provide an acetic anhydride to hydrogen peroxide (calculated as 100%) molar ratio of 1.0 to 1.16 to 1, and preferably about 1.08 to 1, and (c) an alkaline catalyst compatible with active oxygen in an amount to provide a pH in the reaction mixture of 5.4 to 7.0, and preferably 5.5 to 6.0, and continuously withdrawing an aqueous peracetic acid reaction product at a concentration of about 0.5 to 7% by weight at a rate to provide in the reaction a residence time of about 30 seconds to 5 minutes, and preferably 1 to 2 minutes. The pressure at which the reactants are introduced is dependent upon the desired residence time and Reynolds number, and normally is about 10 to 250 p.s.i.g.

By carrying out the reaction in this manner under the conditions specified, build-up of and maintenance of diacetyl peroxide in the reaction mixture is held to a minimum so that the product is substantially free of explosive hazard both in preparation and in use. Safety is augmented by the fact that the process is conducted on a demand basis, with reactants being fed into one end of the apparatus and product discharging in as little as one-half minute from the other end, ready for use. Storage of peracid solution is therefore not necessary, and dangerously large quantities of peracetic acid and diacetyl peroxide are not built up. Furthermore, dilute peracid solutions are not very stable (typically, 20% or more of the peracid active oxygen may be lost at 80° F. for 8 hours), so that the ability of the process to deliver peracid for immediate use is extremely valuable.

The apparatus of this invention, in which the herein process is most suitably carried out, comprises a coiled, easily ruptured, tubular reactor having an inside diameter of  $\frac{1}{8}$ " to 1", which is immersed in a tank of liquid. Means are provided for introducing the reactants into the reactor under pressure and at a steady, pulse-free rate, through a mixing apparatus such as a mixing cross, and an outlet is provided for withdrawal of product at the end of the reaction zone opposite the point of introduction of reactants. In this apparatus, the coiled tubular reactor comprises a tube formed from thin-walled tubing which is easily ruptured relative to commonly used construction materials such as standard weight steel piping. By easily ruptured is meant a tube which ruptures at pressures no greater than about 10,000 pounds per square inch of wall area. The lower limit on wall strength is established by the reaction conditions. Where a reaction is run at a pressure of 50 p.s.i., for example, tubing having a rupture strength of as low as on the order of 150 p.s.i. is suitable and provides a satisfactory safety factor.

The liquid, which preferably is water, in which the coil is immersed serves as a safety means since it is able to absorb the shock of any possible explosion should the feed of reactants get out of control and explosive mixtures develop. To this end, the body of liquid is sufficiently large to surround the coil entirely, and preferably extends beyond the periphery of the coil in all directions for at least one foot in order to provide optimum shock-absorbing ability. For best results, the liquid is housed in a steel or equivalent strength tank having a wall thickness of at least about  $\frac{3}{8}$ ". Also importantly as to safety, carrying the reaction out in a coiled tube serves to limit propagation of any explosion which might occur, since such propagation does not extend beyond one loop of the coil. Use of an easily ruptured reactor tube minimizes the possibility of excessive build-up of explosive mixture, since the tube is rupturable by a small detonation which could occur early upon loss of control of reactant feed, temperature and the like, with consequent release of the reactants into, and dilution in, the surrounding liquid.

In the preferred apparatus, the tubular reaction zone is provided as a coil having a coil diameter and spacing which permits it to fit within a reasonably sized tank of liquid; normally the coils have a minimum separation of about  $\frac{1}{4}$ " and the ratio of the total tube length to the coil diameter is about 50 to 500 to 1.

The reactor coils suitably are constructed of tubes of stainless steel, nickel, aluminum or other metal compatible with active oxygen compounds and resistant to corrosion in the herein system, having a wall thickness of up to about 0.02", or plastic materials such as polyethylene, polypropylene, polyvinyl chloride, Teflon and other plastics which are compatible with active oxygen compounds and corrosion resistant. Tubing of these materials are rupturable under a force of less than about 10,000 pounds per square inch of wall area. The tube preferably has a circular cross-section, although this is not necessary and when a tube which is other than circular is used the diameter is calculated as the diameter of a circle having the same area as the cross-sectional area of the tube used.

Tubing rupturable at pressures less than about 10,000 pounds per square inch is light weight, and will be contained by the liquid surrounding the reactor coil in the herein apparatus in the event of an explosion. Stainless steel tubing is preferred for use in this apparatus, and when used at thicknesses of up to 0.02" ruptures at pressures below about 10,000 pounds per square inch to form elongated light weight strips which minimize possible hazards normally associated with explosions.

In the process the reactants are introduced under an even, pulse-free pressure in the range of about 10 to 250 p.s.i.g. which creates a turbulent flow in the reaction zone. This flow is distinguished from a laminar flow, and is described by the so-called Reynolds number which

denotes the degree of mixing in flowing liquids. Although turbulent flow is encountered at Reynolds numbers as low as 5,000, it is preferred to operate this process in such a condition of turbulence as provides a Reynolds number of about 10,000 to 30,000. The Reynolds number is determined from the following formula:

$$N_{Re} = \frac{D\bar{V}\rho}{\mu}$$

where

D=diameter of pipe, ft.

$\bar{V}$ =average linear velocity of fluid, ft./sec.

$\mu$ =viscosity of fluid, lb./ft.-sec.

$\rho$ =density of fluid, lb./ft.<sup>3</sup>

The combination of use of a tubular reaction zone and a turbulent flow of reactants therethrough results in quite rapid and efficient production of a peracetic acid solution without undue build-up of diacetyl peroxide. Under these conditions, the reaction to peracetic acid proceeds to very satisfactory yields in as little as about 30 seconds to one minute, although residence times of as much as 5 minutes can be tolerated safely due to the advantages of this method.

The acetic anhydride and hydrogen peroxide reactants are used in the reaction of this invention in a molar ratio of the former to the latter of about 1.0 to 1.16 to 1, and preferably about 1.08 to 1. This ratio of reactants permits the obtaining of high yields without either forming excessive diacetyl peroxide, which occurs at too high acetic anhydride concentrations, or wasting of hydrogen peroxide, which occurs when excessive amounts of hydrogen peroxide are used.

The hydrogen peroxide is used at a concentration of about 0.8 to 12.0 volumes (0.24 to 3.64% by weight) in the aqueous reaction mixture. This concentration of hydrogen peroxide provides peracetic acid solution directly useful in bleaching fibers, an operation which desirably employs aqueous peracetic acid having an active oxygen volume concentration of 0.7 to 10.3 (0.5 to 7.0 weight percent). The herein process produces peracetic acid having a concentration of up to about 7 weight percent, which if necessary is readily dilutable with water to useful concentrations. The hydrogen peroxide obviously can be replaced in part or in whole by sodium peroxide, which in solution acts the same as an equivalent mixture of hydrogen peroxide and sodium hydroxide. When sodium peroxide is used, its alkalinity must be taken into account.

An alkaline catalyst is used in this reaction to promote conversion of the hydrogen peroxide and acetic anhydride to peracetic acid. It is used in an amount which provides both catalysis of the peracid-forming reaction and a pH in the peracid product solution at which it is useful for bleaching. Accordingly, pH adjustment of the solution prior to bleaching is not necessary. Where desired, however, the pH of the peracid solution can be adjusted with acids such as sulfuric acid, acetic acid, phosphoric acid and the like acids which are compatible with active oxygen, or with alkalis such as ammonium hydroxide, sodium hydroxide, sodium carbonate and the like alkalis which are compatible with active oxygen. The alkaline agents which are used as catalysts likewise are those which are compatible with active oxygen as hydrogen peroxide and peracetic acid, and include sodium hydroxide and ammonium hydroxide. Tetrasodium pyrophosphate or other polyphosphates may be added to overcome impurities in local water supplies which might adversely affect active oxygen stability.

The reaction product is provided at a pH of about 5.4 to 7.0, and preferably 5.5 to 6.0. It is apparent that where sodium peroxide is used in this reaction, the requirements of alkali for catalysis and establishment of desired pH is affected by the alkalinity of the sodium peroxide.

The temperature at which the reaction to form peracetic acid is carried out is about 80° to 140° F., and preferably

110° to 130° F. Operation at temperatures substantially lower than 80° F. increases the amount of diacetyl peroxide formed, while operation above about 140° F. leads to undue losses of active oxygen. The herein continuous process with its inherent safety features and with its ability to produce a peracid solution for immediate use, can be run periodically at higher temperatures than can the batch method. In a batch method operation at elevated temperatures, upwards of 140° F., is deleterious because of the need normally to produce and store the peracid before use; the inherent instability of the peracid on storage at useful pH's of 5.4 to 7.0 is magnified when it is produced under such conditions.

Temperature and pH effects are inter-related; raising either or both of the pH and temperature lowers diacetyl peroxide content, but increases the active oxygen loss. Lowering either or both of pH or temperature below the preferred conditions expressed herein reduces the ratio of conversion of the acetic anhydride and hydrogen peroxide to peracetic acid.

The invention will now be described with reference to the single drawing attached, which shows the apparatus of this invention which is particularly useful in carrying out the herein process.

In the drawing, which is a schematic diagram, there is provided a tubular coiled reaction zone 10, placed within a tank 12 of water or other suitable liquid 14 which serves as a means for absorbing any possible explosive force created by detonation of the reactants or reaction products. Reactants are fed to this reaction zone from three feed tanks; 16 containing hydrogen peroxide, 18 containing acetic anhydride and 20 containing aqueous alkaline catalyst solution. Hydrogen peroxide is fed from tank 16 through line 22 and metering pump head 24; acetic anhydride is fed from tank 18 through line 26 and metering pump head 28; and aqueous alkaline solution is fed from tank 20 through line 30 and metering pump head 32, all to mixer 34, suitably a mixing cross, where they are blended for passage into reaction zone 10. The metering, diaphragm pump heads are driven by a common motor 38 to maintain a predetermined ratio of feed of reactants. A magnetic clutch 40 between the aqueous ammonia feed head 32 and the other two feed heads 24 and 28 engages the drive shaft from the motor 38, and is so designed as to be disengaged upon start-up and shut-down of the apparatus for a predetermined time, which permits the aqueous ammonia feed to be introduced alone to the reactor coil 10, thereby flushing the system and destroying any potentially hazardous residual diacetyl peroxide. Surge dampeners 42 in each of lines 22, 26 and 30 regulate the flow to a steady condition, where a piston, diaphragm or other pump 38 which creates pulsating flow is used. These dampeners function by exposing the process fluid to a suitably sized flexible diaphragm which separates the fluid from a sealed gas chamber in which the pressure of the gas is adjustable. The diaphragm acts like a spring to dampen oscillations in flow pressure.

The tank 12 of liquid 14 is provided with a water or steam inlet 44 and outlet 46; this makes it possible to regulate the temperature of the reaction by controlling the liquid temperature. The reaction is exothermic, but atmospheric cooling sometimes more than compensates for the heat given off by the reaction, and some heating with steam or hot water is desirable to maintain the required reaction temperature. Peracetic acid product from reaction zone 10 is passed from line 48 to a bleaching range or other end use site for the peracid, or to storage.

The following examples are presented by way of illustration of the present invention only, and are not to be considered as limiting the scope thereof in any way.

### Example 1

A coil 10 having 40 turns on 0.9" centers and having a coil diameter of 28.5 inches, was formed of a ½" O.D. 304 stainless steel tube 300 feet long having a wall thick-

ness of 0.02 inch, and inside diameter of 0.46 inch. This coil was immersed centrally in a cylindrical steel tank 12, 6 feet high and 6.4 feet in diameter, and the tank was filled with water 14. The coil was fitted at the bottom with a mixing cross 34, to which three stainless steel lines 22, 26 and 30 were attached for feeding 50% aqueous hydrogen peroxide, acetic anhydride and 1.38% aqueous ammonium hydroxide solutions. These materials were introduced through metering pump heads 24, 28 and 32 run by motor 38. Surges in feed created by pump action were smooth by surge dampeners 42. Product peracetic acid solution was removed via line 48.

The reaction to form peracetic acid was carried out by feeding the acetic anhydride, hydrogen peroxide and aqueous ammonium hydroxide solutions at the following rates.

| Ingredient:                                 |       | Gallons per hour |
|---------------------------------------------|-------|------------------|
| Hydrogen peroxide                           | ----- | 5.9              |
| Acetic anhydride                            | ----- | 10.5             |
| Aqueous ammonia (1.38% as NH <sub>3</sub> ) | ----- | 167.7            |

This provided a pH of 6.0 and a molar ratio of acetic anhydride to hydrogen peroxide of 1.08 to 1 on a 100% hydrogen peroxide basis. The rate of introduction of ingredients was such that a turbulent flow, measured as a Reynolds number of 20,000, was created and the reaction mixture was in the reaction zone for 60 seconds, and the reaction temperature was 120° F.

Analysis for diacetyl peroxide, conducted one minute after introduction of reaction ingredients into the tube (as they issued from the reactor) showed the presence of 0.035% (by weight of total reaction mixture) of diacetyl peroxide. The product contained 3.57% by weight of peracetic acid, a conversion of 85.5% based on the hydrogen peroxide introduced.

### Example 2

The apparatus used in Example 1 was employed in carrying out a series of runs designed to demonstrate the effects of pH and temperature on the conversion of hydrogen peroxide to peracetic acid and on the amount of diacetyl peroxide formed in the production of peracetic acid by the herein reaction of dilute hydrogen peroxide with acetic anhydride, at a Reynolds number flow of 20,000 and using aqueous ammonia as the alkali source. The results of these tests are shown in Table 1 which follows. Table 1 shows the effect of pH on conversion and diacetyl peroxide content at two temperatures, namely 80° F. and 120° F. In these runs the residence time in the reactor was 1 minute, and 3 gallons per minute of reactants were put through the reactor. A hydrogen peroxide concentration of 1.87% (or 6.15 volumes) and a molar ratio of 1.08 acetic anhydride to hydrogen peroxide were employed. Diacetyl peroxide is designated as DAP.

TABLE 1

| pH  | DAP    |         | Percent conversion of H <sub>2</sub> O <sub>2</sub> to peracetic acid, active oxygen basis |         |
|-----|--------|---------|--------------------------------------------------------------------------------------------|---------|
|     | 80° F. | 120° F. | 80° F.                                                                                     | 120° F. |
| 5.3 | 1.13   | 0.38    | 57                                                                                         | 74.8    |
| 5.4 | 1.01   | 0.25    | 63                                                                                         | 79.2    |
| 5.5 | -----  | 0.26    | -----                                                                                      | 79.7    |
| 5.6 | 0.44   | 0.14    | 78.0                                                                                       | 81.3    |
| 5.7 | -----  | 0.07    | -----                                                                                      | 83.0    |
| 5.8 | -----  | 0.04    | -----                                                                                      | 83.5    |
| 5.9 | 0.24   | 0.04    | -----                                                                                      | 82.3    |
| 6.0 | 0.19   | 0.035   | 84.8                                                                                       | 85.5    |
| 6.1 | 0.133  | 0.025   | -----                                                                                      | 77.2    |
| 6.5 | 0.03   | 0.017   | 83.0                                                                                       | -----   |
| 7.0 | 0.013  | 0.01    | 80.1                                                                                       | -----   |
| 7.5 | -----  | -----   | -----                                                                                      | 27.8    |

The results shown in this Table 1 demonstrate how the level of diacetyl peroxide increases at lower temperatures and at lower pH's, and how the active oxygen conversion quite unexpectedly drops off at both ends of the pH range of the process of this invention.

## Example 3

This example demonstrates the effect of mole ratio of acetic anhydride to hydrogen peroxide, the only variant being the mole ratio. The pH employed was 5.7 and the reaction temperature was 120° F., with the other conditions being those employed in Example 2.

Table 2

| Mole ratio: | Percent conversion |
|-------------|--------------------|
| 1.0 -----   | 77.5               |
| 1.08 -----  | 83.0               |
| 1.16 -----  | 85.5               |

The use of excess acetic anhydride carries the reaction of hydrogen peroxide farther, as would be expected; however, there is a practical upper limit on the excess of acetic anhydride which may be employed. If this excess is too high it is costly, involving dilution of the active oxygen material; use of an excess of hydrogen peroxide, on the other hand, is wasteful of this expensive reagent.

## Example 4

This example demonstrates the effect of flow rate and feed pressure in the tubular reaction zone on the Reynolds number. The tests in this case were run with an acetic anhydride-ammonia aqueous solution having the same physical properties as the reaction mixture of Example 1, and involved varying the flow rate and feed pressure in the equipment used in Example 1.

TABLE 3

| Flow rate,<br>gal./hr. | Reynolds<br>number | Pressure<br>drop across<br>coil, p.s.i.g. | Reactor effluent appearance                |
|------------------------|--------------------|-------------------------------------------|--------------------------------------------|
| 10-----                | 1,080              | <2                                        | Two phases present.                        |
| 30-----                | 3,240              | 2                                         | Organic phase apparent as fine dispersion. |
| 50-----                | 5,000              | 10                                        | Single phase.                              |
| 90-----                | 9,750              | 20                                        | Do.                                        |
| 135-----               | 14,600             | 40                                        | Do.                                        |
| 185-----               | 20,000             | 68                                        | Do.                                        |
| 210-----               | 23,000             | 87                                        | Do.                                        |

The following table, Table 4, shows that residence time can be increased and the Reynolds number decreased within the above range without affecting conversion and with no deleterious increasing effect on diacetyl peroxide formation.

TABLE 4

| Residence<br>time, min. | Reynolds<br>number | pH   | Percent<br>conversion | Percent diacetyl<br>peroxide in<br>product after<br>one minute |
|-------------------------|--------------------|------|-----------------------|----------------------------------------------------------------|
| 1.00-----               | 20,000             | 5.67 | 81.6                  | 0.095                                                          |
| 1.25-----               | 16,000             | 5.63 | 82.3                  | 0.065                                                          |
| 1.67-----               | 12,000             | 5.63 | 84.7                  | 0.055                                                          |
| 2.00-----               | 10,000             | 5.63 | 84.0                  | 0.03                                                           |

## Example 5

A coil 10 having 40 turns on 0.9" centers and having a coil diameter of 28.5 inches, was formed of a ½" O.D. 304 stainless steel tube 300 feet long having a wall thickness of 0.02 inch, and inside diameter of 0.46 inch. This coil was immersed centrally in a cylindrical steel tank 12, 6 feet high and 6.4 feet in diameter, and the tank was filled with water 14. The coil was fitted at the bottom with a mixing cross 34, to which three stainless steel lines 22, 26, and 30 were attached, for feeding 50% aqueous hydrogen peroxide, acetic anhydride and 1.30% aqueous ammonium hydroxide solutions. These materials were introduced through metering pump heads 24, 28 and 32 run by motor 38. Surges in feed created by pump action were smoothed by surge dampeners 42. Product peracetic acid solution was removed via line 48.

The reaction to form peracetic acid was carried out by feeding the acetic anhydride, hydrogen peroxide and aqueous ammonium hydroxide solutions at the following rates:

| Ingredient:                   | Gallons per hour |
|-------------------------------|------------------|
| Hydrogen peroxide (50%) ----- | 5.9              |
| Acetic anhydride -----        | 10.5             |
| Aqueous ammonia (1.30%) ----- | 167.7            |

This provided a pH of 5.6 and a molar ratio of acetic anhydride to hydrogen peroxide of 1.08 to 1 on a 100% hydrogen peroxide basis. The rate of introduction of ingredients was such that a turbulent flow, measured as a Reynolds number of 20,000, was created and the reaction mixture was in the reaction zone for 60 seconds, and the reaction temperature was 80° F.

Analysis for diacetyl peroxide conducted one minute after introduction of reaction ingredients into the tube as they issued from the reactor, showed the presence of 0.44% (by weight of total reaction mixture) of diacetyl peroxide. The product contained 3.25% by weight of peracetic acid, a conversion of 78.0% based on the hydrogen peroxide introduced.

## Example 6.—Comparative example—Batch process

This batch experiment was conducted to compare the amount of diacetyl peroxide provided at the same molar ratio of hydrogen peroxide to acetic anhydride as employed in the continuous reaction of Example 5, at the same pH of 5.6 and at the same temperature of 80° F.

Eighty-seven and five tenths milliliters of water, 3.8 ml. of aqua ammonia (26.0%) 6.0 ml. of acetic anhydride and 3.2 ml. of hydrogen peroxide (as 50% aqueous) were fed in that order into a 200 ml. beaker provided with a magnetic stirrer and placed behind a Lucite safety shield to serve in the event of explosion. The reaction time was considered as beginning with the start of anhydride addition, an addition which took 17 seconds to complete. The pH in the reaction mix was 5.6 and the temperature was 80° F. After 60 seconds, measured as indicated above, the reaction mixture contained 1.04% of diacetyl peroxide as weight percent of the total reaction mixture. The conversion of hydrogen peroxide to peracetic acid on an active oxygen basis was 66.7% after 60 seconds, and the product solution contained 2.88% by weight of the peracid.

The above examples demonstrate the manner of carrying out the process of this invention, and its advantages. The comparative runs of Examples 5 and 6 show the advantage of a continuous process of this invention, shown in Example 5, over a typical batch method of the prior art, shown in Example 6. Diacetyl peroxide formation is substantially reduced by the process of this invention without adversely affecting conversion of hydrogen peroxide to peracetic acid. The reason for the relatively poor conversion is that the batch method had to be run at low temperature for peracid stability reasons and for comparison the continuous process (Example 5) was run under the same conditions.

An additional important point is that whereas the continuous method of Example 1 produces sufficient peracetic acid solution to handle a typical commercial bleaching range over an 8-hour day with an accumulation of no greater than about 3 gallons of reactants (it has a 3-gallon throughput per minute and employs a one-minute residence time) a batch method run to provide the required amount of peracetic acid for a corresponding 8-hour bleaching run involves producing 1440 gallons of peracid solution. Even should several batches, rather than one large batch, be run in batch processing it would be necessary to produce large amounts of peracetic acid solution and store it for eventual use. The amount of diacetyl peroxide in such a large reserve of peracetic acid solution is dangerous, particularly because on storage the diacetyl peroxide is apt to separate and to concentrate; the likelihood of separation is magnified at low temperatures such as frequently encountered in bleaching mill practice.

Overall, therefore, the process and apparatus of this invention provide real advantage to users of dilute peracetic acid aqueous solutions, making it possible for the first time to produce dilute, neutral to acidic peracetic acid

economically and safely at the user's site. While the utility of the process is discussed particularly with respect to its use in bleaching operations, it is useful wherever dilute aqueous peracetic acid solutions at a neutral to acid pH are required.

Pursuant to the requirements of the patent statutes, the principle of this invention has been explained and exemplified in a manner so that it can be readily practiced by those skilled in the art, such exemplification including what is considered to represent the best embodiment of the invention. However, it should be clearly understood that, within the scope of the appended claims the invention may be practiced by those skilled in the art, and having the benefit of this disclosure, otherwise than as specifically described and exemplified herein.

What is claimed is:

1. A method of producing an aqueous peracetic acid solution having a concentration of 0.5 to 7.0 weight percent of peracetic acid, a pH of 5.4 to 7.0 and free of deleterious amounts of diacetyl peroxide, comprising continuously introducing into a tubular reaction zone at a rate to produce a turbulent flow designated by a Reynolds number of 5,000 to 30,000 and a residence time of reactants in the reaction zone of 30 seconds to 5 minutes, at a temperature of 80° to 140° F., the following reactants in the following relative proportions: (a) aqueous hydrogen peroxide in an amount to provide in the reaction mixture an active oxygen concentration of 0.8 to 12.0

volumes, (b) acetic anhydride in an amount to provide an acetic anhydride to hydrogen peroxide molar ratio of 1.0 to 1.16 to 1, and (c) an alkaline catalyst compatible with active oxygen in an amount to provide a pH in the reaction mixture of 5.4 to 7.0, and withdrawing the peracetic acid solution reaction product from the reaction zone.

2. The method of claim 1 in which the alkaline catalyst is ammonium hydroxide.

3. The method of claim 1 in which the molar ratio of acetic anhydride to hydrogen peroxide is about 1.08 to 1 and the residence time in the reaction zone is 1 to 2 minutes.

4. The method of claim 1 in which the reaction is carried out at a temperature of 110° to 130° F. and a pH of 5.5 to 6.0.

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