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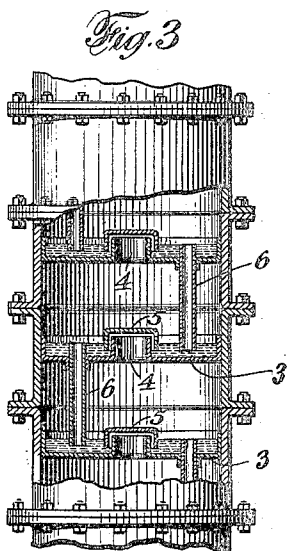
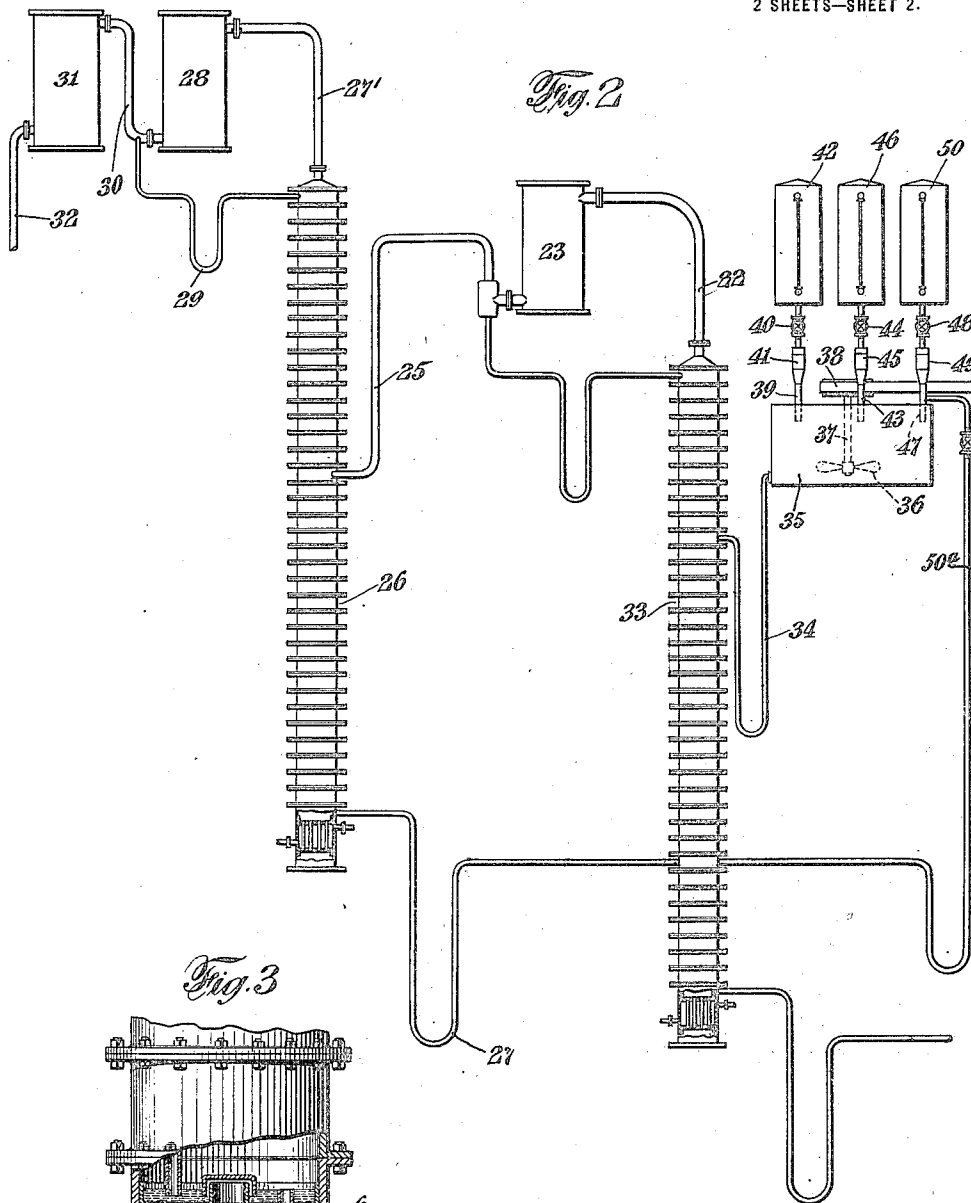
The diagram, labeled "Fig. 1.", illustrates a complex mechanical system. It features two primary vertical cylinders, labeled 1 and 2, which are interconnected by a series of pipes and valves. Cylinder 1 is positioned on the left, and cylinder 2 is on the right. A network of pipes, including lines 25, 24, 22, 26, 27, 20, 21, 29, 30, and 32, connects these cylinders to various components. At the top left, there are two reservoirs, 28 and 31, with associated pipes 27' and 32. A pump or motor unit, labeled 19, is connected to cylinder 2 via pipe 20. To the right of cylinder 2, there are three vertical control or measurement units, labeled 8, 12, and 13, each with a corresponding valve or connector (9, 13, 16) and a long vertical pipe (10, 14, 17). A U-shaped pipe, labeled 7 and 11, is connected to cylinder 2. The entire system is depicted with detailed line work representing the mechanical components and their interconnections.

In witness whereof I have hereunto set my hand and the seal of the said Court, at the City of New York, this 10th day of June, 1884.
 Arthur A. Backhaus, Insignator
 By his Attorney, Prindle, Wright & Knapp.

A. A. BACKHAUS.
 CONTINUOUS PROCESS FOR THE MANUFACTURE OF ESTERS.
 APPLICATION FILED AUG. 7, 1918.

1,400,849.

Patented Dec. 20, 1921.
 2 SHEETS—SHEET 2.



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UNITED STATES PATENT OFFICE.

ARTHUR A. BACKHAUS, OF BALTIMORE, MARYLAND, ASSIGNOR TO U. S. INDUSTRIAL ALCOHOL CO., A CORPORATION OF WEST VIRGINIA.

CONTINUOUS PROCESS FOR THE MANUFACTURE OF ESTERS.

1,400,849.

Specification of Letters Patent. Patented Dec. 20, 1921.

Application filed August 7, 1918. Serial No. 243,754.

To all whom it may concern:

Be it known that I, ARTHUR A. BACKHAUS, of Baltimore, in the State of Maryland, have invented a certain new and useful Improvement in Continuous Processes for the Manufacture of Esters, and do hereby declare that the following is a full, clear, and exact description thereof.

My invention relates to a process by means of which esters may be made continuously, that is to say, without interruption, and has reference to the manufacture of many different kinds of esters in this way.

The object of my invention is to provide a process by means of which esters may be manufactured continuously, instead of requiring the repeated interruption of the process that was hitherto found necessary. A further object is to provide a process of this character by means of which esters, substantially entirely free from water, may be obtained. Further objects of my invention will appear from the detailed description contained hereinafter.

While my invention is capable of being carried out in many different ways, for the purpose of illustration I shall describe only certain ways of carrying out my invention hereinafter, and while it is capable of being carried out in connection with many different types of apparatus, I have shown only two types of apparatus for use in connection therewith in the accompanying drawings, in which—

Figure 1 is a diagrammatic representation of an apparatus which may be used in accordance with my invention,

Fig. 2 is a diagrammatic representation of another type of apparatus which may be used in connection with my invention, and

Fig. 3 is an enlarged vertical section of a detail of one of the columns.

Referring first to Fig. 1, I shall describe my invention as it is applied to the treatment of a weak acid, as for example, dilute acetic acid or vinegar with methyl alcohol in the production of methyl acetate, although it is to be understood that my process is applicable to the production of many different esters and from materials of many different strengths.

In the drawings, referring to the type illustrated in Fig. 1, I have shown a column

still 1 comprised of an outer casing 2, and a large number of plates or pans 3 having central openings 4 covered by hoods or bells 5, the edges of which are sealed in the liquid carried by said plates 3, the adjacent plates being connected by overflow pipes 6. I preferably supply to the upper part of the column still 1 continuously a quantity of sulfuric acid having, for example, a strength of 50° Bé. to 66° Bé. This is preferably done by means of a trapped pipe 7 leading from a sulfuric acid tank such as tank 8, shown as having its outlet controlled by a needle valve 9 and a sight feed 10. The sulfuric acid is preferably fed in the proportion of .33 parts by weight of sulfuric acid to 10 parts by weight of vinegar having a strength of 8% acetic acid, which vinegar is preferably fed continuously to the still 1 by *e. g.*, a trapped pipe 11, leading from an acetic acid tank 12, shown as also provided with a needle valve 13 and a sight feed 14. In addition, methyl alcohol, preferably having a strength of approximately 95% is also fed, preferably continuously, but in the proportion of $\frac{1}{10}$ part by weight, and ordinarily through, *e. g.*, a trapped pipe 15 controlled by a needle valve 16 and a sight feed 17, leading from an alcohol tank 18. Initially, before feeding through the pipes 10, 11 and 15, however, sufficient methyl alcohol is preferably fed into the apparatus to seal all the pans in the column still 1. The proportion of alcohol is varied, however, according to the strength of the acetate, or the like, that is desired to be obtained. The still 1 is preferably heated at its lower end by means such as a tubular heater 19 having inlet and outlet steam pipes 19^a and 19^b. The effluent liquids such as water and sulfuric acid are preferably conducted away from the still 1 by a pipe 20 having a trap 21 therein. From the upper portion of the still 1 a vapor discharge pipe 22 is provided to conduct away the vapors such as the methyl acetate and alcohol, which may have a proportionate composition of 30 parts by weight of methyl acetate and 70 parts by weight of methyl alcohol, to a device such as dephlegmator 23, preferably having a trapped return pipe 24 for returning the condensed alcohol to the top of the column still 1, as well as a discharge pipe 25 for conveying the methyl

acetate or like vapors to a second column 26 constructed in the same manner as the column 1, except that this column is not provided with several inlets, and with the exception
 5 that a trapped discharge pipe 27 preferably conveys away the methyl alcohol from the lower portion of said column 26 to the column 1 at a point which may be opposite to the entry of the pipe 15. In the operation
 10 of the embodiment described the vapors from the pipe 25 ascend in the column 26 through a descending current of methyl alcohol, and the vapors of methyl acetate containing a small amount of methyl alcohol,
 15 are conveyed by a pipe 27' to a dephlegmator 28 from which the condensed methyl alcohol returns by a trapped pipe 29 to the top of the column 26, while the vapors of methyl acetate are conducted by a pipe 30
 20 to a condenser 31 from which the condensed methyl acetate is drawn off by a pipe 32. The methyl acetate produced in this manner is substantially water-free as shown by test with anhydrous copper sulfate.
 25 In case it is desired to use a strong acid, as for example, glacial acetic acid, a somewhat different arrangement of apparatus may be used, as for example, an apparatus, such as shown in Fig. 2. The apparatus
 30 shown in Fig. 2 is constructed the same as the apparatus shown in Fig. 1, except in the following respects: In this instance, I have provided a column 33 constructed the same as the column 1, except that there is only
 35 one trapped inlet pipe 34 which leads from a mixing tank 35 provided with a propeller 36 carried by a shaft 37, and rotated by a pulley 38 from any suitable source of power. Sulfuric acid may be, in this embodiment,
 40 continuously fed to the tank 35 by means of a pipe 39 having a needle valve 40 and a sight feed 41 connected to a sulfuric acid tank 42. In this instance, the sulfuric acid is fed to the mixing tank 35 in the proportion of, *e. g.*, 2 parts by weight of sulfuric acid having a strength of 50° Bé, to 66° Bé., to 10 parts by weight of glacial acetic acid which is fed continuously to the tank 35
 45 by means of a pipe 43 having a needle valve 44 and a sight feed 45 connected to an acetic acid tank 46. At the same time methyl alcohol having a strength of 95 to 98% is continuously fed in the proportion of 6 parts by weight to the tank 35 by means of a pipe
 50 47 having a needle valve 48 and a sight feed 49 connected to an alcohol tank 50. Initially, before feeding through the pipe 34, a quantity of methyl alcohol sufficient to fill the pans in the still 33 is introduced
 60 by means of a valved pipe 50^a. In this instance, the reaction by which methyl acetate is formed takes place partly within the tank 35, although the reaction takes place in part also in the column 33. Said column 33 is as
 65 shown provided with a liquid outlet pipe, a

vapor outlet pipe, alcohol return pipes, and other connections just the same as in the apparatus shown in Fig. 1.

In carrying out my process, reference being had to Fig. 1, the sulfuric acid, the
 70 dilute organic acid, such as, for example, vinegar and methyl alcohol are fed continuously into a countercurrent apparatus such as the column still 1, and the reaction
 75 by which methyl acetate is formed takes place within said column, and the heat which is applied to said column drives off the vapors of the ester, such as methyl acetate and methyl alcohol from the top of the column to the dephlegmator, from which
 80 the condensed water carrying some alcohol is returned to the top of the column to form liquid seals and to provide a descending body of methyl alcohol therein. The methyl acetate or like vapors, thus partly freed
 85 from methyl alcohol, may pass then to the second or rectifying column 26 in which nearly all of the methyl alcohol is removed and may be returned as a liquid to the column 1, while the esters, such as methyl
 90 acetate vapors containing a small amount of methyl alcohol pass out of the same into the dephlegmator 28, from which point the remaining quantity of methyl alcohol is returned to the column 26. The methyl acetate, or like vapors then pass to the condenser 31, from which the condensed acetate such as methyl acetate is continually
 95 drawn off.

In carrying out the process, the esterification is carried out more completely and more
 100 rapidly by reason of the continual removal by distillation of the ester from the esterification zone and because of the provision of much larger quantities of an ester such as
 105 methyl alcohol than are needed for the reaction. The quantity of methyl alcohol present is preferably four or five times the quantity of methyl alcohol required in the reaction. Furthermore, the smaller the percentage of the acetic acid in the descending
 110 current of liquid in the still 1, which becomes weaker in the acid as it descends, the larger the quantity of methyl alcohol required to offset the difficulty of esterification, and, therefore, a large quantity of
 115 methyl alcohol is fed in at a point where the liquid is very weak in the ester-forming acid and in such quantity as to complete the esterification before the liquid reaches the
 120 lower end of the column still 1.

In case it is desired to use a strong organic acid, as for example, glacial acetic acid, the apparatus shown in Fig. 2 may
 125 be used, and in this instance the operation is the same as in the case of the apparatus shown in Fig. 1, except that in the apparatus shown in Fig. 2 the sulfuric acid, the fatty acid such as glacial acetic acid and the alcohol are preferably fed into the mix-
 130

ing tank 35 continually, in which tank the ester such as methyl acetate is partly formed, while the mixed liquids are drawn off from said tank 35 by a single pipe 34 to the column still 33. Here, because of the strength of the fatty acid such as acetic acid, the reaction can be effected to a large degree merely by mixing the reagents and this is done, therefore, in the tank 35, so as to relieve the still 33 correspondingly, in order to increase its capacity. In this instance, the remainder of the process may operate the same as in the case of the process used in the apparatus shown in Fig. 1.

By the term countercurrent in the claims, it is intended to cover the movement of acid and alcohol in opposite directions, either in the form of continuous streams or in the form of intermittent streams, such as streams or currents formed by the successive vaporization and condensation or absorption of one of the reacting materials in a manner to advance the relative position of any given particle of liquid.

It will be understood that other acids and other alcohols may be used instead of the methyl alcohol and acetic acid, such for example, as formic acid and ethyl alcohol. Also crude pyroligneous acid may be used, as it contains acetic acid and methyl alcohol, etc. Also, instead of sulfuric acid another catalyst may be used, as a solution of niter cake, or hydrochloric, or any phosphoric acid, or organic acids, such as acetic acid in excess of the amount required in the ester formed.

While I have described my invention above in detail, I wish it to be understood that many changes may be made therein without departing from the spirit thereof.

I claim:

1. The process of manufacturing esters comprising passing an organic acid in countercurrent to gradually increasing concentrations of an alcohol, and in the presence of a catalytic agent while distilling off the ester formed.

2. The process of manufacturing esters comprising passing an organic acid in countercurrent to gradually increasing concentrations of an alcohol in the presence of a catalytic agent while continuously distilling off the esters and removing the water formed.

3. The process of manufacturing esters comprising passing an organic acid and a catalytic agent in countercurrent to increasing concentrations of an alcohol while distilling off the ester formed.

4. The process of manufacturing esters comprising passing an organic acid and a catalytic agent in countercurrent to increasing concentrations of an alcohol while continuously distilling off the ester formed, and removing the water.

5. The process of manufacturing esters comprising flowing sulfuric acid and an organic acid down a column still provided with plates in countercurrent to an alcohol, and distilling the ester formed from the top of the still.

6. The process of manufacturing esters comprising passing strong sulfuric acid and an organic acid down a column still provided with plates containing an alcohol, in countercurrent to an alcohol, continuously distilling off the ester formed from the top of the still, and continuously removing the water formed from the bottom of the still.

7. The process of manufacturing esters comprising passing a strong catalytic agent and an organic acid down a column still provided with plates containing an alcohol in countercurrent to increasing concentrations of an alcohol, continuously distilling off the ester formed from the top of the still, and continuously removing the water from the bottom of the still.

8. The process of manufacturing esters comprising passing an organic acid in countercurrent to gradually increasing concentrations of an alcohol in the presence of a catalytic agent while distilling off the ester formed, and separating the ester from the alcohol in the distillate.

9. The process of manufacturing esters comprising passing an organic acid in countercurrent to gradually increasing concentrations of an alcohol in the presence of a catalytic agent while distilling off the ester formed, separating the ester from the alcohol in the distillate, and returning the alcohol to the still.

10. The process of manufacturing methyl acetate comprising passing acetic acid in countercurrent to gradually increasing concentrations of methyl alcohol in the presence of strong sulfuric acid while distilling off the methyl acetate formed.

11. The process of manufacturing methyl acetate comprising passing acetic acid in countercurrent to gradually increasing concentrations of methyl alcohol in the presence of strong sulfuric acid, continuously distilling off the methyl acetate formed, and continuously removing the water.

12. The process of manufacturing methyl acetate comprising passing acetic acid in countercurrent to gradually increasing concentrations of methyl alcohol in the presence of strong sulfuric acid, distilling off the ester formed, separating the methyl alcohol from it by condensation, passing the ester vapor into contact with methyl alcohol to condense the remaining alcohol vapors, and collecting the purified methyl acetate.

13. The process of manufacturing methyl acetate comprising passing strong acetic acid and strong sulfuric acid down a column still provided with plates containing methyl al-

cohol, introducing methyl alcohol near the bottom of the still and heating the methyl alcohol near the bottom of the still in order to distil off the methyl acetate at the top of the still.

14. The process of manufacturing methyl acetate comprising passing strong acetic acid and strong sulfuric acid down a column still provided with plates containing methyl alcohol, introducing methyl alcohol near the bottom of the still, heating the methyl alcohol near the bottom of the still in order to distil off the methyl acetate at the top of the still, purifying the methyl acetate by passing it through methyl alcohol and collecting the pure methyl acetate.

15. The process of manufacturing methyl acetate comprising passing strong acetic acid and strong sulfuric acid down a column still provided with plates containing methyl alcohol, continuously replenishing said plates with methyl alcohol, heating the alcohol near the bottom of the still to expel the methyl acetate from the top thereof, passing said acetate vapors into a second still containing methyl alcohol, distilling off the methyl acetate from said second still, condensing methyl alcohol vapors from the acetate vapors, and recovering the purified methyl acetate.

16. The process of manufacturing methyl acetate comprising continuously passing strong acetic acid and strong sulfuric acid down a column still provided with plates containing methyl alcohol, continuously replenishing said plates with methyl alcohol as it is used up, heating the methyl alcohol near the bottom of the still to expel the methyl acetate from the top thereof, continuously removing aqueous liquid from the bottom of the still, continuously distilling off methyl acetate from the top and removing methyl alcohol therefrom, continuously passing the acetate vapors into a second still near the middle thereof, said still having plates containing methyl alcohol, heating the methyl alcohol near the bottom of said second still to expel the methyl acetate from the top thereof, continuously passing the excess methyl alcohol from the bottom of the second still to the first still near its bottom, continuously separating methyl alcohol vapors from the methyl acetate vapors distilled off from the second still, and collecting the purified methyl acetate.

17. The process which comprises forming an ester by feeding methyl alcohol, acetic acid and a catalytic agent to intermingle the same, and at the same time continually removing the vapor of the ester formed while bringing it into contact with an oppositely moving current of the reacting materials.

18. The process which comprises forming an ester by feeding methyl alcohol, glacial

acetic acid and a catalytic agent to intermingle the same, and at the same time continually removing the vapor of the ester formed while bringing it into contact with an oppositely moving current of the reacting materials.

19. The process of manufacturing esters comprising allowing a current of an organic acid to react with successive quantities of an alcohol of progressively increasing concentrations, and in the presence of a catalytic agent while distilling off the ester formed.

20. The process of manufacturing esters comprising allowing a current of an organic acid to react with successive quantities of an alcohol of progressively increasing concentrations in the presence of a catalytic agent while continuously distilling off the esters and removing the water formed.

21. The process of manufacturing esters comprising allowing a current of an organic acid and strong sulfuric acid to react with successive quantities of an alcohol while flowing down a column still provided with plates containing the alcohol, the alcohol on said plates increasing with concentration toward the bottom of the still, and distilling off the ester formed from the top of the still.

22. The process of manufacturing esters comprising allowing a current of an organic acid to react with successive quantities of an alcohol of progressively increasing concentrations in the presence of a catalytic agent while distilling off the ester formed, separating the ester from the alcohol in the distillate, and returning the alcohol to the still.

23. The process of manufacturing esters comprising allowing a current of an organic acid to react with successive separate quantities of an alcohol of progressively increasing concentrations and in the presence of a catalytic agent while distilling off the ester formed.

24. The process of manufacturing esters comprising allowing a current of an organic acid to react with successive separate quantities of an alcohol of progressively increasing concentrations in the presence of a catalytic agent while continuously distilling off the esters and removing the water formed.

25. The process of manufacturing esters comprising allowing a current of an organic acid to react with successive separate quantities of an alcohol of progressively increasing concentrations in the presence of a catalytic agent while distilling off the ester formed, separating the ester from the alcohol in the distillate, and returning the alcohol to the still.

26. The process of manufacturing esters comprising introducing an organic acid and a catalytic agent into a column still, intro-

ducing an alcohol into the still, and heating the latter to distil therefrom the ester formed.

27. The process of manufacturing esters comprising introducing an organic acid and a catalytic agent into a column still, introducing an alcohol near the bottom of the still, and heating the lower part of the still to distil therefrom the ester formed.

28. The process of manufacturing esters comprising introducing an organic acid and a catalytic agent into a column still, intro-

ducing an alcohol into the still below the point of introduction of the acid, and heating the still near the point of introduction of the alcohol in order to vaporize the latter and distil off from the still the ester formed.

In testimony that I claim the foregoing and have hereunto set my hand.

ARTHUR A. BACKHAUS.

Witnesses:

E. J. WINTER,

J. B. JOHNSON.