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PATENT SPECIFICATION

515,720

638

Application Date: June 10, 1938. No. 17340/38.

Complete Specification Accepted: Dec. 12, 1939.

COMPLETE SPECIFICATION

Method of and Apparatus for Mixing Gases and Liquids in the Oxidation of High Molecular Hydrocarbons into Fatty Acids, Alcohols or the like

(A communication to me from abroad by WILHELM AD. FARENHOLTZ, GUSTAV HUBBE, and HERBERT HUBBE, all German Citizens, trading as the Firm VEREINIGTE OELFABRIKEN HUBBE & FARENHOLTZ, of 66, Reichspräsidentenstrasse, Madgeburg - Friedrichstadt, Germany).

I, WILLIAM HANS ARNOLD THIEMANN, Chartered Patent Agent, of the Firm Albert L. Mond & Thiemann, of 19, Southampton Buildings, Chancery Lane, London, W.C.2, a British Subject, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to a process of oxidising high molecular hydrocarbons into fatty acids, alcohols or the like.

In the oxidation of hydrocarbons into fatty acids, alcohols or the like, it is frequently necessary to mix together gases and liquids in a special manner. Thus, in order to bring about the reaction of the hydrocarbons with a gaseous oxidising agent, use has already been made of irrigating towers, through which the liquid or molten hydrocarbons are passed in counterflow to the ascending oxidising gases. Hydrocarbons to be oxidised have also already been mixed by means of a turbo-mixer with air serving as oxidising agent, the hydrocarbons being passed several times through the mixer, if desired. It is also known to atomise liquid or molten hydrocarbons into gaseous oxidising agents. This method, however, has the disadvantage that it is difficult to control the temperature of the reaction. Since the reaction is exothermic, it is practically impossible to avoid overheating of the atomised material, since both the measurement of the temperature and the withdrawal of heat from atomised liquid suspended in gases involve difficulties. Bearing in mind that it is particularly important, in the oxidation of hydrocarbons, to keep as closely as possible to the reaction temperature most favourable for the reaction in question, since the oxidation will not otherwise proceed in the desired direction and valueless or detrimental by-products will be obtained, it can be seen that even by spraying the liquid hydrocarbons into the reaction gases, a usable mixture cannot be obtained.

The present invention aims at obviating the foregoing drawbacks and at providing a method of reliably maintaining the temperatures of the interacting gases and liquids substantially uniform throughout the reaction vessel.

To this end, according to the invention the mixing of the interacting gases and liquids is effected by means of one or more stirrers having apertured or grid-like stirring blades which cut alternately through the gas and liquid phase in rapid succession.

In carrying out the invention the oxidation temperatures may lie between 80 and 180° C. and these temperatures can be very accurately adjusted and kept relatively low by virtue of the invention. Thus, for example, in the oxidation of crude paraffin produced by catalytic conversion of hydrogen and carbon monoxide by the Fischer Tropsch process, it is possible to work with a good reaction velocity even at temperatures of from 100 to 110° C. In the case of other paraffins, which are more difficult to oxidise, it is in many cases not necessary to exceed temperatures of from 120 to 125° C. This accurate temperature control and mixing, in accordance with the invention, ensure a surprisingly high yield of very light fatty acids.

In order to enable the invention to be more readily understood, reference is made to the accompanying drawings which illustrate diagrammatically and by way of example various embodiments of apparatus for carrying the same into practical effect, and in which:—

Fig. 1 is a vertical section viewed from the front of one embodiment;

Fig. 2 is a similar view of a second embodiment having blades disposed at an angle to the stirring spindle;

Fig. 3 is a vertical section through

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another mixer having a horizontally disposed vertically reciprocating stirring member;

Fig. 4 is a section of an embodiment in which the reciprocating stirring surface is shaped like a bell;

Fig. 5 is a vertical section through a further embodiment; equipped with two stirring mechanisms, a froth separator and dephlegmator; and

Figs. 6 to 9 show various embodiments of stirring mechanism.

In Figs. 1, 2 and 7 to 9, 1 denotes the shaft of the stirring mechanism, which is rotatably mounted in known manner in the mixing vessel 2 and driven by a drive 26. The stirring blades are secured on the shaft in such a way that they turn with the latter. The number of stirring blades may vary within wide limits, for example from two to four or even more blades may be secured on one shaft. In the embodiment shown in Fig. 1, perforated plates 3 are used as stirring blades and are disposed radially with respect to the stirrer shaft. The stirrer blades 33, in the embodiment shown in Fig. 2, are rectangular perforated or slotted plates, which are turned (twisted) rather in helical fashion relatively to their longitudinal axis, so that they appear in the Figure to be trapeziform. Different types of stirrer blades may naturally be secured on the same shaft, for example in a cross or star-shaped arrangement. The vessels 2 are kept filled with liquid about up to the height of the level 4, so that the stirrer blades work partly in the liquid and partly in the gas chamber.

The stirrer blades 34 and 35 shown in Figs. 3 and 4 are adapted to be moved up and down by means of the rods 36 in such a way that they are raised out of the liquid and dipped back thereinto in rapid succession. They are operated by means of the crank 38, which can be turned by the shaft 37 and drive 58. At the same time the stirrer blades may also be given a rotary motion, for example by means of the two bevel wheels 39 and 40, the rod 36 being passed through the bevel wheel 39 in such a way that it can move up and down but must participate in the rotary movement of the bevel wheel. The bevel wheels are rotated in known manner by a drive 41.

In the embodiment shown in Fig. 5, a cylindrical drum 9 in which the two stirring mechanisms 12 and 13 are disposed acts as mixing vessel. The shafts 42 and 43 of the stirrers turn in opposite directions. They are disposed at such a height that they are just still covered by the layer of liquid. The grid-like stirrer blades are formed by bars 14 arranged in comb fashion (Fig. 6), fastened and mutually staggered on the shafts 42 and 43 in such a way that, when the two stirrers are turning, the bars of one stirrer move through the corresponding gaps between the bars of the other stirrer. If it be desired to prevent rotary movement of the contents of the drum under the action of the stirring device, and to further improve the mixing of the contents of the drum effected by the stirring device and, if desired, by gases introduced into the liquid, baffle surfaces 17 or the like may be provided at suitable points in the mixing vessels. If such baffle surfaces lie in the region of the stirrers, they may be slotted, so that the bars or other wings of the stirrers will pass through the slots in the plates. The stirrer blades formed by the bars preferably extend over approximately the whole length of the mixing vessels in the direction of the axes 42 and 43. This affords the advantage that the whole contents of the drum are uniformly stirred.

Other constructions may also be employed instead of the stirrer blades illustrated in Figs. 1 to 6. Instead of the stirrer blades 3 and 33 furnished with holes or mutually staggered slits, nets 54 (Fig. 7) may, for example, be employed, or the stirrer blades may consist of a grid-like lattice framework of rods (Fig. 9), or these rods (as shown in Fig. 8) may be joined together in different manner. Rings 52 or perforated plates 53 may also be secured to the rods (Fig. 9) in order to effect a further subdivision of the liquid, in the most favourable manner, when the stirring apparatus is operated.

The material used for making the mixing vessels and stirring apparatus should be of such a nature as to resist attack by the substances to be treated in the mixing vessel. For example, alloy steels, stoneware or like ceramic materials, and also aluminium may be employed. For example, the use of perforated plates of acid-proof steel, possessing numerous perforations about 3 to 4 mm. in diameter, has been found convenient. In order to increase the mixing action, these apertures may be conically shaped (Fig. 3). The mixing apparatus may be equipped in known manner with filling and emptying devices. For example, a charging hopper 6 and an outlet 8 are employed, or the filling and emptying devices 10 and 11 respectively are so designed that they can be connected to the inlet and outlet pipes, through interposed valves or the like.

In addition, the mixing vessels are generally equipped with heating and cooling devices. For example, they may have a jacket 5 or coils 15, which are preferably so designed that they can be used alternately for heating and cooling. The stirrers may also act simultaneously as heating and cooling devices, the shaft 1 being furnished with passages 44 and 45 for passing through a heating or cooling medium, for example, and the stirring blades being made hollow and their hollow passages 46 connected in suitable manner to the passages 44 and 45.

The gases are supplied to the mixing vessel, through the gas admission lines 7, from above into the gas chamber of the mixing vessels, which are equipped with a corresponding gas outlet 47. Cut-off valves 48 and 49 are provided in the gas pipelines. The gas inlets may also be provided at different places in the heating vessels. Thus, it may be convenient in many cases to introduce the gas, for example, air, at about the height of the level of the liquid in the oxidation of hydrocarbons, so that it flows through the vessel parallel to the level of the liquid. The mixing of gas and liquid can in many cases be still further promoted by introducing the gas into the liquid itself, for example with the aid of a nozzle or spray 16. The gas may also be preheated, for example the gas pipe may extend a certain distance in the liquid and only then discharge the gas into the liquid through its mouth. The gas introduced into the liquid, for example by means of nozzles or sprays, causes an intense turbulent flow in the liquid, the particular effect of which is to keep the temperature very uniform in the whole vessel. The gas, or a part thereof, may also be passed into the mixing vessel by the stirring apparatus or by the baffle plates 17, to which end these members are furnished with suitable gas passages 30 and outlet apertures 31. The baffle plates may at the same time be employed as cooling or heating means, for which purpose they are made hollow or are furnished with suitable heating or cooling passages 32, which may also be so arranged that a heating medium and a cooling medium can be alternately passed therethrough. If the mixing is accompanied by intense frothing, froth separators, on which the gas-liquid suspension is broken and from which the liquid separated is passed back into the mixing vessel, are disposed in the top part of the mixing vessel or at its gas outlet. For example, per se known froth basins with reflux line can be provided at the uppermost part of the reaction vessel, or other known devices can be employed. which enable the particles of liquid entrained by the gases in froth or spray form to be separated as completely as possible. For example, a froth separator 19 is mounted above the gas outlet pipe connection 18. This separator consists of a vessel in which suitable inserts or guides 51 form a sudden many time repeated widening and narrowing of the path of flow. Column bells, balls, net or sieve bases or the like may be used as inserts or guides. A reflux line 20 enables the liquid deposited in the dephlegmator to be returned to the mixing vessel.

In order to hold back the last particles of liquid entrained in spray form by the gas current, or in order to separate certain readily condensable vapours from the gas current, dephlegmator 21 may also be provided above the froth separator. Said dephlegmator is filled with packing members 21*a*, for example Raschig rings, and is provided with a cooling coil 22 at its top part. In addition, a connecting pipe 23 is provided for the passage of the gases from the froth separator into the dephlegmator, and a return pipe 24 for the liquid separated in the dephlegmator. The outlet pipe 25 can lead into a further mixing vessel or into a washer or the like, in which, if desired, valuable substances which may be contained in the gases can be recovered, or the purified gases may pass through the outlet pipe 25 into the atmosphere.

The cooperation of the stirrers and the heating and cooling devices enables the temperature of the gases and also of the liquid in the mixing vessel to be kept constant within the most narrow limits, and overheating to be carefully avoided.

If the hereindescribed method is applied to the production of synthetic fatty acids, alcohols, or the like, high molecular hydrocarbons can be used as originating substances, such as illuminating oil or gas oil or hydrocarbons having a higher boiling point, particularly the most diverse paraffins. Lignite paraffin and petroleum paraffin, or crude paraffin produced in the synthetic conversion of carbon monoxide and hydrogen into hydrocarbons by the Fischer Tropsch process, are particularly employed. Naphthenic hydrocarbons or the like can also be used. This oxidation can be carried out in known manner at temperatures above the melting point of the originating substances. The hydrocarbon mixture, pre-purified in known manner if desired, is first brought by heating to the necessary initial temperature. Air or other oxygen-containing gas is then passed through the apparatus. In consequence of the exothermic nature of the reaction, the supply of further heat after commencement of the latter is not necessary. The suitable reaction temperature is maintained, if necessary, by cooling. As a rule temperatures between about 80 and 180° C. are used. However, even lower temperatures lying slightly above the melting point of the originating substances can also be used—i.e. for example, temperatures slightly above 50° C. in the case of hard paraffin.

The oxidation may also be carried out under super-atmospheric pressure. It then proceeds rather more quickly. However, the application of very high pressures is by no means necessary.

For example, it is possible to oxidise hydrocarbons into fatty acids with the hereindescribed apparatus of the invention, by using the process described in the specification of our co-pending application No. 17086/1938 (Serial No. 506,104). The oxidation then takes place in a plurality of serially connected oxidation apparatus, through which the reaction gas is passed and at least one of which is constructed in accordance with the invention. For example, a current of gas, which has been passed through a plurality of oxidation vessels of desired type, is passed into a mixing vessel constructed in accordance with the invention and charged with fresh material to be oxidised. The temperature in the last vessel is preferably kept rather lower than those in the preceding oxidation vessels. In this manner it is possible to collect to a very high extent the valuable substances taken up by the gas current in the preceding vessels and to utilise their catalytic activity for the oxidation. Losses of valuable substances are practically completely avoided in this manner. The further performance of the oxidation of material treated in this manner then proceeds very favourably, and, in addition, a lightening of the colour also frequently occurs at the same time.

The power required by the mixing apparatus of the present invention is relatively low.

When the hereindescribed method is applied to the production of fatty acids the avoidance of overheating and the rapid progress of the reaction enable high grade products to be obtained, which contain predominantly higher molecular fatty acids well utilisable for the soap industry.

The oxidation can then be allowed to proceed to very wide limits, so that about 90% and more of the originating material is oxidised. The small proportion of non-converted originating material can be further oxidised by the same method, after separation from the oxidation products, without the occurrence of detrimental resinification and polymerisation.

EXAMPLES.

1). In a reaction vessel equipped with a horizontally mounted stirring apparatus, according to the invention, comprising four perforated stirring blades extending almost to the cylinder wall, 2000 grams of paraffin (solidification point 42 to 44° C.) were oxidised with air for four hours in known manner. The temperature was initially 160° C. and was gradually lowered to 120° C. The speed of the stirring apparatus was 240 revolutions per minute.

After that space of time the acid number was 103.

A parallel test, made in a reaction tower filled with Raschig rings attained an acid number of only 27 in the same time.

The superiority of the hereindescribed method over the performance of the oxidation by blowing air into the molten hydrocarbons in reaction towers and the like can be seen from the following comparative tests.

2). 1500 grams of paraffin (melting point 46 to 48° C.) together with 8 grams of catalyst, were treated with air for six hours at 130 to 140° C. in an iron vessel equipped with stirring blades according to the invention. After that time an acid number of 140.0 and a saponification number of 276.7 were attained.

3). 1500 grams of soft paraffin (melting point 42 to 44° C.) together with 5 grams of catalyst were treated in the same manner with air at 140 to 145° C. After five hours an acid number of 99.3 and a saponification number of 199.0 were obtained. The yield by weight amounted to 99.25%.

4). 1500 grams of crude paraffin were treated with air at 125 to 135° C. for four hours, together with 10 grams of catalyst, in accordance with the invention. Result: Acid number 154.75, saponification number 306.0 and non-saponifiable matter 22.9%.

5a). Air was blown with a spray nozzle into two iron reaction vessels equipped in accordance with the invention. The filling in each vessel comprised 2000 grams of paraffin (melting point 46 to 48° C.) and 20 grams of catalyst, while the temperature was 110 to 130° C. After twelve hours the acid number in one reaction vessel was 57 and in the other vessel 77.

5b). A reaction tower of iron was lined with Raschig rings and air was blown in for four hours. The filling comprised 1500 grams of paraffin and 15 grams of catalyst, and the temperature was 145° C.

After four hours an acid number of only 27 was reached, and after eight hours an acid number of 46.

6). 144 kgs. of crude paraffin were treated with air, together with 0.6% of catalyst, at 125° C. in an apparatus in accordance with the invention. After twelve hours 50% was oxidised, and after 9 hours more than 91% was oxidised. The saponification number was 304.5. Two parts of manganese stearate with one part of stearic acid were used as catalyst. The oxidation yield amounted to 105%.

7). The same apparatus was filled with 30 litres of water and connected behind three oxidation apparatus traversed by a current of air. The temperature in this apparatus during the passage of the oxidising gases was between 40 and 50° C. On completion of the oxidation 70 litres were drawn off, so that the total oxidation loss amounted to only 3% of the theoretical yield.

8). The same apparatus was filled with the same quantity of raw material as in the oxidation (170 litres) and connected, as in Example 7, as the last of a series of oxidation apparatus. The temperature was again about 50° C. Cooling was effected from time to time, in order to prevent the temperature from rising above 60° C. On completion of the oxidation a total yield of 106% of oxidation products could be attained, the acid number having risen by 8 in the apparatus in question.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1). A process of oxidising high molecular hydrocarbons into fatty acids, alcohols or the like, which is characterised in that the temperatures of the interacting gases and liquids are maintained uniform in all parts of the reaction vessel by effecting the mixing by means of one or more stirrers having apertured or grid-like stirring blades which cut alternately through the gas and liquid phase in rapid succession.

2). Process as claimed in claim 1, in which, when a plurality of stirrers is employed in the same mixing vessel, the stirrers work in opposite directions to one another.

3). Process as claimed in claim 1 or 2, in which the gases are passed through the mixing vessel and thereupon treated for the purpose of separating small drops of liquid, froth, or the like, preferably by passing them repeatedly through alternately narrow and wide spaces.

4). Process as claimed in any of claims 1 to 3, in which the mixing of gases and hydrocarbons takes place in a plurality of oxidation vessels through which the gases are passed in succession.

5). Process as claimed in any of claims 1 to 3, in which the gases from an oxidation vessel or from the last of a series of oxidation vessels, which they traverse in succession, are mixed in a further vessel with the hydrocarbons to be oxidised, or with other liquids, and are thereby freed from valuable substances entrained from the oxidation vessel or vessels.

6). Process as claimed in any of the preceding claims, in which hydrocarbons, gases and catalysts are mixed together, particularly such catalysts as consist of a mixture of higher molecular organic acids of the character of the fatty acids, resin acids or naphthenic acids, and compounds of the metals of the 6th to 8th groups of the periodic table, to which mixtures compounds of the alkali or alkaline earth metals (including magnesium) may also be added.

7). The process of oxidising high molecular hydrocarbons into fatty acids, alcohols or the like, substantially as described.

8). Apparatus when used for carrying out the process claimed in any of the preceding claims, comprising a mixing vessel, for example an oxidising vessel, within which is disposed a stirring apparatus, the stirring blades of which are at right-angles to the direction of the axis of rotation or are inclined relatively thereto and which possess apertures, (for example consist of perforated or slotted plates, networks, bars disposed in comb fashion or the like) said stirring apparatus being so disposed that its stirrer members alternately and in rapid succession cut through the layer of liquid and the layer of gas, and heat exchangers (heating and/or cooling devices) provided on the walls or inside the mixing vessel.

9). Apparatus as claimed in claim 8, in which the stirring apparatus or apparatuses have passages such that they can be used for the supply of gases and/or for the regulation of the temperature.

10). Apparatus as claimed in claim 8 or 9, comprising froth separators connected to the gas outlet of the mixing vessel.

11). Apparatus as claimed in claim 10, in which vessels in which inserts or fillings, for example column bells, balls, net bases, produce a repeated and sudden widening and narrowing of the path of the gas, are employed as froth separators.

12). Apparatus as claimed in claim 10 or 11, comprising a dephlegmator or cooler connected with the froth separator, for example in rear thereof.

13). Apparatus when used for carrying out the process claimed in any of claims 1 to 7, constructed, arranged and adapted to operate substantially as described with reference to the accompanying drawings.

Dated this 10th day of June, 1938.

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Chancery Lane, London, W.C.2,
Agents for the Applicant.

Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1940.

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Fig. 1

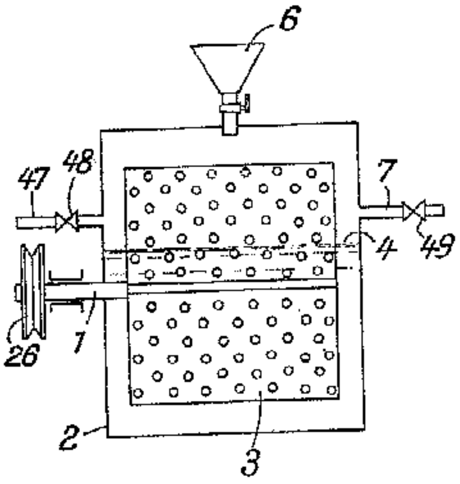

Fig. 2

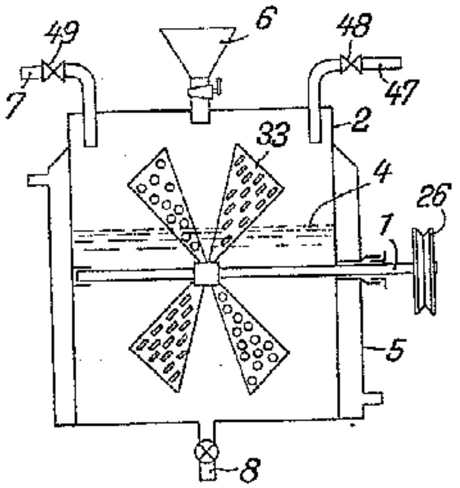

Fig. 3

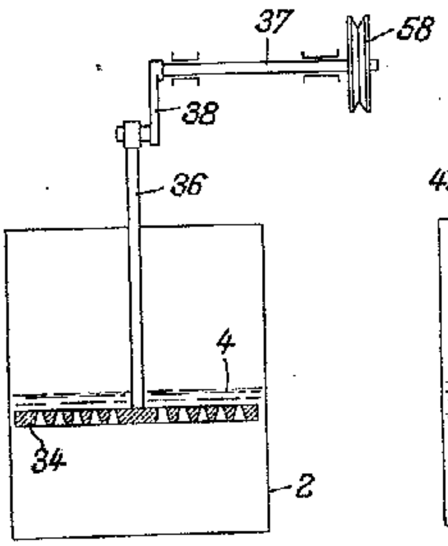

Fig. 4

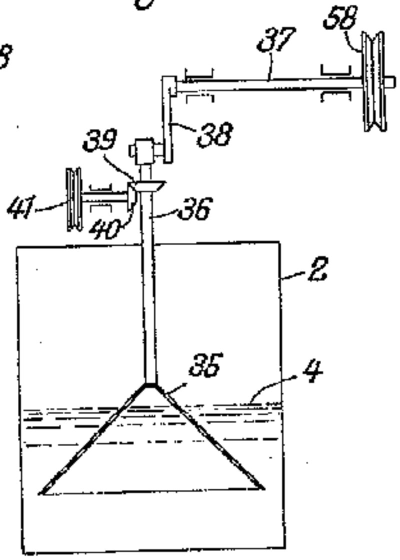

Fig. 5

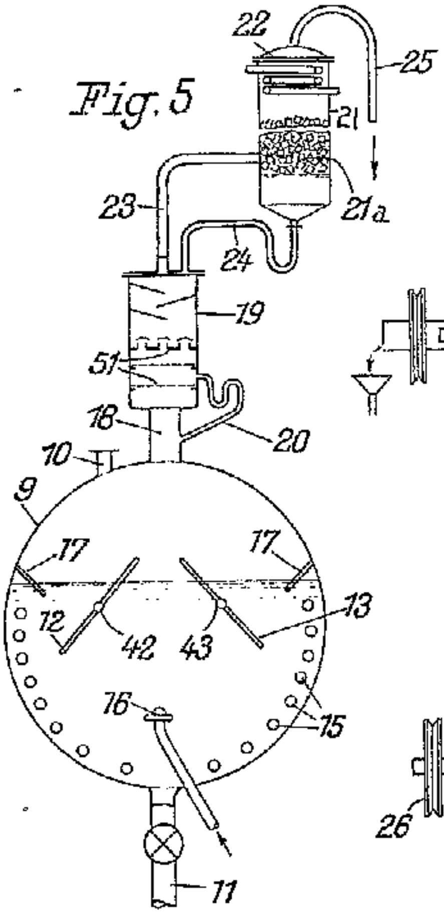

Fig. 8

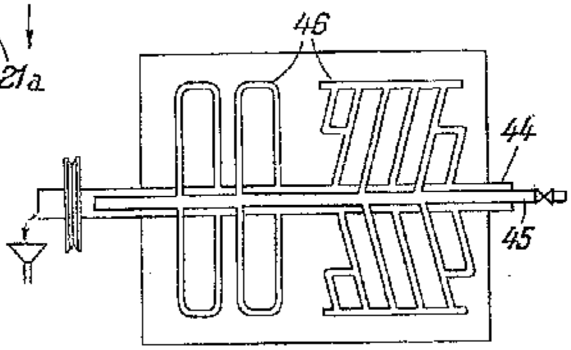

Fig. 7

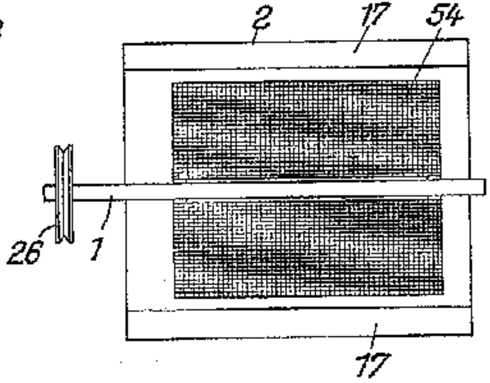

Fig. 6

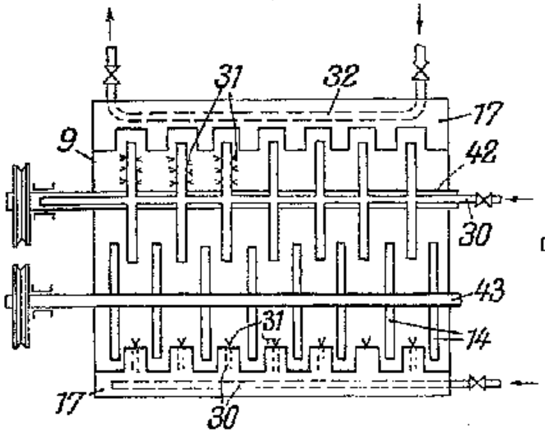

Fig. 9

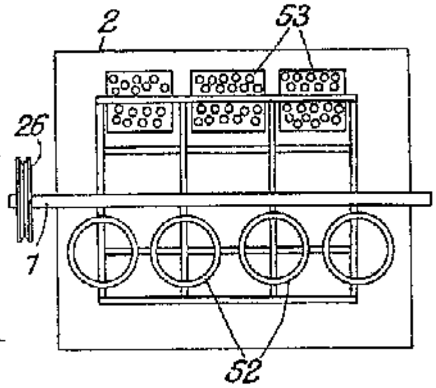

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Fig. 1

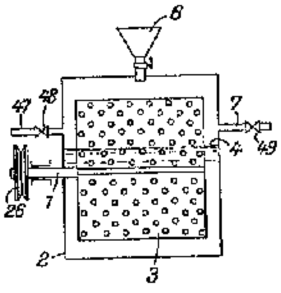

Fig. 2

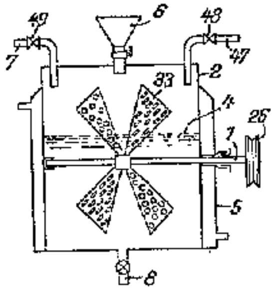

Fig. 3

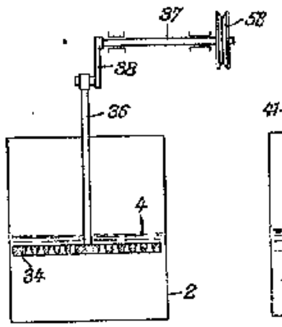

Fig. 4

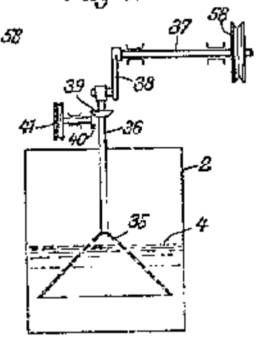

Fig. 5

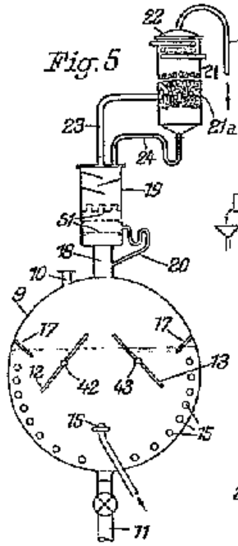

Fig. 8

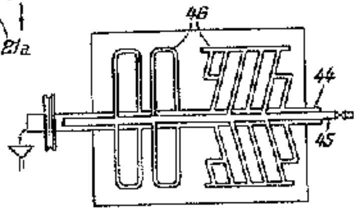

Fig. 7

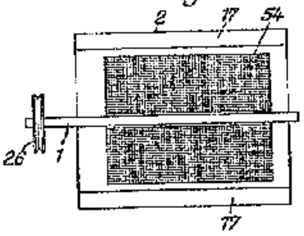

Fig. 6

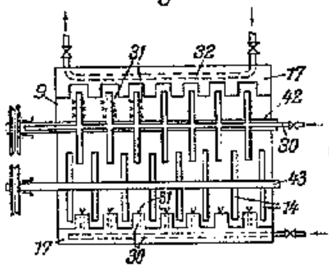

Fig. 9