July 2, 1940. A. P. BEARDSLEY ET AL 2,206,495

ABSORPTION SYSTEM FOR NITRIC ACID

Filed March 30, 1938 4 Sheets-Sheet 1

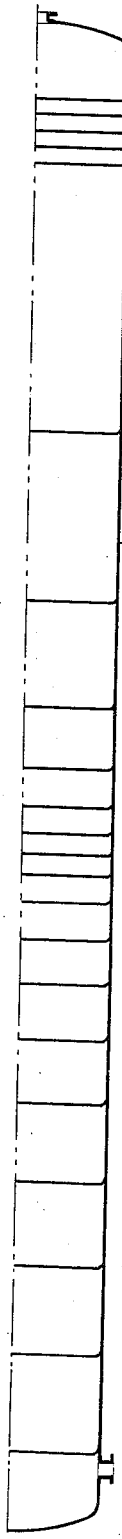


Fig. 1.

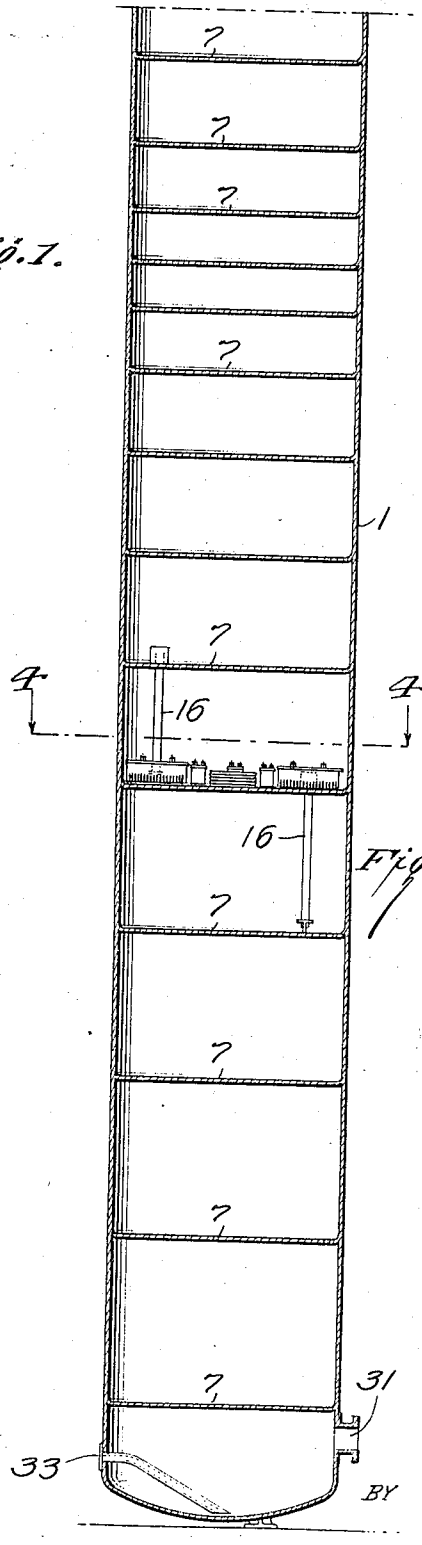


Fig. 2.

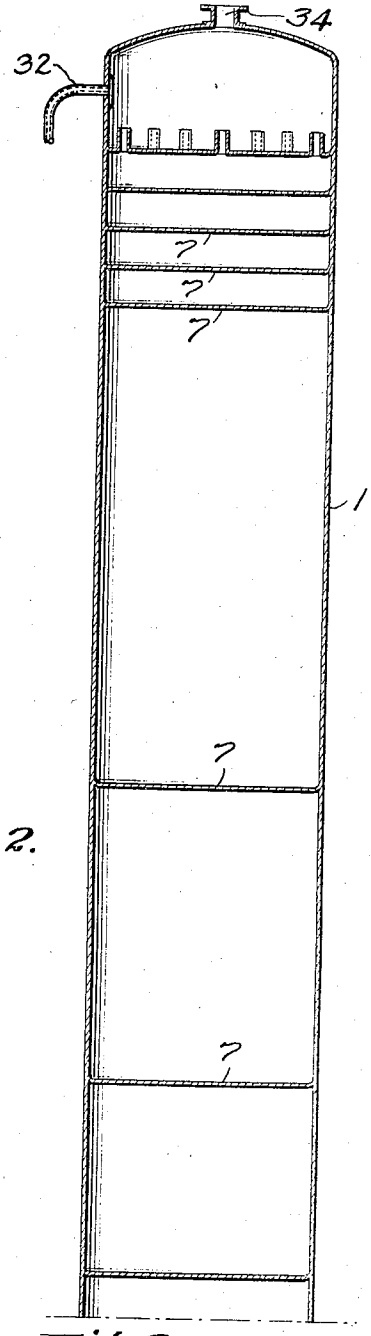


Fig. 3.

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Filed March 30, 1938 4 Sheets-Sheet 2

Fig. 4.

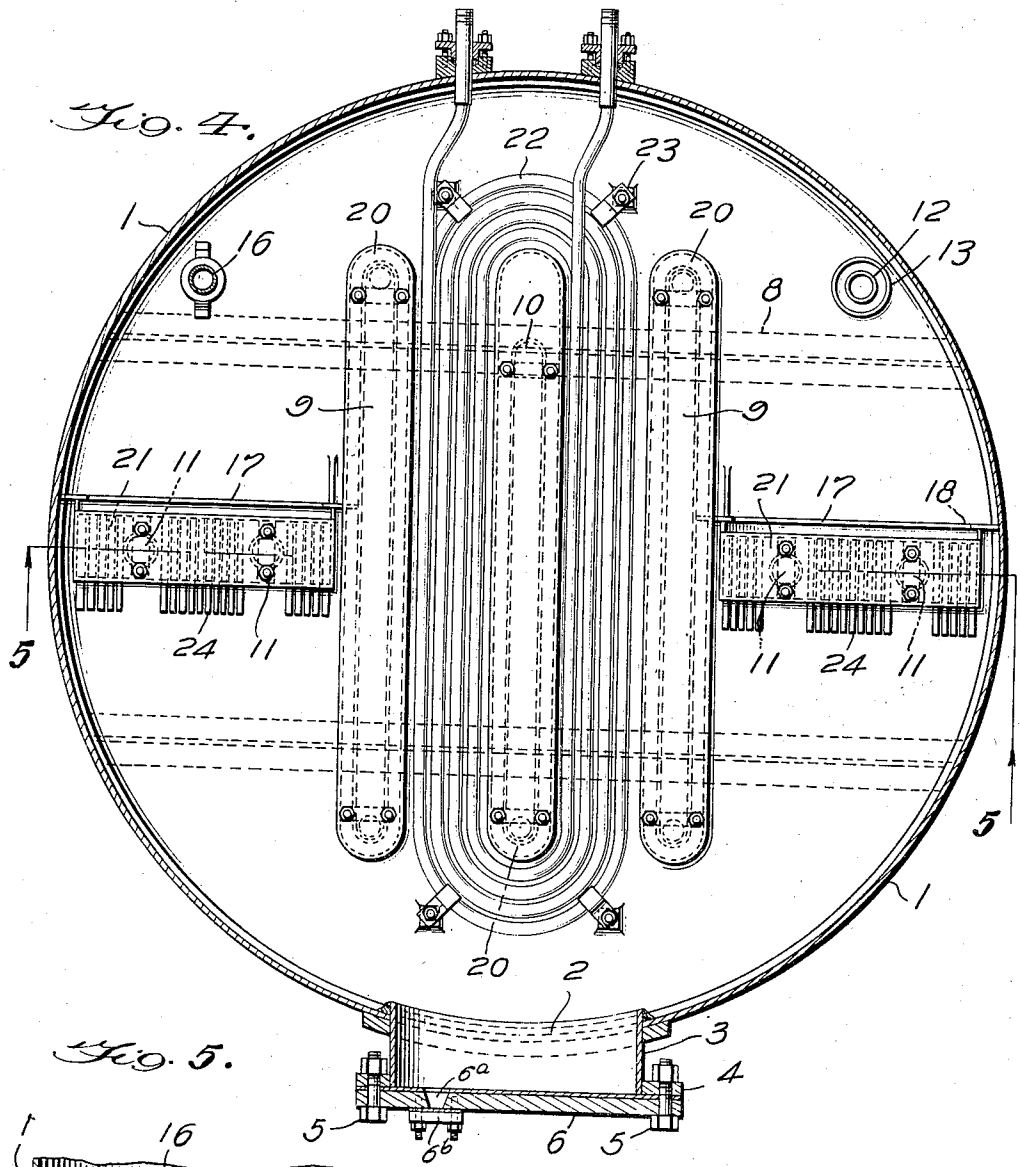
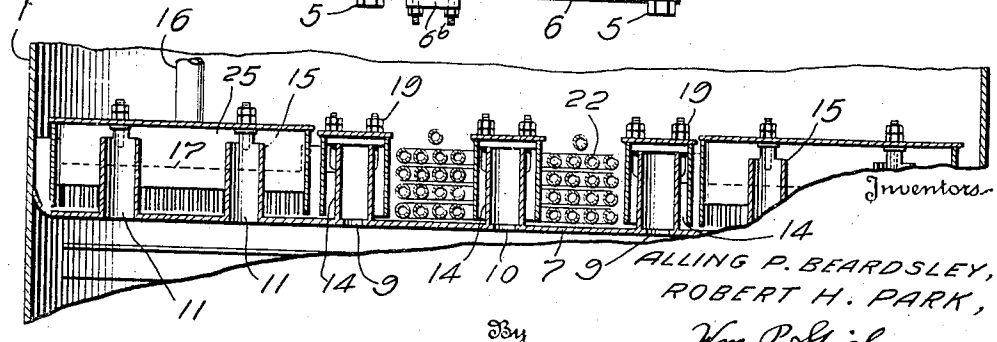


Fig. 5.



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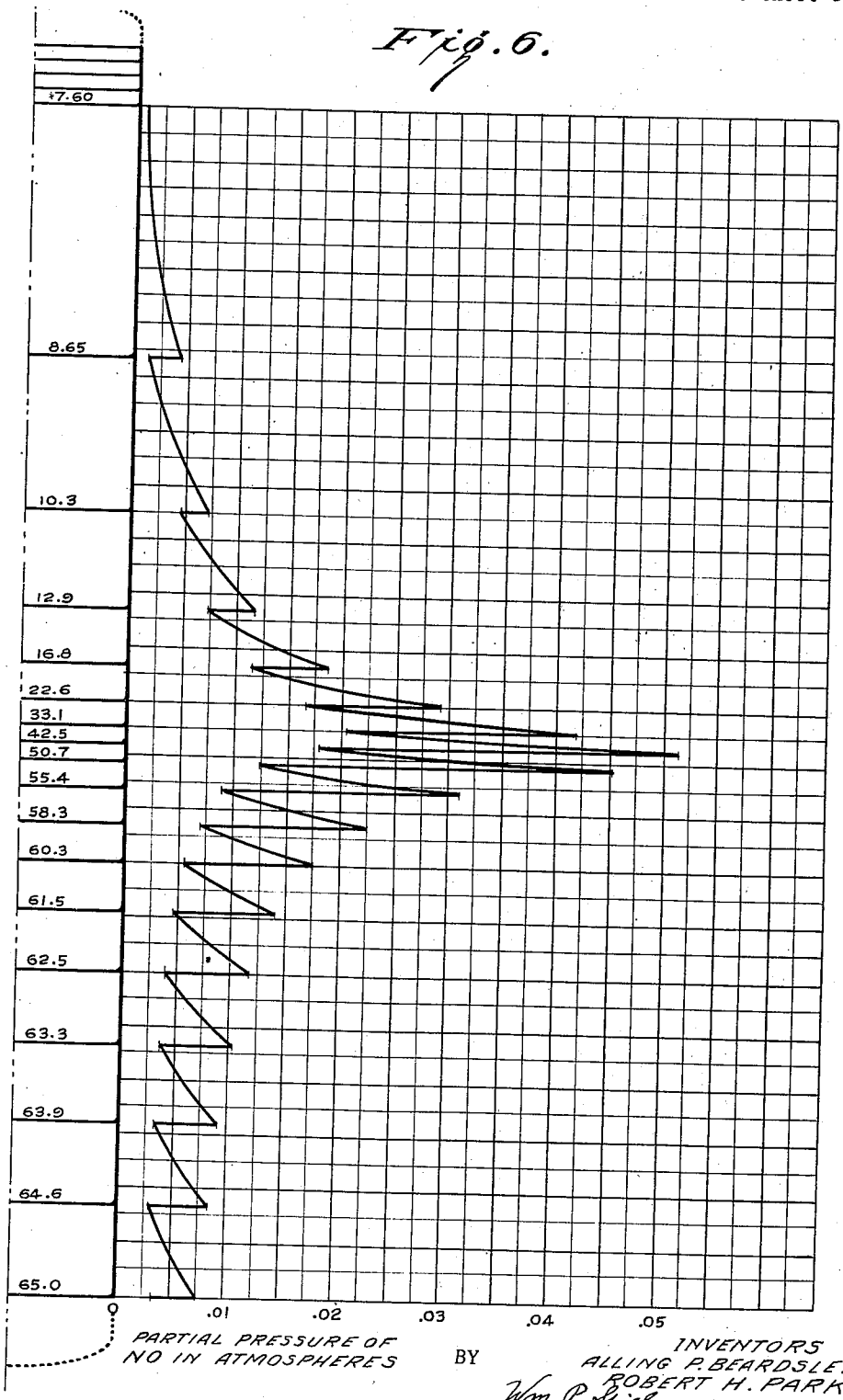
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ABSORPTION SYSTEM FOR NITRIC ACID

Filed March 30, 1938 4 Sheets-Sheet 3

Fig. 6.



BY

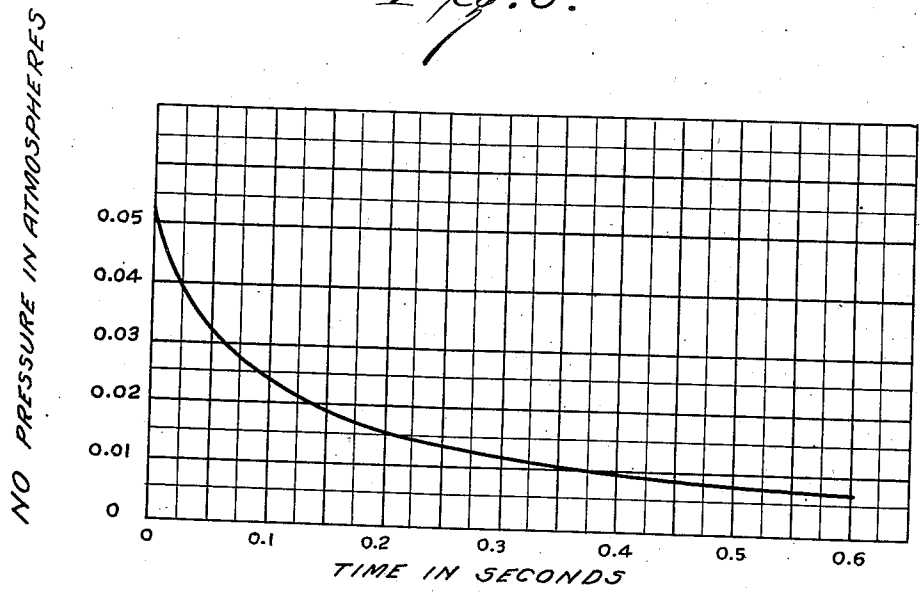
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ABSORPTION SYSTEM FOR NITRIC ACID

Filed March 30, 1938 4 Sheets-Sheet 4

Fig. 8.



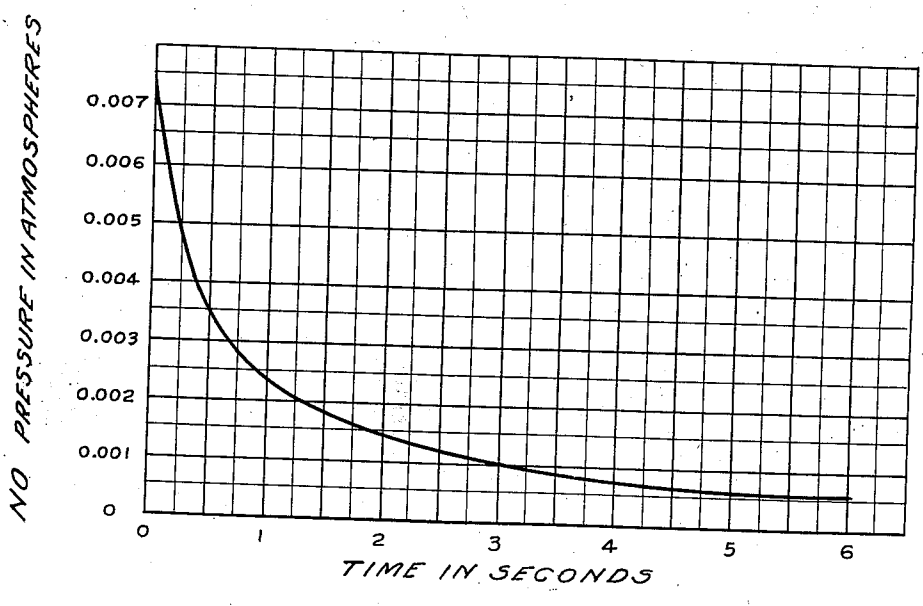


Fig. 7.

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Patented July 2, 1940 2,206,495

UNITED STATES PATENT OFFICE

2,206,495

ABSORPTION SYSTEM FOR NITRIC ACID

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Application March 30, 1938, Serial No. 198,806

8 Claims. (Cl. 23—283)

This invention relates to the design and construction of apparatus for promoting the intimate contact of gases and liquids under atmospheric, subatmospheric or superatmospheric pressures, and to new and improved processes inherent in the operation of such apparatus. While the invention in its broader aspects includes principles which are of general applicability in the design of gas and liquid contact apparatus, it also includes features which are of specific utility in designing towers containing bubble plates. Accordingly, the invention will be described and illustrated in conjunction with a tower of this type, which is used in distillations, fractionations and absorptions, but it should be understood that the invention is not necessarily limited to the constructional features of this embodiment.

The present invention is a result of a study which we have made of the factors involved in reactions which take place between gases and liquids with the evolution of a different gas or vapor. When such reactions are carried out in stages either in bubble towers or in a series of separate communicating receptacles, changes take place in the composition or condition of the gases while passing from each bubble plate or layer of liquid to the next succeeding one. One of the principal features of the invention is the adjustment or control of the extent of such changes to bring about favorable conditions for the next stage of the reaction in a minimum of time, thereby improving the efficiency of the absorption apparatus as a whole.

One of the principal methods of control of the extent of changes in the gases, in accordance with the invention, is the correct proportioning of the volume of the reaction space to the extent of change that may be desired. Since in most cases the most efficient results are obtained by varying the amount of change in different stages of the reaction, it follows that an important feature of the invention resides in the provision of a gas and liquid contact apparatus, and particularly one of the bubble tower type in which the volumes of the reaction spaces are unequal. In a cylindrical absorption tower, this will result in an uneven spacing of the absorption plates, which is a further important feature of the invention.

We have stated that the advantages of the present invention are most fully realized when its principles are applied to the construction of towers for reactions in which a gas is evolved. One of the most troublesome processes of this type is that involving the absorption of nitrogen peroxides in water at low temperatures with the evolution of nitric oxide. We will illustrate these principles by describing the design of an absorption tower for this reaction, but it should be understood that the details given are for purposes of illustration and that the invention in its broader aspects is not limited thereto.

Oxides of nitrogen are produced by the action of an electric arc on air, or by the oxidation of ammonia with air or oxygen in the presence of a platinum or platinum-rhodium catalyst. After cooling, the reacted gases are usually further oxidized until their content of combined nitrogen is almost wholly in the form of NO_2 and N_2O_4, in which condition they are brought into contact with water or nitric acid at temperatures below 50° C. and preferably under super-atmospheric pressure. The reactions which take place are usually stated as follows:

$$3NO_2+H_2O=2HNO_3+NO$$
$$3N_2O_4+2H_2O=4HNO_3+2NO$$

and it will be seen that this is a reaction which takes place with the evolution of a second gas, i. e., nitric oxide. This nitric oxide is not soluble in water to any great extent and must be again oxidized to NO_2 before it can be recovered, the oxidation reaction being:

$$2NO+O_2=2NO_2 \text{ or } N_2O_4$$

It is obvious that an absorption tower for carrying out the above reactions must be constructed of material which is resistant to nitric acid of all concentrations. As such a tower, when constructed in accordance with the present invention, is fitted with plates or trays at uneven intervals, a welded and annealed construction is more desirable than a flanged or riveted one, but presents the difficulty of finding an acid resistant alloy which is capable of being fabricated in this manner. After many investigations we have found that an alloy consisting predominantly of iron and chromium alone, with a carbon content of 0.1% or less is satisfactory for this purpose. Resistance to corrosion by nitric acid increases with an increase of chromium content, but too high a percentage of chromium will result in too brittle a metal. However, a chrome-iron alloy containing from 16.5 to 18% of chromium gives a satisfactory resistance to nitric acid, and with proper welding and annealing technique this alloy can be fabricated into a tower of satisfactory strength and resistance to impact.

When an alloy is used for the manufacture of a nitric acid tower containing 16.5 to 17.5% chromium, the remainder being substantially iron, the finished tower can be satisfactorily annealed by heating it to a temperature of 1450–1500° F. for a suitable period of time followed by a suitably regulated cooling period. A cylindrical tower as large as 70 feet high by 6 feet in diameter has been annealed by this method. In this case the tower was heat treated three times; a heating period of 5 to 6 hours was used in each case to attain the upper temperature of 1500° F. and in each case the metal was held between 1450 and 1500° F. for 1 hour. In the first two treatments the tower was then removed from the furnace for air quenching, while in the final treatment the furnace was shut off for a further one hour period, at the end of which the temperature of the metal was 1100° F. The tower was then slowly cooled in order to avoid mechanical stress.

By the use of a welded and annealed construction of the above type a number of advantages are obtained, particularly in the construction of towers having unevenly spaced trays such as are provided by the present invention. Such a welded construction permits the ready insertion of the trays at intervals best adapted to satisfactory performance without considerations of mechanical strength, for the trays may be inserted at any point within the tower and welded in place and after annealing the tower is obtained as a single unitary structure. Moreover, the construction of the tower as a whole is much cheaper, for one or more trays may be welded to a rolled section of the tower wall which is in turn welded to another rolled section, and in this way the entire tower is built up from sheet metal.

It will thus be seen that the main objects of the present invention are: first, the provision of a gas and liquid contact apparatus having a plurality of reaction zones which vary in size in accordance with the space velocity requirements of gas reactions taking place therein; second, the combination with gas and liquid contact elements of reaction spaces adjacent thereto which are proportioned in size in accordance with certain characteristics of the absorption reactions taking place thereon; third, the construction of a welded and annealed absorption tower of acid proof alloy which is best suited for unevenly mounting gas and liquid contact elements therein; and fourth, a method of designing such a tower or other gas and liquid contact apparatus for obtaining the greatest plate efficiency when used for a reaction in which a gas is absorbed in a liquid with the evolution of a second gas which must be subjected to further treatment in the gas phase before absorption can take place in a subsequent stage. Additional objects will become apparent from the following description, when taken with the claims appended thereto.

The accompanying drawings illustrate a tower which is designed for carrying out in proper sequence the stages of a reaction of the above type. In these drawings:

Fig. 1 is a diagrammatic showing of the plate spacing of a tower constituting an embodiment of the invention.

Figs. 2 and 3 are vertical sections through bottom and top portions, respectively, of the tower shown diagrammatically in Fig. 1, the necessary fittings and equipment being shown only on one plate.

Fig. 4 is a horizontal section through the tower on the line 4—4 of Fig. 2, showing a fully equipped bubble plate in plan view.

Fig. 5 is a vertical section on the line 5—5 of Fig. 4.

Fig. 6 is a graph showing the changes in the partial pressure of nitric oxide which take place in a typical installation of the present invention.

Fig. 7 is a graph showing the rate of change of nitric oxide pressure under the conditions obtaining in the reaction space immediately above the first plate of Fig. 6, and

Fig. 8 is a similar graph showing the rate of change of nitric oxide immediately above the eleventh plate.

Referring to Figs. 2 to 5, the tower consists of a shell 1 of the chrome-iron alloy which has been described, preferably having a chromium content of about 17.25%. The tower is of welded construction, and is preferably provided with manholes 2 fitted with manhole nozzles 3 having flanges 4 receiving bolts 5 for the attachment of cover plates 6 thereto. Any cover plate may be provided with an opening 6a, normally closed by a cover plate 6b, for the introduction of acid drip if desired. A series of plates or trays 7 are rigidly welded at intervals to the tower walls, which are also braced by stiffeners. It is understood that plates of any type may be used in the tower construction, and in many cases a type of plate different from the one shown in Figs. 4 and 5 may be convenient. In fact, the specific details of the plate and fittings shown in Figs. 4 and 5 form in themselves no part of the present invention but are described and claimed in the copending application of Carl E. Mensing, Serial No. 10,021, filed March 13, 1935, now Patent No. 2,120,256, issued June 14, 1938, and are claimed herein only insofar as they cooperate with the novel features of the present invention to produce improved results in tower performance.

Briefly described, each of these plates consists of a rigid tray having outer apertures 9 and a central aperture 10 for the passage of gas therethrough, supplemental apertures 11 for the same purpose, and a circular orifice 12 for the reception of an overflow outlet pipe 13. Permanent tray fittings are welded or otherwise attached to the tray surface and consist of central riser nozzles 14 surrounding the apertures 9 and 10, supplemental riser nozzles 15 surrounding the supplemental apertures 11, bracket 16 for the support of a liquid inlet pipe, and aligned dams 17 having wide central weirs 18 for the passage of liquid thereover. Attached to these permanent tray fittings by bolts 19 are the various elements of the tray equipment which are designed to promote an intimate contact between the plate liquid and the rising gas stream and to cause a recirculation of the liquid over the plate surface in the manner described in the copending application above referred to. This equipment consists of main or central bubble caps 20, supplemental impeller bubble caps 21 and cooling coils 22 attached to bosses on the plate surface by means of brackets 23 and adapted to receive cooling water from outside the tower. It is sufficient here to state that the main bubble caps 20 have slotted lower edges for disseminating gas into the plate liquid in a large number of fine streams, and that the impeller bubble caps 21 are provided with asymmetrically associated liquid conduits 24 which

cooperate with the main gas receiving dome 25 of the bubble cap to produce a recirculating flow of plate liquid over the weirs 18 of the dams 17 and along the main bubble caps 20 and cooling coils 22 through a closed path which includes more than one complete circulation.

In the operation of the tower for the production of nitric acid, a 9% ammonia-air mixture is oxidized at 800–900° C. and the resulting NO gases are cooled to atmospheric temperature with the separation of a condensate containing about 7–8% HNO_3. The gases are then compressed to any desired superatmospheric pressure, for example to a pressure of 5 atmospheres gage. They are again cooled, with separation of a strong acid drip of 62–64% HNO_3, and introduced at 25° C. into the inlet 31 of the absorbing tower shown in Figs. 2 and 3.

The tower is fed with water through a feed leg 32, for example as described in the copending application of A. P. Beardsley, Ser. No. 160,493, filed Aug. 23, 1937, and the weak condensate may be added to this feed if desired. Nitric acid of 65% strength is withdrawn from the base of the tower through the pipe 33 and the strong condensate may be mixed with it and sold as product acid.

The water or weak acid passes downwardly through the tower from plate to plate through the pipes 16 in countercurrent to the gases, which flow upwardly through the bubble plates and reaction spaces. On each plate the strength of nitric acid in the liquid is increased, representative strengths being indicated in the tower shown diagrammatically in Fig. 6, and the content of fixed nitrogen in the gases is correspondingly reduced. The gases finally pass out of the tower through the outlet 34 with a content of about 2% of the oxides of nitrogen originally present. These unabsorbed oxides of nitrogen may be recovered by washing the effluent gases with alkali if desired.

It will be noted from Fig. 1 that there is a large variation in the size of the reaction spaces between the plates in different parts of the tower, and particularly that the average volume of the first five reaction spaces is much larger than the average volume of the next ten. It will be shown that the conditions near the top of the tower are such as to require special treatment and a discussion of the spacing of the plates in this area will be considered later.

In our study of the factors involved in the absorption of oxides of nitrogen, it soon became apparent that one of the most serious limiting factors is the speed of the oxidation reaction

$$2NO+O_2=2NO_2$$

The speed of this reaction at any given temperature is a function of the concentration of the reaction gases and may be expressed by the equation

$$\frac{dx}{dt}=K(a-x)^2(c-x)$$

in which

$2a$=initial molar concentration of NO
c=initial molar concentration of O_2; and
x=the change in the concentration of O_2 during the time t.

Figs. 7 and 8 are examples of this formula, showing the reaction of representative gases in a nitric acid plant operating on a 9% ammonia-air mixture. A similar reaction, although of course with varying concentrations of NO and O_2, takes place in each of the reaction spaces between the absorption plates of a nitric acid tower, or within the voids between the packing of a corresponding packed tower. A study of the curves will show that in every case the velocity coefficient of the reaction, which measures the efficiency of the reaction space as an oxidizing medium, falls off rapidly after an initial period of relatively rapid oxidation. It is an object of the invention to proportion the volume of the reaction spaces to the velocity coefficient or concentration of NO and O_2 in the gases in such a manner that the reactions will proceed along the steep parts of the curves only, and to place the next absorption plates at points where they will interrupt the reactions when the curves begin to flatten out. The efficiency of the tower as an oxidizing apparatus is thereby greatly improved.

The speed of the absorption reaction

$$3NO_2+H_2O=2HNO_3+NO$$

which takes place on each of the absorption plates is much greater than the speed of the oxidation reaction referred to above, and there is relatively little difficulty in approaching equilibrium on each of the absorption plates of the tower. The equilibrium constant of this reaction, however, is a direct function of the molar concentration of NO_2 or N_2O_4 in the gas and an inverse function of the concentration of HNO_3 in the absorbing liquid on the plate. This indicates that for efficient plate operation it is necessary that the concentration of NO_2 in the gases entering any plate should be reasonably high, particularly when the concentration of the absorbing acid is also high. Near the bottom of the tower where the absorbing acid is strongest no reduction in the height or volume of the oxidation space is permissible, for such a reduction would lower the amount of oxidation and reduce the strength of the product acid.

We have discovered, however, that a material reduction which may amount to as much as 25% of the tower volume may be made in the central portions of the tower without sacrificing absorption efficiency if the oxidation spaces in this area of the tower are suitably proportioned to each other and to the concentration of nitric oxide passing through them. By reason of this great saving in oxidation volume in the central part of the tower we are enabled to provide increased volume in the reaction spaces in the lower parts of the tower where it is most needed, thereby giving a stronger product acid and improving the absorption efficiency of the tower as a whole. In the preferred modification of our invention the increase in the volume of the lower reaction spaces corresponds roughly to the increase in strength of the absorbing acid as it flows down the tower in countercurrent to the rising stream of gases, although the strength of the acid is not the only factor involved. The reason why this variation in the volume of the reaction spaces produces improved absorption results may be explained as follows:

In the lower parts of the tower the acid is of maximum strength and its ability to absorb NO_2 is very small. Accordingly, as it is necessary to oxidize to NO_2 substantial proportions of the NO liberated by the reaction on each plate, and since there is a very low concentration of NO in the gases (due to the small amount of reaction) it follows that a relatively longer time and a reaction space of larger volume is necessary to accomplish this. Farther up in the tower the strength of the absorbing acid is weaker and the amount of absorption on each plate is greater;

this results in an increased concentration of NO in the gases given off and a suitable degree of oxidation of NO to NO_2 can be built up in the gases in a much shorter time. Accordingly, the volume of the reaction spaces in the middle and upper parts of the tower can be greatly reduced without seriously affecting the absorption efficiency of the plates in this zone.

We have found, as another feature of the invention, that under the conditions obtaining in ordinary practice a relatively constant extent or degree of oxidation of NO to NO_2 should be maintained in substantially all of the reaction spaces in the lower and middle parts of the tower. In fact, the best results are obtained when a constant degree of oxidation is maintained in all of the reaction spaces except the very top of the tower, as will subsequently be shown. Expressed in other words, we have found that the volume of the reaction spaces in the lower and central portions of the tower should be varied in such a manner that substantially the same proportion of the NO issuing from each plate is oxidized to NO_2 before the next plate is reached. This means, of course, that relatively large reaction volumes should be provided at the bottom and relatively small spaces in the middle of the tower. It is possible, within the scope of the invention, to deviate as widely as 50–75% from these optimum conditions and still retain some of its advantages, and for ordinary commercial installations a tolerance of ±15%, or an outside variance of 30%, is permissible. Frequently such deviations must be resorted to in limited areas of the tower by reason of structural difficulties, and this is particularly true of wider plate spacing than is theoretically necessary in the middle of the tower to provide room for workmen to make the necessary assembly of the bubble caps.

As previously stated an important feature of the invention resides in the extent to which the NO issuing from each plate is oxidized to NO_2 before the next plate is reached. In the lower parts of the tower, where at best the absorption is rather small, we have found that more than 50% of the NO issuing from each plate should be oxidized to NO_2 before the next plate is reached and a range of 50–70% is preferable.

In the middle and upper reaction spaces of the tower, a range of 40–70% of oxidation of NO to NO_2 is most favorable. Reference to Fig. 6 of the drawings will show that this percentage of oxidation can easily be obtained in a relatively short time, whereas, as shown by Fig. 8, any higher percentage of oxidation would require a much greater volume of reaction spaces. This feature of the invention may therefore be described by stating that the reaction spaces in the middle and upper parts of the tower are so proportioned that the oxidation reaction is deliberately interrupted at a point where its relative speed or efficiency has begun to fall off rapidly, this point lying within the range of 40–70% of total oxidation. It will readily be seen, by a comparison of Figs. 7 and 8, that the same is true of the reaction in the bottom parts of the tower.

We have stated that the conditions at the top of the tower may be such as to require special treatment. In this area, which may be defined as the portion of the tower where the strength of the absorbing acid does not exceed 10% HNO_3, the concentration of both NO and O_2 in the gases is very small and an extremely large tower volume must be provided to obtain as much as 50% oxidation of NO to NO_2. We have found, however, that the absorption conditions in this part of the tower are entirely different from those which obtain in the middle and lower parts, for the absorption of NO_2 by dilute acid or by the feed water is relatively small. On the other hand, the absorption of an equimolecular mixture of NO and NO_2 in the water or dilute acid to produce nitrous acid is much more rapid, and the absorbing liquid at the top of the tower is likely to contain large quantities of nitrous acid. Under these circumstances, any NO that may be present in excess of the equimolecular ratio is not absorbed.

As a result of these conditions it is very desirable to carry the oxidation of NO to NO_2 to the point where an equimolecular mixture of NO and NO_2 is obtained but a higher degree of oxidation is of little value. Accordingly, the present invention provides relatively large oxidation spaces in the upper parts of the tower, and particularly at the top, in order to obtain an equimolecular mixture, and then provides an absorbing section with no further oxidation volume. This absorbing section may take the form of a number of bubble plates or a packed section may be provided so as merely to promote contact of the gases and liquid without allowing time for further progress of oxidation. The efficiency of such an absorbing section may be further improved, if desired, by inserting a catch basin below it and using a small recirculating pump, in order to pass a part of the liquid over the packing a number of times. The solution of nitrous acid which is thus built up flows down through the tower, where the nitric acid on the absorption plates will expel the gases from solution and the NO_2 will be reacted chemically with water to produce nitric acid. We consider this method and apparatus for obtaining complete absorption as another feature of our invention.

The above description is based on the assumption that it is desired to recover as much as possible of the fixed nitrogen in the absorption tower. In many cases, for example when the stack gases from the tower can be utilized in the production of nitrites, the above considerations will not apply. Thus when the cost of absorbing volume is an important factor and facilities can be provided for absorbing the exit gases in alkalies our invention points to the fact that it is better to eliminate the top section of the tower entirely and absorb the remaining oxides of nitrogen from the gases with alkali. It will thus be seen that the most important advantages of the invention will be found in the design of the lower and middle parts of the tower, but that its principles may be applied to the top section of the tower if desired.

The foregoing is an outline of the general scope of our invention, pointing out the principal features thereof. In Figs. 6, 7 and 8 of the drawings we have illustrated diagrammatically the conditions existing in the tower which has previously been described and shown in Figs. 2 and 3 when it is operated on a 9% ammonia-air mixture using cooling water at 25° C. This tower is designed to operate at 5 atmospheres absolute pressure and to produce 65% HNO_3 using either pure water or water containing weak acid from the drips as feed. The strength of acid on each of the plates is shown on the drawings, and the partial pressure of the nitric oxide, in atmospheres, is shown on the attached graph for all parts of the tower. The nitrous gases as they

enter the base of the tower are 99.5% oxidized; i. e., 99.5% of the NO has been oxidized to NO_2 or N_2O_4. The lowest plate is fed with nitric acid of 64.6% strength which is fortified on the plate to 65% acid by reaction with a small part of the NO_2 in the gases, the absorption coefficient being in the neighborhood of 4%. The nitric oxide liberated by this reaction, together with that already present in the gases amounts to .0075 atmosphere and the partial pressure of oxygen in the gas is approximately .27 atmosphere. In accordance with the invention a 60% oxidation coefficient is maintained in each of the spaces and so the volume of the first reaction space is large enough to permit oxidation of 60% of the NO to NO_2, which results in a partial pressure of NO just prior to entering the second plate of .003 atmosphere. This pressure is increased to .008 atmosphere by the reaction on the second plate, and the alternate liberation and oxidation of 60% of the NO continues on up the tower in the amounts indicated by the graph.

It is apparent from Fig. 6 that the partial pressure of nitric oxide in the middle of the tower is far greater than its pressure in either the lower or upper parts. As has been indicated, the speed of oxidation of NO to NO_2 is proportional to the pressure of NO in the gases, and accordingly, the initial rate of oxidation of the gases leaving the middle plates of the tower is much higher than at the top or bottom. This is shown by a comparison of Fig. 7, which shows the oxidation curve under the conditions obtaining in the first reaction space, with Fig. 8, which shows the corresponding reaction curve for the eleventh reaction space. It will be noted that one second is required to bring the NO pressure from .007 to .0023 atmosphere, a 67% reduction whereas less than .05 second is required to make the same percentage reduction in a NO gas having a partial pressure of .05, even with the smaller amount of oxygen present in the eleventh reaction space. However it will also be noted that the rate of reaction in any oxidation space falls off quite rapidly from its initial value as the nitric oxide is used up in the reaction. Accordingly, by spacing the absorption plates so closely together in the central part of the tower that the oxidation is interrupted at the point of 60% completion, a much more efficient use is made of the tower volume in this area. On the other hand, by spacing the plates so far apart in the lower parts of the tower that 60% oxidation is obtained, the very low absorption efficiency of the absorption plates is greatly improved and a stronger product acid can be more readily obtained.

The extreme slowness of the oxidation reaction near the top of the tower is very forcibly brought out in Fig. 6, and it will be readily appreciated that this part of the tower is very inefficient as an oxidizing medium. However, the figure also shows the futility of employing the usual number of absorption plates in this part of the tower, and by simply eliminating the greater part of these plates the cost of this part of the tower can be greatly reduced without any loss of absorption efficiency. It will be noted that only two of the regular absorption plates are used in the entire top section of the tower and even then a tower absorption efficiency factor of 98% can be obtained simply by providing sufficient oxidation spaces to reach a 50% oxidation factor in the gases.

While the invention has been illustrated by the description of a specific modification thereof, and while optimum figures and results have been used in its explanation it is understood that suitable equivalents may be resorted to within the scope of the appended claims. For example, the principles of the invention may be equally well applied to the well known drum type of absorbing system for oxides of nitrogen, in which the absorption plates and reaction spaces of a tower are replaced by a plurality of communicating cylinders or drums in cascade. Accordingly, in the subjoined claims it is understood that the term "liquid receptacle" will mean any receptacle capable of gas and liquid contact, and that the term "reaction space" will cover any space in which the regeneration or re-formation of the gases to their original characteristics may take place.

What we claim is:

1. Apparatus for the manufacture of nitric acid by the absorption of oxides of nitrogen in an aqueous absorbing liquid which comprises a series of alternating absorption vessels and oxidation spaces, means for passing the absorbing liquid through said vessels in series, means for passing a gas mixture containing oxygen and oxides of nitrogen through the last vessel of the series wherein the higher oxides of nitrogen are absorbed and nitric oxide is evolved, then through an oxidation space wherein nitric oxide is oxidized, and then through the remaining vessels and reaction spaces wherein these alternate reactions are repeated, the volumes of said reaction spaces being progressively decreased in the direction of gas flow from the gas inlet and toward the central part of the series and being so proporticned to the concentration of nitric oxide in the gases entering them that not less than 40% nor more than 70% of the nitric oxide entering is oxidized when normal oxidizing conditions exist therein.

2. Apparatus according to claim 1 in which the sizes of the reaction spaces are such that substantially the same percentage of the nitric oxide issuing from each absorption vessel is oxidized in each space.

3. Apparatus according to claim 1 in which the sizes of the reaction spaces are such that substantially 60% of the nitric oxide issuing from each absorption vessel is oxidized in the next succeeding space.

4. Apparatus for the manufacture of nitric acid comprising an absorption tower having a number of gas and liquid contact plates separated by reaction spaces, means for passing an aqueous liquid downwardly over the plates in series, and means for passing a gas containing oxygen and oxides of nitrogen upwardly through the plates and reaction spaces in series, the plates being so spaced that the volumes of representative reaction spaces in the central and lower parts of the tower are unequal and are such that not less than 40% nor more than 70% of the nitric oxide evolved on the plate below is oxidized when normal oxidizing conditions exist therein.

5. A system for the manufacture of nitric acid by the absorption of higher oxides of nitrogen in an aqueous absorbing medium comprising a number of gas and liquid contact elements separated by reaction spaces, means for passing the liquid downwardly over the contact elements in series, and means for passing the gas upwardly through the contact elements in series, the reaction spaces in the central portions of the system being smaller than those in the lower por-

tions and the volume of representative reaction spaces in the lower and central portions of the system being a variable quantity such that the coefficient of the oxidation reaction taking place therein is maintained substantially constant when normal oxidizing conditions exist therein.

6. A system for the manufacture of nitric acid by the absorption of higher oxides of nitrogen in an aqueous absorbing medium comprising a number of gas and liquid contact elements separated by reaction spaces, means for passing the liquid downwardly over the contact elements in series, and means for passing the gas upwardly through the contact elements in series, the reaction spaces in the central portions of the system being smaller than those in the lower portions and the volume of representative reaction spaces in the lower and central portions of the system being a variable quantity such that the coefficient of the oxidation reaction taking place therein is 0.6 ± 0.1 when normal oxidizing conditions exist therein.

7. Apparatus for the manufacture of nitric acid comprising an absorption tower composed of acid resisting material and containing unevenly spaced gas and liquid contact elements separated by reaction spaces, the volumes of the reaction spaces in the central part of the tower being smaller than those in the upper part.

8. A system for the manufacture of nitric acid by the absorption of higher oxides of nitrogen in an aqueous absorbing medium comprising a number of gas and liquid contact elements separated by reaction spaces, means for passing the absorbing medium downwardly over the contact elements in series, and means for passing the gas upwardly through the contact elements in series, the volumes of representative reaction spaces being progressively decreased in the direction of gas flow from the gas inlet end toward the central part of the series, the volume of each such representative reaction space being a quantity such that 40–70% of the NO in the gas leaving each contact element will be oxidized to higher oxides of nitrogen when normal oxidizing conditions exist therein.

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