July 27, 1926. 1,594,264

H. HOWARD

CHEMICAL ANALYSIS APPARATUS AND PROCESS

Filed March 1, 1924 4 Sheets-Sheet 1

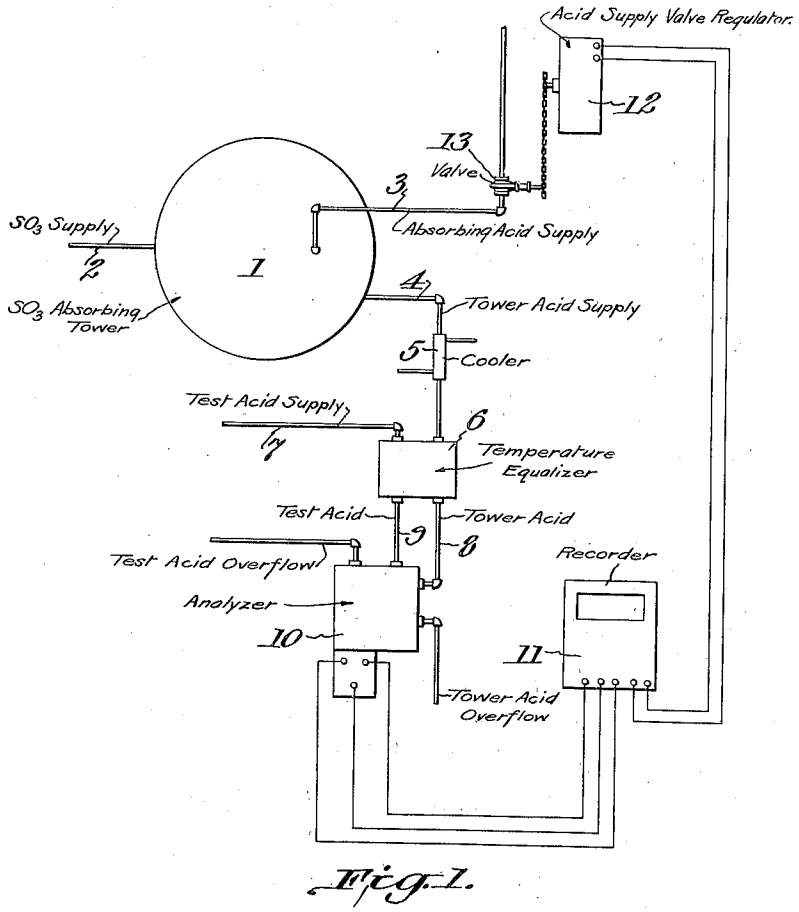


Fig. 1.

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Fig. 2.

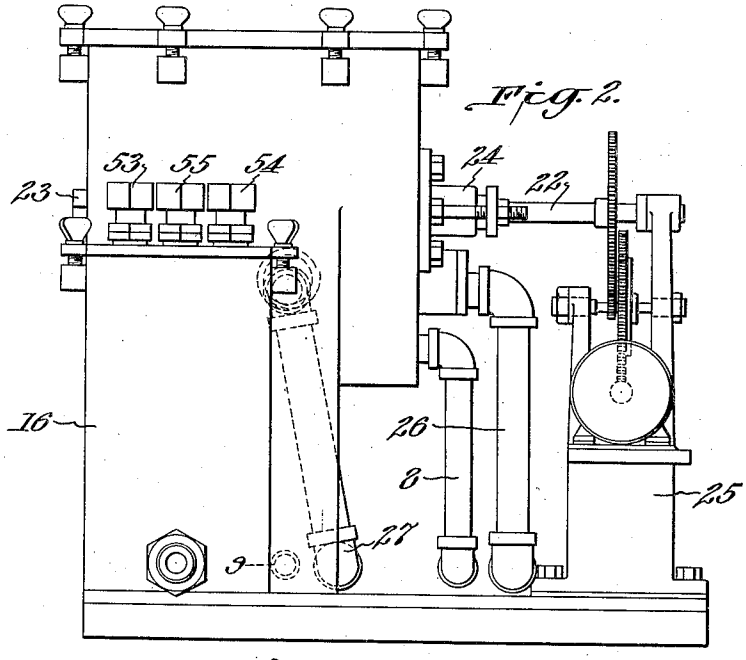
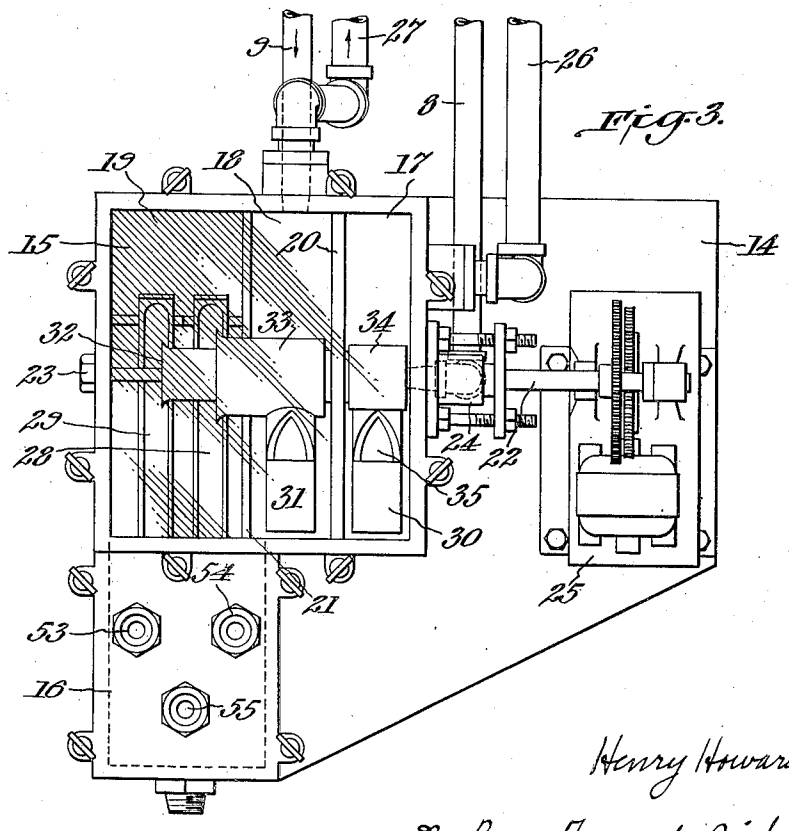


Fig. 3.



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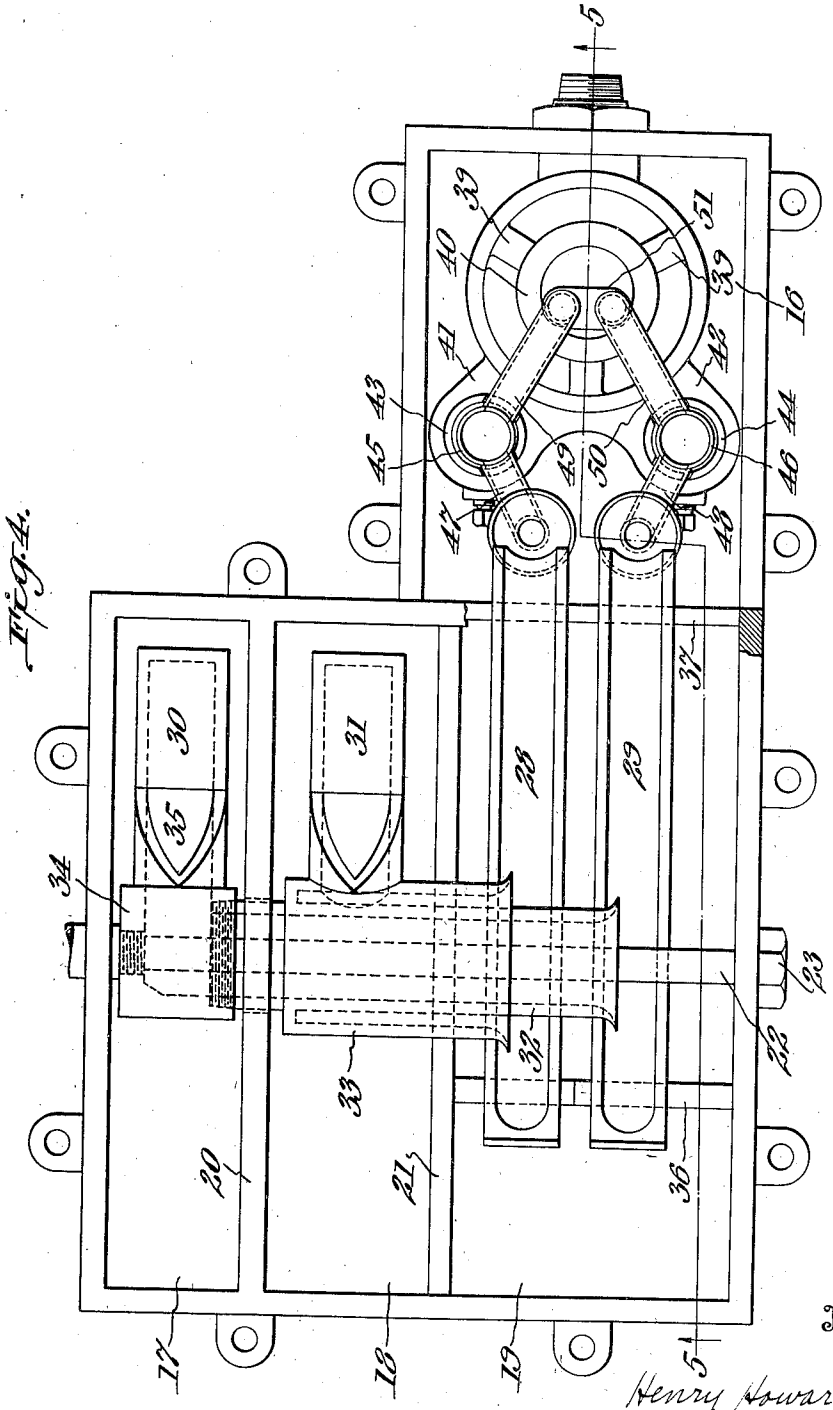
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Fig. 4.



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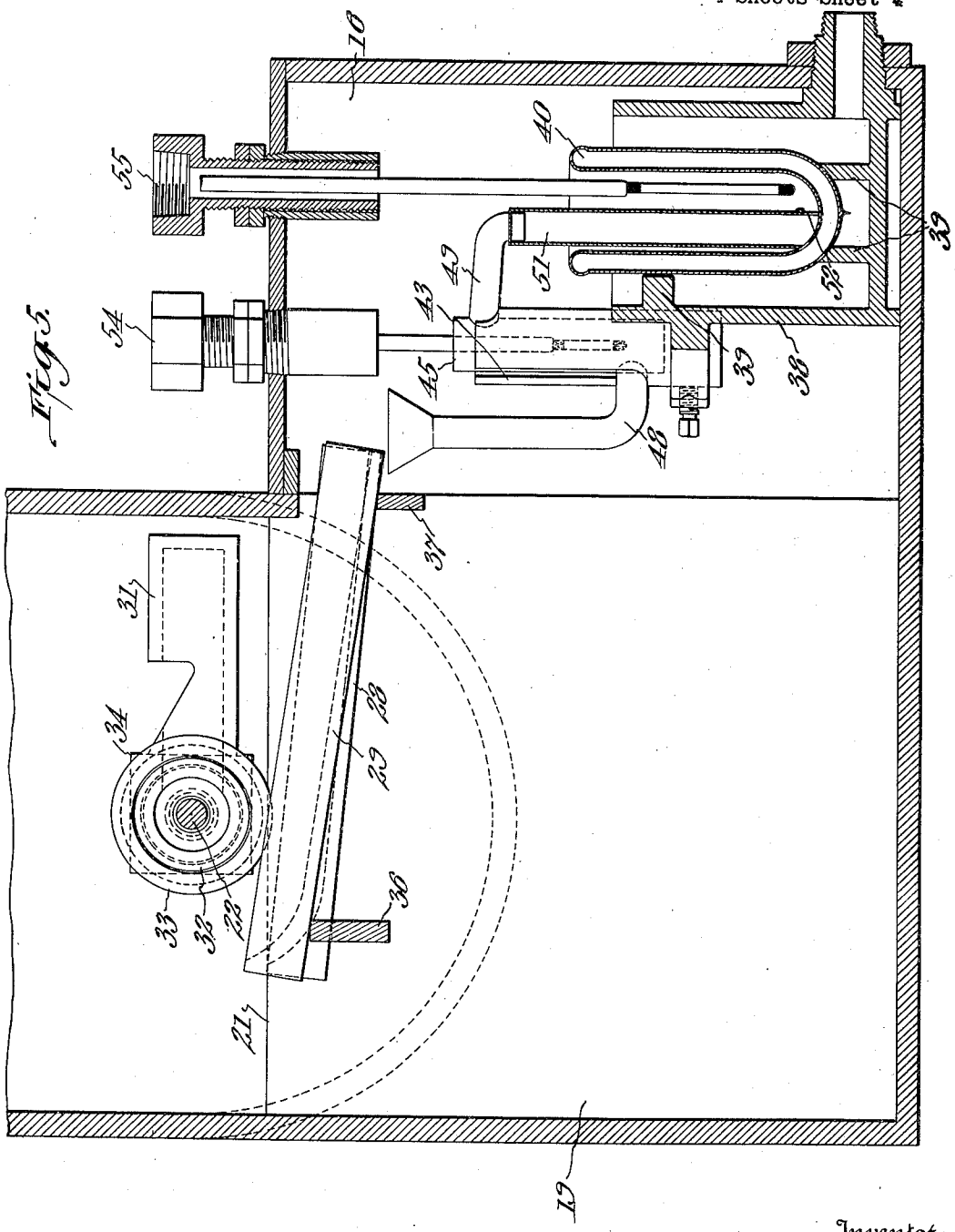
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CHEMICAL ANALYSIS APPARATUS AND PROCESS

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Fig. 5.



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Patented July 27, 1926. 1,594,264

UNITED STATES PATENT OFFICE.

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CHEMICAL-ANALYSIS APPARATUS AND PROCESS.

Application filed March 1, 1924. Serial No. 696,274.

In an article published in the Journal of the Society of Chemical Industry, vol. 29, 1910, page 3 et seq., there is described a method for the quantitative analysis of chemical products which is based upon the determination of the heat of reaction of the material to be analyzed with some other material. The method consists in mixing the material to be analyzed, for instance oleum, with a material capable of reacting therewith to produce a temperature change, for instance water or dilute sulfuric acid, measuring the resulting temperature change and calculating therefrom the composition of the oleum. As is explained in the article referred to the method is of general application and may be used for the analysis of any material which is capable of reacting with some other material or reagent to give a temperature change. So far as I am aware the process referred to has never been carried out other than by manual operation.

The present invention relates to improvements in said method, and more particularly to a procedure designed to be carried out automatically and to give not only an indication and record, if desired, of the composition of the material under consideration but also to control the production of the material. The invention relates further to an apparatus for carrying the process into effect.

For convenience the invention will be described in connection with the manufacture of oleum for which the process and apparatus are particularly designed, but the invention is applicable generally to the analysis of, for instance, acids and alkalies and in fact all chemical substances and compounds which give exothermic or endothermic reactions with other substances or compounds, as will be readily understood, and the application of the invention to such other materials is therefore embraced by my invention.

Referring to the drawings,

Figure 1 is a plan view of the analysis and control apparatus associated with an oleum producting apparatus for analyzing the product therefrom and controlling the operation thereof;

Fig. 2 is a front elevation of the analyzer;

Fig. 3 is a top plan view of the analyzer;

Fig. 4 is an enlarged plan view of the analyzer as illustrated in Figs. 2 and 3 with the driving mechanism, the covers, the base and the acid feed and overflow pipes omitted; and,

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

Referring now to Fig. 1 of the drawing, 1 represents an absorbing apparatus with the usual SO_3 and absorbing acid supplies 2 and 3 and the oleum discharge 4. The oleum passes through a cooler 5 and then through the temperature equalizer 6 in which it and the test acid supplied through a pipe 7 are brought to substantially the same temperature. The temperature equalizer 6 is not an essential part of the apparatus and may be omitted as will appear hereinafter. The oleum and the test acid then flow through pipes 8 and 9, respectively, to the analyzer 10 in which they are mixed in measured quantities and the resulting change in temperature measured or caused to act upon a temperature sensitive device, for instance, an electrical resistance thermometer, the effect being indicated and recorded in any suitable units, for instance, in the case of oleum, in the percent of free SO_3, by the recorder 11 which also controls the operation of the regulator 12 for the absorbing acid supply valve 13.

The absorbing apparatus 1 and its accessories are of any suitable construction and arrangement and do not require further description excepting, as will appear hereinafter, that the absorbing acid supply is automatically regulated so that acid of a uniform predetermined concentration is produced. The cooler 5 and the temperature equalizer 6 are of any well known and approved construction. The acid supply valve regulator is a well known piece of apparatus and does not require detailed description. It may be of that type which comprises a continuously moving power driven mechanism, mechanism connected with the valve 13 for actuating the same, means for transmitting motion from the power driven mechanism to the valve actuating mechanism in forward or reverse direction under the influence of the recorder 11 and time controlled means for periodically bringing the means for transmitting motion into operation.

The recorder 11 also is a known device which does not require detailed description.

It may be of the type involving the principles of operation of the Wheatstone bridge, so arranged that a flow of electric current will cause a deflection of a galvanometer needle, which may in the well known manner be arranged to indicate and record the deflection in any suitable units of measurement and to control a flow of electric current to the regulator 12.

The analyzer 10 illustrated in Figs. 2, 3, 4 and 5 has a suitable base 14 upon which is supported a rectangular box 15 and its rectangular wing 16. Both the box 15 and the wing 16 are provided with removable covers. The box 15 is divided into three compartments 17, 18 and 19 by vertical partition walls 20 and 21, the wall 20 extending to the top of the box and the wall 21 extending upwardly to about the level of the top of the wing 16. The compartment 17 does not extend to the base 14 but is cut off and provided with a semicylindrical bottom, as is illustrated in Figs. 2 and 5. The shaft 22 is mounted with one end in the bearing nut 23 carried by one side wall of the box 15 and extends over the top of the partition 21, through an opening in the partition 20, through a stuffing box 24 carried by the opposite side wall of the box 15, and to the driving motor and reducing gears 25. A constant level of oleum to be tested or analyzed is maintained in the compartment 17 by means of the supply pipe 8 and the overflow pipe 26 and a constant level of testing acid is maintained in the compartment 18 by the test acid supply 9 and the overflow pipe 27. The compartment 19 houses two troughs 28 and 29 for delivering test acid and oleum supplied thereto by the measuring apparatus now to be described to the analyzing apparatus housed in the wing 16.

The test acid and oleum measuring apparatus comprises the two dippers 30 and 31 which communicate respectively with the two concentric tubular conduits 32 and 33, said dippers and conduits being mounted to rotate with the shaft 22. The dippers 30 and 31 are mounted to dip into the acid held in the compartments 17 and 18, respectively, and to deliver acid therefrom into the conduits 32 and 33, respectively, which in turn deliver into the troughs 29 and 28, respectively. The dipper 30 is in the form of a hollow cylinder closed at one end. The other end of the cylinder is open and communicates with an L-shaped canal in the block 34. In the side of the dipper is a V-shaped notch or opening 35 for the admission of acid as it dips into the body of acid maintained in the compartment 17. The block 34, as stated, has an L-shaped canal, one arm of which is co-axial with the shaft 22 and tubular conduit 32. The other arm of the L-shaped canal extends at right angles to the shaft 22 and receives the open end of the dipper 30. The block 34 also has a screw threaded opening co-axial with and extending from that arm of the L-shaped canal which is co-axial with the shaft 22. This opening engages a screw threaded portion of the shaft 22 and serves to support the block 34 with the dipper 30 and the conduit 32 upon the shaft. The conduit 33 is mounted upon and concentric with the conduit 32 and is closed at its end opposite to the trough 28 where it engages the conduit 32. It has a lateral opening in which it receives the open end of the dipper 31. The dipper 31 is similar in construction to the dipper 30 described above.

The troughs 28 and 29 are carried in the compartment 19 by transverse supports 36 and 37 and are inclined to permit the flow of acid to the analyzing apparatus in the wing 16.

In the wing 16 is a supporting structure in the form of a cylindrical receptacle 38 having projections 39 on its inside wall forming a nest for the Dewar flask 40, a lateral outlet near its bottom projecting through the wall of the wing and two similar projections 41 and 42 on its outer wall provided with openings and set screws for receiving and supporting the tubular members 43 and 44, which in turn support the acid receiving vessels 45 and 46. The vessels 45 and 46 preferably are made of glass and therefore are supported as described. Acid is delivered from the troughs 28 and 29 to the vessels 45 and 46, respectively, through the spouts 47 and 48, respectively, and is delivered from the vessels 45 and 46 into the mixing tube 51 by the overflow spouts 49 and 50. The mixture of acids formed in the mixing tube then flows into the Dewar flask 40.

The mixing tube 51 in which the oleum and test acid are mixed and in which a considerable rise in temperature takes place preferably is made of gold. It is a cylindrical tube having an enlarged mouth receiving the delivery ends of the spouts 49 and 50 and the lower end is shaped to fit the bottom of the Dewar flask upon which it rests. Near the bottom of the tube 51 is an opening 52 through which the mixed acid discharges into the Dewar flask. The cover to the wing 16 has three openings 53, 54 and 55, provided with stuffing boxes which support thermometers in the vessels 45 and 46 and the Dewar flask 40. These three thermometers are connected as indicated in Fig. 1 with the recorder 11. The analyzer, excepting of course the driving mechanism which is of the ordinary construction, and the cover to the box 15, the Dewar flask and the units comprising the parts 45, 46, 47, 48, 49 and 50, which preferably are made of glass, and the mixing tube which preferably is made of gold, are made of any suitable structural material. Steel is a satis-

factory material for the construction of an analyzer designed for the analysis of oleum. The receptacle 38 may be made of cast iron.

The operation of the process and apparatus for the analysis of olem and control of the production thereof is as follows:

All or a portion sufficient to supply the analyzer of the oleum produced in the absorber 1 flows through the cooler 5 where it is brought to about room temperature and then passes to the temperature equilizer 6 which is supplied also with test acid through the pipe 7. The oleum and test acid are brought to substantially the same temperature and then flow by way of pipes 8 and 9 into the receptacles 17 and 18. Excess oleum and test acid delivered to the receptacles 17 and 18 overflow through the pipes 26 and 27, thus maintaining constant levels of liquid in the receptacles. The dippers 30 and 31 at each revolution dip into the receptacles 17 and 18 and deliver the oleum and test acid picked up through the conduits 32 and 33, the troughs 28 and 29 and the spouts 47 and 48 into the vessels 45 and 46. The dippers may be rotated continuously at a predetermined uniform rate or they may be given an intermittent or pediodic motion by means of suitable time controlled mechanism as will be readily understood. The dippers may be made to deliver measured quantities of the oleum and test acid at any suitable frequency, for instance, once each minute or once each ten minutes as conditions may require. The equalizing temperature of the oleum and test acid delivered into the vessels 45 and 46 is measured, in the particular form of apparatus illustrated, by two 25-ohm electrical resistance thermometers connected in series. At the next revolution of the dippers 30 and 31 fresh batches of oleum and test acid delivered into the vessels 45 and 46, displacing the oleum and test acid therein and causing it to flow through spouts 49 and 50 into the mixing tube 51 and into the Dewar flask 40 in which the temperature of the mixture is measured by a 50-ohm electrical resistance thermometer. At the next revolution of the dippers 30 and 31 fresh batches of oleum and test acid are delivered into the vessels 45 and 46, oleum and test acid flowing therefrom into the Dewar flask 40 and displacing the mixture therein which flows over the edge of the flask into the receptacle 38 and to waste.

The two 25-ohm electrical resistance thermometers connected in series and the 50-ohm electrical resistance thermometer are counterbalanced in a Wheatstone bridge arrangement including the recorder 11, in which the deflection of a galvanometer needle responsive to potential difference produced by the thermometers due to the differences in the temperatures to which they are subjected, is, by means of a suitably calibrated scale, made to indicate the composition of the oleum, for instance, its content of free SO_3. The deflection of the galvanometer needle is also made to produce a continuous record of the analysis in the well know way and through the control of electric circuits to the regulator 12 to control its operation, that is, to cause it to operate to close the absorbing acid supply valve 13 if the oleum falls below the desired concentration or to open the valve to admit more absorbing acid if the concentration of the oleum exceeds the predetermined concentration.

The recorder 11 is adjusted so that the position of the pointer at which it does not cause any change in the supply of absorbing acid corresponds to the concentration of the product desired and the galvanometer scale is calibrated with reference to the rise in temperature which corresponds to the change in composition of the oleum, as will be apparent from the disclosure in the article in the Journal of the Society of Chemical Industry referred to.

The apparatus described is capable of considerable modification without departing from my invention or the principles involved. For instance, when using an efficient temperature equalizer for the oleum and test acid the two 25-ohm electrical resistance thermometers in series with each other as described are not necessary. A single thermometer may be used to measure the temperature of only the oleum or the test acid and this temperature taken as the equalizing temperature of the two acids, since the other is at approximately the same temperature. Or, if the acids are supplied to the analyzer at a constant temperature the continuous measurement of the temperature of the unmixed acids is unnecessary. In this case the temperature of the mixture may be made to indicate directly the composition of the oleum. It will also be apparent that the invention is applicable where more than two materials are caused to react. The specific form of analyzer illustrated may be replaced by other devices capable of preparing the same or equivalent functions. For instance, the dippers 30 and 31 with their associated parts may be replaced by other means such as time-controlled valve mechanism for periodically delivering batches of oleum and test acid or in place of mechanism for delivering the oleum and test acid periodically and in batches means such as adjustable valves or orifices or jets supplied with oleum and test acid under constant pressure or head may be employed for delivering continuous uniform supplies of the oleum and test acid. An apparatus of the latter type is disclosed and claimed in an application in the name of John C. Boertlein filed March 1, 1924, Serial No. 696,301.

Instead of analyzing oleum as described above, the oleum may serve as the reagent in the analysis of sulfuric acid containing free water. In this case sufficient oleum is used to combine with all of the free water in the acid being analyzed.

It is further noted that in the foregoing description the production of the oleum may be regulated by controlling the supply of SO_3 instead of the supply of absorbing acid to the absorber or both supplies may be regulated.

As is stated in the article above referred to, small differences in the composition of the oleum give comparatively large changes in the temperature of the reaction product. The method therefore is very accurate, although of course the composition of the test acid must be fairly constant and its temperature must not change too rapidly because changes in the composition of the test acid as well as sudden changes in its temperature will produce corresponding changes, although relatively small, in the results.

In the foregoing description and in the appended claims reference is made to heat of reaction, it being understood that heat of reaction is intended to include not only the heat generated or absorbed when true chemical reactions take place, but also heat changes produced by hydrations and dehydrations, solution and precipitation, solidification and liquefaction, and in fact to all known phenomena in which a heat change takes place which bears a definite relation to the composition of the material involved.

I claim:

1. Chemical analysis apparatus comprising a reaction vessel, a source of supply of a material to be analyzed, a source of supply of a material capable when mixed with said material to be analyzed of producing a heat reaction, means for delivering measured quantities of said materials into the reaction vessel, and means comprising heat responsive elements for directly indicating a characteristic of the difference between the equalizing temperature of said materials and the temperature of the mixture thereof in said reaction vessel.

2. Chemical analysis apparatus comprising a source of supply of a material to be analyzed, a source of supply of a material capable when mixed with said material to be analyzed of producing a heat reaction, a temperature equalizer, means for delivering said materials from said sources of supply to said temperature equalizer, a reaction vessel, means for delivering measured quantities of said material from said temperature equalizer to said reaction vessel, and means comprising heat responsive elements for directly indicating a characteristic of the difference between the temperature of one of said materials at a point between said temperature equalizer and said reaction vessel and the temperature of the mixture thereof in said reaction vessel.

3. The combination with apparatus for the continuous formation of a chemical product by the interaction of at least two reagents, said apparatus including a reaction chamber, feed lines for separately delivering the reagents into the reaction chamber, and means for removing the product of reaction from the reaction chamber, of means for regulating the rate of feed in at least one of said feed lines, said means for regulating the rate of feed comprising a reaction vessel, means for delivering thereto measured quantities of said product and of a material adapted when mixed therewith to give a heat reaction, means including a heat-responsive element in the vessel for indicating by changes of temperature therein changes in a characteristic of the product, and means actuated by the last named means for varying said rate of feed.

4. In apparatus for continuous formation of sulfuric acid including an absorbing apparatus, feed lines for feeding absorbing acid and SO_3 respectively thereto, means for varying the rate of flow in one of said feed lines and means for withdrawing the sulfuric acid product from the absorbing apparatus, the combination of a reaction vessel, a source of supply of liquid adapted when mixed with said sulfuric acid product to produce a heat reaction, means connected with the said withdrawing means and with the said source of supply for delivering measured quantities of said sulfuric acid product and of the said liquid into the reaction vessel, means including a heat-responsive element in the said vessel for indicating by changes of temperature in the vessel changes in the degree of concentration of said sulfuric acid product, and means actuated by the last named means for actuating said varying means.

5. In a chemical analysis apparatus the combination of a reaction vessel, separate reservoirs, means for maintaining substantially constant levels of liquids in said reservoirs, dippers mounted to move in fixed paths dipping into said reservoirs, means for delivering liquids from said dippers into said reaction vessel, and means comprising heat responsive elements for directly indicating a characteristic of the difference between the equalizing temperature of the liquids in said reservoirs and the temperature of the mixture of liquids in said reaction vessel.

6. In chemical analysis apparatus a reaction vessel, separate reservoirs, means for maintaining supplies of liquids in said reservoirs, means for delivering liquid from each of said reservoirs at a constant rate into said reaction vessel and means comprising heat responsive elements for directly in-

dicating a characteristic of the difference between the equalizing temperature of the liquids in said reservoirs and the temperature of the mixture of liquids in the reaction vessel.

7. In chemical analysis apparatus a source of supply of a material to be analyzed, a source of supply of a material capable when mixed with said material to be analyzed of producing a heat reaction, a temperature equalizer, means for delivering said materials from said soucres of supply to said equalizer, reservoirs, means for separately delivering said materials from said temperature equalizer to said reservoirs, a reaction vessel, means comprising dippers mounted to move in fixed paths dipping into said reservoirs for delivering said materials from said reservoirs into said reaction vessel at constant rates, and means comprising temperature responsive elements for directly indicating a characteristic of the difference between the temperature of the liquid in one of said reservoirs and the temperature of the mixture of liquids in said reaction vessel.

8. Process of controlling the production of a chemical product which comprises supplying a raw material and forming said product in a continuous operation, causing a portion at least of said product to undergo a phenomenon involving a spontaneous temperature change in the presence of a temperature sensitive device, and causing the effect upon said device to automatically control the supply of said raw material.

9. Process of controlling the production of a chemical product which comprises supplying a raw material and forming said product in a continuous operation, causing a supply of said product immediately following its formation to undergo a phenomenon involving a spontaneous temperature change in the presence of a temperature sensitive device, automatically indicating and recording the temperature effect upon said device, and causing said effect to automatically control the supply of said raw material.

In testimony whereof, I affix my signature.

HENRY HOWARD.