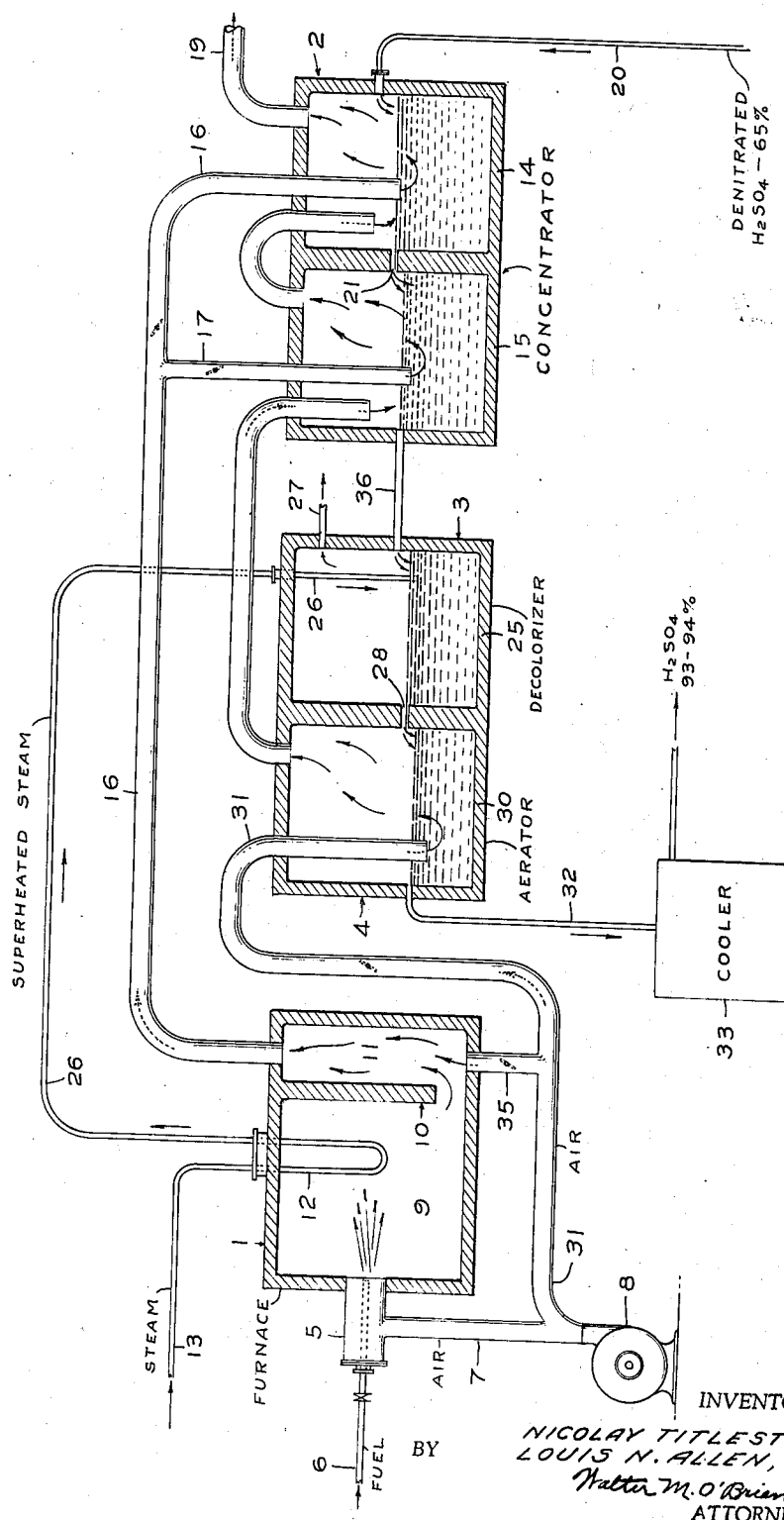


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SULPHURIC ACID CONCENTRATION

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INVENTORS
NICOLAY TITLESTAD,
LOUIS N. ALLEN, JR.,
Walter M. O'Brien
ATTORNEY.

UNITED STATES PATENT OFFICE

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SULPHURIC ACID CONCENTRATION

Nicolay Titlestad, White Plains, N. Y., and Louis
Nathan Allen, Jr., Nutley, N. J., assignors to
Chemical Construction Corporation, New York,
N. Y., a corporation of Delaware

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This invention relates to the concentration and decolorization of denitrated spent sulphuric acid, for example the sulphuric acid remaining after driving off the nitric acid content from the spent or waste acid from the manufacture of nitro-cellulose or of nitroglycerine in munitions plants. Such acid, as obtained from the denitrating towers, is usually of 65–70% concentration and contains appreciable quantities of dark organic compounds which are derived from the nitration process.

Heretofore this acid has been concentrated by boiling it in cast iron pots over an open flame to a final concentration of from 93–96%. In this way the dark organic compounds are broken down and the acid becomes very light in color, but the process is expensive and wasteful as the pots break very frequently and large charges of acid are lost. The fuel consumption is also extremely high because the heat transfer is limited to the surface exposed to the flame and the transfer coefficient is low.

We have attempted to concentrate the spent acid by passing hot gases through it which has the advantage of reducing the boiling temperature of the acid due to the reduced vapor pressure caused by the passage of the hot gases. We found, however, that while this method of treatment would concentrate the acid satisfactorily, it would not decolorize it because this reduced boiling temperature is then too low. We then found that superheated steam, either when used alone or in admixture with other hot gases, will decolorize the dark concentrated acid produced by concentrating denitrated spent acid to approximately the proper strength either by means of hot gases or in a vacuum concentrator or by other methods in which the concentration is effected at a temperature at or below the normal boiling point (i. e. the boiling point under atmospheric pressure) of the acid.

Our invention consists, therefore, in concentrating denitrated spent acid with hot gases or otherwise and thereupon blowing superheated steam into it, either alone or in admixture with other hot gases. Satisfactory results have been obtained by the following methods:

(a) Blowing superheated steam into the liquid whereby the steam is condensed and enters into the acid partly diluting it and raising its temperature to the boiling point by virtue of the heat evolved during dilution together with the latent heat of condensation.

(b) Blowing superheated steam into the liquid, condensing the steam and raising the tempera-

ture to somewhat below the boiling point, thereby diluting the acid correspondingly.

(c) Blowing an excess of superheated steam into the liquid, condensing part of the steam. The uncondensed part is removed and temperature is raised to the boiling point, with corresponding dilution of the acid.

(d) Blowing an excess of superheated steam and hot combustion gases into the liquid, condensing part of the steam. The uncondensed part is removed and the temperature is raised to below the boiling point without diluting the acid.

(e) Blowing an excess of superheated steam into the liquid without condensing any of the steam and raising the acid to the boiling point or slightly below, with or without concentrating the acid further.

A particularly effective method and apparatus constituting a specific feature of the invention is illustrated in the accompanying drawing, in which the single figure is a diagrammatic illustration of the furnace, concentrators and piping system for accomplishing the concentration and decolorization.

In this drawing the apparatus consists generally of the combination of a furnace 1, which may be of any known or approved type, a concentrator 2 of the Mast type such as is described in Reissue Patent No. 19,064 and a decolorizer 3 together with an aerator or concentrator 4 for cooling and further concentrating the decolorized acid obtained in the decolorizer 3.

In the modification shown the furnace 1 is of the oil or powdered coal burning type, which is especially well suited for the generation and/or superheating of steam and the production of hot gases in accordance with the present invention. This furnace is equipped with a burner 5 having a fuel supply line 6 and an air supply line 7, the latter being connected to an air blower 8. The furnace is divided by a baffle 10 into a fire box 9, which may contain water tubes in the usual manner for generating steam, and a dilution chamber 11 for diluting the stack gases to suitable temperatures for use in acid concentration. In addition to the steam generating equipment, which is not shown, the fire box 9 also contains steam superheating coils or tubes which are illustrated diagrammatically by the steam tube 12, and it is understood that these coils are connected directly with the steam generating equipment if this is also contained in the boiler. On the other hand, steam such as waste steam from any suitable outside source may be introduced to the coils 12, as through an inlet pipe 13, and it is

understood that the invention is not limited in this respect.

As has been stated, the acid concentrator 2 is of a known type, and need not be described in detail. It consists generally of a plurality of drums or concentrating chambers 14 and 15 in which the acid to be concentrated is passed in countercurrent contact with hot products of combustion from the furnace 1 which are admitted through pipes 16 and 17. Spent denitrated sulphuric acid of about 65% strength is fed to the drum or concentrating chamber 14 by inlet pipe 20 and is heated and partially concentrated by the gases entering through the pipe 16 which then leave through gas outlet pipe 19. The partially concentrated acid then overflows through the outlet 21 into the second drum or concentrating chamber 15 where it is further concentrated by a second flow of hot gases entering through pipe 17. Although the acid concentrator is shown as consisting of only two drums or concentrating chambers, it is understood that further stages of concentration may be employed if desired, the chief requisite being that the acid is finally brought to the desired concentration, such as 94-96% strength.

The decolorizing chamber 3 which in operation constitutes a principal feature of the invention is preferably similar in form and construction to one of the concentrating drums or chambers 14 and 15 and is made of acid-proof material adapted to withstand the high temperatures at which it operates. In the modification shown it consists of a rectangular or cylindrical chamber 25 provided with a steam inlet pipe 26 extending nearly to the bottom thereof and also preferably provided with an outlet pipe 27 for excess steam. A liquid outlet 28 in the form of a pipe or channel is located at one side of the decolorizing chamber 3 at such a level as to maintain therein a body of acid of substantial depth, thus retaining the acid within the chamber for a substantial period of time when the apparatus is in continuous operation. The volume of acid so retained in the chamber 3 is adjusted to the speed of decolorization by the superheated steam so that the acid is bleached as fast as it is concentrated in the concentrator 2.

As has been pointed out above the process of our invention may be operated with or without a partial condensation of steam and consequent dilution of the acid in the decolorizer 3. In all cases, however, the acid leaving the chamber 25 is very hot and its high heat content may be used for purposes of further concentration by blowing air or other inert gases through it. For the accomplishment of this purpose the decolorizer 3 is directly connected with an aerator or concentrator 4, which consists of a chamber 30 preferably similar in shape and construction to the chamber 25, but having an air inlet pipe 31 extending below the level of the acid therein. Decolorized acid enters this chamber through the pipe 28 and is maintained as a body of substantial depth by the location of an outlet pipe 32 which is provided at a suitable elevation in the side wall thereof. Decolorized and concentrated acid leaving the chamber 30 through this pipe is passed to a cooler 33, from which it may be obtained as a light colored, concentrated sulphuric acid of 93-94% strength.

As has been stated the method of our invention comprises, in its broadest aspects, the decolorizing of concentrated sulphuric acid containing organic coloring impurities by blowing super-heated

steam into a hot body of the acid. The necessity for this step arises from the fact that the concentration temperatures in a drum type concentrator such as the concentrator 2 are below those at which the organic coloring impurities are decomposed or removed. Nitrating acid derived from the manufacture of nitrocellulose or nitroglycerine in munition plants contains organic impurities of this nature which remain in the sulphuric acid after it is denitrated and result in a dark colored product when concentration is accomplished by the use of hot gases alone. Spent alcohol acid recovered as a by-product from the production of secondary alcohols by the absorption of olefins in sulphuric acid and subsequent hydrolysis also presents a similar problem, as it contains organic impurities which darken the acid when it is concentrated at low temperatures.

Accordingly, it will be seen that the process of our invention retains all the advantages accompanying the use of hot gases in concentrating dilute sulphuric acid containing organic impurities and simply adds the additional decolorizing step of blowing superheated steam into the acid. It is an additional important advantage of the invention that this steam can be superheated and/or generated in the same equipment that is ordinarily used for generating the hot gases used in concentrating, and therefore the fuel consumption of the process is not materially altered. In fact, we have found that spent denitrating acid may be concentrated and decolorized to a strength and color suitable for reuse with an expenditure of fuel only 5% greater than that used in the concentrators alone. In other words, the present invention provides light colored acid at a fuel cost of only 5% greater than that required for the production of dark colored concentrated acid, and with very little additional capital expenditure for equipment.

The process of our invention will be illustrated as being carried out in the apparatus which has been described, but it should be understood that in its broader aspects it is not limited thereto. On the contrary, it is understood that the substitution of alternative and equivalent steps may be resorted to within the scope of the claims appended hereto. Hot combustion gases produced in the furnace 1 by the burning of a fuel such as oil, gas or powdered coal are passed over the super-heating steam coils 12, and may then be passed over steam generating tubes in the usual manner if desired. The combustion gases then enter the chamber 11 where they are diluted with air from the blower 8 introduced through the branch pipe 35 in the air line 31. Sufficient air is added from this source to cool the combustion gases to about 1100° F., and they pass at this temperature through the pipe 16 and through branch pipe 17 into the concentrating drums or chambers 14 and 15 where they serve to concentrate spent denitrated sulphuric acid of about 65% strength introduced through the feed line 20 in the usual manner. In a preferred method of operation the acid in the first concentrating drum or chamber 14 is held at 80-85% strength and the acid in the concentrating drum or chamber 15 is held at 94-96% strength. The hot gases passing through these bodies of acid evaporate water therefrom, but at temperatures too low to decompose the impurities which they contain. Thus, for example, the acid in chamber 15 is concentrated to 94-96% at a temperature of about 440° F., and therefore

leaves this chamber as a dark colored concentrated acid which requires decolorization before it is suitable for reuse.

The dark colored acid leaving the concentrator 2 is preferably continuously introduced into the decolorizer 3 through a connecting pipe 36, at a temperature of 440-450° F. In the decolorizer it is maintained as a body of substantial depth and volume while steam which has been superheated in the coil 12 to temperatures of about 1000° F. is passed into it through pipe 26. The temperature of the acid is thereby raised to about 520-530° F., partly by taking up sensible heat from the steam and partly by the heat of dilution resulting from condensation of steam. At these temperatures the color forming impurities in the acid are rapidly decomposed. The size of the chamber 25 and the depth of acid therein are such that the acid is held for a sufficient length of time to remove substantially all of its colored and color forming impurities, after which it is discharged into the chamber 30 through the pipe 28 as a decolorized acid of 92-93% strength.

As has been pointed out above, it is not always necessary to condense a part of the steam into the acid. On the contrary, an excess of superheated steam may be blown through it without condensing any of the steam, and the acid is heated to temperatures near its boiling point simply by the sensible heat, or superheat, contained in the steam. In this way superheated steam at a temperature of 1000-1200° F. or more may be used to both decolorize and concentrate the acid. It is also possible, as is pointed out above, to employ a mixture of superheated steam and hot combustion gases in this stage of the process, in which case a further concentration of the acid may be obtained in the chamber 25. It will be noted that when a mixture of hot gases and superheated steam is used the presence of the steam serves to offset the temperature reducing action of the gases, and this constitutes an important additional feature of the invention.

Where part of the superheated steam is condensed in the acid, which is probably the most economical procedure from the standpoint of fuel consumption, it is necessary to further concentrate the acid and this is accomplished as a part of the aerating and cooling step in the chamber 30. Acid from the chamber 25 is preferably con-

tinuously introduced into this chamber through the inlet pipe 28 and air from the blower 8 is passed through it by way of the pipe 31. Since the acid enters at the extremely high temperatures of 520-530° F., its sensible heat content is sufficient to provide the heat necessary for vaporizing its excess content of water, and the acid is therefore concentrated by the passage of air through it to a concentration of about 93-94%. At the same time, the air stream also serves to cool the acid and to further bleach it by carrying away any volatile colored impurities which it may contain. The same result may be accomplished by using a vacuum evaporator at this point if desired.

From the foregoing description it will be seen that our invention provides a process and a preferred form of apparatus which accomplishes all the objects thereof both cheaply and efficiently. It should be understood, however, that the invention in its broader aspects is not limited to the details given above, which are primarily for purposes of illustration.

What we claim is:

1. In a process of decolorizing dilute impure sulphuric acid containing organic coloring impurities in which the dilute acid is heated to concentrate and decolorize the same, the improvement which comprises, concentrating the dilute acid to about 94-96% strength by heating it to temperatures which are below the normal boiling point, and thereupon blowing superheated steam into the hot concentrated acid to raise the acid temperature to about the normal boiling point to decolorize the acid, part of the superheated steam being condensed in and diluting the acid, and thereafter reconcentrating and cooling the hot decolorized acid by blowing cool air therethrough.

2. In a process of decolorizing dilute impure sulphuric acid containing organic coloring impurities in which the dilute acid is heated to concentrate and decolorize the same, the improvement which comprises, concentrating the dilute acid to about 94-96% strength by the introduction of hot combustion gases therinto, and thereupon blowing superheated steam into the hot concentrated acid to raise the acid temperature to at least about the normal boiling point to decolorize the acid.

NICOLAY TITLESTAD.

LOUIS NATHAN ALLEN, JR.