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H. B. HASS ET AL
PROCESS OF NITRATING ETHANE
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Fig. 1.

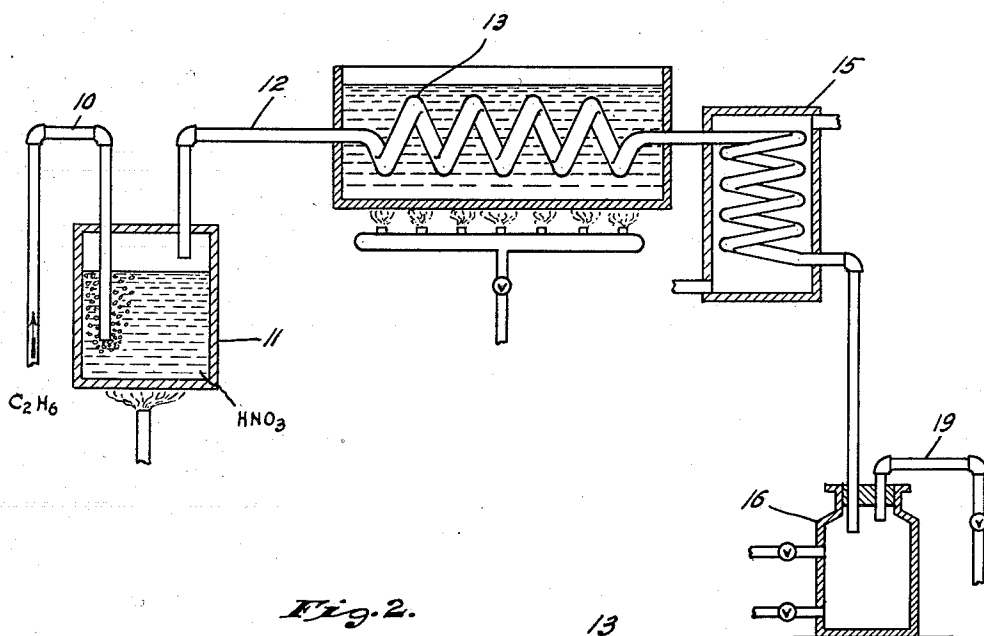
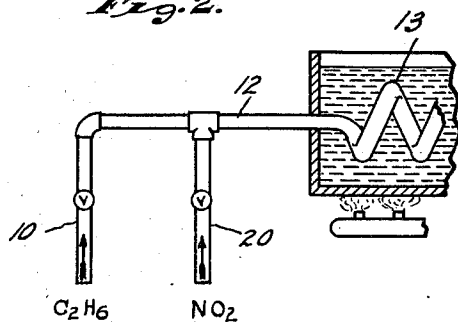


Fig. 2.



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PROCESS OF NITRATING ETHANE

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Application May 16, 1936, Serial No. 80,070

8 Claims. (Cl. 260-144)

It is the object of our invention to effect the nitration of ethane.

In Patent No. 1,967,667, of July 24, 1934, granted to us in association with Byron M. Vanderbilt, there was disclosed for the first time the vapor-phase nitration of saturated aliphatic hydrocarbons having from 3 to 8 carbon atoms; but that application was limited to hydrocarbons within that range, in which in addition to primary carbon atoms there were also secondary and/or tertiary carbon atoms; for the nitration at the specific temperatures there named tended to occur principally on tertiary carbon atoms, and to somewhat smaller extent on secondary carbon atoms, while it occurred only to a relatively small extent on primary carbon atoms. There was no indication at the time of the application for that patent, or from the disclosure of that patent, that a similar nitration could be obtained with ethane, in which only primary carbon atoms are present.

We have now found that even with ethane, which has no secondary or tertiary carbon atoms, nitration is possible by a process otherwise largely like that shown in said Hass, Vanderbilt and Hodge Patent No. 1,967,667; and to do this for the most advantageous reaction it is desirable that the temperature be raised above the 135° to 300° C. mentioned in that patent (although some nitration can be obtained at that range of temperatures) and brought to somewhere between 300° and 500° C.

A suitable apparatus for doing this by a continuous process is that shown in the accompanying drawing. In that drawing, Fig. 1 shows diagrammatically an apparatus in which vapors of heated nitric acid are used to produce the nitration; and Fig. 2 shows fragmentally a modification in which nitrogen dioxide is supplied as such for that purpose instead of by the heating of nitric acid.

Ethane at atmospheric pressure is supplied through a pipe 10 in vapor phase, and in the apparatus of Fig. 1 is bubbled through hot concentrated nitric acid in a suitable container 11. The concentration of nitric acid vapor in the hydrocarbon is determined by the temperature of the nitric acid in the container 11; for by maintaining this temperature at about 108° C. and carrying on the evaporation at atmospheric pressure about one mole of nitric acid is vaporized for each two moles of ethane, which we find to be a satisfactory ratio. The mixture of ethane and nitric acid vapor passes from the container 11 by a pipe 12 to a reaction tube 13 which is suitably heated to a temperature at least above 150° C.

and preferably between 300° C. and 500° C. We find that about 420° C. gives good results. This heating is desirably obtained by having the reaction tube 13 immersed in a bath containing a molten salt mixture that is maintained at such temperature. A suitable mixture for this is a eutectic mixture of sodium nitrite and potassium nitrate. The temperature mentioned is sufficiently high to keep both the reagents and the reaction products in gaseous phase. The vaporized nitric acid is in part decomposed when heated, and yields various decomposition products, among which is nitrogen dioxide. That nitrogen dioxide undoubtedly enters into the nitration reaction with the ethane.

The supply of ethane is desirably such that the passage of the gases through the reaction tube permits the nitration to occur without leaving any substantial amount of nitrogen dioxide in the exit gases. To determine this the speed of gas passage is increased until appreciable amounts of nitrogen dioxide appear in those exit gases; and then the rate of flow is gradually decreased until the nitrogen dioxide has just disappeared from the exit gases. We find this to be approximately the optimum velocity of flow.

The mixed gases from the reaction tube 13 are passed through a cooler 15, in which they are cooled sufficiently to condense most of the nitroethane which has been formed. When the operation is conducted at atmospheric pressure, 0° C. is a satisfactory cooling temperature for this cooler 15.

In this nitration, it is found that some nitromethane accompanies the nitroethane in the exit gases. Perhaps this is because of the formation of acetic acid, and its subsequent nitration and decarboxylation. It may also be due to the addition of nitrogen dioxide to methyl radicals which may be present.

The condensed liquid from the cooler 15, with any accompanying gases, passes to a liquid-gas separator 16, in which the condensed nitroethane and spent acid are removed from the uncondensed gases. The liquid separated in the separator 16 separates in turn into two layers, one of which consists of the spent nitric acid and the other of which consists essentially of nitroethane with some nitromethane. These layers may be drawn off at different levels, or the whole drawn off and the two layers separated by decantation. The nitroethane can be purified, if desired, by washing with water and rectification under atmospheric or sub-atmospheric pressure. The gases from the separator 16 con-

sist of ethane, nitric oxide, carbon monoxide, carbon dioxide, water vapor, and some vapor of nitroparaffins. These gases and vapors may be taken off through the pipe 19 which leads from the upper part of the separator 16, and carried by that pipe to any convenient apparatus for the separation of the component gases.

The nitric oxide is preferably reconverted to nitric acid or to nitrogen dioxide, for further use in this process; and the separated ethane may be and desirably is recycled.

If desired, the whole operation may be carried on under a pressure which is sufficient to cause liquefaction of ethane in the cooler 15.

Instead of vaporizing and decomposing nitric acid, which yields nitrogen dioxide, we may supply nitrogen dioxide as such. This is shown in Fig. 2. There ethane is supplied as before by a pipe 10, desirably a valve pipe, but is supplied directly therefrom to the pipe 12. Nitrogen dioxide is also supplied to the pipe 12 by a valved pipe 20. The valves are adjusted so that there will be a sufficient excess of ethane to avoid explosion. The remainder of the apparatus is as in Fig. 1.

We claim as our invention:

1. The process of nitrating ethane, which consists in producing contact between ethane and nitric acid with both reagents in the gas or vapor phase.

2. The process of nitrating ethane, which consists in producing contact between ethane and

nitric acid with both reagents in the gas or vapor phase and at a temperature between 300° and 500° C.

3. The process of nitrating ethane, which consists in producing contact between ethane and nitric acid with both reagents in the gas or vapor phase and at a temperature above 150° C.

4. The process of nitrating ethane, which consists in producing contact between ethane in the gas or vapor phase and the gases or vapors formed by heating nitric acid.

5. The process of nitrating ethane, which consists in producing contact between ethane in the gas or vapor phase and the gases or vapors formed by heating nitric acid and at a temperature between 300° and 500° C.

6. The process of nitrating ethane, which consists in producing contact between ethane in the gas or vapor phase and the gases or vapors formed by heating nitric acid and at a temperature above 150° C.

7. The process of nitrating ethane which consists in producing contact between ethane and nitrogen dioxide at a temperature above 150° C.

8. The process of nitrating ethane, which consists in producing contact between ethane and a compound in the class consisting of nitric acid and nitrogen dioxide, with both reagents in the gas or vapor phase.

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