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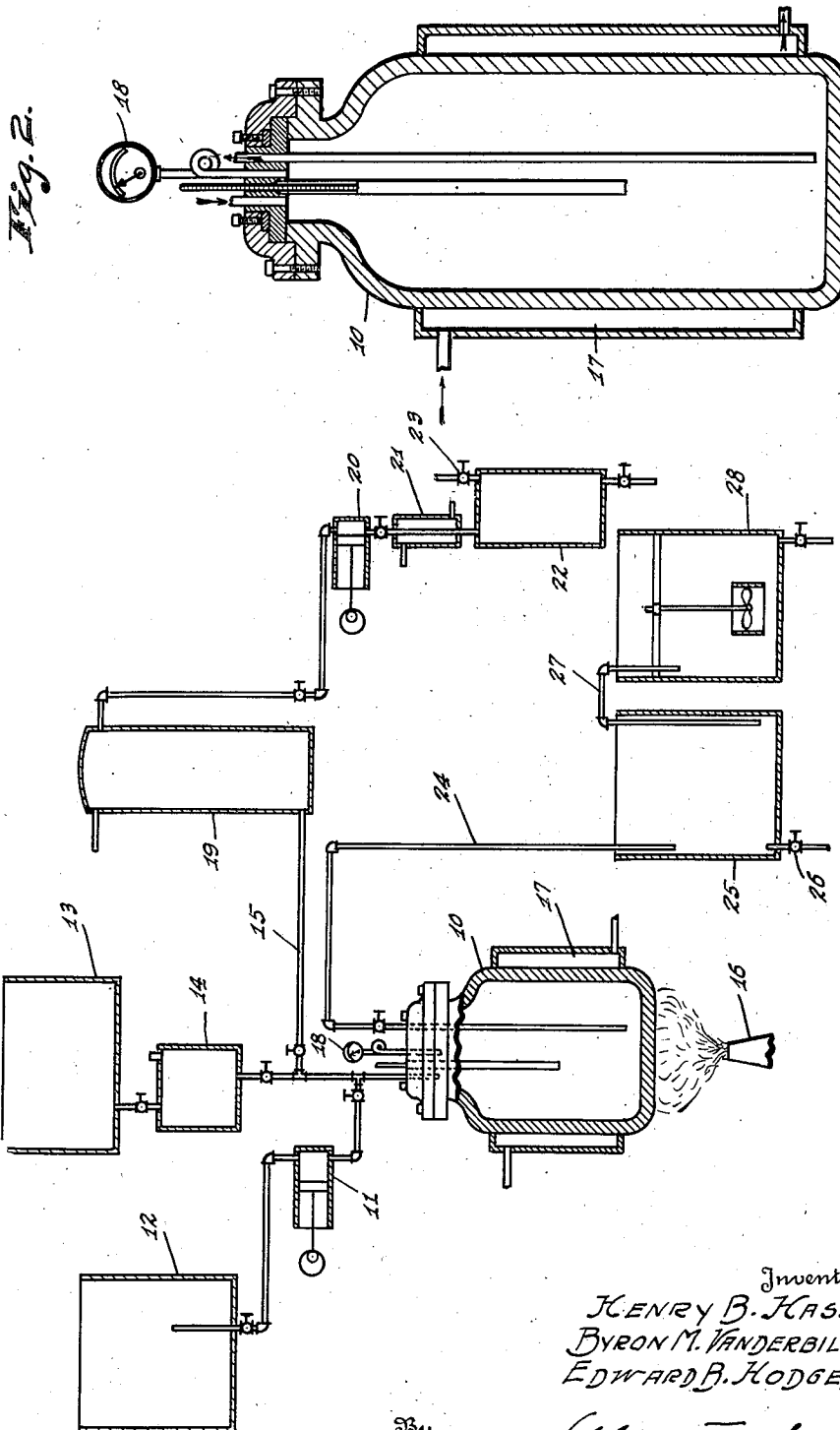
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PROCESS OF NITRATING PARAFFIN HYDROCARBONS AND PRODUCT THEREOF

Filed Oct. 4, 1933

2 Sheets-Sheet 1



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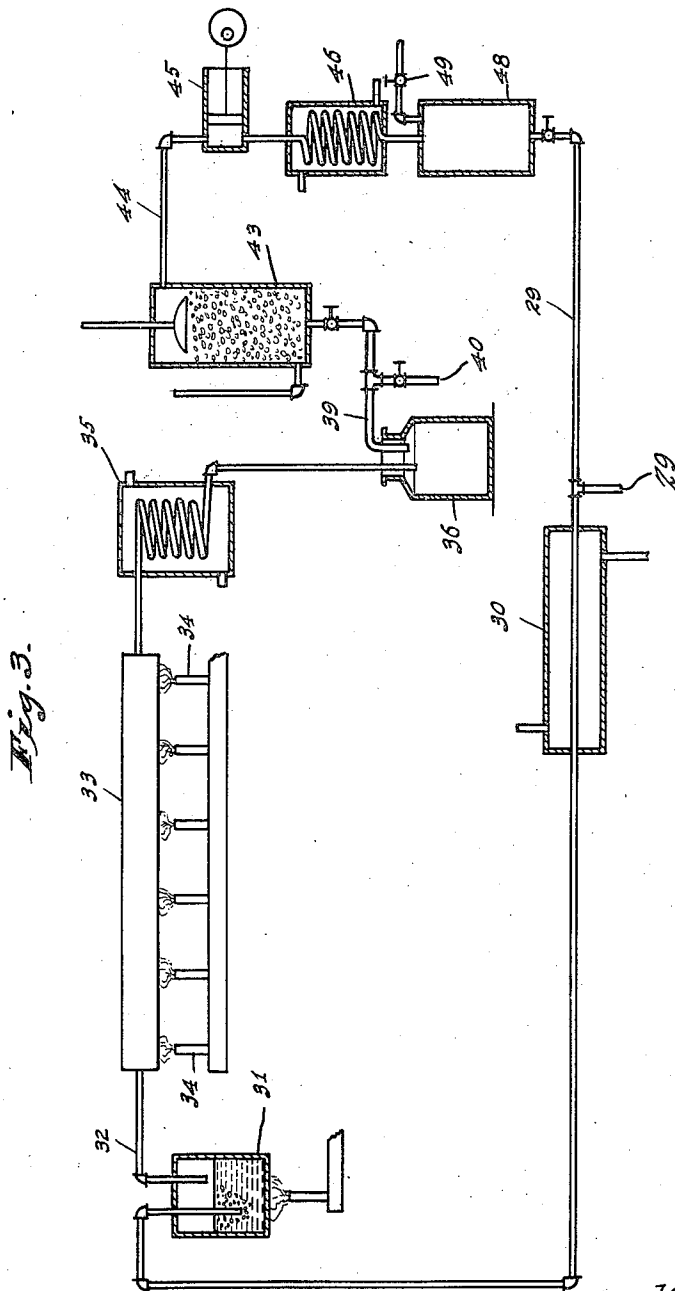
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UNITED STATES PATENT OFFICE

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PROCESS OF NITRATING PARAFFIN HYDROCARBONS AND PRODUCT THEREOF

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16 Claims. (Cl. 260—144)

It is the object of our invention to effect the nitration of saturated aliphatic hydrocarbons which contain other than primary carbon atoms; and more especially to effect the nitration of paraffin hydrocarbons having from 3 to 8 carbon atoms.

On account of the great abundance of saturated aliphatic hydrocarbons, especially of paraffin hydrocarbons such as occur in petroleum and in natural gas, extensive and intensive study has been made of the relatively few chemical reactions which they will undergo. Among such reactions is nitration.

Nitration of these hydrocarbons, however, has not hitherto resulted in any successful commercial application, so far as we know. In fact, in his book entitled "Petroleum and its Products", (McGraw-Hill, 1928, page 60,) Gruse says that "The nitration of petroleum fractions has been studied to some extent but no results of either scientific or technical importance have been obtained because of the mixed nature of the fractions and the complexity of the reactions."

In most if not all of the previous work on nitration of these saturated aliphatic hydrocarbons, the same general technique has been used as that which has been successful with aromatic hydrocarbons—that is, a liquid-phase reaction, and relatively low reaction-temperatures. In the course of that previous work it was learned that in many respects the nitration of aliphatic hydrocarbons was not strictly analogous to the nitration of aromatic hydrocarbons, as, for instance, that more dilute nitric acid should be employed with paraffins than with aromatics; and that it is inadvisable to use sulphuric acid to aid the reaction in attempting to nitrate paraffins, although sulphuric acid helps the reaction in nitrating aromatics. Nevertheless, investigators continued to adhere to the same general method, of attempting to cause a reaction between nitric acid and the various paraffin hydrocarbons with both reagents in the liquid phase.

We have discovered that the reason for the uniformly negative and indifferent results previously obtained has been that the reagents were in the liquid phase, and at low temperatures. Nitric acid and the paraffin hydrocarbons are not soluble in each other to any considerable extent. The nitrated product, however, is much more soluble in nitric acid than is the hydrocarbon from which it is derived. Because of this situation, the initial nitration reaction occurs slowly, but the more soluble nitrated product is more readily at-

tacked by the nitric acid, so that the principal ultimate products are oxides of nitrogen, water, and carbon dioxide. Attempts have been made to increase the mutual solubility of the original reagents by using some mutual solvent in addition; and the most advantageous mutual solvent so far discovered is acetic acid. But the choice of a mutual solvent is greatly limited by the nature of nitric acid, which under the reaction conditions attacks almost all organic compounds. Even acetic acid is oxidized by nitric acid within the temperature range employed by us for the nitration of paraffin hydrocarbons, and we have also found that the presence of acetic acid seems to favor oxidation of the hydrocarbon rather than nitration.

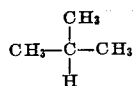
We have discovered that these difficulties may be avoided by departing from the old procedure, of trying to obtain a reaction between two immiscible liquids; and producing the reaction with both the nitric acid in part and the saturated aliphatic hydrocarbon in the vapor or gaseous phase, by using such temperatures and pressures as are necessary to produce this. Since all vapors and gases are miscible with one another in all proportions, the maintenance of the vapor or gaseous phase produces effective mixing; and in consequence causes the reaction to be rapid, and makes it possible to secure relatively good yields of the nitro-aliphatic compounds, such as nitro-paraffins.

Therefore, according to our invention, we operate under conditions in which both of the reagents are in the vapor or gaseous phase; and desirably operate under considerable pressure, and above the critical temperature of the hydrocarbon reagent.

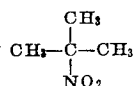
Our process may be used for the nitration of those saturated aliphatic hydrocarbons which have other carbon atoms than primary ones, and especially those which have tertiary carbon atoms. It is applicable to the nitration of aliphatic hydrocarbons having from 3 to 8 carbon atoms; but we have not attempted it with hydrocarbons having more than 8 carbon atoms, nor with such simple hydrocarbons as methane or ethane which have only primary carbon atoms. Our process is especially applicable where there are tertiary carbon atoms, as in the iso-hydrocarbons, for the nitration by our process tends to occur principally on tertiary carbon atoms, and to a somewhat smaller extent on secondary carbon atoms, but to a relatively small extent on primary carbon atoms. Our process is especially advantageous for the nitration of paraffins, such as propane,

n-butane, iso-butane, the pentanes, the hexanes, the heptanes, and the octanes; but it is also applicable with advantage to other saturated aliphatic hydrocarbons such for instance as the naphthenes (cycloparaffins).

We have gotten our best results with iso-paraffins, by nitration of the tertiary carbon atoms. An excellent example of this is isobutane, which has one tertiary carbon atom and three primary carbon atoms, with the general formula:



When this is nitrated, one of the principal products is tertiary nitrobutane, with the following formula:



Small amounts of primary nitro-isobutane are also produced; and some carbon dioxide and some water; and also a solid which has not been identified but which is probably 1,2-dinitro isobutane.

In nitrating these saturated aliphatic hydrocarbons which have secondary and/or tertiary carbon atoms, and of which isobutane is taken as an example, we may carry out the process either in batches or in continuous process. In using isobutane as an example, we do so with no intent to limit the invention; for it is applicable without change to other hydrocarbons of the class mentioned, such for instance as n-butane, propane, etc., as already noted.

The apparatus for doing this is illustrated in the accompanying drawings. Fig. 1 shows an apparatus for carrying out our process in batches; Fig. 2 is a sectional view of a water-cooled bomb which is especially suitable for the batch method of Fig. 1; and Fig. 3 shows an apparatus for carrying out our process continuously.

In the batch process, we may proceed as follows:

A reaction vessel or bomb 10, constructed of material which is resistant to dilute nitric acid, such for instance as Allegheny metal, and capable of withstanding high pressure, is filled with a mixture of liquid isobutane and dilute nitric acid—one mole of nitric acid to two moles of isobutane. We prefer to make the mixture within the bomb by putting in 35% nitric acid in sufficient amount to give the desired molar proportion to the isobutane used and then run in the isobutane in sufficient quantity to fill the bomb to the extent of 5-20%. The isobutane may be supplied by a pump 11 from an isobutane storage tank 12, and the nitric acid from a nitric-acid storage reservoir 13 by way of a measuring tank 14, all suitably connected to the bomb by suitable valved piping 15 shown diagrammatically. The bomb is then closed, and gradually heated by a burner 16 until abundant reaction starts, which is at about 135°-145° C. This temperature is above the critical temperature of isobutane, for such critical temperature is 134° C., but with some hydrocarbons abundant reaction starts below the critical temperature although with the reagents in the gas or vapor phase. The reaction develops a pressure within the bomb of the order of 600 to 2400 pounds per square inch—the fuller the bomb the greater the pressure—; but in spite of the increased pressure, the hydrocarbon remains in the gas or vapor phase by the increase in tem-

perature produced by the heat of the reaction, and the nitric acid is at least partly in vapor phase. Thus the reaction is practically wholly between gases or vapors.

As the reaction is exothermic, it tends to become very violent once it has started, and hence we provide means for cooling the bomb, as by circulating water through an outside jacket 17 with which it is provided as shown in Fig. 2.

When the reaction has substantially ceased, by the using up of the nitric acid, the pressure substantially stops rising and the bomb is cooled to room temperature. We prefer to have a suitable manometer 18 connected with the bomb, for indicating the pressure within it.

When the bomb has been cooled to room temperature, and the pressure sufficiently lowered, the gases therefrom are released through the valved piping 15 into a scrubbing tower 19, and there scrubbed with some reagent which removes nitric-acid vapor from them, such as sodium carbonate. The gases leaving the tower 19 are compressed by means of a compressor 20 and cooled by a condenser 21. A sufficient pressure is produced to condense substantially all of the isobutane, which is removed from the gaseous reaction products in a separator 22. The undensified gases are vented from a valve 23 on the separator 22, and the condensed isobutane is recycled or sent to storage. If desired the oxides of nitrogen may be converted to nitric acid in known manner.

The tertiary nitrobutane may be recovered from the contents of reaction vessel 10 by the following procedure. Such contents are removed by piping 24 from the reaction vessel or bomb 10 to a separating tank 25. The spent acid, which forms a lower layer, is removed from the separating tank 25 through a drain-valve 26. The crude tertiary nitrobutane which remains is transferred by piping 27 to a washing tank 28; where it is agitated with concentrated sodium hydroxide to dissolve any primary nitrobutane, and the alkali is allowed to settle and is drawn off. The tertiary nitrobutane is then further purified by rectification. If desired it may be still further purified by crystallization.

(In case the starting hydrocarbon is such that a secondary nitroparaffin is produced, agitation with sodium hydroxide is not a suitable procedure, since both primary and secondary nitroparaffins are alkali-soluble. In this case a sodium carbonate solution is used to remove traces of nitric acid prior to rectification.)

The tertiary nitrobutane thus obtained boils at about 126.4° C., corrected. It is of very high purity; for it melts at about 25° to 26° C., usually about 25.5° C., instead of at the 24° C. which the literature gives for the melting point of tertiary nitrobutane. The tertiary nitrobutane produced by our process is not lachrymatory, as is the tertiary nitrobutane described in the literature (Berichte 26, 129, 1893); and it has no peppermint odor, as has an uncrystallizable substance reported as tertiary nitrobutane by Tscherniak (Liebig's Annalen der Chemie, 180, 155), but has an odor somewhat similar to that of nitromethane but rather milder.

In the continuous process, we may use various kinds of apparatus, of which that shown in Fig. 3 is an example. Here again we describe the process in connection with isobutane.

Isobutane at atmospheric pressure is supplied through a pipe 29 and vaporizer 30 and bubbled through hot concentrated nitric acid in a suit-

able container 31. The mixture of isobutane and nitric acid vapor passes from the container 31 by a pipe 32 to a reaction tube 33 which is heated by burners 34 to a temperature of about 300° C.—
 5 which is sufficiently high to keep both reagents in the gas or vapor phase. The supply of isobutane is desirably such that it takes about 15 seconds to pass through the tube 33. The nitration occurs within about this time, to produce a
 10 mixture of which tertiary nitrobutane is a predominant constituent. The mixed gases from the reaction tube 33 pass through a cooler 35, in which they are desirably cooled to atmospheric temperature or lower, and then to a separator 36
 15 where the condensed nitrobutane and spent acid are removed from the uncondensed gases. The crude tertiary nitrobutane is purified as in the previous example. The remaining gases, mostly unreacted isobutane, oxides of nitrogen, and of
 20 carbon, pass out from the separator 36 by a pipe 39, and are mixed with air entering through inlet 40 and converted to nitric acid in known manner in tower 43.

The gases leaving the top of tower 43 by way
 25 of pipe 44 are compressed by pump 45 and the isobutane condensed in a cooler 46. The condensed isobutane is separated from uncondensed gases (nitrogen, oxides of carbon, etc.) in a separator 48. The isobutane is recycled, while the
 30 uncondensed gases are vented through a valve 49.

If desired, the whole system of operation in the apparatus of Fig. 3 may be carried out under
 35 pressure, by supplying the isobutane under pressure to the pipe 29 and otherwise maintaining the pressure.

In either the batch method or the continuous method, an increase in yield may be obtained by:

1. Increasing the pressure at which the reaction is carried out.
- 40 2. Increasing the excess of the hydrocarbon over the nitric acid.
3. The use of more dilute nitric acid.

If desired, air or oxygen may be mixed with the hydrocarbon, (such as isobutane,) in order
 45 to reoxidize the oxides of nitrogen to nitric acid; but if this is done, care must be taken to avoid explosive proportions.

In both examples isobutane is used as an example only. Any of the other saturated aliphatic
 50 hydrocarbons indicated above, having from 3 to 8 carbon atoms, may be used instead of isobutane as the starting hydrocarbon in either the batch process or the continuous process.

We claim as our invention:

55 1. The process of nitrating a saturated aliphatic hydrocarbon having from 3 to 8 carbon atoms inclusive, which consists in producing contact between such saturated aliphatic hydrocarbon and nitric acid with both reagents in the
 60 gas or vapor phase.

2. The process of nitrating a saturated aliphatic hydrocarbon having from 3 to 8 carbon atoms inclusive, which consists in producing contact
 65 between such saturated aliphatic hydrocarbon and nitric acid at a temperature higher than the critical temperature of said saturated aliphatic hydrocarbon.

3. The process of nitrating a saturated aliphatic hydrocarbon having from 3 to 8 carbon
 70 atoms inclusive, which consists in producing contact between such saturated aliphatic hydrocar-

bon and the vapor formed by heating nitric acid at a temperature higher than the critical temperature of said saturated aliphatic hydrocarbon.

8 4. The process of nitrating a paraffin hydrocarbon having from 3 to 8 carbon atoms inclusive, which consists in producing contact between such paraffin hydrocarbon and nitric acid with both reagents in the gas or vapor phase.

8 5. The process of nitrating a paraffin hydrocarbon having from 3 to 8 carbon atoms inclusive, which consists in producing contact between such paraffin hydrocarbon and nitric acid at a temperature higher than the critical temperature of said paraffin hydrocarbon.

9 6. The process of nitrating isobutane, which consists in producing contact between such isobutane and nitric acid with both reagents in the gas or vapor phase.

9 7. The process of nitrating isobutane, which consists in producing contact between such isobutane and nitric acid at a temperature higher than the critical temperature of isobutane.

10 8. The process of nitrating n-butane, which consists in producing contact between such n-butane and nitric acid with both reagents in the gas or vapor phase.

10 9. The process of nitrating n-butane, which consists in producing contact between such n-butane and nitric acid at a temperature higher than the critical temperature of n-butane.

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

11 11. The process of nitrating propane, which consists in producing contact between such propane and nitric acid at a temperature higher than the critical temperature of propane.

11 12. The process of nitrating a saturated aliphatic hydrocarbon having from 3 to 8 carbon atoms inclusive, which consists in producing contact between such saturated aliphatic hydrocarbon and nitric acid with both reagents in the gas or vapor phase and at a pressure materially
 12 elevated above atmospheric pressure.

12 13. The process of nitrating a saturated aliphatic hydrocarbon having from 3 to 8 carbon atoms inclusive, which consists in producing contact between such saturated aliphatic hydrocarbon and nitric acid in the presence of free oxygen in excess of that formed by the decomposition of the nitric acid, with the reagents in the gas or vapor phase.

13 14. A composition of matter, consisting of tertiary nitrobutane which is in crystalline form below 25° C., has a melting point between 25° C. and 26° C., and which is substantially free from lachrymatory effects.

13 15. A composition of matter, consisting of tertiary nitrobutane which is in crystalline form below 25° C., has a melting point of substantially 25.5° C., and which is substantially free from lachrymatory effects.

14 16. A composition of matter, consisting of tertiary nitrobutane in solid form free from lachrymatory effects.

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