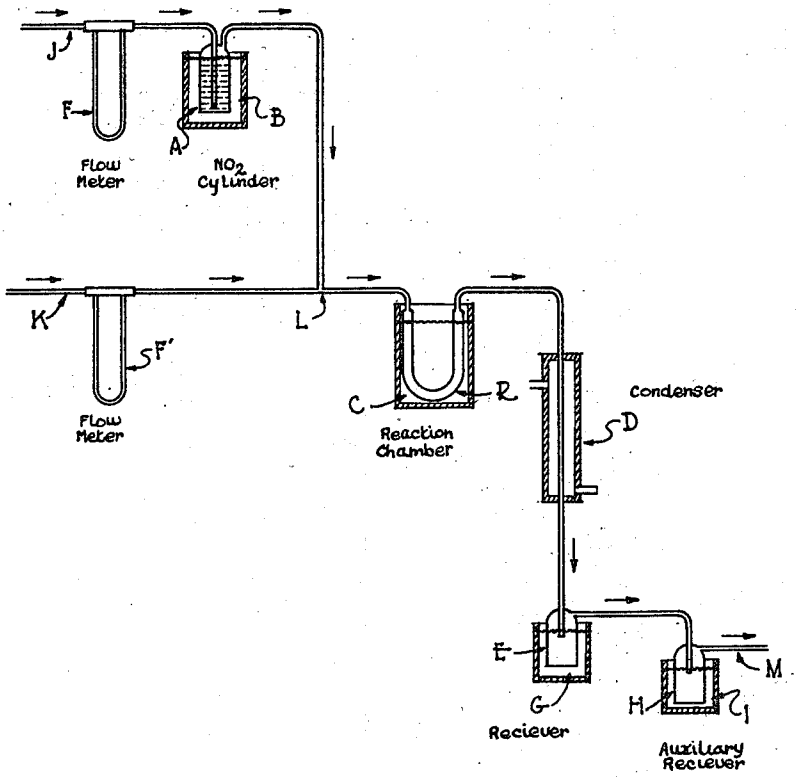
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PROCESS OF NITRATING HYDROCARBONS

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PROCESS OF NITRATING HYDROCARBONS

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Our invention relates to the nitration of saturated aliphatic hydrocarbons, and more particularly to the nitration of saturated hydrocarbons of the paraffin series having in excess of two carbon atoms, by means of nitrogen dioxide.

Numerous efforts have been made in the past to develop a satisfactory method of obtaining nitro derivatives of the saturated hydrocarbons. Regardless of availability and cheapness of the latter, however, no practical commercial process has been developed prior to that disclosed in United States Patent No. 1,967,667, of July 24, 1934, granted to us with Byron M. Vanderbilt as co-inventor. According to that process, saturated aliphatic hydrocarbons having from three to eight carbon atoms, and especially those having secondary or tertiary carbon atoms, are nitrated in the gaseous or vapor phase by the aid of vapors obtained by heating nitric acid, which contain nitrogen dioxide mixed with other substances.

We have now found that we may also obtain effective vapor phase nitration of hydrocarbons higher than those having eight carbon atoms, such as decane, eicosane, triacontane, or paraffin wax, which is a mixture of a number of high molecular weight hydrocarbons.

We have also found that saturated aliphatic hydrocarbons may be more satisfactorily nitrated by substantially pure nitrogen dioxide in place of the vapors formed by heating nitric acid. The use of substantially pure nitrogen dioxide permits improvements in operating procedure which will be apparent from the description of our improved process which follows. Among such improvements are these: By using substantially pure nitrogen dioxide we can obtain more nearly optimum yields, over a wider temperature range, and thus eliminate the necessity for such precise temperature control as is necessary for obtaining such optimum yields, at any given space velocity when vapors of nitric acid are used. Also, by using nitrogen dioxide substantially free from water and nitric acid, we facilitate operation under pressure, lessen condensation, obtain a more selective nitrating action on secondary and tertiary carbon atoms, and obtain greater economy in the recovery of the nitrating agent used.

Our process may be illustrated by reference to the figure, which shows a laboratory apparatus suitable for the application of our process. In the apparatus shown in the diagram, carbon dioxide, or other inert gas, passes through the pipe J, the rate of flow of the inert gas being regulated by the aid of the flow-meter F. The carbon dioxide bubbles through liquid nitrogen dioxide in the cylinder A, the temperature of which is regulated by the bath B maintained slightly below the boiling point of the nitrogen dioxide. By regulating the flow of carbon dioxide through the liquid nitrogen dioxide the proportion of gaseous nitrogen dioxide to hydrocarbon in the reaction mixture may be changed as desired. It is to be understood, however, that other suitable methods of regulating the proportion of nitrogen dioxide to hydrocarbon may be employed without departing from the scope of our invention. In commercial scale operations, for example, the carbon dioxide, or other inert gas, may be dispensed with, if desired, and the gaseous or liquid nitrogen dioxide pumped into the system at determined rates in order to give the desired proportion of reactants.

The hydrocarbon to be nitrated enters the system in a gaseous state through the pipe K, the amount of gas admitted being regulated by the aid of the flowmeter F', or other suitable means. The gaseous reactants meet at L and pass through the coil R maintained at the reaction temperature. This may be accomplished by any suitable means permitting satisfactory temperature control, such as, for example, by the use of electrical heating coils, a molten lead bath or a bath of the molten eutectic mixture of sodium nitrite and potassium nitrate, a bath of this latter type being represented as C in the drawing.

The gaseous reaction products pass through a condenser D where part of the nitrated product is condensed and collected in the receiver E, preferably surrounded by an ice bath G. The uncondensed gases are then preferably conducted to an auxiliary condenser H, cooled by a solid carbon dioxide bath I, or a refrigerating coil, which serves to remove the greater part if not all of the remainder of the nitroparaffins and a substantial portion of any nitrogen dioxide and hydrocarbon remaining in the gaseous reaction mixture. The uncondensed gases leave the system at M and consist mainly of unreacted hydrocarbon together with smaller proportions of carbon dioxide, carbon monoxide, nitric oxide, and nitrogen dioxide. Obviously, however, the composition of the gaseous by-products depends to a large extent upon the particular reactants employed and whether or not an inert diluent gas is used to regulate the admixture of the nitrogen dioxide with the hydrocarbon being nitrated.

The operation of our process will be specifically illustrated by the nitration of isobutane. Carbon dioxide gas, at the rate of two liters per hour, was passed through the cylinder of nitrogen dioxide A, maintained at approximately 18° C. At the same time gaseous isobutane was passed through the flowmeter F', at a rate of fifty liters per hour. The two gaseous reactants after mixing at L were passed through the coil R of 17 ml. capacity, maintained in a $NaNO_2$-KNO_3 salt bath kept at a temperature of 420° C. The exit gases were cooled in the water cooled condenser D and then passed through the receiver E, and the aux-

iliary condenser H which was cooled by solid carbon dioxide, and the nitrated products were collected in both vessels E and H. The nitrated product thus obtained represented 41% of the theoretical conversion of the nitrogen dioxide to nitro compounds.

The procedure outlined above for the nitration of isobutane is applicable to other saturated nonbenzenoid hydrocarbons having more than two carbon atoms, such as, for example, propane, n-butane, pentane, hexane, heptane, octane, decane, eicosane, triacontane, cyclohexane, decahydronaphthalene, etc., as well as mixtures of hydrocarbons, such, for example, as paraffin wax. With the different hydrocarbons, however, the rate of reaction varies somewhat, and hence in order to obtain the best results in any particular case it is usually necessary to vary to some extent the temperature of reaction, the proportion of the reactants, and the space velocity of the reaction mixture. These slight variations in operating conditions, however, ordinarily present no particular difficulties. When, for example, it is desired to operate at some particular temperature the space velocity of the reaction mixture may be regulated by observing the gases from the reaction vessel and adjusting the space velocity so that the brown color characteristic of nitrogen dioxide is no longer, or only barely, visible therein. By way of example, if an operating temperature of 475° C. is selected, the space velocity for the reaction mixture used in the isobutane example described above may be varied between 3000 and 20,000, the preferred range, however, being between 8000 and 15,000.

The proportion of hydrocarbon to nitrogen dioxide may be varied within fairly wide limits. By decreasing the proportion of hydrocarbon to nitrogen dioxide the conversion of the hydrocarbon is increased. This proportion of hydrocarbon, however, should not be lowered sufficiently to approach too closely an explosive mixture. The presence or absence of inert gases and the character and amount of same, as well as the character of the hydrocarbon, determine the exact ratios below which it is impractical to go on account of danger of explosions. On the other hand, increasing the ratio of hydrocarbon to nitrogen dioxide increases the conversion of the nitrogen dioxide to nitro compounds. The cost of handling and recirculating large excesses of hydrocarbon limits from a practical and economical point of view the upper limits of the ratio of hydrocarbon to nitrogen dioxide. In the case of isobutane, a practical ratio for most purposes appears to be of the order of 4–6 mol parts of hydrocarbon to 1 mol part of nitrogen dioxide. As the molecular weight of the hydrocarbon increases, the molecular ratio of hydrocarbon to nitrogen dioxide may be decreased.

The temperature may be varied through a fairly wide range without greatly affecting the degree of conversion, although it is necessary to vary the space velocity to compensate for temperature changes. Temperatures ranging from 300° C. to 600° C. may in general be employed. For most purposes a temperature of the order of 475° C. is satisfactory.

The data shown in the following table will illustrate the results obtained by our process when carried out according to the example set forth above.

Table I

Hydrocarbon	Amount of hydrocarbon, weight in grams	Amount of NO_2, weight in grams	Rate of flow of CO_2, liters/hr.	Partial pressure of reactants	Temperature, °C.	Space velocity, liters reactants per liter space per hour	Conversion, percent NO_2
Propane	66	13.6	2	0.968	420	3,530	18
Do	66	15.0	2	0.968	475	3,580	17
Do	40.4	15.4	3.4	0.971	515	14,400	12
Do	40.4	14.1	3.6	0.970	550	14,200	18
N-butane	108.1	15.6	4	0.968	370	1,820	30.2
Do	104.4	9.3	4.2	0.955	420	5,360	31
Do	92.3	18.2	2	0.967	475	3,480	27
Do	108.1	19.5	4	0.968	540	15,350	28.4
Isobutane	97.2	16.4	2	0.968	420	3,560	44
Do	86.4	13.8	2	0.968	480	3,530	25
Do	129.7	15.4	8	0.967	450	13,530	36
Do	86.4	23.2	2	0.971	540	8,360	29.2
Do	64.8	14.1	4	0.971	540	15,940	39.2
Do	108.1	18.9	4	0.968	525	15,280	39.4

As has previously been pointed out, our invention is applicable to the vapor phase nitration of liquid or normally solid hydrocarbons as well as gaseous hydrocarbons. For example, nitrations of decane and cetane were effected in an apparatus similar to that shown in Figure 1, with the exception that the flow-meter F' was omitted, the rate of flow of the hydrocarbon being controlled in the liquid state; a vaporizer for the hydrocarbons was inserted in the bath C preceding the reaction coil R; and the CO_2-NO_2 mixture was introduced into the reaction coil R in the form of a jet, simultaneously with the vaporized hydrocarbon. The data shown in Table II illustrate the results obtained when operating according to this procedure.

Table II

Hydrocarbon	Amount of hydrocarbon, weight in grams	Amount of NO_2, weight in grams	Rate of flow of CO_2, liters/hr.	Partial pressure of reactants	Temperature, °C.	Space velocity, liters reactants per liter space per hour	Conversion, percent NO_2
Decane	158	40.9	5.5	0.891	330	472	23
Cetane	36	8.2	5.5	0.846	320	317	25

The vapor phase nitration of normally solid hydrocarbons may be illustrated by the nitration of paraffin wax in which case an apparatus similar to that employed in the nitration of the liquid hydrocarbons in the preceding example was used, with the exception that all of the hydrocarbon was placed in the vaporizer and a stream of carbon dioxide was passed through the molten wax, the rate of hydrocarbon feed being controlled by the rate of carbon dioxide flow. Nitrations were effected under the operating conditions shown in Table III.

Table III

Hydrocarbon	Amount of hydrocarbon, weight in grams	Amount of NO_2, weight in grams	Rate of flow of CO_2 through NO_2, liters/hr.	Rate of flow of CO_2 through hydrocarbon, liters/hr.	Partial pressure of reactants	Temperature, ° C.	Space velocity, liters reactants per liter space per hour
Paraffin wax	155	29.5	3.2	8.6	0.636	375-400	217
Do	50	41	1.2	32	0.300	300-335	150

Conversions were not calculated for these nitrations in view of the unknown molecular composition of the original hydrocarbon mixture and of the products, but in both cases satisfactory nitrations were secured as evidenced by complete utilization of the NO_2 and isolation of nitro compounds in the products.

It is to be understood, of course, that our invention is not to be construed as limited to the particular procedures set forth in the above examples. Numerous modifications of the process will naturally occur to those skilled in the art. For example, the process may be operated in a cyclic manner if desired. The exit gases from the condensation and scrubbing systems contain nitrogen oxides, carbon monoxide, carbon dioxide, water vapor, nitroparaffins and hydrocarbons, the amounts and proportions of which vary widely with the particular hydrocarbon being nitrated, the proportion of reactants used, and the character of the recovery system. In the case of low boiling hydrocarbons such as, for example, propane and isobutane, the greater portion of the unreacted hydrocarbon may remain in the exit gases after the condensation of the nitroparaffins. In such cases, additional hydrocarbon and nitrogen dioxide may be added to give a gas mixture of substantially the original composition, which may then be recirculated through the reaction system.

Likewise, if desired, the exit gases may be compressed sufficiently to permit the separation of unconverted hydrocarbon from the nitric oxide, carbon monoxide, etc., and the nitric oxide then reconverted to nitrogen dioxide. The entire nitration operation may even be carried out under sufficiently elevated pressures to cause liquefaction of the unconverted hydrocarbon in the receiver along with the nitroparaffins. It may also be conducted under reduced pressure, which is often desirable in the case of higher boiling hydrocarbons. Numerous other modifications of our process will naturally occur to those skilled in the art. It is to be understood that any such modifications or the use of any equivalents which would naturally occur to those skilled in the art are included within the scope of our invention.

It is to be understood, also, that with respect to the nitration of hydrocarbons having more than eight carbon atoms we do not limit ourselves to the use of substantially pure nitrogen dioxide as the nitrating agent, but may also use less pure materials such as nitrogen dioxide obtained by thermal decomposition of nitric acid, in which case the nitrogen dioxide need not be separated from any undecomposed nitric acid.

Now having described our invention, what we claim is:

1. A process for the production of nitrohydrocarbons which comprises chemically combining, by contacting wholly in the vapor phase, substantially pure nitrogen dioxide and a saturated hydrocarbon containing more than two carbon atoms, at a temperature of 300 to 600° C.

2. A process for the production of nitrohydrocarbons which comprises chemically combining, by contacting wholly in the vapor phase, substantially pure nitrogen dioxide and a saturated hydrocarbon containing more than two carbon atoms, at a temperature of approximately 475° C.

3. The continuous process of nitrating saturated hydrocarbons having in excess of two carbon atoms, which comprises passing a mixture of substantially pure nitrogen dioxide and a saturated hydrocarbon through a reaction vessel maintained at a temperature between 300° and 600° C., and regulating the space velocity of the reactants so that the characteristic brown color of nitrogen dioxide is practically invisible in the gaseous reaction products.

4. A continuous process for the production of nitrohydrocarbons which comprises chemically combining, by contacting wholly in the vapor phase, substantially pure nitrogen dioxide and a saturated hydrocarbon containing more than two carbon atoms, at a temperature of 300° to 600° C., and at a space velocity of 3,000 to 20,000.

5. A process of nitrating a saturated aliphatic hydrocarbon having more than 2 carbon atoms, which comprises producing contact between and chemically combining such saturated aliphatic hydrocarbon and substantially pure nitrogen dioxide, with both reagents wholly in the gas or vapor phase.

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