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METHOD OF SEPARATING OLEFINS FROM HYDROCARBON MIXTURES

George R. Bond, Jr., Paulsboro, N. J., assignor to Houdry Process Corporation, Wilmington, Del., a corporation of Delaware

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2 Claims. (Cl. 260—666)

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The present invention relates to the separation of olefins from mineral oils and other hydrocarbon liquids. An important application of the invention is in the preparation of petroleum fractions, such as products boiling in the range of gasoline or up to heavy naphtha, substantially free of olefinic unsaturates.

I have found that nitrogen tetroxide (N_2O_4) rapidly reacts completely and quantitatively with all commonly available olefinic compounds present in liquid hydrocarbon fractions to convert the same to nitroso addition compounds which are but slightly, if at all, volatile with steam. The unreacted material present in the liquid hydrocarbon fraction, which may contain paraffins, naphthenes and aromatics, can then be readily separated by simple steam distillation.

In accordance with the invention, nitrogen tetroxide vapor is run into the liquid hydrocarbon fraction at temperatures below that of thermal decomposition and in quantity at least sufficient to react with olefins present. The nitrogenous addition compounds of the olefins are then separated from the unreacted products, preferably by subjecting the entire mixture to steam distillation and recovering the distillate of unreacted products by condensation. The hydrocarbons in the condensed distillate are readily separable from the water layer by decantation; any nitroso compounds that may have been entrained or dissolved by the steam vapors are easily separated, for instance by an alkaline wash.

The extreme selectivity of the reaction between the nitrogen tetroxide and olefins has been successfully demonstrated by extensive preliminary experimentation particularly on known and synthetic mixtures containing various paraffins, naphthenes, olefins, diolefins, acetylenes, aromatics, etc. in compositions boiling up to 450° F. In all instances it was found that the olefins (including conjugated and non-conjugated diolefins and aromatics having an olefinic side-chain) reacted completely, while aromatics (free from side chain unsaturation), paraffins and naphthenes remained substantially unchanged.

Although it is preferred to carry out the described reaction with the hydrocarbon fraction in liquid phase, the reaction will also take place in vapor phase. The reaction is strongly exothermic and it is preferred to control the temperature of the reaction so as to maintain the same at 80° to 100° F., which may be readily accomplished by controlling the rate of introduction of the nitrogen tetroxide, or if desired, provision may be made for heat exchange.

The nitrogen tetroxide in vapor form may be obtained from any suitable source such as by vaporization of liquid nitrogen tetroxide at appropriate temperature. The vapor is introduced

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directly into the body of the hydrocarbon liquid and thorough contact of the reactants may be enhanced by agitation during treatment. The completion of the reaction is readily ascertained by the cessation of the exothermic phenomenon (significant temperature decline) and by the marked formation of brown fumes above the surface of the liquid being treated. When it is observed from these indications that the reaction has gone to completion, further addition of N_2O_4 should be stopped. Any excess of N_2O_4 in the reaction mix may be destroyed by the addition of water to convert the same to nitric and nitrous acids, or by other well known methods such as the addition of aqueous solutions of sulfamic acid, as is done in the azo dye industry, or by the addition of aqueous solution of urea to destroy nitrous acid.

In accordance with one embodiment of the invention, a crude naphtha fraction, produced for instance by high temperature cracking of a petroleum stock, may be selectively solvent extracted to obtain an extract containing aromatic materials including styrene; olefins, and diolefins. By treatment with N_2O_4, nitrosates of the unsaturated materials are formed which are then readily separated from the unreacted substantially pure saturated aromatics. These purified aromatics find important uses as solvents and intermediates in the chemical industries.

Alternatively, the separation may be carried out in two stages. Thus, the solvent extract of naphtha may be initially treated with nitrogen trioxide (N_2O_3), under conditions substantially similar to that employed with the nitrogen tetroxide, whereby nitrosites are formed of the aralkenes and conjugated diolefins present, leaving substantially unreacted the mono-olefin content of the naphtha. The aromatics may then be purified by the removal of these remaining olefins by treatment with N_2O_4 forming the nitrosates which can be separated by distillation.

In either the one-stage or two-stage treatment above described, the unreacted hydrocarbons are preferably separated from the nitrosites or nitrosates by steam distillation. If desired, separation may be effected by precipitation of the nitrosates or nitrosites on dilution of the treated naphtha with petroleum ether or the like, the precipitate being removed by filtration or decantation. Any desired narrow aromatic cut may be removed before or after formation of the nitroso compound. For instance by taking out a toluene cut, a pure enough toluene is obtained to meet the required standards for nitration grade toluene.

In the reaction of the N_2O_4 with an olefin-containing fraction, a wide range of temperatures is available; formation of nitroso compounds has been obtained at temperatures rang-

ing from below 32° F. (with liquid butene) to somewhat above 130° F. It is preferred, however, to carry out the reaction at about room temperature or slightly above as in the range of 80° to 100° F. At low temperatures the rate of reaction is slower and in some instances less stable reaction products may be formed, while at temperatures above 100° F. complicated side reactions may take place to form less easily separated products. The use of super-atmospheric pressure is unnecessary and it is preferred to carry out the reaction at atmospheric or sub-atmospheric pressures. Higher pressure may be used when it is not extended to the point of causing undesirable side reactions such as oxidation, nitration, and others which may occur. The reaction of the nitrogen oxides with the unsaturated hydrocarbons proceeds rapidly so that time limitations are imposed only by operating conditions to assure completeness of the reaction. For complete reaction the amount of nitrogen oxide, whether it be N_2O_3 or N_2O_4, should be at least one mol of the oxide for each bond of olefinic unsaturation. Excess nitrogen oxide should be destroyed, as described.

Steam distillation is preferably effected by running steam directly into the nitrogen tetroxide-treated mix, but if desired the mix may be diluted with at least an equal volume of water and then boiled, collecting the vapors in a cooled receiver to condense the same. Usually in the case of hydrocarbons boiling below 430° F., the reaction products are heavier than water. Thus when steam distillation is effected, the unreacted material being lighter than water collects above the surface of the water in the distillate and completion of the separation is indicated when distillate material heavier than water distills over and collects at the bottom of the water layer. However, in certain instances, as for example, in the case of tri-isobutylene nitrosate and some other reaction products which are lighter than water, it is desirable to stop the steam distillation when the ratio of oil to water in fresh portions of the distillate decreases to about 1 to 4. Such reaction products as are carried over during the steam distillation may be removed from the unreacted portion of the oil distillate by reaction with aqueous or alcoholic alkali metal hydroxide such as sodium or potassium hydroxide. Instead of or in addition to the hydroxide, removal of impurities may be effected with aqueous or alcoholic alkali metal sulfide such as sodium or potassium sulfide. Reaction of N_2O_4 with olefinic hydrocarbons in hydrocarbon mixtures boiling above 430° F. is readily effected with, however, increased tendency to side reactions such as nitration or oxidation and increasing difficulty of separation by steam distillation of the reacted from the unreacted portions as the boiling point of the material increases.

The oily reaction products of olefins and N_2O_4, composed chiefly of nitrosates, may be hydrolyzed to nitro-alcohols or rearranged to nitro-oximes during steam distillation. No serious decomposition of these compounds, however, has been observed at temperatures up to 212° F., with the possible exception in cases of certain terpenes, which if present in high concentrations, should be substantially diluted with any desired saturated hydrocarbons, before distillation.

Instead of separating the nitrosate formed from the unreacted hydrocarbons in a treated fraction, the nitrosate in the admixture may be further treated or converted to other chemical

compounds, provided that such compounds are easily separable from the unreacted hydrocarbons by conventional methods. For instance, if the reaction mass of nitrosates and unreacted hydrocarbons is treated with aqueous alkaline solutions, before subjecting the mass to steam distillation, the nitrosates are converted to carbonyl compounds, such as ketones or aldehydes, which can then be separated from the unreacted hydrocarbons by fractionation or selective extraction.

The formation of aromatic carbonyl compounds from certain olefins is more fully described and claimed in my copending application Serial No. 725,726 filed of even date herewith, and now Patent No. 2,542,985.

Example I

A sample of 115–200° F. boiling range coal-tar reformer naphtha from destructive distillation of coal was reacted with N_2O_4 (at 70–100° F.) until excess N_2O_4 fumes indicated completion of the reaction, then washed with water and steam distilled. The distillate was washed with about 5 volume per cent of 10% caustic solution, water washed caustic free, and redistilled substantially to dryness. The distillate, amounting to 85.2% by volume of the original sample, had a density of 0.8730, a bromine number of 0.2 (ASTM) and was absorbed practically completely by concentrated sulfuric acid, showing that the composition of the distillate was practically pure aromatic in nature.

A similar treat was made on a 115–200° F. fraction of a high temperature thermal reformer naphtha from petroleum. The distilled unreacted oil, amounting to about one-third of the original sample, had a density of 0.8685, a bromine number of 0.2 and was absorbed to the extent of about 94% by concentrated sulfuric acid, showing that practically all olefinic materials had been removed successfully and that most of the residue was aromatic in nature.

Example II

A sample of a synthetic mixture of paraffin-naphthene base (acid treated gasoline range material) containing about 10% styrene was treated with N_2O_3 until excess of nitrous fumes showed completion of reaction. The precipitate formed during the reaction was separated by filtration and the residual oil, 90% by volume of the original, was washed with about 5 volume per cent of 10% caustic solution, washed with sodium bisulfite (small amount) to remove traces of benzaldehyde, and again with a small amount of 10% caustic solution; then water washed to remove excess caustic, dried over calcium chloride, and distilled to 294° F. cut point. The distillate had the following properties, which show complete removal of styrene.

Refractive index (n_D^{20}) 1.4189

Specific gravity (d_4^{20}) 0.7523

Bromine number (ASTM) 0.0

Specific dispersion $\frac{(n_F - n_C)}{d}$ 99

In the above example and in several of the examples following, reference is made to "acid treated gasoline range material" or to "acid treated naphtha" or "paraffin-naphthene base stock." These designations have reference to various samples of gasolines and light naphthas (as the case may be) that were subjected to the type of acid treatment used in determining an-

alytically the amounts of aromatics and olefins by their absorption in the treating acid. The residue, comprised mainly of paraffins and naphthenes, was washed and neutralized, and after drying constituted a material which showed no reaction with the nitrogen oxides and was therefore satisfactory as a diluent or carrier for the olefinic materials being tested.

Example III

One part of a synthetic mixture containing 23.1% turpentine, 38.45% benzene and 38.45% acid treated naphtha was treated with N_2O_4 at 70–100° F. until the reaction was complete as evidenced by the presence of excess N_2O_4. The excess N_2O_4 was destroyed by the addition of 0.3 part 20% NaOH solution in 50% alcohol. The reaction products were dissolved by mixing this mixture with one part of 25% alcoholic K_2S and separated by centrifuging the mixture after dilution with aqueous alcohol. The residual unreacted oil was found to equal 77.0% by volume of the original, indicating complete removal of the turpentine since previous tests have shown no significant reaction occurring with either benzene or the acid treated naphtha.

Example IV

A crude benzene-toluene fraction from the destructive distillation of coal was treated with N_2O_4 until the persistant presence of unreacted N_2O_4 showed substantial completion of the treatment. The solution, now dark red in color and with a slight gummy precipitate was washed with water and then steam distilled. The distillate was washed with about 2 to 3 volume per cent of 10% caustic solution and then with water until it tested neutral to litmus, and then freed of water by drying over calcium chloride.

Other polymerizable impurities were then removed by treating the fraction with approximately 0.5% by volume of 96–98% H_2SO_4, washing with water, washing with 0.2% by weight of NaOH in 10% aqueous solution and then steam distilling the treated oil. The thus purified hydrocarbon distillate fraction, amounting to 91.2% was colorless, sweet smelling, and distilled completely between 176° F. and 235° F. A satisfactory H_2SO_4 wash test (did not turn black) indicated complete removal of olefinic materials.

Example V

A hydrocarbon fraction containing a major amount of isopropyl benzene and minor amounts of similar boiling range material was subjected to dehydrogention conditions and then treated at room temperature with N_2O_3 until the presence of unreacted N_2O_3 showed completion of reaction; the nitrosite precipitate thus formed was separated from the unreacted oil by decantation. The unreacted oil, amounting to 52.8% by volume of the original sample, was treated with N_2O_4 at room temperature until the reaction was complete. The remaining unreacted oil was then separated by steam distillation and purified by caustic wash of the distillate. The purified distillate amounted to 25.6% by volume of the original sample.

The described method of removal of olefins from mixtures containing the same is adapted to be employed as a direct volumetric measure of olefinic unsaturation in a hydrocarbon sample, as described by me in "Determination of Olefinic Unsaturation," Industrial and Engineering Chemistry, Analytical Edition, (1946) vol. 18, p. 692.

The method of the invention is also applicable to the treatment of higher boiling hydrocarbons, such as those boiling in a range up to about 600° F. In the use of the described method with higher boiling hydrocarbons in this range, as above 450° F., complications may be encountered if substantial amounts of di-cyclic compounds are present, due to the greater facility of nitration taking place.

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof and therefore only such limitations should be imposed as are indicated in the appended claims.

The present application is a continuation-in-part of my application Serial No. 528,948, filed March 31, 1944, now abandoned.

I claim as my invention:

1. The method of removing olefins from low boiling liquid hydrocarbon fractions containing the same, said fractions boiling in the range of up to about 600° F., which comprises contacting such a fraction with vapors of nitrogen tetroxide in quantity approximately sufficient to react with all olefins present in such fraction and at a temperature in the range of 70–100° F. until excess nitrogenous vapors appear, destroying any excess nitrogen tetroxide in the reaction mixture, thereafter steam distilling the reaction mixture, and washing the oil in the distillate with caustic solution to remove therefrom any nitrogenous products present.

2. The method of separating olefins from crude liquid hydrocarbon fractions containing the same, which comprises treating such fraction with nitrogen trioxide at approximately room temperature until no further reaction occurs, separating the formed precipitate, treating the residual liquid fraction with nitrogen tetroxide at approximately room temperature until no further reaction occurs, steam distilling the nitrogen tetroxide-treated fraction, and washing the oil in the distillate with alkali.

GEORGE R. BOND, JR.

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