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PROCESS FOR TREATING A HYDROCARBON MIXTURE WHICH IS CONTAMINATED BY SMALL AMOUNTS OF ORGANIC FLUORINE COMPOUNDS

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1

This invention relates to a process for treating a hydrocarbon or hydrocarbon mixture which is contaminated by small amounts of organic fluorine compounds to remove fluorine therefrom. More specifically, it relates to the treatment of hydrocarbons produced synthetically in the presence of an active fluoride catalyst to remove small amounts of organically combined fluorine present in compounds admixed with the hydrocarbon or hydrocarbon mixture.

The invention is particularly adapted to the treatment of hydrocarbons produced by the alkylation of isoparaffinic hydrocarbons with olefinic hydrocarbons or with alkyl fluorides using active fluoride catalysts including hydrogen fluoride or fluoride mixtures comprising essentially hydrogen fluoride and boron fluoride. The process is also applicable to the removal of alkyl fluorides from propane and butane fractions, said fractions being recovered from the gaseous products discharged from an alkylation plant in which isobutane is alkylated by olefins present in a propane-propylene or butane-butylene fraction.

An object of this invention is to defluorinate a hydrocarbon or hydrocarbon mixture contaminated by relatively small amounts of organic fluorine compounds, particularly alkyl fluorides.

Another object of this invention is to dehydrofluorinate an isoparaffin alkylation product formed in the presence of an active fluoride catalyst.

A further object of this invention is to remove alkyl fluorides from hydrocarbon conversion products formed in the presence of an active fluoride catalyst.

A still further object of this invention is to remove alkyl fluorides from a fraction of normally gaseous paraffinic hydrocarbons recovered from the products formed in the alkylation of isobutane by olefins present in a C^3–C^4 hydrocarbon fraction.

Another object of this invention is to remove ethyl fluoride from a propane fraction recovered from the products formed in the alkylation of isobutane in the presence of hydrogen fluoride with a propane-propylene fraction containing a relatively small amount of ethylene.

One specific embodiment of the present invention comprises a process for treating hydrocarbon material containing as an impurity a relatively small percentage of organically combined fluorine to remove fluorine therefrom which comprises contacting said material with fluosulfonic acid at dehydrofluorinating conditions of temperature

2

and pressure, and recovering the treated hydrocarbon material.

Another embodiment of the present invention comprises a process for treating hydrocarbons recovered from an alkylation process in which an isoparaffin is alkylated with an olefin in the presence of an active fluoride catalyst, by treating said hydrocarbons with fluosulfonic acid at dehydrofluorinating conditions of temperature, pressure and time, and recovering the treated hydrocarbons.

The alkylation of branched chain paraffinic hydrocarbons such as isobutane and isopentane with olefinic hydrocarbons, particularly the olefinic hydrocarbons present in cracked gases, produces saturated liquid hydrocarbons utilizable as constituents of gasoline of high antiknock value. By this means relatively low boiling isoparaffinic hydrocarbons are alkylated with low boiling olefins and thereby converted into materials of higher boiling point and high antiknock values. The higher boiling hydrocarbons so formed from low boiling isoparaffins and olefins in the presence of an active fluoride catalyst including hydrogen fluoride or mixtures of hydrogen fluoride and boron fluoride, frequently contain small amounts of organic fluorine compounds which are not readily removable by washing with caustic and water or by fractional distillation.

These contaminating fluorine compounds which are thus present in alkylation hydrocarbon mixtures are frequently due to the interaction of hydrogen fluoride with olefins to form alkyl fluorides. Some alkyl fluorides are more stable than others in the presence of active fluoride catalysts. Thus, ethyl fluoride is more stable than some of the higher molecular weight alkyl fluorides in an alkylation reaction mixture and is not converted completely into paraffinic alkylation products but admixes with the hydrocarbon products. Some higher boiling alkyl fluorides and other organic fluorine compounds may also remain in hydrocarbon alkylation products. Because of its high stability, boiling point, and the fact that it forms with propane an azeotrope boiling at −47° C., ethyl fluoride is found in the propane fraction recovered from an alkylation process utilizing a propane-propylene fraction as an olefinic charging stock. Such propane-propylene charging stocks frequently contain ethylene in small amounts and ethyl fluoride forms by the addition of hydrogen fluoride to this olefin of lowest molecular weight.

Boron fluoride assists hydrogen fluoride in catalyzing the alkylation of an isoparaffin by

ethylene and higher olefins, but in these cases the alkylation product also contains small quantities of organic fluorides as do those formed in the presence of hydrogen fluoride from an isoparaffin and an olefin of higher molecular weight than ethylene.

Although the fluorine content of the hydrocarbon product of gasoline boiling range resulting from an alkylation treatment is rarely very high, the presence of fluorine is undesirable both from the standpoint that the combustion products of such a fuel are corrosive, as well as the fact that the antiknock value of the gasoline, generally expressed by the term "octane number," is reduced considerably either when the gasoline is used as such, or when a small amount of an antidetonating agent such as lead tetraethyl is added thereto. Thus it may be shown that gasoline fractions containing 0.1% by weight of fluorine have inferior antiknock properties, particularly as concerns their response to lead tetraethyl, as compared to the otherwise same material which contains substantially no fluorine compounds. The present invention offers a method for reducing the fluorine content of the hydrocarbon alkylation product to an amount where this adverse effect is negligible.

Also, propane and normal butane which are not alkylated during the alkylation treatment of an isoparaffin with olefins present in a C_3 or a C_4 hydrocarbon fraction are recovered from alkylation products and marketed as bottled gas for use as domestic fuels and for various industrial uses. Such recovered propane and normal butane fractions are sometimes contaminated by ethyl fluoride and other organic fluorine compounds formed incidentally in the alkylation treatment and it is desirable that these propane and butane fractions be freed from fluorine compounds before being so utilized as fuel.

It is much more difficult to dehydrofluorinate ethyl fluoride than the other alkyl fluorides which may be encountered in products of the hydrogen fluoride alkylation process. It has been observed that alkylation plants which charge a propane-propylene feed stock to the alkylation reactor produce ethyl fluoride from the ethylene which sometimes contaminates the C_3 feed stock. This ethyl fluoride tends to go through the plant unchanged and finally appears in the propane fraction recovered from the effluent gases. The methods used heretofore for removing organic fluorine compounds from alkylate, such as passage through heated contactors containing bauxite or aluminum, do not cause sufficient dehydrofluorination of ethyl fluoride and consequently are ineffective for producing a propane fraction substantially free from fluorine. My process, however, does defluorinate not only the gasoline boiling range material but also propane and butane and makes it possible to produce substantially fluorine-free propane and butane fractions.

As indicated above, ethyl fluoride is more stable than the higher alkyl fluorides encountered in the products of the hydrogen fluoride alkylation process. Possibly one reason for this difference in stability of the alkyl fluorides is the fact that ethyl fluoride is a primary alkyl fluoride, while the alkyl fluorides produced from propylene and higher olefins are either secondary or tertiary alkyl fluorides. I have found that when propane which is contaminated by small amounts of ethyl fluoride is treated at about 25° C. with fluosulfonic acid, the fluorine content is reduced more than 99% to give a propane fraction containing only about 0.001%, or less, by weight of fluorine from a contaminated material containing 1.2% fluorine present as ethyl fluoride. These results are remarkable and unpredictable because I have also found that neither hydrogen fluoride alone nor sulfuric acid alone nor a mixture of hydrogen fluoride and sulfuric acid will defluorinate to anything near this extent, that is, hydrogen fluoride alone or sulfuric acid alone had about 20% of the defluorinating activity of fluosulfonic acid while a mixture of sulfuric acid and hydrogen fluoride was little more than 40% as effective as fluosulfonic acid.

After prolonged use, the fluosulfonic acid may be regenerated by distillation but when only small percentages of fluorine are present in the charging stock, the cheapness of the fluosulfonic acid may permit it to be discarded after it has become contaminated too much for further use.

One method of preparing fluosulfonic acid, used in the process of this invention, consists in treating fluorspar (CaF_2) with fuming sulfuric acid (50–60% SO_3). Fluosulfonic acid is a mobile liquid with a boiling point of 163° C. at 760 mm. pressure and has a faint pungent odor but substantially no harmful action on dry skin. It feels greasy to the touch and is without the intense blistering action of anhydrous hydrogen fluoride.

According to the process of the present invention, hydrocarbon material contaminated by organic fluorine compounds is freed from a substantial proportion of such organically combined fluorine by treatment with fluosulfonic acid at a temperature of from about −50° to about 150° C. and preferably at a temperature of from about 0° to about 50° C. The process is carried out at atmospheric pressure or at a superatmospheric pressure sufficient to maintain the fluorine-containing hydrocarbon or hydrocarbon mixture in substantially liquid phase.

The treatment of the hydrocarbon or hydrocarbon mixture with fluosulfonic acid is effected in either batch or continuous types of treatment. In batch type operation, one volume of the hydrocarbon or hydrocarbon mixture contaminated by organic fluorine compounds is agitated with from about 0.1 to about 2 volumes of fluosulfonic acid at a temperature of from about −50° to about 150° C. and at a pressure sufficient to maintain liquid phase operation and for a time generally of from about 0.1 to about 3 hours. The resultant reaction mixture is then separated into a fluosulfonic acid layer and a hydrocarbon layer and the latter is washed, dried, and distilled or otherwise treated to recover the desired hydrocarbon or hydrocarbons substantially free from fluorine-containing compounds, while the used fluosulfonic acid is returned to the reactor for further use in treating an additional quantity of the hydrocarbon charging stock.

Continuous treatment of a hydrocarbon containing organically combined fluorine is effected by passing said hydrocarbon and a proportioned amount of fluosulfonic acid through a baffled mixer or other suitable type of contacting equipment in which the hydrocarbon and fluosulfonic acid are contacted at the aforementioned conditions of temperature and pressure for a time sufficient to effect the removal of substantially all of the fluorine from the hydrocarbon material. From this treating equipment the mixture of hydrocarbon material and fluosulfonic acid is directed to a separator from which the hydrocarbon layer is removed and then washed, dried, and distilled or otherwise treated to recover the de-

sired hydrocarbons substantially free from fluorine-containing compounds. The used fluosulfonic acid is then withdrawn from the separator and a portion of it is recycled to further use in treating an additional quantity of the mentioned charging stock.

The following examples are given to show results obtained in the operation of the process, but they are not to be considered to unduly limit the broad scope of the invention.

Example I

Several runs were made in each of which 51 grams of a propane fraction containing small amounts of ethyl fluoride was contacted with 174 grams of fluosulfonic acid at 25° C. for 3 hours in a rotatable steel autoclave of 850 cc. capacity. After this treatment the rotation of the autoclave was stopped and the reaction mixture was permitted to stand at 25° C. for 14 hours.

The fluorine content of the propane fraction charged in each of these runs and the defluorination effect by the treatment with fluosulfonic acid are as follows:

Per cent by weight fluorine in propane (present as ethyl fluoride)	1.21	1.53	0.209
Weight per cent fluorine in propane product	0.0013	0.0053	0.0010
Per cent defluorination of propane charged	99.9	99.7	99.5

Example II

For comparative purposes, similar runs were made in a turbomixer of 1000 cc. capacity in which the propane fraction containing ethyl fluoride (1.21% of fluorine relative to propane) was treated with hydrogen fluoride in one run and with sulfuric acid in another run otherwise using the same conditions employed in Example I. The materials charged in these runs, the amount of fluorine present in the treated propane, and the percentage defluorination of propane effected are as follows:

Charge, grams:		
Propane	102	102
Hydrogen fluoride	106	
Sulfuric acid, 96%		183
Weight per cent fluorine in propane product	0.95	0.95
Per cent defluorination of propane charged	21	19

Example III

A run similar to those referred to in Example II was made in which 102 grams of propane containing ethyl fluoride (0.209% by weight fluorine) was contacted at 25° C. with 115 grams of hydrogen fluoride and 27 grams of sulfuric acid of 96% concentration. The propane recovered from this treatment had a fluorine content of 0.12% by weight corresponding to 43% defluorination of the propane charged.

The nature of the present invention and the type of results obtained in the process are evident from the preceding specification and examples, although neither section should be construed to unduly limit the broad scope of the invention.

I claim as my invention:

1. A process for treating a saturated hydrocarbon material containing as an impurity a relatively small percentage of organically combined fluorine to remove fluorine therefrom which comprises contacting said hydrocarbon material with fluosulfonic acid at defluorinating conditions of temperature and pressure, and recovering the treated hydrocarbon material.

2. A process for treating a paraffin hydrocarbon material containing as an impurity a relatively small percentage of an alkyl fluoride to remove fluorine therefrom which comprises contacting said hydrocarbon material with fluosulfonic acid at defluorinating conditions of temperature and pressure, and recovering the treated hydrocarbon material.

3. A process for treating a hydrocarbon material containing as an impurity a relatively small percentage of organically combined fluorine and produced by catalytic alkylation of an isoparaffinic hydrocarbon with an olefinic hydrocarbon in the presence of an active fluoride catalyst which comprises treating said hydrocarbon material with fluosulfonic acid at defluorinating conditions of temperature and pressure, and recovering the treated hydrocarbon material.

4. A process for treating a hydrocarbon material containing as an impurity a relatively small percentage of organically combined fluorine and produced by catalytic alkylation of an isoparaffinic hydrocarbon with an olefinic hydrocarbon of higher molecular weight than ethylene in the presence of a hydrogen fluoride catalyst which comprises treating said hydrocarbon material with fluosulfonic acid at defluorinating conditions of temperature and pressure, and recovering the treated hydrocarbon material.

5. A process for treating a paraffin hydrocarbon material containing as an impurity a relatively small percentage of organically combined fluorine to remove fluorine therefrom which comprises contacting said hydrocarbon material with fluosulfonic acid at a temperature of from about —50° to about 150° C., and recovering the treated hydrocarbon material.

6. A process for treating a paraffin hydrocarbon material containing as an impurity a relatively small percentage of organically combined fluorine to remove fluorine therefrom which comprises contacting said hydrocarbon material with fluosulfonic acid at a temperature of from about —50° to about 150° C. and at a pressure sufficient to maintain the hydrocarbon material in substantially liquid phase, and recovering the treated hydrocarbon material.

7. A process for treating a paraffin hydrocarbon material containing as an impurity a relatively small percentage of an alkyl fluoride to remove fluorine therefrom which comprises contacting said hydrocarbon material with fluosulfonic acid at a temperature of from about —50° to about 150° C., and recovering the treated hydrocarbon material.

8. A process for treating a paraffin hydrocarbon material containing as an impurity a relatively small percentage of an alkyl fluoride to remove fluorine therefrom which comprises contacting said hydrocarbon material with fluosulfonic acid at a temperature of from about —50° to about 150° C. and at a pressure sufficient to maintain the hydrocarbon material in substantially liquid phase, and recovering the treated hydrocarbon material.

9. A process for treating propane containing as an impurity a relatively small percentage of organically combined fluorine to remove fluorine therefrom which comprises contacting said propane with fluosulfonic acid at defluorinating conditions of temperature and pressure, and recovering the treated propane.

10. A process for treating butane containing as an impurity a relatively small percentage of organically combined fluorine to remove fluorine therefrom which comprises contacting said butane with fluosulfonic acid at defluorinating conditions of temperature and pressure, and recovering the treated butane.

11. A process for treating a normally liquid paraffinic hydrocarbon mixture containing as an impurity a relatively small percentage of organically combined fluorine to remove fluorine therefrom which comprises contacting said normally liquid paraffinic hydrocarbon mixture with fluosulfonic acid at defluorinating conditions of temperature and pressure, and recovering the treated normally liquid paraffinic hydrocarbon mixture.

12. A process for treating propane containing as an impurity a relatively small percentage of organically combined fluorine to remove fluorine therefrom which comprises contacting said propane with fluosulfonic acid at a temperature of from about −50° to about 150° C., and recovering the treated propane.

13. A process for treating butane containing as an impurity a relatively small percentage of organically combined fluorine to remove fluorine therefrom which comprises contacting said butane with fluosulfonic acid at a temperature of from about −50° to about 150° C., and recovering the treated butane.

14. A process for treating a normally liquid paraffinic hydrocarbon mixture containing as an impurity a relatively small percentage of organically combined fluorine to remove fluorine therefrom which comprises contacting said normally liquid paraffinic hydrocarbon mixture with fluosulfonic acid at a temperature of from about −50° to about 150° C., and recovering the treated normally liquid paraffinic hydrocarbon mixture.

15. The process of claim 9 further characterized in that said impurity comprises ethyl fluoride.

16. The process of claim 12 further characterized in that said impurity comprises ethyl fluoride.

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