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REMOVAL OF AROMATICS, SULPHUR, OR UNSATURATES FROM HYDROCARBONS

Robert E. Burk, Cleveland Heights, Ohio, assignor to The Standard Oil Company, Cleveland, Ohio, a corporation of Ohio

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Crude petroleum, and the various fractions that can be obtained therefrom by distillation, as well as hydrocarbon mixtures and fractions obtained synthetically and by various processing operations, are comprised of a mixture of a number of different types of compounds. Of these types of compounds the saturates comprise a large portion, particularly the paraffins, and to a lesser extent the naphthenes. Many other compounds are included, among them being aromatics, aliphatic unsaturates, and sulphur compounds.

For many purposes it is undesirable to have all or a plurality of these different types of compounds in admixture. For numerous uses it is essential that a fraction or product be free from one or more of several types of these compounds.

For example, it is important in a great many instances (except in the case of asphalt and tars) that pretroleum and hydrocarbon fractions and products be free from sulphur or at least have a stated minimum sulphur content. Gasoline should be relatively sulphur-free to make it compatible with lead. Motor fuel containing sulphur in the form of mercaptans is undesirable because these sulphur compounds have an unpleasant odor and catalyze gum formation. Sulphur is objectionable in fuel oil and kerosene because it burns to form sulphur dioxide which is obnoxious and harmful.

For many other purposes it is desirable that petroleum fractions and products be free from aromatics (as well as sulphur in many cases). Lubricating oils, for example, which have only a small amount of certain aromatics have much better viscosity characteristics with reference to temperature, i. e., a higher viscosity index. Kerosene free from aromatics has greater freedom from smoking when used as an illuminant.

Certain unsaturates are undesirable in many petroleum products; thus the presence of highly unsaturated compounds in lubricating oil results in polymerization of these unsaturates under the conditions of their use to form gums and other undesirable products; they are also acted upon by oxygen to form sludge. The presence of highly unsaturated compounds in gasoline is undesirable for the same reason.

The above considerations are directed generally to instances where it is desirable to remove unwanted compounds such as sulphur, certain aromatics and highly unsaturated material from saturates which comprise the wanted product. In some cases, however, the compound to be removed may be the wanted product. In the

case of aromatics, for example, it is some times desirable to recover the aromatics present in fractions of natural petroleum, or those formed by aromatizing, or other processing operations on petroleum hydrocarbons or distillates from other sources. The aromatics thus separated and recovered are useful in the production of toluene for nitration, in toluene substitute solvents and other solvents, and in the production of aromatic naphthas having good blending characteristics useful in the manufacture of aviation fuels. In some instances the aromatics may be the major constituent of a product, and it may be desirable to treat the product to separate minor amounts of other compounds therefrom.

It has been proposed previously to remove sulphur from petroleum products and the problem of sulphur removal is as old as the petroleum industry. The character of the crudes available indicates that it will continue to be a problem. Numerous proposals have been made, such as the "doctor" solution which converts the mercaptan sulphur compounds to disulphides. This has the disadvantage that the lead is precipitated as the sulphide and can be regenerated only through time-consuming and high temperature operations. Treatment with copper chloride solution similarly converts mercaptans to disulphides but is objectionable for the same reason as the lead treatment and for the additional reason that traces of copper remain in the hydrocarbon which catalyze gum formation. It has also been proposed to remove sulphur and mercaptans with caustic by conversion to disulphides, but this process like the others discussed above, requires the removal of the disulphides if all sulphur is to be eliminated and also requires large amounts of caustic unless the caustic is regenerated. Adsorption with bauxite and similar oxides is another proposal but this process, too, uses up the adsorbent unless it is regenerated through high temperature operations involving difficulties.

Dearomatizing has also been proposed by means of solvent extraction but the solvents available heretofore have also exerted some solvent action on paraffins and naphthenes, so that the aromatics could not be recovered in a relatively pure state from saturates.

In accordance with this invention, it has been discovered that sulphur, aromatics or highly unsaturated compounds such as di- and polyolefins, or any combination of them, can be removed from petroleum or hydrocarbons containing the same by means of a novel "solvent-catalyst." The compounds separated will depend on the con-

stituents of the hydrocarbon material treated. If the material comprises saturated hydrocarbons containing aromatics, or sulphur, or highly unsaturated compounds, then treatment in accordance with the invention will remove these aromatics, sulphur or unsaturates, respectively. If the material contains any two of them, such as aromatics and sulphur, both will be removed simultaneously, or if the material contains all of them, all three will be removed simultaneously.

By means of the invention, gasoline may be made relatively sulphur free and, therefore, compatible with lead to increase its octane rating. Fuel oils and kerosenes may have their aromatic or sulphur content lowered or removed to improve burning qualities. Lubricating oil may be improved as to its viscosity and anti-sludge forming characteristics. Crudes and reduced crudes may be improved to facilitate their further processing. Diesel fuels may be refined to remove aromatics and thus increase their cetane number as well as reduce their sulphur content. Aromatics may be removed from gas oils in order to improve them as cycle stock for cracking. Other fractions may be treated as will be apparent to one skilled in the art, in view of the disclosure being made herein.

The process is generally applied in the liquid phase, the material being treated and the novel solvent-catalyst being thoroughly mixed and then permitted to stratify or separated centrifugally. The aromatics, sulphur or unsaturates or any combination of them, go in the solvent-catalyst phase. Two layers are formed, the upper being the extracted or raffinate phase and the lower layer containing the solvent-catalyst and the separated compounds. The two layers can be readily separated.

The process has the advantage that the solvent-catalyst is relatively low boiling and can be separated by simple heating to a low temperature and reused. It is not deleteriously affected and can be recycled and reused indefinitely. This is to be distinguished from prior processes of removing sulphur, as discussed heretofore, for example, where the removing agent is used up, or can be regenerated only with high temperature and otherwise difficult operations.

The process also has the advantage that the solvent-catalyst used in accordance with the invention does not separate paraffins or naphthenes. This is of particular advantage when the process is used for dearomatization, and is to be distinguished from processes using solvents proposed heretofore for dearomatizing.

The process of the invention has the additional advantage that it permits the simultaneous removal of a plurality of different types of compounds. In many cases it is desirable to remove unsaturates, sulphur and aromatics, or any two of them if contained in the stock to be treated, and this can be accomplished in accordance with the invention, in a single operation.

In addition, the process has the advantage that the compounds removed with the solvent-catalyst may be recovered. This is important in the case of aromatics, particularly where aromatics and sulphur are not separated simultaneously and where the process is used for recovering, concentrating or purifying aromatics. While the process no doubt could be worked out similarly, with reference to sulphur and unsaturates, possibly in a somewhat changed form, the value of the latter two is not such as to warrant the application of the invention to their recovery.

The solvent-catalyst referred to comprises hydrogen fluoride in the liquid phase and boron trifluoride dissolved therein (generally with pressure) as the active and essential ingredients.

This material seems to form a complex or loose chemical combination with the materials to be removed, or at least some of them. In this respect the material is not a solvent in the sense that organic materials are referred to as selective solvents. The material also is a catalyst for some reactions involving hydrocarbons, although under the conditions of use, in accordance with this invention, there are probably few reactions in which it exerts a catalytic effect. Since the same material also may be used as a catalyst, it will be referred to herein as a "solvent-catalyst" for want of a better term.

The solvent-catalyst is used in the liquid phase. The amount, based on the hydrocarbon fraction or stock to be treated may vary depending on the amount and nature of the material to be removed. The amount is not critical except that enough must be used to permit stratification and separation as two layers. It is obvious that it is not economical to use more than will be necessary to accomplish the particular separation desired. In some instances amounts of the order of 10% are more efficient than larger amounts of the order of 100%. In general, and subject to the above definition, the amount will be about 5 to 300 volume per cent based on the stock to be treated.

The relative proportions of hydrogen fluoride and boron trifluoride may vary from a trace to 50 mol per cent of boron trifluoride based on the amount of hydrogen fluoride. The composition will vary somewhat with the material to be treated and the product to be removed. In the removal of sulphur from heavy stocks, hydrogen fluoride alone may be used, but it alone is not suitable for lighter fractions. The amount of boron trifluoride can be expressed conveniently in terms of its partial pressure. Since it is a gas (B. P. -150° F.) at the temperatures at which the process is carried out, it will be necessary to have it under pressure during the treatment. The larger the amount employed the higher will be the partial pressure exerted by the boron trifluoride. In general, partial pressures from 2 to 500 pounds per square inch may be used.

The temperature employed is generally from about -30° to 225° F. The higher temperatures are sometimes preferable when heavy stocks are to be treated in order to reduce the viscosity. At higher temperatures also there may be some cracking or other reactions occasioned by the catalytic character of the fluorides. The temperature to be used should be selected with this in mind. In general, temperatures from 32° to 150° F. are suitable.

Since hydrogen fluoride is relatively low boiling (B. P. 67° F.) it is necessary to use pressure if temperatures above this are used and a closed system is preferred at any event to prevent loss of the fluoride. In general, a higher pressure is not required than is necessary to maintain the desired amount of the two fluorides in the treating zone.

In carrying out the process the hydrocarbon material to be treated and the solvent-catalyst are mixed thoroughly by any suitable apparatus. The reaction occurs rather promptly and the time required may vary from a few minutes to several hours depending on the temperature and other interrelated factors. Generally half an hour is

sufficient, and with efficient equipment and conditions shorter times are satisfactory. Counter-current extraction is not necessary although it may be used.

After the reaction is complete or has proceeded to the desired extent, the solvent-catalyst phase is separated from the raffinate in a convenient manner, such as by settling, decantation, centrifuging, etc.

If the solvent-catalyst extract is under pressure, the pressure may be released and the fluorides will be liberated upon the application of heat. In general, it is not necessary or desirable to heat the extract beyond that necessary to release the fluorides, both for reasons of efficiency and in order not to modify the extracted materials or to vaporize them if they are low boiling.

Any fluorides that may remain in the raffinate can be removed generally by heating, since the fluorides are volatile at slightly elevated temperatures. Alternatively, the phases may be contacted with water.

The anhydrous fluorides recovered from the extract and any from the raffinate may be condensed for reuse. The process is adapted for a continuous type operation in which the fluorides are continuously recovered and continuously used to treat fresh incoming stock.

The following examples are given as illustrative of the application of the invention to de-aromatizing. In this process the aromatics are thought to form a complex or loose chemical combination with the fluorides which is readily decomposed or broken down at higher temperatures without substantial modification of the aromatics. This suggests that lower temperatures for the treatment may give more complete removal but there are, no doubt, other factors which influence the equilibrium.

As an illustrative example, a hydrocarbon fraction boiling within the range of 117-380° F. derived from Illinois crude, and containing 10% aromatics, was treated at 32° F. for one hour with 104 volume percent hydrogen fluoride based on the volume of the stock and with boron trifluoride to provide a partial pressure of 150 pounds per square inch. The mixture was permitted to stratify and the upper layer was found to contain 5% aromatics (Kattwinkel). A procedure identical therewith, except that a temperature of 14° F. was used, results in an upper layer containing 3% aromatics.

A naphtha from Illinois stock containing 13% aromatics was treated for one-half hour at a temperature of -2° F. with 50 volume percent hydrogen fluoride based on the volume of the naphtha charge. The amount of boron trifluoride used was 0.1225 part by weight of the naphtha charge. The mixture was permitted to stratify and the top layer drawn off. Analysis showed it to contain 4% aromatics (Kattwinkel).

In a further illustration of the invention, a kerosene from Illinois stock containing 17% aromatics was treated for 0.66 hour with 51 volume per cent of hydrogen fluoride based on the kerosene charge and with 0.1115 part by weight boron fluoride based on the weight of the kerosene charge. The raffinate comprises 86.25% by volume of the charge and was found to contain only 4% aromatics (Kattwinkel), and to have a bromine number of 0 indicating that any unsaturates originally present were also removed. The fluorides were removed from the extract layer and it was then distilled. The

portion distilling below 410° F. comprises 40% of this fraction. Analysis of the distillate showed it to contain over 95% aromatics (Kattwinkel). The bromine number of the distillate was 19.6 indicating that unsaturates had been removed from the kerosene by the process.

In the event that a hydrocarbon fraction is to be dearomatized before it is subjected to averaging or other catalytic reactions with hydrogen fluoride and boron trifluoride as the catalyst, it is possible to use the fluoride catalyst remaining from said catalytic reaction for treatment of further stock to be dearomatized.

As illustrative of the application of the invention to the removal of sulphur, a Mississippi gas oil stock was utilized as the material to be treated. This had a sulphur content of .206%, a bromine number of 4.2 (indicating a small amount of unsaturates), and an aromatic content of 20%. The gas oil was treated for one-half hour at 85 to 97° F. with the solvent-catalyst in an amount of 138% by weight based on the amount of gas oil. The solvent-catalyst used comprised 86.4% hydrogen fluoride and 13.6% boron trifluoride. This gave a boron trifluoride partial pressure of 52 pounds per square inch. The total pressure was 60 pounds per square inch. The raffinate was found to contain .063% sulphur indicating a removal of about 65% of the sulphur. The aromatic content was reduced to 6% and the bromine number to 0.16.

The same gas oil stock was treated with a smaller amount of the same solvent-catalyst and at a lower temperature, i. e., the amount used was 71% by weight of the stock and the temperature was 78 to 85° F. The total pressure was 30 pounds per square inch. The raffinate comprises 80.2% of the charge and contained .09% sulphur. The extract, after removal of the solvent-catalyst, contained 1.045% sulphur.

As further illustrative of the application of the invention to the removal of sulphur, a reduced Yazoo crude oil was treated in accordance with the invention. This reduced crude had an initial sulphur content of 0.85% and a viscosity gravity constant of 0.836. The reduced crude was treated for fifteen minutes at a temperature of 110° F. with 10 volume per cent hydrogen fluoride based on the amount of reduced crude, and 4.3 weight per cent boron trifluoride based on the reduced crude. At the end of this treatment the raffinate was found to comprise 77% of the reduced crude charge and to have a sulphur content of 0.17%. The viscosity gravity constant of the raffinate was found to be 0.816.

The invention is applicable to the treatment of lubricating oils to improve their viscosity index (through removal of aromatics) and to decrease their tendency to form carbon and sludge, as well as the removal of sulphur present in the oil. The mode of application of the invention to lubricating oils will be readily apparent.

The invention is also applicable to the treatment of crude oil. The removal of sulphur from crude will be reflected in all later processing operations. The sulphur removal may be accompanied by catalytic cracking, averaging, and other reactions which the solvent-catalyst catalyzes, but these are of minor significance unless appropriate conditions are selected to favor them.

It is recognized that Hofmann et al. have proposed the treatment of lubricating oil with a small amount of hydrogen fluoride. In their

process the fluorides apparently were used to catalyze the polymerization of unsaturates. The amount used also was apparently too small to permit stratification or extraction, as the fluorides in their process were distilled off without any attempt at separation of any constituents with the fluorides in the liquid phase. Following this the lubricating oil was distilled off to leave the impurities behind. The manner in which the invention distinguishes from the process is readily apparent.

This application is a continuation-in-part of application Serial No. 423,303, filed December 17, 1941.

The invention is subject to many modifications and variations as will be apparent from this description and I intend all of the same to be included within the invention as one within the scope of the following claims:

I claim:

1. A process of treating hydrocarbons to separate any compound of an unsaturated, aromatic or sulphurous nature that may be present therein, which comprises admixing said hydrocarbons containing at least one of said compounds with liquid hydrogen fluoride containing a minor proportion of boron trifluoride under a pressure to maintain the hydrogen fluoride liquid under conditions such that the primary action is the formation of a fluoride complex with any of said compounds, and separating the mixture into two layers, the heavier layer containing said fluoride complex.

2. A process of treating hydrocarbons to separate any compound of an unsaturated, aromatic or sulphurous nature that may be present therein, which comprises admixing said hydrocarbons containing at least one of said compounds with 5 to 300 volume percent liquid hydrogen fluoride and an amount of boron trifluoride to provide a partial pressure of 2 to 500 pounds per square inch at a temperature of -30° to 225° F., and under a pressure to maintain the hydrogen fluoride liquid, the conditions within the above recited ranges being selected such that the primary action is the formation of a fluoride complex with any of said compounds, whereupon the mixture may be separated into lighter and heavier layers with said fluoride complex in the heavier layer; and separating the layers.

3. A process of treating hydrocarbons to separate any compound of an unsaturated, aromatic or sulphurous nature that may be present therein, which comprises admixing said hydrocarbons containing at least one of said compounds with 5 to 150 volume percent liquid hydrogen fluoride and an amount of boron trifluoride to provide a partial pressure of 25 to 200 pounds per square inch, at a temperature of 32° to 110° F., and under a pressure to maintain the hydrogen fluoride liquid, the conditions within the above recited ranges being selected such that the primary action is the formation of a fluoride complex with any of said compounds, whereupon the mixture may be separated into lighter and heavier layers the latter containing said fluoride complex; removing the lighter layer; removing the heavier layer and heating it to release the fluorides contained therein.

4. A process for separating any compounds of an unsaturated, aromatic or sulphurous nature that may be contained in petroleum and petroleum fractions; which comprises subjecting the same to the action of liquid hydrogen fluoride

containing a minor proportion of boron trifluoride under conditions such that the primary action is the formation of a fluoride complex with any of said compounds; and separating the resulting mixture into two layers, the heavier comprising the fluorides and said fluoride complex.

5. A process for separating any compounds of an unsaturated, aromatic or sulphurous nature that may be contained in petroleum and petroleum fractions; which comprises subjecting the same to the action of 5 to 300 volume percent liquid hydrogen fluoride and an amount of boron trifluoride to provide a partial pressure of 2 to 500 pounds per square inch, at a temperature of -30° to 225° F., and at a pressure to maintain the hydrogen fluoride liquid, the conditions within the above recited ranges being selected such that the primary action is the formation of a fluoride complex with any of said compounds, separating the resulting mixture into two layers, the heavier comprising the fluorides and said fluoride complex; separating the two layers; and heating the heavier layer to recover the fluorides therefrom.

6. A process for separating any compounds of an unsaturated, aromatic or sulphurous nature that may be contained in petroleum and petroleum fractions; which comprises subjecting the same to the action of 5 to 150 volume percent liquid hydrogen fluoride and an amount of boron trifluoride to provide a partial pressure of 25 to 200 pounds per square inch, at a temperature of 32° to 110° F., and at a pressure to maintain the hydrogen fluoride liquid, the conditions within the above recited ranges being selected such that the primary action is the formation of a fluoride complex with any of said compounds, separating the resulting mixture into two layers, the heavier comprising the fluorides and said fluoride complex; and separating the two layers.

7. A process for separating any compounds of an unsaturated, aromatic or sulphurous nature that may be contained in crude oil; which comprises subjecting the crude to the action of liquid hydrogen fluoride and a minor proportion of boron trifluoride under conditions such that the primary action is the formation of a fluoride complex with any of said compounds; separating the resulting mixture into two layers, the heavier comprising the fluorides and said fluoride complex and separating the two layers.

8. A process for separating any compounds of an unsaturated, aromatic or sulphurous nature that may be contained in a petroleum distillate fraction; which comprises subjecting the same to the action of liquid hydrogen fluoride and a minor proportion of boron trifluoride under conditions such that the primary action is the formation of a fluoride complex with any of said compounds; separating the resulting mixture into two layers, the heavier comprising the fluorides and said fluoride complex; and separating the two layers.

9. A process of treating lubricating oil stock to separate therefrom compounds of an unsaturated, aromatic or sulphurous nature that may be contained therein; which comprises subjecting the same to the action of liquid hydrogen fluoride and a minor proportion of boron trifluoride under conditions such that the primary action is the formation of a fluoride complex with any of said compounds; separating the resulting mixture into two layers, the heavier comprising the fluorides and said fluoride complex; and separating the two layers.

10. A process of treating lubricating oil stock to separate therefrom compounds of an unsaturated, aromatic or sulphurous nature that may be contained therein; which comprises subjecting the same to the action of 5 to 200 volume percent liquid hydrogen fluoride and an amount of boron trifluoride to provide a partial pressure of 2 to 500 pounds per square inch, at a temperature of -30° to 225° F., and at a pressure to maintain the hydrogen fluoride liquid; the conditions within the above recited ranges being selected such that the primary action is the formation of a fluoride complex with any of said compounds, separating the resulting mixture into two layers, the heavier comprising the fluorides and said fluoride complex and the lower layer comprising the treated lubricated oil stock; separating the two layers; and recovering the fluorides from the heavier layer.

11. A process of desulphurizing hydrocarbons; which comprises subjecting a sulphur containing hydrocarbon to the action of liquid hydrogen fluoride and a minor proportion of boron trifluoride under conditions such that the primary action is the separation and transfer of the sulphur

compounds from the hydrocarbons to the fluorides; forming the resulting mixture into two layers, the heavier comprising the fluorides and sulphur compounds separated from the hydrocarbons; and separating the two layers.

12. A process of desulphurizing petroleum and petroleum fractions containing sulphurous compounds; which comprises mixing the same with 5 to 300 volume percent liquid hydrogen fluoride and an amount of boron trifluoride to provide a partial pressure of 2 to 500 pounds per square inch, at a temperature of -30° to 225° F., and at a pressure to maintain the hydrogen fluoride liquid, the conditions within the above recited ranges being selected such that the primary action is the transfer of sulphurous compounds from the petroleum and the petroleum fractions to the liquid fluoride; forming the resulting mixture into two layers, the heavier comprising the fluorides and sulphur compounds separated from the petroleum and petroleum fractions; separating the two layers; and recovering the fluorides from the heavier layer.

ROBERT E. BURK.