May 8, 1945.  M. P. MATUSZAK  

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2,375,675  

PROCE D OF TREATING HYDROCARBON MATERIALS  

Filed March 10, 1942  

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This invention relates to the treatment of hydrocarbon materials, and more particularly to hydrofluoric acid treatment of hydrocarbon materials containing gums, resins, sulfur compounds, or other undesirable constituents under such conditions as to remove substantially all of these constituents. It relates still more particularly to the refining of hydrocarbon materials with used or spent hydrofluoric acid-containing catalyst obtained from the alkylation of alkylatable hydrocarbons. This application is a continuation-in-part of my preceding application, Serial No. 395,280, filed May 26, 1941.

Therefore, hydrocarbon materials containing unsaturated hydrocarbons, sulfur compounds, gum-forming compounds, and/or other undesirable constituents have been generally treated with sulfuric acid to remove such undesirable constituents. For example, it has been a common practice to refine hydrocarbon oils by sulfuric acid treatment. In many cases, this treatment is only partly successful, apparently because of the oxidizing action of the acid, which may be especially pronounced when highly concentrated sulfuric acid is used. This oxidizing action is of such a nature that substances are produced in the main body of the hydrocarbon material which bring about an unstable condition in the material with respect to color and odor.

In accordance with this invention, hydrocarbon materials can be advantageously freed of substantially all unsaturated hydrocarbons, resins, sulfur compounds, color- and/or gum-forming compounds, and the like by treating these hydrocarbon materials with substantial amounts of hydrofluoric acid, which is free from the oxidizing action of sulfuric acid, and which has become spent and comparatively ineffective for further use as a catalyst in the alkylation of alkylatable hydrocarbons with olefin hydrocarbons.

One object of this invention is to remove undesirable constituents of the nature of sulfur compounds, color- and gum-forming compounds, and the like from hydrocarbon materials.

Another object is to provide an improved process for removing such constituents.

Another object of this invention is the gainful use of hydrofluoric acid which has become spent as an alkylation catalyst, before it is subjected to treatment restoring it for reuse as an alkylation catalyst.

Another object is to combine advantageously an acid treatment of hydrocarbon materials with an alkylation step using a hydrofluoric acid-containing catalyst.

Further objects and advantages of this invention will be apparent from the following description, the accompanying drawings, and the appended claims.

During the treatment in accordance with the present invention, the hydrocarbon material and the hydrofluoric acid are preferably in the liquid phase, although application of the invention is not to be limited to treating only in liquid phase; in some instances, as in the treatment of a four-carbon hydrocarbon fraction or similar low-boiling fraction, the hydrocarbon material may be at least partly in the vapor phase. Usually, however, the hydrocarbon material to be treated according to the invention will be one or more hydrocarbon oils ordinarily susceptible to refining by acid treatment, such as petroleum oils, distillates, lubricating oil, kerosine, naphtha, gasoline, or the like. Any well-known or preferred type of acid-treating equipment may be used.

The hydrofluoric acid may be that which has become spent for the alkylation of alkylatable hydrocarbons, preferably isoparaffins, with alkylating agents, preferably olefins, without any intermediate treatment. However, an intermediate treatment with an alkylatable hydrocarbon, preferably the same alkylatable hydrocarbon as that being alkylated in the alkylation step, is advantageous, as thereby the spent hydrofluoric acid loses part of its content of acid-soluble organic compounds, and the alkylatable hydrocarbon becomes saturated with hydrofluoric acid.

Such intermediate treatment is further described hereinafter.

The amount of spent hydrofluoric acid should be sufficient to form a distinct and appreciable liquid phase containing the major proportion of the acid under the conditions of the treatment; it is preferably several times this amount.

The exact amount that is necessary to effect a given extent of refining will vary with the nature of the hydrocarbon material being treated, especially with the content of constituents that are to be removed. Generally, it should not be less than that required to produce a substantially completely saturated hydrocarbon product. An amount of hydrofluoric acid equal to or perhaps several times the volume of the hydrocarbon material to be treated may be set as about the maximum that may need to be used. However, an amount between 10 and 50 per cent by volume of the hydrocarbon material usually will be found satisfactory.

Hydrocarbon materials consisting predominantly or entirely of acid-soluble compounds,
such as unsaturated hydrocarbons, are generally not satisfactorily treated by the present process; however, if for some reason it appears desirable to treat such materials with hydrofluoric acid to remove part or all of the acid-soluble compounds, this treatment is within the spirit of the invention. Furthermore, when acid-soluble compounds are the predominant constituents in a mixture containing also non-hydrocarbon constituents substantially inert to and insoluble in hydrofluoric acid under the prevailing conditions, the invention will find particular application for removing substantially all of the acid-soluble compounds therefrom.

The mutual solubility of liquid or liquefied hydrocarbons and of liquid hydrofluoric acid increases appreciably with increase in temperature, and this effect of temperature should be taken into consideration in establishing the treating conditions in any particular case. Usually, however, the treatment may be satisfactorily conducted at temperatures in the range from about 0°C to about 100°C, although in the most cases a range between about 0°C and about 150°C is preferable. The pressure should be sufficient to insure proper flow through the apparatus; when liquid-phase operation is desired, it should be sufficient to insure the liquid phase at the temperature of operation.

In the treatment of normally liquid hydrocarbon materials, such as motor fuels, kerosines, fuel oils, lubricating oils, and the like, a relatively low-boiling liquefied paraffin, such as propane or a butane, preferably normal butane, or a mixture of relatively low-boiling liquefied paraffins, can be added to the normally liquid hydrocarbon material before, during, or after contacting with the hydrofluoric acid. This low-boiling hydrocarbon material aids in subsequent removal of residual hydrogen fluoride dissolved in the hydrocarbon phase after physical separation of the hydrocarbon phase from the hydrofluoric acid phase. Thus in a preferred manner of operating, a normally liquid hydrocarbon material is treated with spent alkylating hydrofluoric acid; an acid phase is separated from a hydrocarbon phase containing the normally liquid hydrocarbons and dissolved hydrofluoric acid; and then a low-boiling liquefied paraffin or mixture of such paraffins is added to the hydrocarbon phase. Such addition is often preferable to having a low-boiling paraffin hydrocarbon present while an acid phase is also present, as during the acid treatment of the normally liquid hydrocarbons. Regardless of whether the low-boiling paraffin is present during the treatment or is subsequently added, the hydrocarbon phase is fractionally distilled to remove a low-boiling fraction in which the distilled low-boiling paraffin hydrocarbon carries with it the hydrofluoric acid that had been dissolved in the hydrocarbon phase. Such low-boiling hydrocarbon forms minimum-bolting azotropic mixtures with hydrofluoric acid. Under the proper conditions, the low-boiling fraction will be such an azotropic mixture; however, in actual plant operations, the control of conditions need not be so close that the low-boiling fraction is necessarily solely an azotropic mixture. Such treatment removes hydrofluoric acid from the normally liquid hydrocarbon phase without the loss of this material that would occur if the removal were carried by water-washing, alkali-washing, or the like and without the same increase in temperature that would be necessary for removal of the acid by simple fractional distillation. Increase in temperature is undesirable because it promotes a tendency of hydrofluoric acid to react with liquid hydrocarbons to form fluoroine-containing compounds. Nevertheless, if desired, simple fractional distillation of the dissolved hydrofluoric acid from the treated liquid hydrocarbon material, without prior addition of a relatively low-boiling paraffin, may be practiced.

The acid removed by either type of fractional distillation is suitable for re-use in the treatment of additional hydrocarbon material or in the alkylation of an alkylatable hydrocarbon.

One embodiment of the invention will now be described with reference to the accompanying drawing, which forms a part of this specification and which illustrates diagrammatically one specific arrangement of apparatus for carrying out the process, the description serving to exemplify some of the many aspects of the invention.

An alkylatable hydrocarbon, usually an iso-paraffin of four to five carbon atoms per molecule, such as isobutane, which is preferred, is admitted to alkylator 17, as through inlet 11; preferably, it is brought to the alkylator 17 by conduit 27, as will be indicated hereinafter. Simultaneously, an alkylating agent, such as one or more olefins having three to five carbon atoms per molecule, is admitted to alkylator 17 through one or more inlets, such as inlet 19. Hydrofluoric acid, which catalytically promotes the alkylation reaction, is admitted to alkylator 17, as through inlet 15 and/or through conduit 20, the acid is advantageously as concentrated as possible, being preferably anhydrous, although it is known to promote alkylation, even when it contains up to about 20 percent of water.

The conditions in the alkylator may be varied widely, but they are preferably so selected as to favor alkylation and to minimize side reactions such as reactions that consume the alkylating agent to produce relatively heavy unsaturated hydrocarbons or polymers and/or fluorne-containing compounds. To this end, the instantaneous concentration of alkylating agent in the reaction mixture should be low; the isobutane is always in great excess; accordingly, multipoint addition of the alkylating agent to the reaction zone is advantageous. The ratio of hydrofluoric acid to hydrocarbons should be high enough for easy maintenance of a liquid alkylating reagent, but at this high a temperature and at these high pressures, the alkylating reaction will be complete in a few minutes, and the alkylated product can be recovered by fractional distillation. The alkylating temperature is preferably maintained in the range of from about 0°C to about 100°C. A high pressure may be used, but the pressure need not exceed 2000 psi and is normally about 500 psi. Intimate contact of the reactants with the acid is desirable and may be effected by any suitable means, for example, by mechanical agitation, such as agitation of the mixing-tube type, which is preferred.

After a suitable reaction period, or time of
contact, the reaction mixture is passed from alkylation 17 through conduit 18 to separator 20, wherein it is separated, as by gravity, and/or centrifugation, into a hydrocarbon phase and a relatively dense acid phase. During the separation, elevated temperatures preferably should be avoided, since the mutual solubility of liquid hydrofluoric acid and hydrocarbons increases with increase in temperature; for example, in the range of 32 to 140°F, the solubility of hydrofluoric acid in isobutane increases practically linearly from 0.3 to 0.9 per cent by weight, and the solubility of isobutane in hydrofluoric acid increases from 1.8 to 4.0 per cent. For improved separation of the two phases, the temperature may be advantageously lowered somewhat below the temperature preferred for alkylator 17, preferably to a temperature in the range of from about 10 to about 50°F, more or less.

The hydrocarbon phase separated from the alkylation mixture in separator 20 is passed through conduit 21 into fractionating means 22. In this fractionating means, it is fractionally distilled into the desired alkylation products, by-products, and recycle fractions. For example, a low-bolling fraction comprising relatively inert gases such as propane, lighter hydrocarbons, and uncombined hydrogen fluoride may be withdrawn through outlet 24; if desired, this material may be treated, as in a cooler and separator (not shown in the drawing), to condense and recover the hydrogen fluoride which then may be recycled to any appropriate step in the process. A fraction consisting predominantly of isobutane may be recycled directly to alkylator 11, as through conduit 27, but preferably it is passed through line 28 to isobutane treater 41. A fraction comprising chiefly any normal alkanes may be withdrawn from the system, as through outlet 29. A fraction comprising highly branched normally liquid hydrocarbons, which were formed by the alkylation and which are suitable for use in aviation gasoline, may be withdrawn from the system through outlet 31. A relatively small low-bolling fraction comprising heavy by-products may be withdrawn through outlet 33.

The acid layer separated from the alkylation mixture in separator 20 may be recycled to alkylator 11, as through conduit 27. When it is spent to a desired degree, it may be passed through conduit 32, directly to contacting chamber 31. Preferably, however, it is first given a treatment with isobutane in isobutane treater 41, where it is brought through conduit 38. Isobutane is admitted through inlet 38; ordinarily and preferably, such isobutane constitutes the major isobutane feed to the process; it is usually augmented by isobutane passing from fractionating means 22 through line 28. The isobutane and the hydrofluoric acid in treater 41 are intimately contacted together, whereby the isobutane becomes saturated with the acid, some additional alkylation is formed and/or extracted by the isobutane and the used acid becomes partly purified or reactivated, so that it becomes somewhat improved for subsequently effecting the removal of undesirable constituents from hydrocarbon materials.

Passing of the used acid to treater 41 is preferably made as soon as possible, i.e. substantially immediately, after the isobutane is contacted with the hydrocarbon effluent from the alkylation step. Undue delay in effecting the contacting with isobutane appears to produce undesirable chemical changes in the acid-soluble organic material present in the acid, whereby this material becomes relatively resistant to reaction with the isobutane and produces heavy nonreactive carbonaceous compounds, some of which appear to be exceptionally high in fluorine content; consequently contacting within 5 minutes or less after the separation is preferred.

Treater 41 may comprise any suitable means for effecting intimate mixing and/or emulsification of the isobutane with the hydrofluoric acid; it may be a standard mixer having a mechanical stirrer, or it may be an arrangement of piping and/or jets wherein turbulence is maintained by high fluid velocity. Alternatively, it may be designed for effecting a counter-current contacting of the acid and isobutane, as, for example, in a tower in which the isobutane rises through the down-flowing acid; but such counter-current contacting is relatively less satisfactory because intimate contacting of the two liquid phases is not favored as much as it is by the fine subdivision and emulsification produced by a mechanical mixer of the concurrent type, which accordingly is preferred. The treater 41 is preferably operated at atmospheric temperature, though at times some heating or cooling may be advantageous and or or. The pressure should be sufficient to maintain the mixture in the liquid phase. The treating time is not highly critical; usually a time in the range of from 5 minutes to about 2 hours is suitable; the time required usually decreases with increase in temperature, and the optimum time for a selected set of conditions may be readily found by trial.

For best results, the treating time generally must be longer than the time of contact in the alkylation step, since the reactivation reaction is considerably slower than the alkylation reaction; for this reason, the treating time preferably may be at least twice as long as the time of contact in the alkylation step. However, in the present process, the best possible results usually are not necessary, so that a relatively short time—shorter than the time required, for example, if the isobutane-treated acid were to be recycled directly to the alkylation step—is generally satisfactory.

The resulting mixture is passed from treater 41 through conduit 44, wherein it is separated, as by gravity and/or centrifugation, into an isobutane phase and a relatively dense hydrofluoric acid phase. The isobutane phase is passed through conduits 48 and 27 to alkylator 17. The hydrofluoric acid phase is passed through conduits 49 and 33 to contacting chamber 31; if desired, part of it may be recycled to treater 41, for additional treatment with isobutane, as through conduit 48.

In contacting chamber 31, the used hydrofluoric acid passed there from either from treater 41 through line 38 or, after treatment with isobutane in treater 41, from separator 44 through line 46, is utilized for the refining of hydrocarbon material containing gums, resins, sulfur compounds, or similar undesired acid-soluble constituents. This hydrocarbon material enters treater 31 through inlet 32. Ordinarily it is a normally liquid or a liquefied hydrocarbon material, but on occasion a low-bolling hydrocarbon material in the vapor phase may be treated with the acid in the liquid phase. The hydrocarbon material and the acid are intimately contacted in a batch or continuous manner. If continuous, the contacting may be concurrent, but usually it is preferably countercurrent, so that fresh acid comes...
in contact with hydrocarbon material that has already lost most of its content of undesirable acid-soluble constituents, in a manner known to the art. Sufficient hydrofluoric acid is admitted to treater 51 so that under preferred conditions of operation a liquid phase containing a major proportion of hydrofluoric acid, and a minor proportion of hydrocarbon and another liquid phase containing a major proportion of hydrocarbons and a minor proportion of hydrofluoric acid are present. The time of contacting in treater 51 is not critical, provided that sufficiently intimate contacting is obtained to effect substantial extraction of acid-soluble compounds by the acid.

The resulting hydrofluoric acid extract, containing acid-soluble compounds removed from the hydrocarbon material charged through inlet 52, is passed from contacting chamber 51 through conduit 54 to separating means 66, wherein the hydrofluoric acid is processed to free it from the acid-soluble material contained in it. Ordinarily and preferably, separating means 66 consists of a fractionating column wherefrom purified hydrofluoric acid is distilled overhead. Although ordinarily this purified hydrofluoric acid is recycled to alkylator 17, as through conduit 55, under some conditions of operation it preferably is used to fortify the acid in contacting chamber 51 by being passed, at least in part, to this chamber through conduits 60 and 36; if desired, part or all of this purified acid may be withdrawn from the system through outlet 61. From the kettle of such a fractionating column 66 is withdrawn, as through outlet 65, a residue comprising chiefly the acid-soluble material removed from the hydrocarbon material treated in contacting chamber 51 and some heavy acid-soluble by-products produced in the alkylation step. By maintaining the kettle temperature sufficiently high, usually not above about 390°F., any fluoride-containing compounds are decomposed, liberating hydrofluoric acid, so that the residue contains little or no fluoride; the resulting residue may be burned as fuel.

The treated or extracted hydrocarbon material is passed through contacting chamber 51 by being passed through conduit 65 and is usually passed directly through lines 66 and 67 to fractionating means 68, wherein it is freed by distillation from a minor proportion of dissolved hydrofluoric acid. The resulting acid-free and acid-soluble hydrocarbon material is recovered as a product of the process through outlet 69. A low-boiling fraction comprising the dissolved hydrofluoric acid may be withdrawn through outlet 71, but it preferably is recycled to alkylator 17, as through conduit 73; if desired, part or all of this fraction may be withdrawn from the system through outlet 75. When the resulting low-boiling fraction comprises hydrofluoric acid preferably may be recycled to alkylator 17 as already described, if the added low-boiling hydrocarbon is isobutane; otherwise, it may be recycled to contacting chamber 51, as through conduits 73 and through conduits 38 and 50, or alternatively through conduit 83.

However, in some instances it may be desired to separate the acid and the hydrocarbon in this low-boiling fraction. In such case any desired part or all of this fraction is passed through conduit 84 into separating means 86. From separating means 86 a hydrofluoric acid fraction, separated in any desired manner, may be removed through conduit 87; this fraction may be recycled, through conduits 48 and 36 and/or through conduits 15 and 60, to contacting chamber 51 and/or alkylator 17, in proportions controlled by the valves in lines 81 and/or 80, respectively; if desired, any part of this fraction may be removed from the system through outlet 86. A suitable low-boiling paraffin fraction may be removed from separating means 86 and may be returned to the process through conduit 92, leading to inlet conduit 75. At times it may be found that the presence of a low-boiling paraffin in contacting chamber 51 will aid the separation of hydrofluoric acid and hydrocarbon phases in this contacting chamber 51, whereas a portion of the low-boiling paraffin in conduit 75 may be passed through conduit 54 to conduit 63 and contacting chamber 51.

In some instances the purification carried out in contacting chamber 51 will be at a temperature more or less elevated, and a preliminary separation of hydrofluoric acid dissolved in the hydrocarbon stream from this chamber may be advantageously effected by cooling this stream to atmospheric or subatmospheric temperature. Accordingly, any desired portion of this stream is passed from conduit 65 through conduit 96; is cooled in cooler 98 to a desired separation temperature, preferably between about 10°F. and about 50°F.; and is passed through conduit 99 to separator 100, in which separation occurs into two liquid phases. The relatively dense or hydrofluoric acid phase is passed from separator 100 through conduit 101 to conduit 54 for subsequent treatment in separating means 56 as already described; if desired, any part or all of this phase may be discharged from the system through outlet 103. The hydrocarbon phase is passed from separator 100 through conduit 105 back to conduit 65 for subsequent treatment in the system as hereinbefore described. Separator 100 will also be used when the contacting in chamber 51 is made in a concurrent manner instead of in the countercurrent manner specifically indicated, or when the contacting is made in a batch-wise manner.

Although the separation by fractional distillation in the presence of a low-boiling paraffin forms a distinct aspect or feature of the invention, the process should not be restricted to such separation in all cases; it is possible that other separation may be effected in means such as separating means 66; that is, the purified hydrocarbon material may be passed from conduit 65 through conduit 107 to separating means 68, and the purified hydrocarbon product is recovered through outlet 109.
Relative to the purification of a liquid hydrocarbon stock and to the separation of dissolved hydrofluoric acid from the purified material in fractionating means 68, an initial proportion of low-bolling paraffin such as normal butane may be added through inlet 75 at the start of the process, and thereafter this low-bolling paraffin may be recycled within the purification system as hereinbefore described. Further additions of low-bolling paraffin being made only to compensate for unavoidable losses. When the hydrocarbon material fed through inlet 52 contains such low-bolling paraffin, it may be unnecessary to add additional paraffin through inlet 78; after a steady state of operation has been reached with suitable recycle of the low-bolling paraffin, the purified hydrocarbon material recovered through outlet 58 will contain substantially the same proportion of this paraffin as that present in the material introduced through inlet 52.

Example

The following example illustrates some of the many aspects of the invention without necessarily limiting it. A motor fuel having an undesirable content of sulfur and gum-forming compounds is agitated with about a fifth of its own volume of a liquid hydrocarbon stock, containing approximately 5 mole% of the alkylation of isobutane with butylene. After thorough mixing, the mixture is allowed to separate. The hydrocarbon layer is separated from the acid layer; a relatively small proportion of isobutane is added to the hydrocarbon layer; and the resulting mixture is freed from the dissolved acid and the added isobutane by fractional distillation. The thus purified motor fuel has a practically negligible or undetectable content of sulfur and gum-forming compounds. The distilled acid-and-isobutane mixture is passed to the alkylation step. The acid layer is fractionally distilled to purify the hydrofluoric acid, which is also passed to the alkylation step.

Although, for the sake of simplicity and by way of example, the description herein has been devoted primarily to hydrofluoric acid used as an alkylation catalyst, it will be understood that other hydrofluoric acid-containing alkylation catalysts, such as mixtures of hydrofluoric acid with sulfuric acid, with boron fluoride, with metallic halides of the type of phosphorus pentfluoride, or with other promoters or modifiers, may be used in substantially the manner herein described, with only minor modifications that will be obvious from the nature of the additional component or components of the catalyst.

Numerous modifications of this invention will be obvious to those skilled in the art. The drawing is diagrammatic and does not show in detail many pieces of equipment, such as pumps, fractionating columns, and the like, that may be desirable or necessary for obtaining the results indicated. As such pieces of equipment are well-known in principle and use, they may be readily supplied by those skilled in the art. Suitable equipment and operating conditions for any particular application of the invention may be readily ascertained by one skilled in the art in the light of the foregoing description and discussion.

Because of the many modifications and variations of the invention that may be made without departing from the spirit and scope thereof, the invention should be limited only in accordance with the appended claims.

I claim:

1. A process of treating a hydrocarbon material containing normally liquid hydrocarbons and objectionable constituents of the nature of sulfur compounds and color- and gum-forming compounds, which comprises: mixing said hydrocarbon material with a used alkali metal containing a major portion of the used hydrofluoric acid catalyst, obtained from the alkylation of at least one low-bolling isoparaffin with at least one olefin containing three to five carbon atoms per molecule; passing the resulting hydrocarbon-containing mixture to a separating means; removing from said separating means a liquid phase containing normally liquid hydrocarbons substantially free from said objectionable constituents and containing dissolved hydrofluoric acid; admixing with said liquid phase a relatively low-bolling paraffinic material; passing the liquid phase and relatively low-bolling paraffinic material to a fractional distillation means; separating from said distillation means a low-bolling fraction containing at least a portion of the low-bolling paraffinic material and substantially all of the dissolved hydrofluoric acid; passing said fraction to a treating means from which hydrofluoric acid is removed; separating also from the alkylation step a higher-bolling fraction containing saturated normally liquid hydrocarbons substantially free from said objectionable constituents and from hydrofluoric acid; and removing said higher-boiling fraction from the process.

2. A process of treating a hydrocarbon material containing normally liquid hydrocarbons and objectionable constituents of the nature of sulfur compounds and color- and gum-forming compounds, which comprises contacting said hydrocarbon material with a used catalyst, obtained from the alkylation of at least one low-bolling isoparaffin with at least one olefin containing three to five carbon atoms per molecule in the presence of a concentrated hydrofluoric acid catalyst under alkylating conditions; passing the resulting hydrocarbon-containing mixture to a separating means; removing from said separating means a liquid phase containing normally liquid hydrocarbons substantially free from said objectionable constituents and containing dissolved hydrofluoric acid; admixing with said liquid phase a relatively low-bolling paraffinic material; passing the liquid phase and relatively low-bolling paraffinic material to a fractional distillation means; separating from said distillation means a low-bolling fraction containing at least a portion of the low-bolling paraffinic material and substantially all of the dissolved hydrofluoric acid; passing said fraction to a treating means from which hydrofluoric acid is removed; separating also from the alkylation step a higher-bolling fraction containing saturated normally liquid hydrocarbons substantially free from said objectionable constituents and from hydrofluoric acid; and removing said higher-boiling fraction from the process.

3. A process of treating a hydrocarbon material containing normally liquid hydrocarbons and objectionable constituents of the nature of sulfur compounds and color- and gum-forming compounds, which comprises contacting said hydrocarbon material with a used catalyst, obtained from the alkylation of at least one low-bolling isoparaffin with at least one olefin containing three to five carbon atoms per molecule in the presence of a concentrated hydrofluoric acid catalyst under alkylating conditions; passing the resulting hydrocarbon-containing mixture to a separating means; removing from said separating means a liquid phase containing normally liquid hydrocarbons substantially free from said objectionable constituents and containing dissolved hydrofluoric acid; admixing with said liquid phase a relatively low-bolling paraffinic material; passing the liquid phase and relatively low-bolling paraffinic material to a fractional distillation means; separating from said distillation means a low-bolling fraction containing at least a portion of the low-bolling paraffinic material and substantially all of the dissolved hydrofluoric acid; passing said fraction to a treating means from which hydrofluoric acid is removed; separating also from the alkylation step a higher-bolling fraction containing saturated normally liquid hydrocarbons substantially free from said objectionable constituents and from hydrofluoric acid; and removing said higher-boiling fraction from the process.

4. A process of treating a hydrocarbon material containing normally liquid hydrocarbons and objectionable constituents of the nature of sulfur compounds and color- and gum-forming compounds, which comprises contacting said hydrocarbon material with a used catalyst, obtained from the alkylation of at least one low-bolling isoparaffin with at least one olefin containing three to five carbon atoms per molecule in the presence of a concentrated hydrofluoric acid catalyst under alkylating conditions; passing the resulting hydrocarbon-containing mixture to a separating means; removing from said separating means a liquid phase containing normally liquid hydrocarbons substantially free from said objectionable constituents and containing dissolved hydrofluoric acid; admixing with said liquid phase a relatively low-bolling paraffinic material; passing the liquid phase and relatively low-bolling paraffinic material to a fractional distillation means; separating from said distillation means a low-bolling fraction containing at least a portion of the low-bolling paraffinic material and substantially all of the dissolved hydrofluoric acid; passing said fraction to a treating means from which hydrofluoric acid is removed; separating also from the alkylation step a higher-bolling fraction containing saturated normally liquid hydrocarbons substantially free from said objectionable constituents and from hydrofluoric acid; and removing said higher-boiling fraction from the process.

The invention also includes, in addition to the process described, a claim: A process of treating a hydrocarbon material containing normally liquid hydrocarbons and objectionable constituents of the nature of sulfur compounds and color- and gum-forming compounds, which comprises: mixing said hydrocarbon material with a used alkali metal containing a major portion of the used hydrofluoric acid catalyst, obtained from the alkylation of at least one low-bolling isoparaffin with at least one olefin containing three to five carbon atoms per molecule; passing the resulting hydrocarbon-containing mixture to a separating means; removing from said separating means a liquid phase containing normally liquid hydrocarbons substantially free from said objectionable constituents and containing dissolved hydrofluoric acid; admixing with said liquid phase a relatively low-bolling paraffinic material; passing the liquid phase and relatively low-bolling paraffinic material to a fractional distillation means; separating from said distillation means a low-bolling fraction containing at least a portion of the low-bolling paraffinic material and substantially all of the dissolved hydrofluoric acid; passing said fraction to a treating means from which hydrofluoric acid is removed; separating also from the alkylation step a higher-bolling fraction containing saturated normally liquid hydrocarbons substantially free from said objectionable constituents and from hydrofluoric acid; and removing said higher-boiling fraction from the process.

Additionally, the invention includes a claim: A process of treating a hydrocarbon material containing normally liquid hydrocarbons and objectionable constituents of the nature of sulfur compounds and color- and gum-forming compounds, which comprises: mixing said hydrocarbon material with a used alkali metal containing a major portion of the used hydrofluoric acid catalyst, obtained from the alkylation of at least one low-bolling isoparaffin with at least one olefin containing three to five carbon atoms per molecule; passing the resulting hydrocarbon-containing mixture to a separating means; removing from said separating means a liquid phase containing normally liquid hydrocarbons substantially free from said objectionable constituents and containing dissolved hydrofluoric acid; admixing with said liquid phase a relatively low-bolling paraffinic material; passing the liquid phase and relatively low-bolling paraffinic material to a fractional distillation means; separating from said distillation means a low-bolling fraction containing at least a portion of the low-bolling paraffinic material and substantially all of the dissolved hydrofluoric acid; passing said fraction to a treating means from which hydrofluoric acid is removed; separating also from the alkylation step a higher-bolling fraction containing saturated normally liquid hydrocarbons substantially free from said objectionable constituents and from hydrofluoric acid; and removing said higher-boiling fraction from the process.
3. A process of treating a hydrocarbon material containing normally liquid hydrocarbons and objectionable constituents of the nature of sulfur compounds and color- and gum-forming compounds, which comprises admixing such hydrocarbon material with a spent acid catalyst obtained from the alkylation of at least one low-bollling isoparaffin with at least one olefin containing three to five carbon atoms per molecule in the presence of a concentrated hydrofluoric acid catalyst under alkylation conditions and said catalyst being spent with respect to said alkylation reaction, in a contacting chamber, passing a resulting hydrocarbon-containing mixture to a separating means, removing therefrom a liquid phase containing normally liquid substantially saturated hydrocarbons substantially free from said objectionable constituents and containing dissolved hydrofluoric acid, admixing with the liquid phase a relatively low-bollling paraffinic material, passing the liquid phase and relatively low-bollling paraffinic material to a fractional distillation means, separating from said distillation means a low-bollling fraction containing at least a portion of the low-bollling paraffinic material, and substantially all of the dissolved hydrofluoric acid, passing said fraction to a treating means from which hydrofluoric acid is removed, circulating said hydrofluoric acid to the contacting chamber, separating also from the fractional distillation means a higher bollling fraction containing saturated normally liquid hydrocarbons substantially free from said objectionable constituents and hydrofluoric acid, and removing said higher bollling fraction from the process.

4. A process of treating a hydrocarbon material containing at least some objectionable constituents of the nature of color- and gum-forming compounds, which comprises contacting the hydrocarbon material with a spent catalyst obtained from the alkylation of at least one low-bollling isoparaffin with at least one olefin containing three to five carbon atoms in the presence of a concentrated hydrofluoric acid catalyst, in a contacting chamber and in sufficient amount to form a liquid phase containing a major portion of the spent catalyst and a liquid phase containing a mixture of the hydrocarbon material and the remaining spent catalyst, passing said mixture of hydrocarbon material and remaining spent catalyst to a first separating means, removing therefrom a liquid phase containing hydrofluoric acid and passing said phase along with the liquid phase containing a major portion of the spent catalyst to a second separating means wherein hydrofluoric acid suitable for reuse in the treatment of additional hydrocarbon material is separated and returned to the contacting chamber; removing also from the first separating means a second phase containing substantially saturated hydrocarbons and dissolved hydrofluoric acid, admixing with this second phase a relatively low-bollling paraffinic material in an amount at least sufficient to form an azeotropic mixture with said dissolved hydrofluoric acid, passing this second phase with admixed low-bollling paraffinic material to a fractional distillation means, separating therefrom a low-bollling fraction containing at least a portion of the low-bollling paraffinic material and substantially all of the dissolved hydrofluoric acid, passing said fraction to a treating means from which hydrofluoric acid is removed and circulating said hydrofluoric acid to the contact chamber, and separating from the treating means and from the fractional distillation means higher bollling fractions containing saturated normally liquid hydrocarbons substantially free from said objectionable constituents and substantially free of hydrofluoric acid, and removing said saturated hydrocarbons from the process.

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