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HYDROFLUORIC ACID ALKYLATION OF
PARAFFINS

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This invention relates to a process for the alkylation of hydrocarbons, and more particularly to alkylation of hydrocarbons in the presence of hydrofluoric acid. This application is a continuation-in-part of my copending application, Serial No. 327,497, filed April 2, 1940.

In the presence of suitable catalysts, saturated-type hydrocarbons, such as paraffins, aromatics, and naphthenes react with unsaturated hydrocarbons or other alkylating agents to form higher boiling alkyl derivatives. Thus, propylene can be used as an alkylating agent with isobutane to give isoheptanes, with benzene to give propylbenzene, and the cyclohexane to give propylcyclohexane. The alkylation is promoted especially well by hydrofluoric acid. This catalyst yields best results with aromatics and isoparaffins, or paraffins having at least one tertiary carbon atom per molecule, and with olefins having more than two carbon atoms per molecule; however, under especially favorable conditions, other paraffins and/or olefins may react. Suitable alkylating agents other than olefins include alkyl compounds, advantageously relatively polar nonprimary alkyl compounds, such as tertiary and secondary alcohols, alkyl halides, preferably fluorides and chlorides, and the like. The hydrofluoric acid preferably should be above about 80 per cent in strength; it is most advantageous when it is substantially anhydrous, or about 100 per cent in strength.

Because of its nonoxidizing character, hydrofluoric acid does not produce oxidation by-products such as those formed in alkylation with catalysts of the type of sulfuric acid. Furthermore, it is relatively free of the tendency to form complex tarry addition products such as those formed in alkylation with certain other well-known catalysts, particularly halides of some polyvalent metals. However, when the reaction vessel is of iron, it tends to form tarry residues that are absent when copper vessels are used, apparently because of the formation of iron fluoride (Simons, Ind. Eng. Chem., vol 32, page 178 (1940)); nickel-containing reaction vessels have been believed to form tarry residues similarly. Moreover, under some reaction conditions, hydrofluoric acid is so highly corrosive that ordinary and stainless steels and soft metals like copper are inadequately resistant to it, necessitating an undesirably frequent replacement of processing equipment and subjecting workmen to the hazard of serious burns from escaping acid.

In accordance with this invention, hydrofluoric acid alkylation of saturated-type hydrocar-

bons is effected in equipment made of a high-nickel alloy, which is exceptionally resistant to corrosion by hydrofluoric acid and which is rather unexpectedly free from the tendency to promote tar-formation.

An object of this invention is to alkylate saturated-type hydrocarbons.

Another object of this invention is to alkylate paraffins in the presence of hydrofluoric acid under conditions under which ordinary steels are disadvantageous because of relatively high rates of corrosion and of tar-formation.

Other objects and advantages of the invention will be evident to those skilled in the art, from the accompanying disclosure and discussion.

In an extensive experience with processes involving alkylation of hydrocarbons in the presence of hydrofluoric acid, various materials were investigated to determine their fitness for equipment that comes in contact with hydrofluoric acid, especially under alkylation conditions that may tend to promote corrosion and/or tar-formation, such as an elevated temperature, the presence of considerable moisture, or the like.

Among the materials investigated were ordinary and stainless steels and alloys, including many chromium-iron alloys of various contents of chromium and of other metals, such as copper, nickel, molybdenum, vanadium, and manganese. This experience indicated, somewhat unexpectedly in view of published statements, that iron-nickel alloys having a high content of nickel are exceptionally resistant to corrosion by hydrofluoric acid under alkylation conditions and are also relatively free from promoting tar-formations.

A preferred alloy is one containing 50 to 80 per cent nickel, the balance being chiefly or entirely iron. Various other metals, such as copper and chromium, may replace part of the iron, but they do not appear to make any outstanding contribution; minor proportions of still other metals, such as vanadium, molybdenum, cadmium, and manganese, may be present as components conferring special working qualities or as incidental components. The content of nickel preferably exceeds that of any other single component.

The practice of this invention is advantageous in the hydrofluoric acid alkylation of saturated-type hydrocarbons under all alkylation conditions; but it is especially valuable under conditions known to promote corrosion and/or tar-formation. Sometimes a corrosion-promoting condition, such as an elevated temperature (i. e., above room temperature) or the presence of considerable water, is unavoidable or is necessary to

cause the alkylation to proceed at a reasonably rapid rate. For example, alkylation of paraffins with alcohols inevitably causes considerable water to be present in the reaction mixture. Similarly, alkylation of relatively refractory paraffins, or alkylation with relatively refractory alkylating agents, requires an elevated temperature to expedite the reaction; alkylation with secondary alkyl compounds requires a temperature appreciably higher than that which is suitable for alkylation with tertiary alkyl compounds.

No specifications as to dimension, shape, or specific function of the alkylation equipment need be given, as these may vary widely, as is well known in the art of alkylating hydrocarbons. For example, the essential intimate mixing of the alkylation reactants and the hydrofluoric acid may be obtained in various ways, such as mechanical stirring, turbo-mixing, turbulence created by jets or orifices, and the like. Preferably the process is carried out in a system in which the concentration of the alkylating agent is low, with additional alkylating agent being added during the reaction, and with a suitable arrangement for taking up the heat of reaction. What is an essential feature of the present invention is to conduct the alkylation reaction in a reaction zone whose bounding surfaces are of a high-nickel alloy. It is sufficient in many instances for the equipment to be constructed of iron, steel, or other common material, provided that it is lined with a high-nickel alloy at the surfaces bounding the reaction zone. The reaction zone includes not only the zone in which the primary alkylation reaction occurs but also any zone in which secondary treatments may be carried out, such as a settling or separating zone in which the reaction mixture is separated into an alkylate-containing liquid phase and a predominantly hydrofluoric acid liquid phase.

The following example is illustrative of the invention without being restrictive.

Example

A liquid having the approximate composition of 52 per cent by weight isobutane, 5 per cent olefins (mostly butylenes and a little propylene), and 43 per cent inert hydrocarbons (mostly normal butane and some propane) is contacted with about a sixth of its own weight of liquid concentrated hydrofluoric acid at about 130° F. for an average contact period of 5 minutes in a turbo-mixer type of reactor made of an alloy containing 65 per cent nickel, the balance of the alloy being chiefly iron. The resulting reaction mixture is allowed to separate into a hydrocarbon phase and a hydrofluoric acid phase in a separator made of the same high-nickel alloy. The

alkylate isolated from the hydrocarbon phase amounts to about 190 per cent by weight of the original olefins; 89.5 per cent by volume of it distills in the octane range or below. The fraction boiling above 410° F., which may be taken as a rough index of the tendency to form tarry residues, amounts to less than 0.6 per cent by volume, whereas in an alkylate prepared in the same way except in a reactor and a separator made of ordinary steel it is generally more than 2.0 per cent.

In comparative tests of corrosion by hydrofluoric acid, the alloys containing nickel as the major constituent lose only about a sixth as much weight per unit surface per unit time as do ordinary and stainless steels.

Because the invention may be practiced otherwise than as specifically described or illustrated, and because many modifications and variations within the spirit and scope of it will be obvious to those skilled in the art of alkylating hydrocarbons, the invention should not be necessarily restricted by the foregoing illustrative example.

What is claimed is:

1. The process which comprises alkylating an alkylatable paraffin with an alkylating agent in the presence of liquid hydrofluoric acid in a reaction zone of which the confining surface is an alloy containing 50 to 80 per cent by weight of nickel, the balance of the alloy being chiefly iron.

2. In a process of alkylating an alkylatable, saturated-type hydrocarbon in the presence of hydrofluoric acid under corrosion-promoting conditions, the step which comprises effecting the alkylation in equipment constructed from an alloy comprising essentially only nickel and iron and containing 50 to 80 per cent by weight of nickel.

3. In a process of alkylating paraffins in the presence of hydrofluoric acid and of water, the step which comprises effecting the alkylation in equipment constructed of an alloy comprising essentially only nickel and iron and containing 50 to 80 per cent by weight of nickel.

4. In a process of alkylating an alkylatable paraffin with a non-primary alcohol in the presence of hydrofluoric acid, the step which comprises effecting the alkylation in a reaction zone of which the confining surface is an alloy containing 50 to 80 per cent nickel, the balance of the alloy being chiefly iron.

5. The process which comprises alkylating an alkylatable hydrocarbon with an alkylating agent in the presence of liquid hydrofluoric acid in a reaction zone of which the confining surface is an alloy containing at least 50 per cent nickel, the balance of the alloy being chiefly iron.

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