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TREATMENT OF HYDROCARBONS

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This invention relates more particularly to the manufacture of hydrocarbons of suitable boiling point for use as components of motor fuel.

5 In a more specific sense the invention has reference to a process which both conserves materials which are ordinarily considered as waste products in cracking processes and at the same time produces hydrocarbons having specially high anti-detonating characteristics.

10 Owing to the adoption of high compression ratios in automobile engines to increase their thermodynamic efficiency, a demand has been made upon the petroleum refining and other industries which furnish hydrocarbon motor fuels, for fuels of a high anti-knocking and slow-burning character. The cracking process which generally produces both unsaturated hydrocarbons and cyclic hydrocarbons due to the primary dehydrogenating and secondary condensing character of the decomposition reactions is employed quite generally to meet the demand for a high anti-knock motor fuel. However, complete control of the proportion of cyclic hydrocarbons to olefins is not always possible as the character of the charging oil varies with the type of crude from which it is produced, and when intensive cracking conditions are employed in an effort to increase the amount of cyclic hydrocarbons and hence the anti-knock value, undesirably large losses in gas and coke may be encountered and frequently the amount of olefins, particularly those of a highly unsaturated and unstable character, may increase roughly in proportion to the increase in aromatics and other cyclic hydrocarbons.

35 The fixed gases produced in cracking processes contain notable amounts of the normal olefins, including ethylene, propylene, and butylenes and other gases of a more highly unsaturated and still more reactive character such as iso-olefins, acetylene, butadienes, et cetera. Extensive experimenting has been conducted to find ways of utilizing the reactive constituents of gases from cracking plants and convert them into more valuable products.

40 The present process enables the effective utilization of the olefinic constituents of cracked gases and similar olefins produced in any manner.

50 In one specific embodiment the present invention comprises treatment of aromatic or similarly reactive cyclic hydrocarbons with olefinic or unsaturated gases in the presence of catalytic agents comprising acids of phosphorus and car-

rying or spacing materials of a porous and adsorptive character, at an elevated temperature above 100° C.

The essential ingredient of the solid catalysts which are employed to alkylate aromatics with 5 olefins according to the present invention is phosphoric acid, which may constitute 80% or more of the catalyst mixture, and in most cases is over 30% by weight thereof. Of the various acids of phosphorus, the orthophosphoric acid 10 (H_3PO_4) is generally preferred on account of its polymerizing ability, its cheapness and the readiness with which it may be procured although the invention is not restricted to its use but may employ any of the other acids of phosphorus insofar as they are adaptable. It is not intended to infer, however, that the different acids of phosphorus which may be employed will produce identical effects upon any given alkylation reaction, as each acid will exert its own 20 characteristic action.

In using orthophosphoric acid as one of the primary components of a catalyst mixture, different concentrations may be employed from approximately 85 to 100% or acid containing 25 some free phosphorus pentoxide may even be used. Within these concentration ranges, the acids will be thick liquids of varying viscosity and readily incorporated with the absorbent materials. In practice it has been found that pyrophosphoric acid corresponding to the formula 30 $H_4P_2O_7$ is readily incorporated with siliceous and relatively inert carriers at temperatures somewhat above its melting point (61° C.) and that the period of heating which is given to the acid-absorbent mixtures may be changed from that employed with the ortho acid. This point will be developed more in detail in a later paragraph.

40 A feature of the present invention resides in the employment of ordinarily liquid phosphoric acid as a catalyst for alkylation reactions in substantially solid form, this being accomplished by the alternative use of a number of different adsorbent carrying materials which vary somewhat 45 in their absorptive capacity and also in their chemical and physical properties and their influence upon the catalytic effect of the mixtures. The materials which may be employed are divisible roughly into two classes. The first class 50 comprises materials of a predominately siliceous character and includes diatomaceous earth, kieselguhr and artificially prepared porous silica such as, for example, Sil-O-Cel. In the case of naturally occurring diatoms it is believed that 55

they sometimes contain minor amounts of highly active aluminum oxide which in some instances seems to contribute to the total catalytic effect of the solid catalyst. This active material is not present in the artificially prepared forms of silica.

The second class of materials which may be employed either alone or in conjunction with the first class (and with certain other optional ingredients to be later described) comprises generally certain members of the class of aluminum silicates and includes such naturally occurring substances as the various fuller's earths and clays such as bentonite, montmorillonite, et cetera. This class also includes certain artificially prepared aluminum silicates of which the product known as Tonall is representative, this substance being in a sense a purified aluminum silicate made by treating certain selected clays with sulfuric, hydrochloric or other mineral acid and washing out the reaction products. The naturally occurring substances in this general class are characterized by a high adsorptive capacity which is particularly in evidence in making up the present type of phosphoric acid catalyst, and they may also contain traces of active ingredients which may assist in producing the desired polymerizing effects. Again each silicate material which may be used alternatively will exert its own specific influence upon the net effectiveness of the catalyst composite which will not necessarily be identical with that of the other members of the class.

In some cases the structure of the solid phosphoric acid catalysts may be improved by the primary incorporation of organic materials which yield a carbonaceous residue on heating. Substances which may be used in this manner include such materials as cellulose, starches, sugars, glue, gelatin, flour, molasses, agar-agar, et cetera. They evidently function as binders to some extent to prevent the breakdown of the catalyst structure when subjected to elevated temperatures and the action of hydrocarbon vapors or liquids in service.

Catalysts of the character comprised within the scope of the present invention are producible by a series of relatively simple steps comprising generally: mixing a liquid phosphoric acid and adsorbent materials in selected proportions, heating at temperatures of approximately 180 to 20° C. and grinding and sizing the resultant product to produce particles of the desired size. The catalyst may be used in particle sizes of from approximately 4 to 20 mesh or may be made up into small briquettes. When carbonaceous materials are used somewhat higher temperatures may be employed to decompose them. The optimum temperature of heating when employing these materials varies considerably. Good results have been obtained at temperatures as high as 300° C., though in some instances it would appear that too high temperatures above this point have a deleterious effect. The exact maximum temperature employed in the calcining step will be to some extent a matter of trial.

When pyrophosphoric acid is employed in the original mixes the temperatures employed in the mixing step are commonly those comprised within the range of from 120 to 180° C. Within this temperature range the acid is sufficiently fluid to enable rapid mixing by mechanical devices. Such mixes may then be calcined at temperatures from approximately 180 to 300° C. without deleterious effect upon the structure, strength or catalytic efficiency of the particles finally produced.

When starting with this acid and heating at the somewhat higher permissible temperatures the heating or calcining period may be reduced in some instances from 48 to 60 hours down to about 20 hours.

Catalysts of the present character are hydroscopic to a variable extent and are best ground, sized and preserved for use out of contact with moist air.

Owing to the possibility of varying both the active ingredients and the relatively inert adsorbent materials which go to form the catalyst masses, a number of alternatives exists each of which will have its own peculiar catalyzing character which will not be exactly equivalent to masses of different composition.

By the use of phosphoric acid catalysts in solid form it has been found convenient and feasible to alkylate aromatic hydrocarbons with olefin hydrocarbons while adjusting the conditions of operation in respect to the activity of the reacting constituents, particularly in regard to the olefins. It is known that the iso olefins (for example, isobutylene) are generally more reactive than the straight chain isomers and in cases involving these iso compounds less severe conditions of temperature, pressure, time of contact and amount and strength of acid catalyst are necessary than when employing the normal compounds. The most difficult alkylation reaction involves the use of ethylene as the first member of the olefin series. When working with this compound, more active catalysts, considerably higher temperatures and increased superatmospheric pressures are preferable within ranges which will be later more accurately designated.

Contrasting the action of solid phosphoric acid catalyst for alkylation reactions with sulfuric acid used for the same purpose, I have found that the phosphoric acids have a more moderate and controllable action with practically no tendency to oxidize or unduly favor polymerization reactions at the expense of the desired alkylation. This is particularly in evidence in the case of the iso olefins. When using sulfuric acid and alkylating with gaseous olefin mixtures such as those produced as by-products in oil cracking reactions, the polymerization reactions may proceed to the extent of forming polymers of too high molecular weight and boiling point for use in commercial motor fuels and may even produce gummy and resinous polymers which are insoluble and entirely objectionable for this reason. It is not to be inferred, however, that polymerization can be entirely obviated with phosphoric acid catalyst since the catalytic acid mixtures are not miscible with the hydrocarbons and only multi-phase reactions are possible, which leaves the question of effective contact between reacting constituents to the efficiency of mechanical agitation and mixing.

The reactions between olefins and aromatics in the presence of solid phosphoric acid catalyst are basically of a simple character, although there may be a certain amount of side reactions due principally to a certain amount of ester formation with the phosphoric acid. Apparently the intermediate-compound theory of catalysis best explains the observed reactions, which means in the present instance that both types of reacting components probably form primary transient addition compounds with the phosphoric acids which then further react to produce the synthetic hydrocarbons and regenerate the acids. The following equations may represent the course

of a typical reaction induced between a mono-olefin and an aromatic by orthophosphoric acid:



Propylene Benzol Iso-propyl benzol

The reaction which takes place when iso-butylene is reacted with benzol in the presence of orthophosphoric acid is also characteristic and may be expressed by the following equation:



Iso-butylene Benzol Iso-butyl benzol

These equations show the union of one molecule each of olefin and benzol. The reactions in both cases may proceed further to the production of di and even tri-alkyl derivatives, depending upon conditions of operation, the relative proportions of olefins and aromatics and the usual controlling factors such as temperature, pressure and efficiency and time of contact.

Below is given a tabulation of the known acids of phosphorus along with their melting points and temperatures of decomposition:

Acids of phosphorus		M. P. ° C.	Dec. ° C.
Hypophosphorous...	H_3PO_2	26.5	Above 200
Orthophosphorous...	H_3PO_3	70.0	200
Pyrophosphorous...	$\text{H}_4\text{P}_2\text{O}_5$	38.0	130
Hypophosphoric...	$\text{H}_4\text{P}_2\text{O}_6$	55.0	70
Metaphosphoric...	HPO_3	Sublimes	-----
Pyrophosphoric...	$\text{H}_4\text{P}_2\text{O}_7$	61	Looses $\frac{1}{2}$ H_2O at 213
Orthophosphoric...	H_3PO_4	38.6	

Of those listed the use of the more ordinary and stable acids is preferred in making up the solid composites, to wit, orthophosphoric acid H_3PO_4 , pyrophosphoric acid $\text{H}_4\text{P}_2\text{O}_7$, orthophosphorous acid H_3PO_3 , etc., these being utilizable alternatively though without identically equivalent catalytic effects. The strengths and amounts of these acids used in the composite materials may be varied considerably in dealing with different specific reactions to compensate principally for the different degrees of reactivity in the olefins. In the case of the orthophosphoric acid, 100% strength may be used or a certain proportion of it with the less highly hydrated acids, to wit, the pyro and meta acids having the formulas $\text{H}_4\text{P}_2\text{O}_7$ and HPO_3 respectively. The catalytic effectiveness of the acids of phosphorus in which this element has a valence of 5 is considerably greater than the acids in which it has only a valence of 3 so that as a rule the phosphoric acids are preferable over the phosphorous acids.

The solid phosphoric acid catalysts characteristic of the present process may be used to induce or accelerate reactions of alkylation in any manner found convenient. In one mode of operation the granules of catalyst may be used as filler in the interior of a vertical cylindrical treater and a mixture of the vapors of an aromatic hydrocarbon and an olefin in regulated proportions are passed downwardly therethrough at suitably elevated temperature and pressure. Products from the bottom of the treater may be admitted directly to a fractionating column designed to separate the alkylated products produced from the unreacted substances, which latter may then be returned to further contact with the catalyst until the reactions are substantially complete. Alkylation may be caused to proceed to the formation of more highly alkylated compounds by increasing the proportion of olefin and the time and temperature of the reaction.

While the foregoing is the more customary procedure in conducting alkylation reactions with the fresh type of catalyst, reactions may also be brought about under relatively high pressure in closed vessels in which some of the reacting constituents are in liquid phase and in which the catalyst particles are maintained in suspension by some form of agitation. Reacting constituents in mixed phase may also be forced together through stationary beds of catalyst to effect the same type of results. The choice of any particular type of operation will depend upon such circumstances as the temperature and pressure found to be most effective in producing the desired type of alkylation to a predetermined extent.

The following example is given to illustrate the character of results obtained in a normal operation of the present process, although the data presented are only from a selected case and are not introduced with the intent of unduly restricting the scope of the invention.

Benzol was alkylated with isobutylene by passing an approximately equimolecular mixture of their vapors downwardly through a solid phosphoric acid catalyst mass at a temperature of approximately 120° C. and a pressure of 50 to 75 pounds per square inch.

The catalyst was made by the following general procedure

- About 65 parts by weight of pyrophosphoric acid was thoroughly mixed with 35 parts by weight of an air-dried sample of kieselguhr at a temperature of approximately 170° C., the mixing being completed in about 5 minutes;

- The mixture was then heated at a temperature of about 280° C. for 20 hours to produce a solid cake;

- The cake was ground in a dry atmosphere and the ground particles were sized with recovery of the 6-10 mesh granules for use as filler in the catalyst tower.

Using this catalyst and the conditions of temperature, pressure and concentration mentioned, it was found possible to produce the desired alkylation reaction up to about a 75% efficiency in a single pass through the catalyst bed. Fractionation of the reactive material enables the recovery of the alkylated product which was principally mono isobutyl benzol having a specific gravity of 0.874, a boiling point of about 180° C. and a blending octane number of motor fuel mixes of approximately 110. The unreacted benzol and isobutylene were mixed with fresh material and recycled so that ultimate yields approaching 100% were possible.

The character of the present invention is evident from a consideration of the foregoing specification and the novelty and utility of results obtained by its use will be seen from the single example although neither specification nor illustrative data are to be construed as limiting the generally broad scope of the invention.

I claim as my invention:

- A process for the treatment of aromatic hydrocarbons to improve their knock rating when used as motor fuel which comprises, subjecting the said aromatic hydrocarbon to the action of an olefin containing gas in the presence of a calcined mixture of an acid of phosphorus and an adsorbent, and at an alkylating temperature.

- A process for the treatment of aromatic hydrocarbons to improve their knock rating when used as motor fuel which comprises, subjecting the said aromatic hydrocarbon to the action of an olefin containing gas in the presence of a calcined

mixture of pyrophosphoric acid and a siliceous material, and at an alkylating temperature.

3. A process for the treatment of aromatic hydrocarbons to improve their knock rating when used as motor fuel which comprises, subjecting the said aromatic hydrocarbon to the action of an olefin containing gas in the presence of a calcined mixture of metaphosphoric acid and a siliceous material, and at an alkylating temperature.

4. A process for the treatment of aromatic hydrocarbons to improve their knock rating when used as motor fuel which comprises, subjecting

the said aromatic hydrocarbon to the action of an olefin containing gas in the presence of a calcined mixture of an acid of phosphorus and infusorial earth, and at an alkylating temperature.

5. A process for the treatment of aromatic hydrocarbons to improve their knock rating when used as motor fuel which comprises, subjecting the said aromatic hydrocarbon to the action of an olefin containing gas in the presence of a calcined mixture of pyrophosphoric acid and infusorial earth, and at an alkylating temperature.

VLADIMIR IPATIEFF.

Certificate of Correction

Patent No. 2,067,764.

January 12, 1937.

VLADIMIR IPATIEFF

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, first column, line 51, for "20° C." read 220° C.; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 27th day of July, A. D. 1937.

[SEAL]

HENRY VAN ARSDALE,
Acting Commissioner of Patents.

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