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TREATMENT OF HYDROCARBONS

Vladimir Ipatieff and Raymond E. Schaad, Chicago, Ill., assignors to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware

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This invention relates particularly to the treatment of hydrocarbons of an unsaturated character, such as the mono-olefins, the present application being a continuation-in-part of our earlier applications, Serial Nos. 17,254 and 17,255, filed April 19, 1935.

In a more specific sense, the invention is concerned with the selective treatment of the mono-olefins which are normally gaseous to produce particular compounds which are of superior value as antiknock blending fluids for gasolines inferior in this respect.

Oil cracking processes which are in use as a means of supplementing the supply of gasoline obtainable by straight run distillation from crudes, and also for producing higher antiknock value material than the so-called "natural" gasolines i. e. gasolines which are produced by straight distillation of crude oils, are also productive of considerable quantities of fixed gases and heavy residual products, both liquid and solid, which are in a sense waste products of the process in that very little utilization of them has been made other than as fuels. The fixed gases produced, for example, in cracking a topped crude with the primary object of producing gasoline may run as high as 10% by weight of the charging oil under intensive cracking conditions. The composition of these gases will vary with the severity of the cracking operation, the nature of the charging stock, the phase prevalent during the operation, and other factors.

Intensive researches have been conducted to find a practical method for augmenting the supply of cracked gasoline by forming liquid polymers from the gaseous olefins present in cracked hydrocarbon gas mixtures. Fortunately, all of the dimers and many of the trimers and mixed polymers of the normally gaseous mono-olefins boil within the range of commercial motor fuel and are characterized by a satisfactory stability and particularly by a good antiknock value, which generally exceeds that of any of the components of cracked gasoline. For purposes of reference the following table is introduced to show the boiling ranges of the dimers of the lower boiling mono-olefins:

Boiling points of olefin dimers

	°F.
Hexylene	155
Octylene	255
Decylene	323
Dodecylene	417

The tendency of the gaseous mono-olefins to polymerize varies considerably when using different catalysts and also with the same catalyst. The present process is an adaptation of a particular type of catalyst to selectively polymerize the olefins in hydrocarbon gas mixture, and particularly those present in the gases from oil cracking operations.

In one specific embodiment the present invention comprises treatment of olefin-containing hydrocarbon gas mixtures for the polymerization of the olefins therein contained in successive stages characterized by the use of orthophosphoric acid in the primary stage and pyrophosphoric acid in succeeding stages.

In a preferred embodiment the process is directed to the treatment of the fixed hydrocarbon gas mixtures produced incidental to oil cracking operations.

According to the present invention the olefins present in gas mixtures can be selectively and successively polymerized in order of their reactivity by employing phosphoric acids of graded strength and particularly by employing first orthophosphoric acid and then the pyroacid which corresponds to the ortho with one less molecule of water in combination with phosphorus pentoxide. In general, the olefins of higher molecular weight and of condensed or iso-structure are removed first. As a rule the amount of five carbon atom hydrocarbons in cracked gas mixtures is small and not a considerable item either in the matter of direct recovery by absorption processes or indirect recovery by polymerization by processes of the present character. For example, in cracked gas mixtures isobutylene may be first more or less selectively polymerized, then the n-butylenes and lastly the propylene. In this sense isobutylene may be considered as the most reactive and readily polymerizable of the compounds normally encountered and in the following description of the operation of the process it will be so considered.

While the respective liquid acids may be employed with proper modification of procedure, the catalysts which are preferably used in the present connection are essentially solids of a special and unique character which warrant detailed description, as they are evidently peculiar in their action. They are made generally by mixing the ortho or the pyro acid with a substantially unreactive and generally siliceous adsorbent until a paste is obtained, this paste being then calcined to produce a solid cake, which is ground and sized to produce catalyst granules. It has

been found in the case of highly adsorbent materials, such as kieselguhr, that primary composites may be made in which the acid of phosphorus is the major constituent by weight. Thus a stiff paste is produced when 80 parts of commercial ortho-phosphoric acid is mixed at ordinary temperatures with 20 parts of kieselguhr. Conversely, relatively dry mixes result when about 30 parts of this acid is mixed with 70 parts by weight of the adsorbent. By incorporating varying quantities of the two phosphoric acids with these adsorbents, catalyst masses are produced which have varying polymerizing effectiveness which may be due to the variation in the actual contact surface of the acid which is exposed during service.

By controlling the proportions of adsorbent and acid and also the temperature employed in the drying or calcining step, granular catalyst composites may be produced which vary both in the type and percentage of the acidic component and in the strength of said component. Thus for the polymerization of such readily polymerizable compounds as iso-butylene catalysts are utilized which have been produced by merely mixing commercial orthophosphoric acid of approximately 90% concentration with a siliceous and finely divided adsorbent material and drying at temperatures of approximately 250° F. to 300° F., which operation if conducted for periods of time which vary somewhat with the amount of acid present in the mix, ultimately yields solid catalysts which contain 100% orthophosphoric acid as their essential constituent.

When a catalyst composite comprising the pyroacid as the essential active ingredient is to be manufactured, and the orthoacid has been used in the primary mixtures, the most effective catalysts are produced when the pasty mixtures are heated at temperatures from approximately 400 to 600° F. for a considerable period of time, usually from 40 to 60 hours. During this heating water is evolved and analysis shows that the remaining acid has a composition closely approaching that of the pyroacid. Advantages are frequently gained in utilizing the higher temperatures and also in starting with the pyroacid. If dehydration of the acid is found to have taken place to too great an extent so that its polymerizing effectiveness is reduced (as shown by small scale tests) the particles may be contacted with superheated steam at temperatures within the approximate range of 400 to 500° F. to rehydrate the acid and produce a catalyst of maximum effectiveness. When utilizing pyroacid in the initial mixes it is preferable to use somewhat elevated temperatures in the mixing step, usually between 250 and 350° F., to increase the fluidity of the acid and insure rapid and uniform distribution throughout the adsorbent.

One of the principal features of the present invention resides in the employment of ordinarily liquid phosphoric acids as polymerizing catalysts in substantially solid form, this being accomplished by the alternative use of a number of different adsorbent carrying materials which vary somewhat in their adsorptive 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 comprises materials of a predominately siliceous character and includes diatomaceous earth, kieselguhr and artificially prepared porous silicas such as, for example, "Sil-O-Cel". In the case of naturally occurring diatoms it is believed that they sometimes contain minor amounts of highly active aluminum oxide which in some instances seem 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, etc. The class also includes certain artificially prepared aluminum silicates of which the product known as "Tonsil" is representative, this substance being in a sense a purified aluminum silicate made by treating certain selected clays with hydrochloric or other mineral acid and washing out the soluble reaction products. Both the naturally occurring and acid-treated 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 catalysts, and they may also contain traces of active ingredients which assist in producing the desired polymerizing effects. Again each substance which may be used alternatively will exert its own specific influence which will not necessarily be identical with that of the other members of the class.

In carrying out the process on a mixture of olefin-containing hydrocarbon gases the general procedure is to contact the gas mixture successively with contact masses containing first orthophosphoric acid and then the pyroacid. Thus, isobutylene is selectively removed from a gas mixture by first contacting the mixture with a solid catalyst mass which is relatively weak in its polymerizing action and which may contain from approximately 30 to as high as 80% by weight of orthophosphoric acid adsorbed in and upon some siliceous carrier such as, for example, kieselguhr though certain finely divided clays of the bentonite and montmorillonite type may be alternately employed. Under temperature conditions of from approximately 200° F. to 250° F. with a catalyst of this character and even pressures as high as 300 lbs., there is substantially no action upon olefins other than isobutylene, which is converted principally into its dimer, iso-octene. In a simple two-stage operation the next step consists in contacting the residual gases after separation of liquid polymers with solid phosphoric acid catalysts containing approximately 70% of pyrophosphoric acid and 30% of absorbent by weight at temperatures of approximately 400° to 500° F. and moderately superatmospheric pressures of the order of 100 to 200 lbs. per square inch, or higher, which obtain in the receivers of cracking plants or in stabilizers operating on primary cracked distillates. In this second stage, residual butenes, propylene, and to some extent ethylene, are polymerized to form gasoline boiling range liquids.

Where separation and selective polymerizing of isobutylene, normal butenes and propylene, is required or desirable, the operation may be conducted in three stages. In the first stage the conditions will be the same as those recited in the preceding paragraph. In the second stage, wherein alpha and beta butenes are polymerized, catalyst composites containing about 50% by weight of pyrophosphoric acid may be used, and

temperatures of from approximately 250° F. to 400° F. After the removal of the butenes in this stage the severity of treatment in respect to amount of pyrophosphoric acid in the catalyst and the temperatures employed is then increased to correspond to those necessary for the polymerization of propylene to wit, about 400–500° F. In this third stage the polymers will be produced principally from propylene, with minor percentages originating from reactions involving residual butenes and propylene on the one hand and propylene and ethylene on the other hand.

The invention may employ for the preliminary treatment of the gases to be processed any suitable method for the removal of hydrogen sulphide, low boiling mercaptans, dienes and other gases which may interfere with the normal functioning of the catalysts or the production of polymers of sufficient purity for ready incorporation with refined gasolines. Furthermore, the liquid polymer products may be subjected to any of the ordinary treatments commonly employed on cracked distillates, such as a limited amount of sulphuric acid, caustic soda, sweetening reagents and the addition of small amounts of inhibitors.

The catalysts are best employed in vertical cylindrical towers and best results are commonly obtained by passing olefin-containing gas mixtures downwardly therethrough after preheating the gases to some temperature found to be most suitable for the selective removal of the olefins. The down flow keeps any liquid condensates washed from the catalyst particles and prevents contamination of their surfaces by the gradual deposition of high boiling polymers, which eventually carbonize and make regeneration of the catalyst particles necessary. The regeneration steps commonly comprise: (1) removal of distillable materials by the use of superheated steam at temperatures of approximately 600° to 700° F.; (2) the use of oxidizing gas mixtures of graded oxygen content to burn out the carbonaceous material; and (3) the rehydration of the acid by steam at temperatures of 400° to 600° F. In the burning step it is most advantageous in commercial units to employ primarily instead of air a flue gas mixture produced by using only a very slight excess of air in the combustion of the fuel, so that the total oxygen content is below 1%. If air is used at first too high temperatures are likely to develop and portions of the catalyst will be over-burned, causing a loss of the volatile meta acid, which is formed as a result of too extensive dehydration. In the burning step the temperature of 950° F. should not generally be exceeded.

The reactions of polymerization of olefins are exothermic and consequently the temperature of a gas mixture on passage through a bed of preferred catalysts tends to rise in proportion to the percentage of olefins present, the strength of the catalyst and the rate of passage of the gas, and advantages are sometimes gained by intermediate cooling between towers connected in series. This may be extended not only to the removal of the initially formed liquid polymers by partial cooling but also to the complete liquefaction of liquid polymers and intermediate stabilization to permit only the residual gases to contact with further quantities of the catalyst.

Solid phosphoric acid catalysts are characterized by their ability to polymerize olefins to produce relatively low boiling hydrocarbon polymers rather than heavy tars or pitches and by their long life due to the absence of such highly carbonaceous reaction products and also due to lack of oxidizing tendency in the phosphoric acid which constitutes the major portion thereof. In contrast to this it is notable that when employing sulphuric acid as a polymerizing agent, caution is necessary to prevent oxidation and undesirable side reactions such as ester formation and that, when employing metal holides such as aluminum chloride or zinc chloride, the tendency toward the formation of heavy polymers is very pronounced, so that it is not possible to produce more than minor amounts of desired low boiling hydrocarbons without the concurrent production of large quantities of heavy materials. Furthermore, such catalysts are readily regenerated after they have been contaminated by surface carbon deposits after long periods of service by merely burning off the deposits with air or other oxidizing gas at moderate temperatures. A still further advantage resides in the fact that they are substantially of a non-corrosive character as compared with the decided corrosive action of liquid phosphoric acid and other polymerizing agents. The peculiar structural strength of catalyst masses of the present type should be noted in connection with the general advantages which they possess, this being of special commercial value.

The following examples are given to indicate the character of the results obtainable by the use of the present process, although not with the intention of correspondingly limiting the scope of the invention:

Example I

A gas mixture consisting of 89% by volume of propylene and 11% by volume of isobutylene was passed at 140 pounds pressure and a temperature of 305° F. over a catalyst prepared by incorporating 30 parts by weight of 89% orthophosphoric acid and 70 parts by weight of diatomaceous earth and heating the mixture according to the general method described in preceding paragraphs. By controlling the space velocity it was possible to selectively polymerize 85% of the isobutylene present in the mixture without affecting the propylene. By contacting the gas mixture further with a catalyst made by mixing 60 parts by weight of pyrophosphoric acid and 40 parts by weight of diatomaceous earth and calcining according to the preferred procedure the complete polymerization of the remaining olefins was effected.

Example II

This illustrates the applicability of the process to the treatment of cracked hydrocarbon gas mixtures. The idea of selective and successive polymerization was applied to a light hydrocarbon reflux produced in stabilizing a primary cracked naphtha to a given vapor pressure. The following table shows the olefin content of the mixture treated:

	Percent
Ethylene	5
Propylene	25
n-Butenes	15
Isobutylene	5

The gas mixture was passed successively through three treating towers containing solid phosphoric acid catalysts. The first tower contained a granular catalyst bed in which orthophosphoric acid was approximately 40% by weight of the total material. At a temperature

of 175° F. the isobutylene was selectively polymerized and removed as liquid polymers. This liquid material had a blending octane number of approximately 120.

Prior to their admission to the second tower, the gases were heated to a temperature of 270° F. and passed downwardly through a bed of catalyst which consisted of 60% by weight of a phosphoric acid corresponding to the pyroacid in composition and 40% by weight of kieselguhr and some silicophosphoric acid complexes. In this step residual 4-carbon atom olefins were polymerized to form a liquid polymer having a blending octane number of 105–110.

In the final stage of the process the gases were heated to a temperature of 450° F. and passed through a bed of catalyst similar in composition to that employed in the second stage. This removed about 85% of the residual propylene and furnished a yield of liquid polymers having a blending octane number of about 90. In this stage some of the ethylene was removed by condensation with the propylene as shown by the presence of some pentenes and heptenes in the polymers. The major portion, however, of the ethylene was unaffected.

The character of the invention is evident from the preceding specification and the results obtainable are illustrated by the three preceding examples although neither the descriptive material nor the numerical data are given with the intention of unduly limiting its scope.

We claim as our invention:

1. A process for the treatment of olefin-containing hydrocarbon gas mixtures for the formation of liquid polymers from the olefins contained therein, which comprises subjecting said gas mixtures at polymerizing temperatures and pressures first to the action of solid contact materials comprising orthophosphoric acid and thereafter subjecting the gas mixture to the action of solid contact materials comprising pyrophosphoric acid.

2. A process for the treatment of olefin-containing hydrocarbon gas mixtures for the formation of liquid polymers from the olefins therein contained, which comprises subjecting said gas mixtures at polymerizing temperatures and pressures first to the action of solid contact materials comprising essentially orthophosphoric acid and an inert carrier, and thereafter subjecting the gas mixture to the action of solid contact materials comprising essentially pyrophosphoric acid and an inert carrier.

3. A process for the treatment of olefin-containing hydrocarbon gas mixtures for the formation of liquid polymers from the olefins therein contained, which comprises subjecting said gas mixtures at polymerizing temperatures and pressures, first to the action of solid contact materials comprising essentially orthophosphoric acid and a siliceous carrier, and thereafter subjecting the gas mixture to the action of solid contact materials comprising essentially pyrophosphoric acid and a siliceous carrier.

4. A process for the selective and successive polymerization of the olefins contained in hydrocarbon gas mixtures in the order of their reactivity, which comprises subjecting said gas mixtures at polymerizing temperatures and pressures first to the action of contact materials comprising orthophosphoric acid to polymerize the more reactive olefins, and thereafter to the action of contact materials comprising pyrophosphoric acid to remove the less reactive residual olefins in order of decreasing reactivity.

5. A process for the selective and successive polymerization of the olefins contained in hydrocarbon gas mixtures in the order of their reactivity, which comprises subjecting said gas mixtures at polymerizing temperatures and pressures first to the action of contact materials comprising essentially orthophosphoric acid and an inert carrier to polymerize the more reactive olefins, and thereafter to the action of contact materials comprising essentially pyrophosphoric acid and an inert carrier to remove the less reactive residual olefins in order of decreasing reactivity.

6. A process for the selective and successive polymerization of the olefins contained in hydrocarbon gas mixtures in the order of their reactivity, which comprises subjecting said gas mixtures at polymerizing temperatures and pressures first to the action of contact materials comprising essentially orthophosphoric acid and a siliceous carrier to polymerize the more reactive olefins, and thereafter to the action of contact materials comprising essentially pyrophosphoric acid and a siliceous carrier to remove the less reactive residual olefins in order of decreasing reactivity.

7. A process for the selective and successive polymerization of the olefins contained in hydrocarbon gas mixtures in the order of their reactivity, which comprises subjecting said gas mixtures at temperatures within the approximate range of 250 to 500° F. and superatmospheric pressures up to 200 lbs. per square inch first to the action of contact materials comprising essentially orthophosphoric acid and a siliceous carrier to polymerize the more reactive olefins, and thereafter to the action of contact materials comprising essentially pyrophosphoric acid and a siliceous carrier to remove the less reactive residual olefins in order of decreasing reactivity.

8. A process for producing liquid hydrocarbons from normally gaseous olefin mixtures which comprises subjecting the mixture successively to the action of orthophosphoric acid and pyrophosphoric acid under polymerizing conditions.

VLADIMIR IPATIEFF.
RAYMOND E. SCHAAD.