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SELECTIVE REMOVAL OF CYCLOPENTADIENE FROM A MIXTURE CONTAINING AT LEAST ONE OTHER HYDROCARBON

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ABSTRACT OF THE DISCLOSURE

A method of removing 1,3-cyclopentadiene from a mixture consisting essentially of at least one hydrocarbon and 1,3-cyclopentadiene comprising contacting the said mixture with at least one oxide of a metal selected from the group consisting of copper, chromium and mixtures thereof.

This invention relates to a method of treating hydrocarbons. More particularly, this invention relates to a method of removing 1,3-cyclopentadiene from hydrocarbons.

It is known that 1,3-cyclopentadiene deactivates or retards the catalytic action of various catalysts used for the polymerization of various unsaturated hydrocarbons. Thus, it is usually desirable to reduce or eliminate the 1,3-cyclopentadiene content of those unsaturated hydrocarbons which are to be polymerized or used as diluents in polymerizations. For similar reasons it is usually desirable to reduce or eliminate 1,3-cyclopentadiene from other hydrocarbons such as saturated hydrocarbons and aromatic hydrocarbons, particularly where they are used as diluents in polymerizations.

Therefore, it is an object of this invention to provide a method of reducing the 1,3-cyclopentadiene content of hydrocarbons.

According to this invention, it was unexpectedly found that 1,3-cyclopentadiene can be selectively and substantially removed from a mixture comprising at least one hydrocarbon and 1,3-cyclopentadiene comprising treating the said mixture with at least one oxide of a metal selected from the group consisting of copper, chromium, and mixtures thereof. The oxides of such metals include cupric oxide, cuprous oxide, chromic oxide, chromous oxide and mixtures thereof including copper chromite.

It is a particular advantage of this invention that 1,3-cyclopentadiene can be selectively and almost completely removed from hydrocarbon mixtures comprising 1,3-cyclopentadiene with at least one other hydrocarbon exemplatory of which are saturated aliphatic, saturated cycloaliphatic, unsaturated aliphatic, unsaturated cycloaliphatic, and aromatic hydrocarbons, and mixtures of such hydrocarbons, without an appreciable removal of the saturated, unsaturated or aromatic hydrocarbons from the hydrocarbon mixture. Other methods utilized for removal of 1,3-cyclopentadiene from hydrocarbons, particularly unsaturated hydrocarbons, such as extraactive distillation, chemical reaction, and hydrogenation, generally may also remove an appreciable portion of the unsaturated hydrocarbons from such a mixture.

It has been found in the practice of this invention that a hydrocarbon which contains 1,3-cyclopentadiene can be treated to reduce the 1,3-cyclopentadiene content of the hydrocarbon to at least as low as 0.1 parts of 1,3-cyclopentadiene per million parts (p.p.m.) by weight of the hydrocarbon.

Various saturated, unsaturated and aromatic hydrocarbons and their mixtures which contain 1,3-cyclopentadiene can be treated by the oxides of this invention. Suitable hydrocarbon mixtures can be petroleum or coal tar

distillates having a boiling point at atmospheric pressure of from about —10° C. to about 150° C. and usually from about 0° C. to about 80° C. Representative examples of these and other various saturated hydrocarbons which can be treated are aliphatic hydrocarbons such as the butanes, the pentanes, the hexanes, the heptanes and the octanes; aromatic hydrocarbons such as benzene, and toluene and various unsaturated hydrocarbons representative of which are olefins such as ethylene, propylene, butene and methyl butene, and diolefins such as isoprene, 2-ethyl butadiene, and butadiene. Various mixtures of the saturated, unsaturated and aromatic hydrocarbons can also be treated.

Hydrocarbons used in polymerization processes either as monomers or as diluents can contain 1,3-cyclopentadiene in amounts of from about 500 to about 5,000 p.p.m. depending on the origin of the hydrocarbons. If the hydrocarbons have undergone special treatment, their 1,3-cyclopentadiene content can be as low as from about 2 to about 50 p.p.m. and in some instances as low as 1 p.p.m.

The oxides of the metals used in this invention may be used in their pure form, or they may be supported by various carriers. Generally, it is desired to combine the oxides with carriers such as structural materials having less density and more porosity than that of the said oxides in order to provide a greater surface area per unit of weight of the oxides. It is usually desired that such carriers are inert in that they do not adversely affect the removal of 1,3-cyclopentadiene from the hydrocarbon. Although it is understood that some carriers may be acidic in nature, and thus promote in some degree the polymerization of some unsaturated hydrocarbons, such a property does not itself prevent thesse carriers from being classified as inert within the scope of this invention. Various materials may be used as a structural support for the oxides and are generally known to those skilled in the catalyst art. Representative examples of such supporting materials are relatively low surface area and relatively non-porous materials such as alundum and silicon carbide. Representative relatively low surface area and relatively porous materials are pumice and diatomaceous earths. Representative relatively high surface area and relatively non-pourous materials are kaolin and carbon black. Representative relatively high surface area and relatively porous materials are attapulgite, alumina, magnesia, silica gel, silica-alumina, silica-magnesia, and charcoals from coal, bone and wood. Thus, the supporting materials can be inorganic or they can be organic in composition such as the carbon blacks and charcoals. For example, an oxide of copper, chromium and/or their mixtures may be deposited by coprecipitation or by other techniques known to those skilled in the catalyst art on particles of silica, alumina, or a mixture of silica or alumina. A suitable particle size for the oxides or supported oxides is from about 2 to about 100 mesh size (Tyler standard sieve scale) although usually other particle sizes may be used.

In this invention it is usually desired to pass the hydrocarbons containing the 1,3-cyclopentadiene while in a gaseous state through a bed of the oxide particles or particles of a carrier-supported oxide, although the hydrocarbons can be treated in their liquid state. The invention may be practiced as a continuous or a batch process whereby the hydrocarbon mixture is contacted with the said particles for a sufficient time to remove at least a portion of the 1,3-cyclopentadiene.

The invention can be practiced over a wide temperature range such as temperatures from about 0° C., to about 200° C., and even up to about 300° C., although the temperature should not substantially exceed that at which appreciable cracking of the hydrocarbons occurs. It is usually desired to conduct the reaction at a tempera-

ture of from about 80 to about 180 C. At these temperatures the pressure can vary from above to below atmospheric pressure. A suitable reaction pressure is from about 10 to about 80 pounds per square inch to facilitate control over process variables such as pumping rates.

When the invention is practiced as a continuous process the flow rate of the hydrocarbon through the catalyst bed can be measured by volumes of liquid hydrocarbon treated at about 25° C. and at a pressure of about one atmosphere, per volume of catalyst particles per hour and is known as the liquid hourly space velocity or LHSV. The volume of the catalyst particles is measured as the volume of the reactor displaced by the bulk of such particles which is the sum of the volumes of the particles and their void space. A suitable LHSV is generally from about 0.1 to about 50. The LHSV can be adjusted by one skilled in the art to remove the amount of 1,3-cyclopentadiene desired. Thus, for a hydrocarbon such as pentane containing about 100 parts per million of 1,3-cyclopentadiene by weight wherein it is desired to remove 99 percent of the 1,3-cyclopentadiene, a maximum LHSV may be from about 5 to about 10 at a temperature of from about 120° C. to about 150° C. and a pressure of from about 10 to about 50 pounds per inch gauge.

In some instances, in the practice of this invention, the oxides become less effective in removing the 1,3-cyclopentadiene after a continued exposure of the oxides to hydrocarbons which contain 1,3-cyclopentadiene. It has been found that the effectiveness of the oxides can be restored by regeneration. Various methods for regeneration of the oxides are treatment with steam, by treatment in various oxidizing atmospheres and by a combination of such methods. Various oxidizing atmospheres can be used for such treatments representative of which are air, oxygen and nitrogen dioxide atmospheres.

The following examples further illustrate this invention. The parts and percentages are by weight unless otherwise indicated.

EXAMPLE 1

To a suitable reactor was charged one-eighth inch pellets comprising 10 percent by weight of cupric oxide on alumina, (Cu–0803–T ⅛" from the Harshaw Chemical Company), to form a fixed bed of the pellets. The reactor was heated to 138° C. The reaction was conducted as a continuous process by continuously charging to the reactor isoprene containing 150 p.p.m. of 1,3-cyclopentadiene at 138° C., at atmospheric pressure, and at an LHSV of 4.8. The isoprene leaving the reactor contained 0.5 p.p.m. of 1,3-cyclopentadiene according to gas chromatographic analysis.

EXAMPLE 2

To a reactor was charged pellets of copper chromite (Girdler G–22 from the Girdler Chemicals Department of Chemetron Chemicals). The reactor was heated to 138° C. To the reactor was continuously charged a mixture of a hydrocarbon mixture comprising 20 percent by weight of isoprene and 80 percent by weight of pentane, and containing 200 p.p.m. of 1,3-cyclopentadiene at 138° C., a pressure of 82 pounds per square inch gauge and at an LHSV of 2. The resulting treated hydrocarbon mixture contained 2 parts of 1,3-cyclopentadiene per million parts by weight of the hydrocarbon mixture.

EXAMPLE 3

To a reactor was charged one-eighth inch pellets of chromous oxide on alumina, (Cu–1404–T ⅛" from the Harshaw Chemical). The reactor was heated to 138° C. To the reactor was then continuously charged pentane containing 75 p.p.m. of 1,3-cyclopentadiene at 138° C., 42 pounds per square inch gauge and at an LHSV of 2.5. The resulting treated pentane contained 3 p.p.m. of 1,3-cyclopentadiene.

EXAMPLE 4

To a reactor was charged pellets of material comprising 10 percent cupric oxide on alumina (Cu–0803–T ⅛" from the Harshaw Chemical Company). The reactor was heated to 138° C. To the reactor was then continuously charged with pure-grade n-hexane (99 percent by weight n-hexane from the Phillips Petroleum Company) containing 935 p.p.m. of 1,3-cyclopentadiene at 138° C., 45 pounds per square inch gauge, and at an LHSV of 3.8. The resulting treated n-hexane contained less than 0.1 p.p.m. of 1,3-cyclopentadiene.

While certain representative embodiments and details have been shown for the purpose of illustrating the invention, it will be apparent to those skilled in this art that various changes and modifications may be made therein without departing from the spirit or scope of the invention.

What is claimed is:

1. A method of removing a 1,3-cyclopentadiene from a mixture consisting essentially of at least one hydrocarbon and 1,3-cyclopentadiene comprising contacting the said mixture with at least one oxide of a metal selected from the group consisting of copper, chromium and mixtures thereof at a temperature of from about 0° C. to about 200° C. but not exceeding the cracking temperature of the hydrocarbons.

2. A method according to claim **1** wherein the said oxide is selected from the group consisting of cupric oxide, cuprous oxide, chromic oxide, chromous oxide and mixtures thereof.

3. A method according to claim **10** wherein the 1,3-cyclopentadiene content is reduced to as low as 0.1 part of 1,3-cyclopentadiene per million parts by weight of hydrocarbon.

4. A method according to claim **10** wherein the said oxides are supported on a solid inert carrier having a practical size of from about a 2 to about a 100 mesh size.

5. A method according to claim **10** wherein the said mixture comprises 1,3-cyclopentadiene, saturated aliphatic hydrocarbons, saturated cycloaliphatic hydrocarbons, unsaturated aliphatic hydrocarbons, unsaturated cycloaliphatic hydrocarbons, and aromatic hydrocarbons or mixtures of 1,3-cyclopentadiene and such hydrocarbons.

6. A method according to claim **10** wherein the said hydrocarbon is a petroleum or coal tar distillate having a boiling point at atmospheric pressure of from about −10° C. to about 150° C.

7. A method of removing 1,3-cyclopentadiene from a mixture consisting essentially of 1,3-cyclopentadiene and at least one diene selected from the group consisting of isoprene and 1,3-butadiene which comprises contacting the said mixture with at least one oxide of a metal selected from the group consisting of copper, chromium and mixtures thereof.

8. A method according to claim **7** wherein the said mixture is treated at a temperature of from about 0° C. to about 200° C.

9. A method according to claim **7** wherein the said mixture is treated in its gaseous state.

10. A method according to claim **9** wherein the said oxide is selected from the group consisting of cupric oxide, cuprous oxide, chromic oxide, chromous oxide and mixtures thereof.

11. A method according to claim **10** wherein the said oxide is cupric oxide supported on an inert carrier.

12. A method according to claim **10** wherein the said oxides are supported on a solid inert carrier having a particle size of from about a 2 to about a 100 mesh size.

13. A method according to claim **12** wherein the mixture is contacted with the oxides at a pressure of from about 10 to about 80 pounds per square inch and the

flow rate of the mixture through the particles has a liquid hourly space velocity of from about 0.1 to about 50.

14. A method according to claim **2** wherein the said mixture is treated in its gaseous state.

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