

UNITED STATES PATENT OFFICE

2,436,550

DESULFURIZATION OF TRIISOBUTYLENE

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No Drawing. Application May 2, 1946,
Serial No. 666,839

5 Claims. (Cl. 260-677)

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This invention relates to the purification of tri-isobutylene and more particularly relates to the removal of sulfur from tri-isobutylene prior to hydrogenation.

In order to reduce the hazard from fire which is attendant to the crash landing of aircraft, it has been proposed that the customary flammable gasoline used as fuel be replaced by a material which will not readily ignite at atmospheric temperature, yet will perform satisfactorily in an internal combustion engine of the conventional Otto type. The requirements for such a fuel are that it be substantially equal in antiknock quality and heating value to conventional high octane number aviation gasolines, yet have a "flash point" high enough so that its vapors will not readily ignite from a spark under atmospheric conditions. A fuel having a Tag closed cup flash point of at least 100° F. may be properly designated as "safety fuel."

It is known that isobutylene may be polymerized by means of sulfuric acid to a liquid boiling between 350°-355° F. and having the essential composition of $(C_4H_8)_3$ and known as tri-isobutylene or trimer. This material is then hydrogenated to produce a high flash and high octane number safety fuel. However, difficulty is encountered in the hydrogenation due to the presence of 0.01% sulfur in the trimer. While the hydrogenation can be carried out with a catalyst, such as molybdenum sulfide deposited on charcoal, which is not poisoned by the sulfur, high temperatures and pressures are required and a substantial portion of the trimer is cracked back to isobutylene. On the other hand, a sulfur-sensitive catalyst such as nickel can be used at lower temperatures where cracking does not occur. For this reason it is necessary to remove sulfur from the trimer prior to hydrogenation.

It is, therefore, the main object of this invention to provide a method for removing sulfur from the trimer prior to hydrogenation.

According to this invention the sulfur content of the trimer can be reduced to a point where a sulfur-sensitive catalyst such as nickel can be used for the hydrogenation by contacting the trimer with activated alumina, particularly dehydrated bauxite of a particular type.

The raw bauxite that is particularly desirable in accordance with this invention is preferably a bauxite of the Arkansas type, that is, one that has been mined in Arkansas and which contains from 50 to 70% of aluminum oxide and from 25 to 30% of water. The term "Arkansas" type bauxite or such similar expression is not intended

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as a limitation on the origin of the bauxite, but merely as a limitation upon the properties and generic structural characteristics of a bauxite which has been found operative in accordance with this invention.

It is thus intended to include bauxites of other origins and activated alumina in general having substantially the same structure and possessing, when activated, substantially the same potency for selective absorption of the sulfur from the trimer. It is, of course, understood that the water of constitution is not critical and that bauxites with lower percentages may be used although it has been found that bauxites with water of constitution around 25% will give best results.

Prior to its use, the bauxite is preferably dehydrated by heating from 800° to 1200° F. to remove all but about 2 to 3% of its contained water. This bauxite may be regenerated for re-use by suitable treatment which consists in roasting it at elevated temperatures between 800° and 1200° F. This roasting, as well as the first dehydration, is usually carried out in a furnace of the Herreshoff type, in a rotary kiln, or in a vertical stationary furnace. In case of regeneration, the organic matter absorbed by the bauxite is carbonized and substantially completely removed by maintaining an oxidizing atmosphere in the furnace. This regeneration and subsequent re-use of the bauxite may be carried out repeatedly so that the process is very economical.

In the practical application of this invention, the trimer is contacted at ordinary temperatures with a bauxite dehydrated as described above for a period of time sufficient to remove the sulfur. The method of contact between the trimer and the bauxite is not of critical importance and may be achieved by either adding the bauxite to the trimer in a tank or other suitable receptacle and thereafter separating the trimer from the bauxite; or by percolating the trimer through a layer of the bauxite of sufficient thickness to substantially ensure the desired adsorption. In all cases, care should be taken that the bauxite be regenerated or revived as soon as its adsorptive power has been exhausted.

It is, of course, understood that the method according to this invention is not limited to the use of dehydrated bauxite but is also applicable in connection with any type of activated alumina containing not more than 3% of water. Likewise, it is not to be limited to the desulfurization of tri-isobutylene since any other isobutylene

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polymer or copolymer may be desulfurized in like manner.

The following examples are given to indicate the general character of the treating effects obtainable in the practical application of this invention and while they are illustrative, they are not given with the intent of limiting the scope of the invention to the specific instances cited.

The following table illustrates the effectiveness of the process of this invention.

	Sample	Sulfur, Wt. per cent
1	Untreated trimer (commercial product).....	0.0103
2	(1) after percolation through burned bauxite at 150° F.....	0.0026
3	(1) after percolation through burned bauxite at room temperature (75° F.).....	0.0018
4	(1) after percolation through burned bauxite at 25° F.....	0.0022

The above data show that percolation of trimer through bauxite effects appreciable reduction in the sulfur content particularly at temperatures below 100° F.

While it is known that the sulfur content of various petroleum fractions may be reduced by percolation through bauxite or other activated alumina, the reduction in sulfur content of the usual petroleum fractions as shown by the prior art is not sufficient to allow a sulfur sensitive catalyst to be used for a subsequent hydrogenation step. However, the discovery has been made that when tri-isobutylene is thus treated an unexpectedly large amount of sulfur is removed as shown in the following table.

Removal of sulfur by bauxite percolation

Feed Stock	Approximate Boiling Range, °F.	Sulfur, Wt. per cent		Sulfur Removal, per cent
		Feed	Product	
Commercial Trimer.....	350-355	0.0103	0.0018	83
Thermally Cracked Naphtha.....	175-430	0.231	0.143	38
Thermally Cracked Naphtha after acid treating.....	125-310	0.071	0.063	11
Light Cracked Naphtha.....	90-160	0.106	0.038	64
Light P. C. Naphtha.....	115-270	0.054	0.027	50
Kerosene.....	330-550	0.067	0.053	21

The above data show that bauxite is unexpectedly more effective for removing sulfur from tri-isobutylene than for the usual petroleum stocks. It should be noted in particular that only

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21% of sulfur is removed from kerosene as compared with a reduction of 83% in the case of trimer which boils within the range of kerosene.

The features and advantages of the present invention are obvious from the consideration of the preceding specification and numerical data presented, although neither should be construed as imposing undue limitations upon the invention's generally broad scope.

The nature and objects of this invention having thus been set forth and specific examples of the same given, what is claimed as new and useful and desired to be secured by Letters Patent is:

1. A process for desulfurizing polymerized isobutylene to a sulfur content of less than 0.01% comprising treating said polymerized isobutylene in the liquid phase with a dehydrated alumina containing no more than 3% water.

2. Process according to claim 1 in which the dehydrated alumina is dehydrated bauxite.

3. Process for desulfurizing tri-isobutylene to a sulfur content of less than 0.01% comprising contacting said tri-isobutylene at temperatures below 100° F. with dehydrated alumina containing no more than 3% water.

4. Process according to claim 3 in which the dehydrated alumina is dehydrated bauxite.

5. A process for desulfurizing tri-isobutylene to a sulfur content of less than 0.01% comprising contacting the tri-isobutylene at ordinary temperatures with bauxite dehydrated to a water content of no more than 3% by heating to between 800° and 1200° F. and derived from bauxite having at least 25% of water of constitution and maintaining such contact for a period of time sufficient to remove sulfur from said tri-isobutylene.

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