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HYDROLYSIS OF ALKYL CHLORIDES IN HYDROCARBONS

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The present invention is directed to a method of removing alkyl chlorides from hydrocarbons containing them. More particularly, the invention is concerned with removing alkyl chlorides from hydrocarbons in the gasoline boiling range.

In the catalytic conversion of hydrocarbons in which aluminum chloride is used as a catalyst, such as in the alkylation of an isoparaffin with an olefin or in the isomerization of a normal paraffin to an isoparaffin, the product frequently contains alkyl chlorides which act as contaminants. The products, when isoparaffins are alkylated with olefins, usually boil in the gasoline boiling range and the alkyl chloride contaminating the product also boils in the gasoline boiling range and as a result it is difficult to remove the contaminating alkyl chloride from the desired product.

The presence of alkyl chlorides in hydrocarbons, when the hydrocarbons are to be used as a motor fuel, is quite detrimental in that certain of the alkyl chlorides act as detonating agents or may react with anti-knock agents which are added to the gasoline. It is, therefore, quite desirable that alkyl chlorides present in hydrocarbons for any reason and frequently as a result of a catalytic conversion operation should be removed therefrom before the hydrocarbon is generally suitable as a gasoline component and particularly an aviation gasoline component.

Accordingly, the present invention may be briefly described as involving treating a hydrocarbon containing an alkyl chloride by contacting the hydrocarbon with an aqueous solution of an alkali metal hydroxide at an elevated temperature for a sufficient length of time to convert the alkyl chloride to an alcohol following which the alcohol may be removed from the hydrocarbon and the treated hydrocarbon is recovered substantially free of alkyl halide.

Ordinarily the hydrocarbon fraction which forms a feed stock of the present invention will contain an amount no greater than 5% by volume of an alkyl chloride. Usually when the hydrocarbon feed stock is an alkylate the feed may contain in the range from about 1% to about 2% of ethyl or isopropyl chloride when aluminum chloride is employed as an alkylating agent for producing the hydrocarbon feed stock. The hydrocarbon feed stock may result from any processing operation in which it becomes contaminated with an alkyl chloride. As mentioned before, such operation may include the alkylation of an isoparaffin with an olefin when employing aluminum chloride as a catalyst or the isomerization of a normal paraffin to an isoparaffin employing aluminum chloride as a catalyst. Likewise the hydrocarbon mixture may result from the chlorination of a hydrocarbon wherein a mixture of a hydrocarbon and alkyl chloride is obtained in which the mixture contains an amount no greater than 5% by volume of an alkyl chloride.

The hydrocarbon feed stock, as mentioned before, may boil in the gasoline boiling range from about 65° F. up to about 450° F. The hydrocarbon feed stock may have

such a boiling range especially if it is formed by the alkylation of an isoparaffin with an olefin with the isoparaffin having 4 carbon atoms in the molecule and the olefins having from 2 to 4 carbon atoms in the molecule. Generally the gasoline boiling hydrocarbons in an alkylate fraction of this nature may contain from about 5 to 16 carbon atoms in the molecule.

The alkyl chlorides present in the hydrocarbon feed of the present invention will usually comprise ethyl and isopropyl chlorides. The alkyl chlorides serving as a contaminant in the feed stock of the present invention may be exemplified by the following compounds: tertiary butyl chloride and secondary butyl chloride.

In practicing the present invention it is desirable to contact the contaminated hydrocarbon feed stock containing alkyl chlorides with an aqueous solution of an alkali metal hydroxide at an elevated temperature. The elevated temperatures will range ordinarily from 180° to 500° F. with a preferred temperature in the range from about 290° to 500° F.

At the lower temperatures in the range given it is necessary that a longer time of contact be employed than at the higher temperatures. For example, at the lower temperatures it will be necessary to use longer contact times of the order of 50 to 60 minutes, whereas at the higher temperatures shorter contact times may be employed; for example, the time should usually be in excess of about 3 minutes depending on the temperature level at which the treating operation occurs. At about 325° F. in removing isopropyl chloride from an alkylate of the nature given a contact time of about 35 minutes will give substantially complete removal of isopropyl chloride.

It is desirable to maintain the hydrocarbon which is being treated in the liquid phase; therefore, pressures may be superimposed during the reaction to maintain a liquid phase treatment.

The alkali metal hydroxide may be an aqueous solution of an alkali metal hydroxide, such as sodium, potassium or lithium hydroxide. It will be preferred, however, to use an aqueous solution of sodium hydroxide containing an amount of sodium hydroxide in the range between 1% and 30% by weight of the solution. A preferred range of sodium hydroxide concentration in the aqueous solution is an amount in the range between 2% and 15% by weight.

The present invention will be further illustrated by the following examples:

EXAMPLE I

Normal pentane which contained approximately 1 volume per cent of isopropyl chloride was divided into 8 portions each of which was contacted with an aqueous solution of sodium hydroxide at temperatures ranging from 250° to 330° F. In conducting runs on the 8 portions of feed stock a charge to each run consisted of about 2 volumes of either 2.4% or 11% aqueous sodium hydroxide solution and 2 volumes of hydrocarbon containing isopropyl chloride. The hydrocarbon and the isopropyl chloride differed in boiling points not more than 2° F. This charge was introduced into a turbo-treater having a capacity of approximately 5 volumes, the treater being equipped with a stirring device turning at a constant rate of about 850 R. P. M. The power consumption for this treater, according to the method of Olney and Carlson, "Chemical Engineering Progress" vol. 43, page 473 was found to be about 0.93 H. P. an hour per barrel, assuming a contact time of 30 minutes.

After the 8 portions had been contacted as has been described with the sodium hydroxide solution, samples were removed after varying contact times and analyzed for chloride content expressed as weight per cent chlo-

rine. Pertinent data for the 8 runs are presented in Table I.

Table I

HYDROLYSIS OF ISOPROPYL CHLORIDE

Run	Temp., ° F.	Caustic Strength, Wt. Percent NaOH	Wt. Percent Cl [1]					
			Charge	After 10 Min.	After 20 Min.	After 30 Min.	After 50 Min.	After 60 Min.
A	330	11	0.6603	0.0852	0.0154	0.0012	----------	----------
B	320	11	0.6603	0.1716	0.0485	0.0118	----------	0.0012
G	320	2.4	0.4899	0.1586	0.0426	0.0083	----------	Nil
H	290	11	0.4899	0.2355	0.1350	0.0698	----------	0.0104
C	250	11	0.3881	0.3716	0.3337	----------	0.2047	----------
D	250	11	0.3834	0.3325	0.3029	----------	0.2710	----------
E	250	2.4	0.3739	0.3278	0.3017	----------	0.3153	----------
F	250	2.4	0.3716	0.3266	0.2970	----------	0.2449	----------

[1] ±0.0006.

It will be seen from an inspection of the results given in Table I that at the higher temperatures the isopropyl chloride has been substantially removed after 30 minutes contact time, whereas at the lower temperatures, such as 250° F., longer contact times were necessary to effect substantial removal of the chloride.

EXAMPLE II

In order to illustrate the invention further, runs were made in which a hydrocarbon solution containing ethyl chloride was subjected to hydrolysis at elevated temperatures ranging from 150° to 305° F. in a contacting device as described in Example I. Samples were removed from the contacting apparatus after 15, 30 and 60 minutes contact time and analyzed for chloride content. The results of these runs are presented in Table II.

Table II

Temperature, ° F.	Percent Removal of Ethylchloride at Indicated Contact Time		
	15 Minutes	30 Minutes	60 Minutes
150	----------	4	6
200	19	25	42
250	87	97	[1] 100
305	92	[1] 100	----------

[1] 100% conversion was reached before the indicated time, because the ethylchloride content was zero.

It will be noted from the data in Table II that at 150° F. only a small amount of ethyl chloride was removed after 60 minutes contacting time. Whereas at 200° F. 42% of ethyl chloride was hydrolyzed. On the other hand, at the higher temperatures ranging from 250° to 305° F. from 87% to 100% removal of ethyl chloride was realized.

In the contacting operation of the present invention in which the hydrocarbon contaminated with alkyl chloride is contacted with aqueous alkali metal hydroxide solution at an elevated temperature, it is believed that the alkyl chloride is hydrolyzed to the corresponding alcohol. The alcohol on formation may go into solution in the aqueous solution of alkali metal hydroxide and may be recovered therefrom. In general, ethyl and isopropyl alcohol, formed from the corresponding alkyl chlorides, will dissolve in the aqueous caustic solution. The higher alcohols will remain in solution in the hydrocarbon. In the small quantities involved, such alcohols are beneficial to the performance rating of the fuel. The hydrocarbon is separated from the aqueous solution of alkali metal hydroxide and then may be water washed, if desired, to remove traces of caustic therefrom and may be used as a component of aviation fuel or as a feed stock to a conversion operation, as may be desired, depending on its boiling points and properties.

It will be seen from the foregoing description and examples that the practice of the present invention involves treating an alkyl chloride contaminated hydrocarbon fraction at an elevated temperature with an aqueous solution of an alkali metal hydroxide for a sufficient period of time to cause conversion of the alkyl chloride to the corresponding alcohol. The lower alcohols dissolve in the alkali metal hydroxide solution which is then separated from the hydrocarbon. As stated, the hydrocarbon may be washed with water to remove traces of caustic therefrom and then may be used as a blending agent in processing operations common to petroleum refining processes. The process, it will be clear from the foregoing description, is a simple one readily adaptable and easy to use in the modern petroleum refinery where many operations involve the use of chloride-containing materials which serve to contaminate the desired hydrocarbon fractions.

While the present invention has been described and illustrated primarily in the removal of alkyl chlorides from alkylates and from gasoline boiling hydrocarbons, it is to be understood that the invention is not to be restricted to fractions boiling in the gasoline boiling range. As mentioned before, isomerization products may become contaminated with alkyl chlorides, such as isobutane resulting from the isomerization of normal butane. Likewise the invention is not restricted to paraffinic hydrocarbons. It is frequently desirable to convert by isomerization one naphthenic hydrocarbon to another. For example, methylcyclopentane may be isomerized to cyclohexane, employing aluminum chloride as the catalyst. Since feed stocks to these processes may contain either naphthenic or paraffin hydrocarbons, the present invention is applicable to treatment of products therefrom for the removal of alkyl chlorides therefrom.

The nature and objects of the present invention having been completely described and illustrated, what we wish to claim as new and useful and to secure by Letters Patent is:

1. A method for treating a hydrocarbon in the gasoline boiling range containing an amount in the range from about 1% to about 2% by volume of an alkyl chloride selected from the group consisting of the secondary and tertiary alkyl chlorides having 3 to 4 carbon atoms in the molecule which comprises contacting said hydrocarbon with an aqueous solution of an alkali metal hydroxide at an elevated temperature in the range between 180° and 500° F. for a sufficient length of time in the range from about 3 minutes to about 50 minutes to form an alcohol from said alkyl chloride and recovering a contacted fraction substantially free of chloride.

2. A method for treating a substantially saturated hydrocarbon fraction in the gasoline boiling range containing an amount in the range from about 1% to about 2% by volume of an alkyl chloride selected from the group consisting of the secondary and tertiary alkyl chlorides having 3 to 4 carbon atoms in the molecule which comprises contacting said hydrocarbon fraction with an aqueous solution of an alkali metal hydroxide at a temperature in the range between 180° and 500° F. for a time in the range from about 3 minutes to about 50

minutes to form an alcohol from said alkyl chloride and recovering a contacted fraction substantially free of chloride.

3. A method for treating an alkylate of an isoparaffin with an olefin, said isoparaffin and olefin having from 2 to 4 carbon atoms in the molecule, in the gasoline boiling range containing an amount in the range from about 1% to about 2% by volume of an alkyl chloride selected from the group consisting of the secondary and tertiary alkyl chlorides having from 3 to 4 carbon atoms in the molecule which comprises contacting said alkylate with an aqueous solution of an alkali metal hydroxide at a temperature in the range between 180° and 500° F. for a time in the range from about 3 minutes to about 50 minutes to form an alcohol from said alkyl halide and removing said alcohol from said treated alkylate to obtain a contacted alkylate substantially free of chloride and alcohol.

4. A method in accordance with claim 3 in which the alkylate is a fraction resulting from alkylating isobutane with ethylene in the presence of an aluminum chloride catalyst.

5. A method for treating an alkylate of an isoparaffin with an olefin, said isoparaffin and olefin having from 2 to 4 carbon atoms in the molecule, in the gasoline boiling range containing an amount in the range from about 1% to about 2% by volume of an alkyl chloride selected from the group consisting of the secondary and tertiary alkyl chlorides having from 3 to 4 carbon atoms in the molecule which comprises contacting said alkylate with an aqueous solution of sodium hydroxide at a temperature in the range between 180° and 500° F. for a time in the range from about 3 minutes to about 50 minutes to form an alcohol from said alkyl chloride, separating

said solution from said contacted alkylate, and recovering said contacted alkylate substantially free of chloride and alcohol.

6. A method in accordance with claim 5 in which the solution of sodium hydroxide contains an amount of NaOH in the range between 1% and 30% by weight.

7. A method for treating a substantially saturated hydrocarbon fraction in the gasoline boiling range containing an amount in the range from about 1% to about 2% by volume of an alkyl chloride selected from the group consisting of isopropyl chloride, tertiary butyl chloride, and secondary butyl chloride which comprises contacting said hydrocarbon fraction with an aqueous solution of sodium hydroxide at a temperature in the range between 250° and 330° F. for a time in the range from about 3 minutes to about 50 minutes to form an alcohol from said alkyl chloride and recovering a contacted fraction substantially free of chloride.

8. A method in accordance with claim 1 in which the hydrocarbon boils in the range between about 65° and about 450° F.

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