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TREATING HYDROCARBON FLUIDS

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This invention relates to the treatment of hydrocarbon fluids to separate paraffins or saturated hydrocarbons from unsaturated hydrocarbons and more specifically relates to the use of inorganic halide-hydrocarbon complexes such as aluminum chloride-hydrocarbon complexes as selective solvents for treating hydrocarbon fluids to separate paraffin hydrocarbons from unsaturated hydrocarbons.

It is known that there are various types of petroleum and that the different petroleums contain different types of constituents. Certain petroleums contain substantially all paraffin compounds, whereas other petroleums contain saturated and aromatic compounds. Also distillates obtained from petroleum oils comprise mixtures which contain different constituents or different types of hydrocarbon constituents.

My invention may be used to treat mixtures of hydrocarbons which contain aromatic or unsaturated constituents by using an aluminum chloride-hydrocarbon complex to remove the aromatic or unsaturated constituents. In such cases the raffinate will be more paraffinic than the hydrocarbon mixture before it is treated.

For example, when a hydrocarbon distillate such as a Mid-Continent gas oil is subjected to a conversion or cracking operation to produce lower boiling hydrocarbons, olefinic and aromatic compounds or compounds having a deficiency of hydrogen are obtained along with saturated or paraffin hydrocarbons and a gasoline separated from the products of conversion will contain olefinic and aromatic hydrocarbons and saturated hydrocarbons. Such a cracked gasoline may be subjected to a solvent extraction according to my invention using an inorganic halide-hydrocarbon complex as a selective solvent to separate a fraction from the cracked gasoline which will contain the olefinic and aromatic hydrocarbons and which will have a high anti-knock value and will be valuable as a motor fuel or as a blending agent.

Prior processes for separating unsaturated or aromatic compounds from hydrocarbon oils are relatively expensive and the processes must be carried out under specific or critical temperature and pressure conditions in order to get the treated oil to separate into the extract and raffinate phases. In my invention the selective solvent is a complex compound containing aluminum chloride and carbon and hydrogen atoms as a hydrocarbon radical or radicals and this complex compound is relatively cheap compared to the organic compounds which are used in certain other processes. Using my selective solvent, higher temperatures and lower pressures may be used than are used in present commercial processes. In addition the aluminum chloride-hydrocarbon complex is relatively insoluble in the upper layer or raffinate and two layers are formed with the complex and its dissolved unsaturated compounds forming the lower layer. The extraction and separation into layers take place through a relatively long range of temperatures and pressures.

My invention may also be used for treating lubricating oils to improve the viscosity-temperature characteristics and to obtain a lubricating oil having a low carbon residue and a high viscosity index. My invention may also be used for treating other hydrocarbon fluids to separate paraffinic from unsaturated constituents. For example, hydrocarbon gases containing paraffinic constituents and olefinic constituents, preferably in liquefied form, may be treated with my selective solvent complex to separate paraffinic constituents from unsaturated constituents.

In practicing my invention batches of hydrocarbon fluids may be treated or continuous streams of hydrocarbon fluid may be treated to separate paraffinic from unsaturated constituents. Where the batch process is used, the aluminum chloride-hydrocarbon complex is shaken or mixed or otherwise intimately contacted with the hydrocarbon fluid to be treated. The mixture is then allowed to settle and stratify, the upper layer containing mostly paraffinic constituents. The lower layer contains the solvent complex together with the dissolved unsaturated constituents. The layers may be separated by decantation or any other suitable manner and the lower layer or extract is heated to drive off the unsaturated constituents and the complex may then be again used for another solvent treatment. The separated unsaturated constituents may be further treated in any desired manner.

Where a continuous process is used, the complex selective solvent is passed countercurrent to a stream of the hydrocarbon fluid preferably in a tower. The complex is introduced into the upper portion of the tower and the hydrocarbon fluid to be treated is introduced into the lower portion of the tower and an extract phase is withdrawn from the lower portion of the tower and a raffinate phase is withdrawn from the upper portion of the tower.

My invention will now be more specifically described. A hydrocarbon fluid such as an oil

containing saturated and unsaturated hydrocarbon constituents is intimately contacted with about an equal amount of aluminum chloride-hydrocarbon complex. The non-paraffinic or unsaturated constituents, such as olefins, aromatic or other ring compounds or the like, are more soluble in the complex compound than in the oil and the complex compound extracts the non-paraffinic constituents from the oil. After sufficient time of contact or mixing of the oil and the complex, the oil is allowed to settle and stratification occurs. The upper layer contains mostly paraffinic constituents and the lower layer contains the complex compound with its dissolved unsaturated constituents. The unsaturated hydrocarbons are recovered from the complex compound by heat and the complex compound or solvent can be used again for another solvent extraction. The extraction with the solvent may be made at normal or elevated temperatures and at normal or elevated pressures.

The aluminum chloride-hydrocarbon complex may be prepared by reacting anhydrous aluminum chloride and paraffinic hydrocarbons such as normally liquid saturated hydrocarbons. The character of the hydrocarbon constituent in the complex is not definitely known nor is the chemical structure of the complex definitely known. By changing the relative amounts of aluminum chloride and paraffin hydrocarbons or by selecting different types of paraffin hydrocarbons, aluminum chloride complexes may be obtained which apparently have different compositions. For example, various complexes may be made in which the proportions of the various constituents vary as shown in the following table:

	Per cent
Aluminum	7 to 15
Chlorine	30 to 50
Hydrocarbon	30 to 60

The atomic ratio of chlorine to aluminum varies from 1.7 to 3.7. The aluminum chloride hydrocarbon compound is a very complex mixture and no single constituent thereof has been isolated or identified. The character of the hydrocarbon constituent of the complex is not definitely known.

The aluminum chloride complexes which have been made are unsaturated and high boiling and it is believed that the complex forms loose molecular compounds with unsaturated hydrocarbons which are relatively immiscible with the uncombined oil being treated. I believe, but do not wish to be restricted thereto, that the hydrocarbon forming part of the complex selective solvent is chemically combined with aluminum chloride because it can only be separated from the aluminum chloride by treatment with water whereby the aluminum chloride is destroyed or by thermal treatment whereby the complex hydrocarbon is coked. The complex after it has been used in an extraction contains dissolved unsaturated hydrocarbon constituents which can be removed from the complex by heating under normal pressure or higher pressures and the complex then reused for another extraction.

In order to test the solvent action of aluminum chloride-hydrocarbon complexes a synthetic solution of benzene and n-heptane was used so that the extractions could be followed on the refractometer. The aluminum chloride-hydrocarbon complex was prepared by agitating about one part by weight of anhydrous aluminum chloride with about three parts by weight of a paraffinic oil having an initial boiling point of about 400° F. and an end point of about 550° F. for a period of several hours at a temperature about 200° F. The aluminum chloride-hydrocarbon complex settled as a red liquid and was separated from the oil. The prepared hydrocarbon solution to be extracted contained equal amounts of n-heptane and benzene and gave on one extraction with an equal volume of the aluminum chloride-hydrocarbon complex a raffinate containing 21% of benzene. The extract or aromatic-rich fraction which was distilled from the aluminum chloride-hydrocarbon complex at 20 mm. contained 60% benzene. Larger volumes of the aluminum chloride-hydrocarbon complex solvent may be used as for example, in the ratio of two or three of the complex to one of the oil to be extracted. Higher ratios may be used, if desired.

In another example a 20% solution by volume of benzene in n-heptane was extracted four times with aluminum chloride-hydrocarbon complex prepared as above described. About 25 cc. of the hydrocarbon solution and about 25 cc. of the aluminum chloride-hydrocarbon complex were used in the first extraction. In the succeeding extractions smaller volumes of hydrocarbon solution were used while about 25 cc. of the complex were used in each extraction. The following results were obtained:

Extraction	Initial vol. of hydrocar. solution	Volume of raffinate	Percent benzene in oil treated	Percent of benz. in raff.
1	25	20	20	8.8
2	19	18	8.8	6.0
3	17	16	6	1.25
4	15		1.25	1.25

Since the fourth extraction gave no drop in refractive index, the product was washed with water whereupon the refractive index became about the same as that of n-heptane. From this it was concluded that part of the liquid complex was dissolved in the raffinate phase and that this raised the refractive index and that the extraction was complete after the third extraction. Benzene was completely recovered from the complex by heat under normal pressure. The complex was just as effective when used a second time.

Instead of reacting aluminum chloride with a saturated hydrocarbon oil, other inorganic compounds can be used such as sodium aluminum chloride, and anhydrous aluminum bromide and complexes made with these latter compounds which may be used as selective solvents according to my invention.

While I have given specific examples it is to be understood that these are by way of illustration only to show the selective solvent action of aluminum chloride-hydrocarbon complexes and that other hydrocarbon mixtures may be treated to separate paraffinic or saturated hydrocarbons from non-paraffinic or unsaturated hydrocarbons without digressing from my invention.

I claim:

1. A method of treating hydrocarbon fluids to separate paraffinic constituents from unsaturated constituents which comprises intimately mixing a hydrocarbon fluid containing saturated and unsaturated constituents with a liquid containing an aluminum chloride-hydrocarbon complex formed by reacting anhydrous aluminum chlo-

ride with hydrocarbon oil to extract unsaturated constituents from the hydrocarbon fluid.

2. A method of treating hydrocarbon fluids to separate paraffinic constituents from unsaturated constituents which comprises intimately mixing a hydrocarbon fluid containing saturated and unsaturated constituents with a liquid containing an aluminum chloride-hydrocarbon complex formed by reacting anhydrous aluminum chloride with a paraffin oil to extract unsaturated constituents from the hydrocarbon fluid.

3. A method of treating hydrocarbon fluids containing saturated and unsaturated hydrocarbons to separate paraffinic constituents from unsaturated constituents which comprises intimately admixing anhydrous aluminum chloride with a paraffinic oil at a temperature of the order of 200° F. to form a liquid product in the form of an aluminum chloride-hydrocarbon complex, and contacting the hydrocarbon fluid to be treated with said aluminum chloride-hydrocarbon complex to extract unsaturated constituents therefrom.

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