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TREATMENT OF HYDROCARBONS

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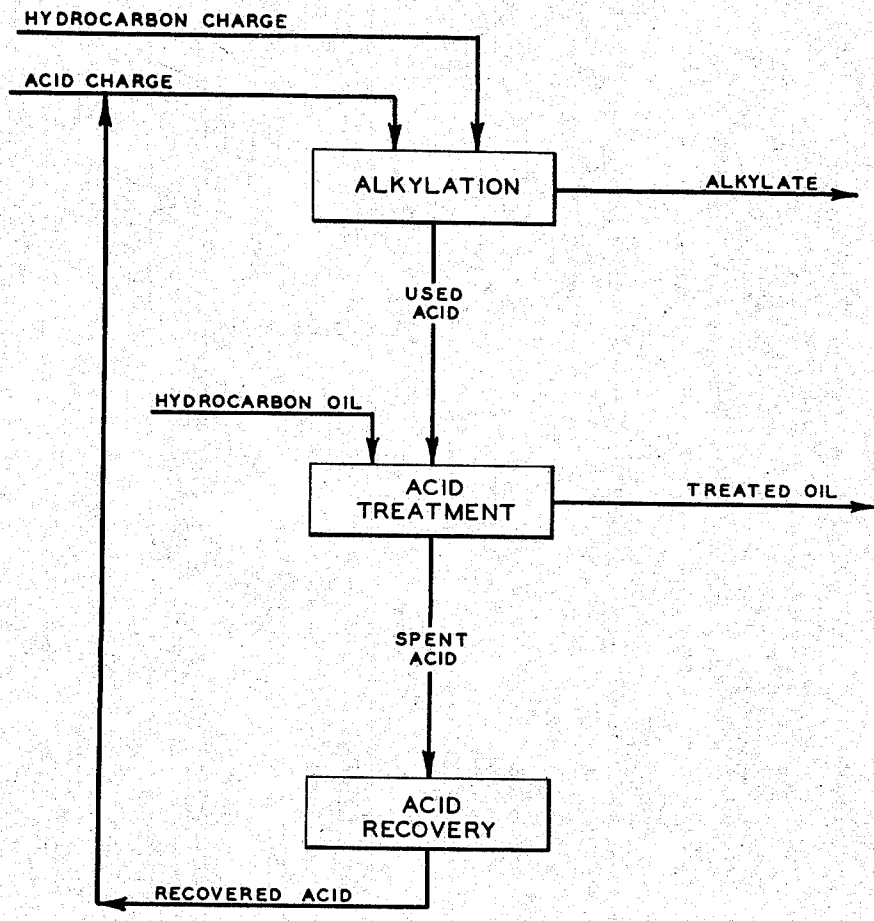

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TREATMENT OF HYDROCARBONS

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8 Claims. (Cl. 196—31)

This invention relates to the refining of hydrocarbon oils by acid treatment and has to do particularly with the utilization of a used or spent acid, formed by previously alkylating isoparaffin hydrocarbons with olefin hydrocarbons in the presence of sulfuric acid, as the acid treating reagent.

In the alkylation of low boiling isoparaffins, such as isobutane and isopentane with olefins, for example normally gaseous olefins or polymers thereof, in the presence of sulfuric acid to produce branch chain saturated gasoline hydrocarbons of high antiknock value, the acid gradually becomes spent and ineffective as a catalyst for such purpose.

The spent acid comprises mainly sulfuric acid and organic carbon containing materials, principally as hydrocarbon compounds, and differs from ordinary sludge acid obtained from the acid treatment of hydrocarbon oils in that the water content is very low. The organic carbon containing materials may run from 1 to 20% and usually about 4 to 10%. While the acid is no longer effective as an alkylation catalyst, it has been found that the acid can be used advantageously for the acid treatment of hydrocarbon oils to refine the oil by removing undesirable constituents therefrom, such as gums, resins, sulfur compounds and the like.

The oils that may be treated according to the invention are any hydrocarbon oils ordinarily subjected to refining by acid treatment. It is intended that petroleum oils, such as distillates, including lubricating oil, kerosene and naphtha or gasoline may be used. The invention is particularly applicable to the treatment of cracked distillates or cracked gasoline wherein the distillate is ordinarily given an acid dosage of about 3 to 5 pounds and the acid treated oil, after the separation of the acid sludge, neutralized and rerun by steam distillation. The amount of used acid required for acid treatment is ordinarily in the same proportion by weight as that used in the case of new acid. In some cases, however, it may be desirable to use spent acid in an amount equivalent to new acid on a percentage acidity basis; or the spent acid may be fortified with a stronger acid, such as 98% acid, or fuming acid to bring the acidity up to the equivalent of new acid and then a dosage, equivalent by weight to that used in the treatment with the new acid, used.

Any well known or preferred type of acid treating equipment may be used and the conventional methods of acid treatment employed. The sludge acid separated from the treating operation is subjected to conventional acid recovery methods whereby a restored acid, suitable for reuse in the alkylation operation may be obtained.

The accompanying drawing is a flow chart showing the operation of the process.

An example will now be given of the process of the invention as applied to the use of spent acid derived from an alkylation operation in which isobutane was alkylated, in the presence of about 93% sulfuric acid, by an unsaturated hydrocarbon fraction of cracking still gases containing C_3 and C_4 hydrocarbons, using a fresh feed ratio of isobutane to olefins of about 3:1, a ratio by weight of acid to olefins in the feed of about 0.6:1, and a temperature of about 65° F. The used acid from the operation analyzed as follows:

Percent H_2SO_4 by titration	86.6
Percent H_2SO_4 $(CH_2)_n$ free	91.1
Percent organic calculated as carbon	6.48
Percent organic calculated as $(CH_2)_n$	5.04
Specific gravity at 60° F	1.702

A cracked naphtha having an initial boiling point of 113° F. and an end point of 402° F. was treated with the used acid. The results obtained, as compared with those from treating the same naphtha without any acid and with fresh acid are shown in the following table. The oils in each case were neutralized, steam distilled and sweetened.

Kind of acid	None	Spent Alkylation	66 Bé.
Acid dosage lbs./barrel	None	3	3
Tests on oil:			
A. P. I. gravity	54.3	53.7	52.3
Color (18 in. Lovibond)	6.5	0.6	1.1
Sulfur percent	0.094	0.05	0.056
Gum	28	1	3

The spent acid from the acid treating operation may be run to the acid recovery plant wherein it is restored to desired concentration and reused in the alkylation operation.

The use of the spent alkylation acid in the refining of oils by acid treatment may produce a refined oil of improved properties, such as color, sulfur and gum content, and less sludge formation and acid treating loss, as compared to normal acid treating operations.

Obviously many modifications and variations of the invention as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. A process for refining hydrocarbon oils containing objectionable sulfur, color and gum-forming compounds, which comprises subjecting the oil to treatment with used sulfuric acid, which has been obtained from the alkylation of isoparaffins with olefins in the presence of strong sulfuric acid, whereby such objectionable compounds are substantially removed.

2. A process for the refining of hydrocarbon distillates containing undesirable sulfur, color and gum-forming compounds, which comprises treating the distillate with used sulfuric acid, which has been obtained from an alkylation operation wherein isoparaffins are alkylated with olefin hydrocarbons in the presence of strong sulfuric acid as a catalyst, whereby such undesirable compounds are substantially removed.

3. A process for the refining of light petroleum distillates to remove sulfur, color and gum-forming compounds, which comprises contacting the distillate with used sulfuric acid, which has been obtained by alkylating low boiling isoparaffins with olefins in the presence of strong sulfuric acid as the catalyst, said used acid containing about 1 to 20% of organic material soluble therein, and separating the acid sludge from the treated distillate.

4. A process for the refining of cracked hydrocarbon distillates to remove sulfur, color and gum-forming compounds, which comprises contacting the distillate with used sulfuric acid, which has been formed in the alkylation of low boiling isoparaffins with olefins in the presence of strong sulfuric acid as a catalyst, said used acid consisting essentially of sulfuric acid and organic material soluble therein, and separating the acid sludge from the treated oil.

5. A process which comprises subjecting an excess of low boiling isoparaffins and olefins to the reaction of strong sulfuric acid under alkylating conditions, whereby saturated branched chain hydrocarbons are formed by the alkylation of the isoparaffins with the olefins and the acid deteriorates, and then utilizing the used alkylation acid containing organic material soluble therein for the acid treatment of petroleum distillates to remove color and gum-forming compounds therefrom.

6. A process which comprises alkylating low boiling isoparaffins with normally gaseous olefins and polymers thereof in the presence of strong sulfuric acid, whereby saturated high antiknock gasoline hydrocarbons are formed, separating the used acid containing organic material soluble therein from the reaction products, treating a petroleum distillate with said used acid containing said soluble organic material to refine the distillate by removing sulfur, color and gum-forming compounds therefrom, separating a sludge acid from the last mentioned treating operation, recovering a strong sulfuric acid of alkylation strength from said sludge acid and returning the recovered acid to the alkylation operation.

7. In the refining of hydrocarbon oil containing undesirable sulfur, color and gum forming compounds, the process which comprises treating the oil with preformed acid sludge, derived from an alkylation operation wherein an isoparaffin is alkylated with an olefin hydrocarbon in the presence of sulfuric acid as a catalyst, whereby such undesirable compounds are substantially removed from the oil.

8. In the refining of cracked naphtha containing undesirable sulfur, color and gum forming compounds, the process which comprises treating the cracked naphtha with preformed acid sludge, derived from an alkylation operation wherein an isoparaffin is alkylated with an olefin hydrocarbon in the presence of sulfuric acid as a catalyst, whereby such undesirable compounds are substantially removed from the oil.

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