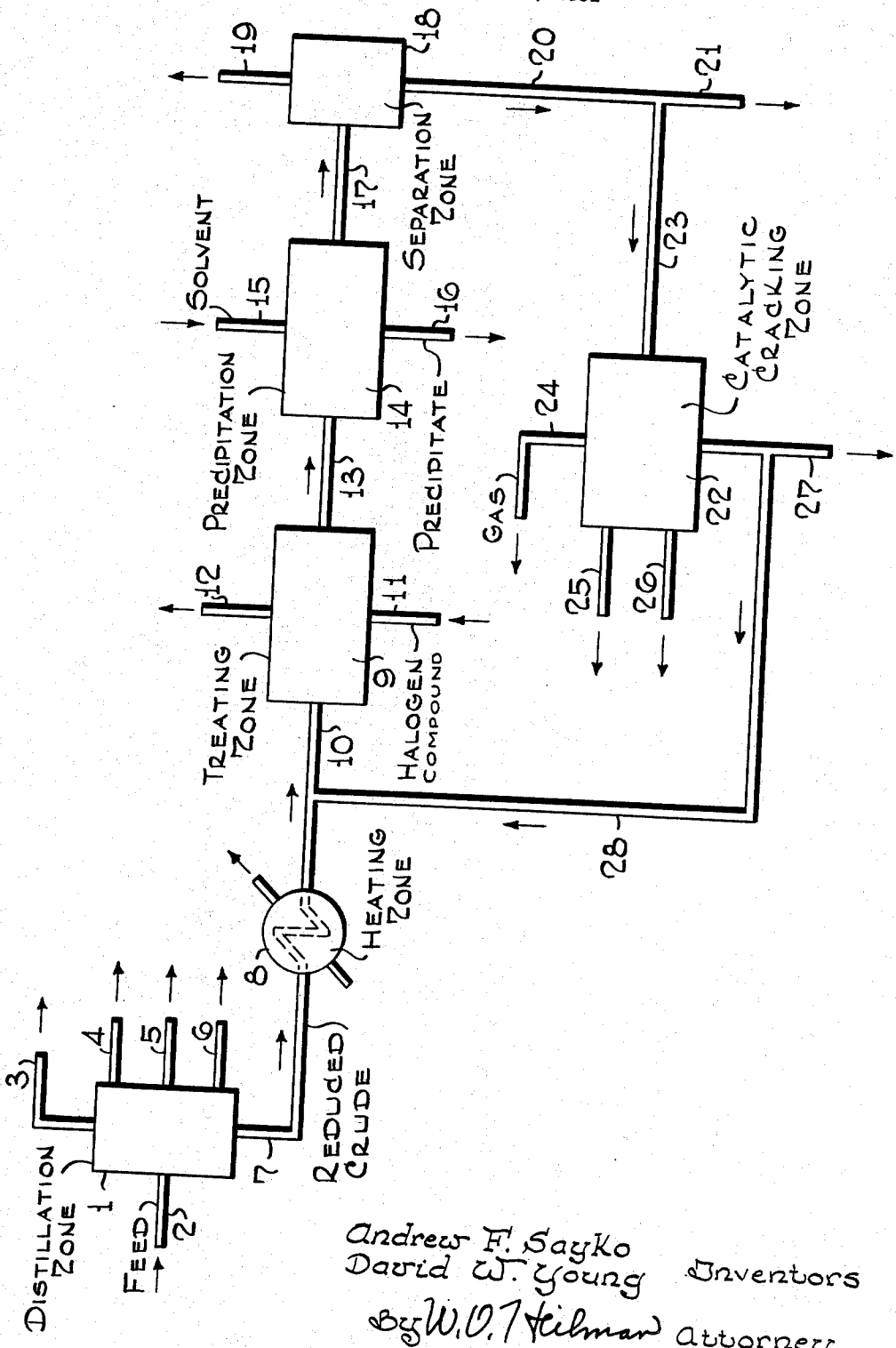
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PROCESS FOR REMOVAL OF COMPLEX HIGH MOLECULAR WEIGHT AROMATIC CONSTITUENTS FROM HIGH BOILING OILS

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PROCESS FOR REMOVAL OF COMPLEX HIGH MOLECULAR WEIGHT AROMATIC CONSTITUENTS FROM HIGH BOILING OILS

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The present invention is concerned with an improved process for the removal of high molecular weight and highly aromatic constituents from petroleum oils, particularly from petroleum oils remaining after distillation of volatile components. The invention is more particularly concerned with an improved process for the preparation of high quality heating oils and for the preparation of satisfactory feed stocks for a catalytic cracking operation. In accordance with the present invention, undesirable high boiling highly aromatic constituents are removed from petroleum oils, particularly high boiling petroleum oils by an operation which comprises treating these oils with a halogen compound followed by the precipitation of these constituents with a solvent, preferably with a light hydrocarbon solvent.

It is well known in the art to treat mineral oils with various solvents in order to precipitate undesirable constituents from these oils. For example, it is known to employ light hydrocarbon solvents, as for example, hydrocarbons such as propane and butane in order to remove undesirable constituents, as for example, asphaltic constituents therefrom. In these operations various temperatures and pressures are employed, as well as, various solvent to oil ratios. It is also known in the art to use various processes for the preparation of high quality heating oils by using various operations for the removal of gum and ash-forming constituents therefrom. Other processes have been directed toward the preparation of satisfactory high boiling feed stocks for a catalytic cracking operation. In a catalytic cracking operation, the removal of high molecular weight and highly aromatic material from feed stocks is desirable since the use of feed stocks, as for example reduced crudes, containing these undesirable constituents is prohibitive due to the excessive formation of carbon and ash.

It has now been discovered that undesirable high molecular weight and highly aromatic constituents may be more efficiently removed from feed stocks boiling in their reduced crude boiling range, providing the crude is first treated with a halogen compound preferably at elevated temperatures followed by contacting the same with a solvent, as for example, a light hydrocarbon solvent containing from about 3 to 8 carbon atoms in the molecule. The process of the present invention may be readily understood by reference to the drawing illustrating one embodiment of the same.

Referring specifically to the drawing, a feed

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oil, as for example, a West Texas crude, is introduced into distillation zone 1 by means of feed line 2. Temperature and pressure conditions are adjusted in zone 1 to secure the desired fractionation of the crude oil. Light hydrocarbon gases are removed overhead by means of line 3; a lower boiling hydrocarbon fraction is removed by means of line 4, a higher boiling hydrocarbon fraction is removed by means of line 5, and a somewhat higher boiling fraction is removed by means of line 6. A fraction boiling in the reduced crude boiling range, as for example, in the range above about 600° to 700° F., preferably boiling in the range above 850° F., is segregated as a bottoms fraction by means of line 7. It is to be understood that zone 1 may comprise any suitable number and arrangement of distillation zones or stages.

In accordance with the present invention, the high boiling oil is raised to an elevated temperature in heating zone 8 and passed to treating zone 9 by means of line 10 wherein it is contacted with a halogen compound introduced into zone 9 by means of line 11. Evolved gases are removed from zone 9 by means of line 12. It is to be understood that treating zone 9 likewise may comprise any suitable number and arrangement of stages.

The treated oil is withdrawn from zone 9 by means of line 13 and introduced into solvent or precipitation zone 14. The oil is contacted in zone 14 with a suitable precipitation solvent which is introduced by means of line 15. Temperature and pressure conditions as well as solvent to oil ratios in zone 14 are adjusted to secure the desired precipitation of the high molecular weight and highly aromatic material from the oil. The precipitate comprising these constituents is removed from zone 14 by means of line 16 and further handled and refined as desired. Precipitation zone 14 may comprise any suitable number and arrangement of stages.

The treated oil free of undesirable high molecular weight highly aromatic type constituents is removed from zone 14 by means of line 17 and introduced into a solvent separation zone 18 which may comprise a distillation zone. The solvent is removed by means of line 19 while the treated oil free of solvent and undesirable constituents is removed by means of line 20. This oil may be removed from the system by means of line 21 and used as a heating oil or as a feed stock for various other processes which require that the oil be free or substantially free of high

molecular weight highly aromatic type constituents.

However, a preferred adaptation of the invention is to combine the foregoing with a catalytic cracking operation. As pointed out heretofore, the use of reduced crudes in a catalytic cracking operation has presented problems due to the fact that it has not been possible heretofore to remove high molecular weight highly aromatic constituents from these high boiling reduced crudes to a satisfactory extent. The presence of these constituents in a feed oil in a catalytic cracking operation causes excessive formation of carbon on the catalyst, thus substantially decreasing the activity of the catalyst. Therefore, in accordance with a preferred adaptation of the present invention, the treated oil removed by means of line 20 is introduced into a catalytic cracking zone 22 by means of line 23.

Temperature and pressure conditions in cracking zone 22 are adjusted so as to secure the desired conversion of the feed oil. Constituents boiling in the vapor phase are removed by means of line 24; constituents boiling in the motor fuel boiling range are removed by means of line 25, while higher boiling constituents are removed by means of line 26. A high boiling oil, as for example, a cycle oil is removed by means of line 27 and disposed of as desired. In accordance with a preferred adaptation of the present invention, at least a portion of this oil is recycled by means of line 28 to the halogen compound treating zone.

The invention is broadly concerned with the removal of high molecular weight and highly aromatic materials from petroleum oils, particularly from petroleum oils boiling in the reduced crude boiling range. Petroleum oils treated in accordance with the present invention are particularly adapted as feed stocks for a catalytic cracking reaction. Although the invention may be adapted for the treatment of mineral oils boiling over wide ranges as pointed out above, it is particularly adapted for the treatment of oils boiling above about 700° F., preferably boiling above about 860° F.

Various halogenated compounds may be employed, as for example,

CH_2Cl_2, $CHCl_3$, CH_3CCl_2H, $CH_3CH_2CCl_3$, $CHCl{=}CCl_2$, $CCl_2{=}CCl_2$, CH_2ClCH_2Cl, $CH_2ClCHCl_2$, $CHCl_2CCl_3$, CCl_3CCl_3, $CH_3CHClCH_2Cl$

Mixtures of compounds, as for example, CCl_4 and $ClCH_2OC_2H_5$ may also be used. Particularly desirable treating agents comprise carbon tetrachloride and tetrachloroethane.

Pressures may vary from atmospheric to 1000 p. s. i. g., while temperatures are in the range from about 300° F. to 600° F. A preferred temperature range is from about 350° F. to 400° F. The time of treatment may likewise vary appreciably depending upon the feed stock and upon the particular halogen treating agent utilized. It is preferred that the time of treatment be in the range of about 120 to 180 minutes.

The amount of halogen compound employed will depend upon other operating variables, as for example, temperature, pressure and the particular halogen compound employed. Usually the amount employed is in the range from ½ to 10% by weight and a preferred amount is in the range from about 3 to 5% by weight, based upon the feed oil being treated.

The particular precipitating solvent or solvent mixture employed in the precipitation zone may

be selected from a wide class of light hydrocarbon and low boiling oxygenated compounds, as for example, various ketones and the like. Desirable solvents comprise paraffinic hydrocarbons having from about 3 to 8 carbon atoms in the molecule, while the preferred solvents have 3 to 4 carbon atoms in the molecule. Temperatures utilized are in the range from about 50° F. to 150° F., while pressures vary from atmospheric to 1000 p. s. i. g. The amount of solvent employed is usually in the range from about 1 to 5 volumes of solvent or solvent mixture per volume of oil being treated.

As discussed above, the invention is particularly concerned with an improved operation which comprises the treatment of a reduced crude by contacting it with a halogen compound, precipitating a residue and utilizing the treated stock to secure an improved catalytic cracking operation. It is well known in the art to produce cracked naphthas by a fluidized solids catalytic operation wherein the cracked product comprises constituents boiling in the motor fuel boiling range, as for example, below about 430° F. The cracked product also comprises normally gaseous constituents, as for example, those containing three carbon atoms and less in the molecule. The fluidized solids technique for processing feed fractions, as for example, gas oils, heavy residuums and other feed stocks for the production of hydrocarbon fractions boiling in the motor fuel boiling range is a conventional one. One system of a fluidized solids technique comprises a reaction zone and a regeneration zone, employed in conjunction with a fractionation zone. The reactor and the catalyst regenerator are arranged at approximately an even level. The operation of the reaction zone and the regeneration zone is conventional, which preferably is as follows:

An overflow pan is provided in the regeneration zone at the desired catalyst level. The catalyst overflows into a withdrawal line which preferably has the form of a U-shaped seal leg connecting the regeneration zone with the reaction zone. The feed stream introduced is usually preheated to a temperature in the range from about 500° to 650° F. in exchangers in heat exchange with regenerator flue gases which are removed overhead from the regeneration zone, or with cracked products. The heated feed stream is withdrawn from the exchangers and introduced into the reactor. The seal leg is usually sufficiently below the point of feed oil injection to prevent oil vapors from backing into the regenerator in case of normal surges. Since there is no restriction in the overflow line from the regenerator, satisfactory catalyst flow will occur as long as the catalyst level in the reactor is slightly below the catalyst level in the regenerator when vessels are carried at about the same pressure. Spent catalyst from the reactor flows through a second U-shaped seal leg from the bottom of the reactor into the bottom of the regenerator. The rate of catalyst flow is controlled by injecting some of the air into catalyst transfer line to the regenerator.

The pressure in the regenerator may be controlled at the desired level by a throttle valve in the overhead line from the regenerator. Thus, the pressure in the regenerator may be controlled at any desired level by a throttle valve which may be operated, if desired, by a differential pressure controller. If the pressure differential between the two vessels is maintained at a minimum, the seal legs will prevent gases from passing from one

vessel into the other in the event that the catalyst flow in the legs should cease.

The reactor and the regenerator may be designed for high velocity operation involving linear superficial gas velocities of from about 2.5 to 4 feet per second. However, the superficial velocity of the upflowing gases may vary from about 1–5 and higher. Catalyst losses are minimized and substantially prevented in the reactor by the use of multiple stages of cyclone separators. The regeneration zone is provided with cyclone separators. These cyclone separators are usually from 2 to 3 and more stages.

Distributing grids may be employed in the reaction and regeneration zones. Operating temperatures and pressures may vary appreciably depending upon the feed stocks being processed and upon the products desired. Operating temperatures are, for example, in the range from about 800° to 1000° F., preferably about 850°–950° F., in the reaction zone. Elevated pressures may be employed, but in general pressures below 100 lbs. per sq. in. gauge are utilized. Pressures generally in the range from 1 to 30 lbs. per sq. in. gauge are preferred. A catalyst holdup corresponding to a space velocity of 1 to 20 weights per hour of feed per weight of catalyst is utilized. A preferred ratio is 2 to 4. Catalyst to oil ratios of about 3 to 10, preferably about 6 to 8 by weight are used.

The catalytic materials used in the fluidized catalyst cracking operation, in accordance with the present invention, are conventional cracking catalysts. These catalysts are oxides of metals of groups II, III, IV and V of the periodic table. A preferred catalyst comprises silica-alumina wherein the weight per cent of the alumina is in the range from about 5 to 20%. Another preferred catalyst comprises silica-magnesium where the weight per cent of the magnesia is about 5% to 20%. These catalysts may also contain a third constituent, as for example, ThO_2, WO_3, MoO, BeO, Bi_2O_3, CdO, UO_3, B_2O_3, SnO_2, Fe_2O_3, V_2O_5, MnO, Cr_2O_3, CaO, Tl_2O_3, MgO and Ce_2O_3 present in the concentration from 0.05% to 0.5%. The size of the catalyst particles is usually below about 200 microns. Usually at least 50% of the catalyst has a micron size in the range from about 20–80. Under these conditions with the superficial velocities as given, a fluidized bed is maintained wherein the lower section of the reactor, a dense catalyst phase exists while in the upper area of the reactor a dispersed phase exists.

The above described operation as pointed out, has not been entirely satisfactory for cracking heavy oils such as a reduced crude due to excessive formation of carbon on the catalyst. However, by combining the halogen treating stage with the precipitation stage and the catalytic cracking stage, an improved operation results when using feed stocks of this character. The process of the present invention may be further understood by the following examples, further illustrating the same.

Example I

In one operation a West Texas crude oil was distilled to secure a residuum which comprises about 16% of the original crude. This residuum was treated with normal heptane for two hours at a reflux temperature using 5 volumes of normal heptane per volume of residuum.

The precipitate segregated was about 3% of the oil contacted.

Example II

In another operation the identical feed oil was treated as described. The precipitate obtained was 3.6% based upon the oil contacted with the normal heptane. The precipitate and raffinate had the following inspections:

Precipitate:		
Carbon		83.31
Hydrogen		7.96
Hydrogen-carbon atomic ratio		1.14
Yield	wt. per cent	3.6
Raffinate		
Carbon		85.48
Hydrogen		11.35
Hydrogen-carbon atomic ratio		1.60
Ash (at 800° C.)	per cent	.02

Example III

In a third operation the West Texas residuum was contacted with 5% by weight of carbon tetrachloride prior to contacting with normal heptane. The oil was contacted under reflux with carbon tetrachloride at a temperature of 350° to 400° F. for a time period of 140 minutes. The reaction was discontinued after no further hydrogen chloride gas was evolved. The oil was then contacted with normal heptane as described in Example I. The precipitate secured was 8.5% by weight. The physical properties of the precipitate were identical as well as the atomic hydrogen to carbon ratio with the precipitate secured in Example I. The precipitate and the raffinate had the following inspections:

Precipitate:		
Carbon		83.14
Hydrogen		8.38
Chlorine		1.13
Hydrogen-carbon atomic ratio		1.21
Yield	wt. per cent	8.5
Raffinate		
Carbon		85.43
Hydrogen		11.55
Hydrogen-carbon atomic ratio		1.62

Example IV

A 16% West Texas atmospheric residuum (200 grams) was treated with 10 grams of tetrachloroethane as described with respect to Example III. The formation of hydrogen chloride was noted at 380° F. Vigorous evolution of hydrogen chloride was obtained at 405° F. The reaction was completed after 2½ hours with a maximum temperature of 450° F. The resultant residuum when treated with 5 volumes of normal heptane gave a yield of 7.3 weight percent of asphaltic precipitate. The analysis was as follows:

	Per cent
Carbon	85.11
Hydrogen	8.60
Hydrogen-carbon ratio	1.20

The tetrachloroethane treated residuum gives somewhat lower yields of asphalt, but still appreciably more than the untreated residuum. There is only a slight difference in aromaticity and paraffinicity of the products from Example III and tetrachloroethane treatment as indicated by hydrogen-carbon atomic ratios.

The precipitate in Example III contains increased amounts of highly aromatic asphaltic materials not removable by the technique of Example II. The presence of 1.13 wt. percent chlorine in the asphalt results in increased melt-

ing point and ductility, as well as in decreased penetration.

The raffinate from Example III having a slightly higher hydrogen-carbon atomic ratio is more highly paraffinic. This results in an improved cracking feed stock as compared to the raffinate of Example II.

While the invention has been described with respect to an improved catalytic cracking operation, it is to be understood that in its broader aspects the halogen treatment increases the yield and quality of asphalts obtained by the deasphalting process utilizing as solvents propane or butane. In the deasphalting process of the present invention the quantities of solvent necessary to produce a definite asphalt yield are decreased.

What is claimed is:

1. Improved process for the removal of highly aromatic constituents from a feed oil containing the same which comprises treating said feed oil in an initial stage at a temperature in the range from about 300° F. to 600° F. with a treating agent consisting of a halogen compound selected from the class consisting of carbon tetrachloride and tetrachloroethane, then contacting said oil in a secondary stage with a precipitating light hydrocarbon solvent containing from about 3 to 8 carbon atoms in the molecule.

2. Process as defined by claim 1 wherein said feed oil boils in the range above about 700° F.

3. Process as defined by claim 1 wherein said halogen compound comprises carbon tetrachloride.

4. Improved process for the production of hydrocarbon constituents boiling in the motor fuel boiling range from a feed oil boiling above about 700° F. which comprises contacting said feed oil in an initial stage at a temperature in the range from about 300° F. to 600° F. with a treating agent consisting of a halogen compound selected from the class consisting of carbon tetrachloride and tetrachloroethane, removing the oil and contacting the same in a secondary stage with a precipitating light hydrocarbon solvent having from about 3 to 8 carbon atoms in the molecule, separating the residue from the treated oil and then contacting said oil with a suitable fluidized cracking catalyst at elevated temperatures and pressures adapted to crack the oil and produce hydrocarbon constituents boiling in the motor fuel boiling range.

5. Process as defined by claim 4 wherein the feed oil is an oil which boils above about 860° F.

6. Process as defined by claim 4 wherein the temperature utilized in said cracking zone is above about 900° F. and wherein the pressure is below about 100 lbs. per square inch gauge.

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