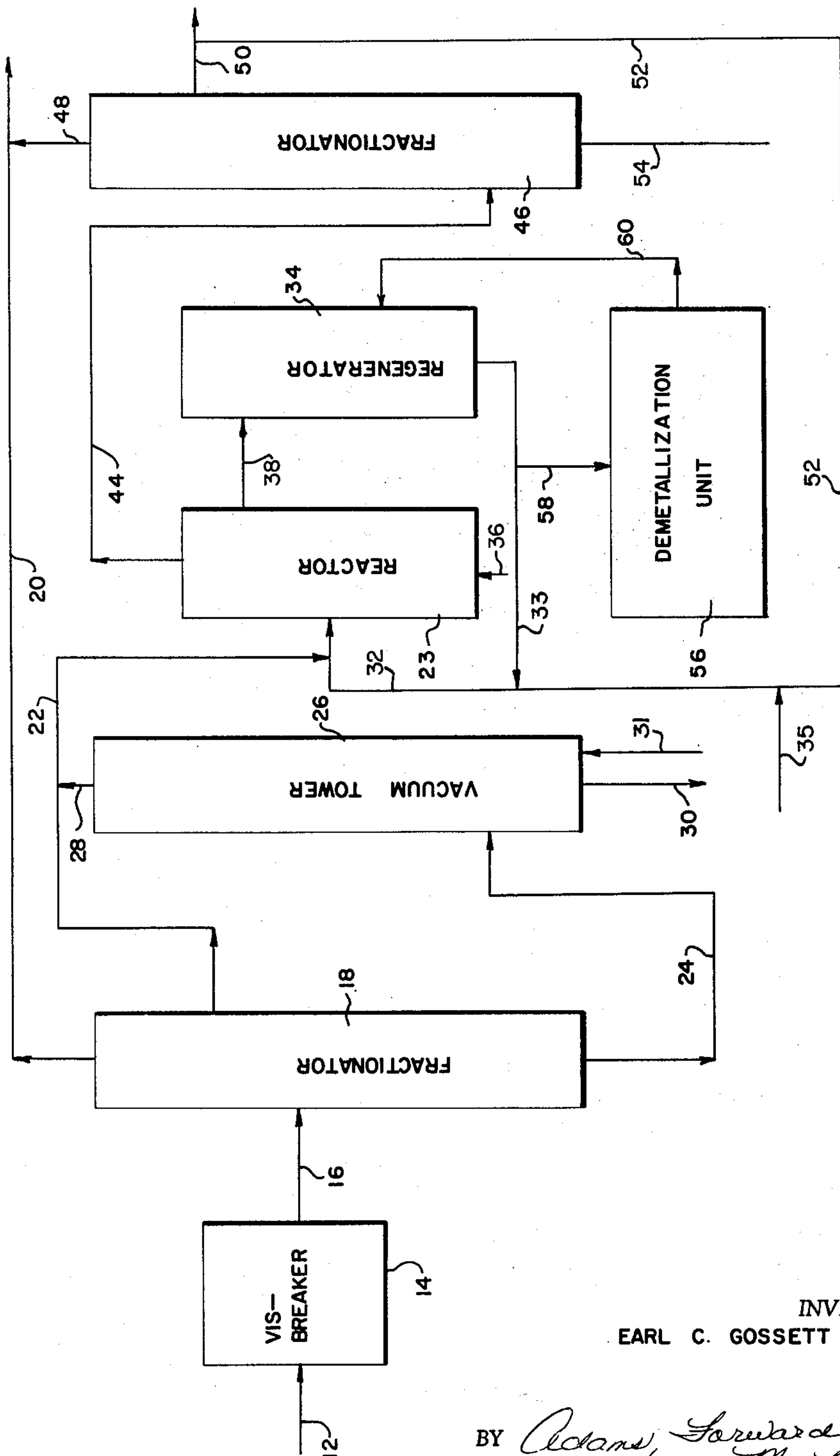


Aug. 25, 1964

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CONTAINING METALLIC IMPURITIES
Filed Feb. 9, 1961

3,146,188



INVENTOR
EARL C. GOSSETT

BY *Adams, Forward & McLean*
ATTORNEYS

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PROCESS FOR CRACKING A RESIDUAL OIL CONTAINING METALLIC IMPURITIES

Earl C. Gossett, South Holland, Ill., assignor, by mesne assignments, to Sinclair Research, Inc., New York, N.Y., a corporation of Delaware

Filed Feb. 9, 1961, Ser. No. 88,150

15 Claims. (Cl. 208—73)

This invention relates to an improved process for the treatment of petroleum oils for the production of motor fuels or motor fuel components. More particularly, this invention relates to the treatment of a petroleum crude oil or crude oil fraction, particularly a heavy residuum asphaltic fraction such as an asphaltic long residuum, by a combination of operations wherein there is produced a feedstock particularly suitable for use in a catalytic cracking operation for the production of gasoline, motor fuels and the like. Principally, this invention pertains to a process adapted for the production and catalytic cracking of distillates of the character of gas oils to obtain gasoline.

The behavior of a hydrocarbon feedstock in a cracking reaction depends upon various factors including its boiling point, carbon-forming tendencies, content of catalyst contaminating metals, etc., and these characteristics may affect the operation to an extent making a given feedstock uneconomical to employ. Until relatively recently, the gas oil distillate fraction employed as a catalytic cracking feedstock was a fraction boiling primarily in the relatively low range of about 500° to 900° F. However, in order to secure greater yields of cracked products and to reduce the portion of the petroleum oil constituting the residual portion higher boiling than gas oil, there has been a great deal of incentive for extending catalytic cracking to higher boiling feedstocks. Toward this end, the end point of the gas oil fraction subjected to catalytic cracking has in some cases risen to greater than about 900° F. Difficulties, such as the presence of metal contaminants, have been encountered in attempting to crack gas oils of this character including a substantial portion boiling above about 900° F. These metal contaminants include nickel and vanadium which are particularly deleterious. High boiling fractions for catalytic cracking have also been produced by solvent deasphalting, and deasphalted oils thus produced are also frequently very high in such metal contaminants.

The metal compounds are inherently and unavoidably carried over into the high boiling gas oils when including products boiling above about 900° F., because of entrainment and volatility of metal compounds in high temperature fractionation and because of the solubility of metal compounds in deasphalted oil produced from deasphalting higher boiling fractions.

These metals affect fluid catalytic cracking operations by increasing the hydrogen content of the gases produced. There is also a significant increase in coke production at a given conversion level and a corresponding decrease in yield of liquid products. The adverse economic effects of these factors may be extremely high as a result of loss in unit capacity, decrease in liquid yield and increased catalyst replacement rates required to minimize the effect of the buildup of active metal contaminants on the catalyst.

Gas oils is a broad general term that covers a variety of stocks, for instance, those having an initial boiling point of at least about 400° F. and an end boiling point of at least about 600° F., and boiling over a range of at least about 100° F. The portion of a petroleum crude oil which is not distilled is considered residual stock. The exact boiling range of gas oil, therefore, will be determined by the initial boiling point and the temperature at which distillation is cut off, the end point.

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In practice, petroleum distillations have been made under vacuum to recover gas oils boiling up to temperatures as high as about 1100–1200° F. Accordingly, in the broad sense, a gas oil is a petroleum fraction which boils essentially between two temperatures that establish a range falling within from about 400° F. to about 1100–1200° F. Thus, a gas oil could boil over the entire range 400–1200° F., or it could boil over a narrower range, e.g. 500–900° F. The gas oils can be roughly classified by overlapping boiling ranges. Thus, a light gas oil boils between about 400° F. and about 600–650° F. A medium gas oil distills between about 600–650° F. and about 700–750° F. A heavy gas oil will boil between about 600–650° F. and about 800–900° F. A gas oil boiling between about 800–850° F. and about 1100–1200° F. is sometimes designated as a vacuum gas oil. It must be understood, however, that a gas oil can overlap the foregoing ranges. It can even span several ranges, i.e., include light and medium gas oils.

Since the distillates or gas oil fractions boiling higher than gasoline are converted by catalytic cracking to gasoline of high-octane number, it is a general practice, where catalytic cracking capacity is available, to attempt to pre-treat heavier petroleum oil materials to obtain a maximum proportion of distillate gas oil product to be utilized as catalytic cracking feedstock. For example, "topped crudes" and short residues, as well as certain heavy crudes are often subjected to a thermal treatment known as "visbreaking" to effect a viscosity reduction.

Visbreaking of the residuum serves to crack or otherwise alter high molecular weight, high-boiling constituents of the reduced crude into lower molecular weight, lower boiling, constituents. The visbreaking operation tends to produce lower boiling and more highly aromatic constituents which are generally more refractory in the subsequent catalytic cracking operation than the paraffinic hydrocarbons which are also produced. In spite of the amount of visbreaking, substantial amounts of the metal contaminants in the feedstock e.g., nickel and vanadium, are generally carried through to the visbreaker effluent. Fractionation of the visbreaker effluent, however, can remove for use as a gas oil, a distillate containing a minor, frequently an insignificant, amount of metal poisons. As pointed out above, the metal poisons tend to concentrate in the materials boiling above about 900° F., which frequently is the end-point of gas oils from conventional distillations conducted under atmospheric pressure. The present invention, however, utilizes a heavy gas oil fraction boiling in the 900° F. to 1200° F. range as at least part of a catalytic cracking feedstock. The cracking process of this invention includes procedures for demetallizing the cracking catalyst which is poisoned by the metals contained in the cracking feed, that is, procedures for removing the metal poisons from the cracking catalyst.

In this invention, heavy asphaltic petroleum fractions, particularly asphaltic fractions which contain a substantial amount of metal contaminants such as nickel and vanadium are vis-broken and fractionated to provide a gas oil boiling essentially in the range of about 400–1200° F., with at least a portion boiling above about 900° F. This gas oil is sent to catalytic cracking to produce gasoline and the cracking catalyst is continuously demetallized. This process, by recovering and using heavy gas oil from the vis-breaker effluent, is able to produce more gasoline and other desirable products from a given amount of feed to the vis-breaker without encountering severe catalyst losses.

The mineral hydrocarbon oils charged to the vis-breaking operation are asphaltic residual stocks which are exemplified by reduced crude, atmospheric or vacuum distillation bottoms, etc., and will, in general, contain greater

amounts of the poisoning metals than distillate oils. For instance, the residuals frequently contain more than about 25 p.p.m. nickel and 50 p.p.m. vanadium. The maximum amount of metals in the residuals can vary widely; but most often the maximum amount of these poisoning metals in the residual stock will not exceed about 500 p.p.m. nickel and/or about 1000 p.p.m. vanadium. Therefore, any fraction, regardless of its initial boiling point, which includes all the heavy bottoms such as tars, asphalts, etc., is a residual fraction. Accordingly, the residual stock used as a feed to the vis-breaking operation of this invention can be the portion of the crude boiling above about 1100–1200° F., or it can be made up of a gas oil fraction plus the portion boiling above about 1100–1200° F. For instance, a topped crude, that is, the entire portion of the crude remaining after the light ends, the portion boiling up to about 400° F., have been removed by distillation, may be used as a feed to the process of this invention. The residual may be, for example, a Mid-Continent vacuum asphalt having an initial boiling point greater than about 550° F. usually an initial boiling point greater than about 650° F. and amounting for instance to about 10–60% by volume of the original crude petroleum.

The vis-breaking operation subjects this feedstock to elevated conditions of temperature and pressure to produce some thermal cracking of feedstock components and some lowering of the feedstock viscosity. Vis-breaking conditions may include a temperature in the range of about 800–1000° F. and a pressure in the range of about 50–500 p.s.i.g. The feed is held under these temperature and pressure conditions for a period sufficient to reduce the viscosity of the oil. The vis-breaking performed in this invention is generally more severe in its cracking effects than conventional vis-breaking runs. Vis-breaking conditions are generally regulated to give a vis-breaker effluent comprising about 25 to 50 percent by volume, based on asphaltic feed, of gas oil components boiling from about 400 to 1100–1200° F. About 40 to 85%, preferably about 50 to 75% of this gas oil component boils primarily in the range of about 900° F. to 1200° F. The vis-breaker effluent also comprises gas and gasoline components having an end boiling point of up to about 430° F. in the amount of perhaps 5 to 15 volume percent of the feed to the visbreaker. Also contained in the vis-breaker effluent are constituents boiling higher than about 1200° F. The gas oil fraction, boiling primarily in the range of about 400 to 1100–1200° F. is separated from the other components and sent to the catalytic cracking.

Separation is by distillation which may be conducted in a single stage or a plurality of stages. A single separation at a subatmospheric pressure, as by vacuum flashing, can isolate the gas oil fraction. Alternatively, a preliminary distillation at atmospheric pressure may isolate a 400° F. to 900° F. boiling point gas oil fraction. This fraction may comprise about 15 to 35% by volume of the visbreaker feed. The residue from this preliminary distillation usually has a gravity in the range of about 3–15 API and a Conradson carbon residue in the range of about 10–35%, more or less. It may be sent to a reduced pressure distillation to vaporize the heavy gas oil fraction boiling primarily between about 400° F. and 1200° F. This second distillation may employ vacuum or steam stripping, and the fraction so distilled may amount to about 40 to 45% by volume of the charge to the vacuum still. About 50 to 90% by volume of this fraction is material boiling primarily in the range of about 900° F. to 1200° F. and preferably about 60 to 85% by volume. The gas oil fractions are combined and sent to catalytic cracking. The bottoms from a single stage fractionation or from the vacuum tower of a two-stage system generally has an API gravity of from about 0 to 6, a Conradson carbon residue in the range of about 26–33%, and a penetration at 77° F. of about 1–40. It is withdrawn from the system, and may be blended with other hydro-

carbon components to meet specifications for residual fuel oils.

Visbreaking itself does not significantly reduce the metal poisons content of the petroleum; however, the metal poisons appear in the visbreaker effluent bottoms in greater proportions than in the distillate fractions. The gas oil from the visbreaker effluent contains at least about 1 p.p.m. of metal poison and often contains vanadium in amounts of at least about 1.5 p.p.m. and in addition nickel is frequently found along with vanadium and in amounts of at least about 0.8 p.p.m. nickel, but usually less than about 25 p.p.m. nickel and/or 50 p.p.m. vanadium, reported as their oxides. The relatively high metal content of the vis-breaker effluent gas oil would under normal circumstances make it an undesirable catalytic cracking feedstock because of the high catalyst make up rates which would be required to maintain catalytic activity, and selectivity. Even dilution of this gas oil with gas oils relatively free of metals would still usually produce poisoning of the cracking catalyst, although at a lower rate. In the practice of this invention, vis-breaker effluent gas oils are sent to a catalytic cracker, preferably blended with gas oils from extraneous sources, and the cracking catalyst is demetallized to avoid poisoning effects. Poisoning metals are removed from the catalyst by the use of a demetallization unit associated with the cracking unit.

The hydrocarbon feedstock for the catalytic cracking operation can be entirely the visbreaker effluent gas oil boiling primarily above the gasoline range or may include other gas oil components, for example, from extraneous sources. The cracker feed generally comprises at least about 5% of gas oils derived from the asphalt visbreaker feedstock, usually about 10 to 50%. The remaining portion of cracker feed may comprise cracking feeds of more or less conventional types, that is, virgin gas oil fractions, recycle gas oils from this cracker or other catalytic crackers, etc. The proportion of visbreaker gas oil included in the cracker feed will be adjusted to provide a feed containing more than about 0.3 p.p.m. nickel and/or 0.5 p.p.m. vanadium in order to justify the provisions made in this invention for cracking catalyst demetallization and preferably the total feed to cracking will contain more than about 1 p.p.m. nickel and about 2 p.p.m. vanadium, but less than about 10 p.p.m. nickel and/or 20 p.p.m. vanadium. At least about 1 p.p.m. nickel and/or about 1 or 2 p.p.m. vanadium is contributed to the cracker feed by the visbreaker effluent.

The feed to the cracking zone is vaporized and catalytically treated under more or less conventional fluid catalytic cracking conditions. These conditions generally include a temperature of about 750 to 1000° F., preferably about 850 to 975° F. and a pressure between atmospheric and 100 p.s.i.g., preferably about 5 and 25 p.s.i.g., at a weight hourly space velocity from about 0.1 to 10 to obtain about a 40–70 volume percent, preferably about 50 to 60%, conversion of the 400° F.+ gas oil to gasoline and other desired lighter components. The products of the cracking are conducted to a fractionator. In the fractionation, which may be conducted under partial vacuum, the lower boiling gasoline constituents of the cracker effluents having an approximate 375–430° F. end point are vaporized and removed from the system and may be used as gasoline blending components or other products. The gas oil cycle stock, usually boiling between about 400° F. and about 850–950° F. may be sent back to the catalytic cracking zone along with the poisoned visbreaker effluent fractions, while the bottoms may be sent back to the visbreaker or discarded from the system. In the cracking operation a batch, semi-continuous or continuous system is used but most often it is the latter.

The cracking catalyst is of the solid refractory metal oxide type known in the art, for instance silica, alumina, magnesia, titania, etc., or their mixtures. Of most im-

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portance are the synthetic gel-containing catalysts such as the synthetic and the semi-synthetic, i.e. synthetic gel supported on a carrier such as natural clay, cracking catalysts. The cracking catalysts which have received the widest acceptance today are usually predominantly silica, that is silica-based, and may contain solid acidic oxide promoters, e.g. alumina, magnesia, etc., with the promoters usually being less than about 35% of the catalyst, preferably about 5 to 25%. These compositions are calcined to a state of very slight hydration. The cracking catalyst can be of macrosized, for instance, bead form, or finely divided form, and employed as a fixed, moving or fluidized bed. In a highly preferred form of this invention finely divided (fluidized) catalyst, for instance, having particles predominantly in the 20 to 150 micron range, is disposed as a fluidized bed in the reaction zone to which the feed is charged continuously and is reacted essentially in the vapor phase.

Vaporous products are taken overhead and a portion of the catalyst is continuously withdrawn and passed to a regeneration zone where coke or carbon is burned from the catalyst in a fluidized bed by contact with a free oxygen-containing gas, before its return to the reaction zone.

The invention will be better understood by reference to the accompanying drawing which is a schematic representation of the processing system of this invention, but is not to be considered as limiting.

The residual feed is introduced via line 12 to vis-breaker 14. Within the vis-breaker the vacuum asphalt, for example, is subjected to elevated conditions of temperature and pressure and other conditions perhaps in a coil reactor, to lower the viscosity of the charge. Vis-broken product is introduced via line 16 into fractionator 18, where the vis-broken products are distilled. Gas and gasoline having an end boiling point of about 430° F., amounting perhaps to about 5 to 15 volume percent of the feed are removed from the system via line 20 and recovered. A gas oil fraction boiling in the range of about 400° to a maximum of about 900° F. is removed via line 22 to reactor 23 and a bottoms fraction boiling essentially higher than the end point of the distillate from the fractionator 18 is removed from this fractionator by line 24 to a second distillation stage, for example, the vacuum tower 26. The vaporized products from the vacuum flash tower 26, having boiling points up to about 1100° or 1200° F., pass overhead through lines 28 and 22 to the reactor 23. Vacuum tower bottoms may be removed from the system by line 30. If desired, steam or other stripping gas may be introduced into the vacuum tower 26, by way of line 31 to aid in vaporizing the heavy fractions therein.

The combined vaporized stream from fractionator 18 and vacuum tower 26 and also, perhaps, additional cracking feedstock from line 32 is intermixed with a finely divided active cracking catalyst from line 33 from the regenerator 34. The additional cracking feedstock may be recycle gas oil or may come from the external source 35. The gas oil feed from line 22 may be passed to reactor 23 at substantially the same temperature at which it is recovered from fractionator 18 and/or vacuum tower 26, or, if desired, the gas oil may be preheated to about 700–750° F. Diluents for the feed such as steam, other inert gases, and low end-point hydrocarbon vapors may also be passed to reactor 23 by line 36. The fluidized catalytic cracking system of this invention also comprises a regenerator 34. Catalyst transfer to the regenerator is effected through line 38 and catalyst is returned from the regenerator by line 33.

The products from reactor 23 are removed overhead through line 44 and introduced into product fractionator 46. This distillation zone may be operated to permit removal of gas and gasoline from the catalytically cracked products through line 48. Gas oil fractions of the catalytically cracked products may be removed from fractionator 46 through line 50 and may be recovered or

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recycled to the cracker by line 52. Heavy material is removed from the bottom of the fractionator 46 through line 54 for discard from the system.

As previously mentioned, the process of this invention employs procedures for controlling the level of poisoning metal on the catalyst by subjecting the catalyst to one or more demetallization techniques hereinafter described outside the catalytic cracking system. Apparatus for performing these techniques is represented by the demetallization unit 56 which is provided with catalyst line 58 by which a slip-stream of regenerated catalyst may be withdrawn from the line 33 and with the line 60 for return of the demetallized catalyst to the cracking system. Thus, the catalytic cracking to produce gasoline is combined with a procedure for reducing poisoning metals on the cracking catalyst to present a more attractive processing procedure. The vis-breaking operation and cracking catalyst demetallization enable heretofore marginal stocks to be used for the production of a superior motor fuel or motor fuel component.

Regeneration of a catalyst to remove carbon is a relatively quick procedure in most commercial catalytic conversion operations. For instance, in a typical fluidized cracking unit, the catalyst is contacted with a free oxygen-containing regenerating gas such as air at about 950–1200° F., more usually about 1000 to 1150° F. Combustion of coke from the catalyst is rapid and for reasons of economy only enough air is used to supply the needed oxygen. The free oxygen content of the effluent gases from the regenerator is often in the range of about 2 to 5%.

In the treatment to take poisoning metals from the cracking catalyst the amount of metal is removed which is necessary to keep the average metal content of the catalyst in the cracking system below the limit of the unit's tolerance for poison. The tolerance of the cracker for poison in turn determines to a large extent the amount of metals removed in the catalyst demetallization procedure. Where the catalyst contains a greater amount of poisoning metal, a particular treatment will remove a greater amount of metal; for example, if the cracker can tolerate an average of 100 p.p.m. Ni and the demetallization process can remove 50% of the nickel content of the catalyst, only 50 p.p.m. of nickel can be removed in a pass through the catalyst demetallization system. However, where the cracker can tolerate 500 p.p.m. of nickel, it is possible to remove 250 p.p.m. nickel from the catalyst with each pass through the demetallization system. It is advisable, therefore, to operate the cracking and demetallization procedures with a catalyst having a metals content near the limit of tolerance of the cracker for poisoning metals. This tolerance for poisoning metal oxide is seldom greater than about 5,000–10,000 p.p.m. Catalyst demetallization is not economically justified unless the catalyst contains at least about 50 p.p.m. nickel and/or 50 p.p.m. vanadium. Preferably the equilibrium metals level is allowed to exceed about 200 p.p.m. nickel and/or 500 p.p.m. vanadium so that total metals removal will be greater per pass through the demetallizer.

In the treatment to take poisoning metals from the cracking catalyst a large or small amount of metal can be removed as desired. The demetallization treatment generally removes about 10 to 90% of one or more poisoning metals from a catalyst portion which passes through the treatment. Advantageously a demetallization system is used which removes about 60 to 90% nickel and 20 to 40% vanadium from the treated portion of catalyst. Preferably at least 50% of the equilibrium nickel content and 15% of the equilibrium vanadium content is removed. The actual time or extent of treating depends on various factors, and is controlled by the operator according to the situation he faces, e.g. the extent of metals content in the feed, the level of conversion unit tolerance for poison, the sensitivity of the particular catalyst toward a particular phase of the demetallization procedure, etc. Also, the thoroughness of treatment of

any quantum of catalyst in commercial practice is balanced against the demetallization rate chosen; that is, the amount of catalyst, as compared to the total catalyst in the conversion system proper, which is subjected to the demetallization treatment per unit of time. A high rate of catalyst withdrawal from the conversion system and quick passage through a mild demetallization procedure may suffice as readily as a more intensive demetallization at a slower rate to keep the total of poisoning metal in the conversion reactor within the tolerance of the unit for poison. In a continuous operation of the commercial type a satisfactory treating rate may be about 5 to 50% of the total catalyst inventory in the system, per twenty-four hour day of operation although other treating rates may be used. With a continuously circulating catalyst stream, such as in the ordinary "fluid" system a slip-stream of catalyst, at the "equilibrium" level of poisoning metals may be removed intermittently or continuously from the regenerator standpipe of the cracking system. The catalyst is subjected to one or more of the demetallization procedures described hereinafter and then the catalyst, substantially reduced in contaminating metal content, is returned to the cracking system.

The demetallization of the catalyst will generally include one or more processing steps. Copending patent applications Serial Nos. 758,681, filed September 3, 1958; 763,833, and 763,834, filed September 29, 1958; 767,794, filed October 17, 1958; 842,618, filed September 28, 1959; 849,119, filed October 28, 1959; 19,313, filed April 1, 1960; 39,810, filed June 30, 1960; 47,598, filed August 4, 1960; 53,380, filed September 1, 1960; 53,623, filed September 2, 1960; 54,368; 54,405 and 54,532, filed September 7, 1960; 55,129; 55,160 and 55,184, filed September 12, 1960; 55,703, filed September 13, 1960; 55,838, filed September 14, 1960; 67,518, filed November 7, 1960; and 73,199, filed December 2, 1960; and 81,256 and 81,257, filed January 9, 1961; all of which are hereby incorporated by reference, describe procedures by which vanadium and other poisoning metals included in a solid oxide hydrocarbon conversion catalyst are removed by dissolving them from the catalyst or subjecting the catalyst, outside the hydrocarbon conversion system, to elevated temperature conditions which put the metal contaminants into the chloride, sulfate or other volatile, water-dispersible or more available form. A significant advantage of these processes lies in the fact that the overall metals removal operation, even if repeated, does not unduly deleteriously affect the activity, selectivity, bore structure and other desirable characteristics of the catalyst.

Treatment of the regenerated catalyst with molecular oxygen-containing gas is employed to improve the removal of vanadium from the poisoned catalyst. This treatment is described in copending application Serial No. 19,313, and is preferably performed at a temperature at least about 50° F. higher than the regeneration temperature, that is, the average temperature at which the major portion of carbon is removed from the catalyst. The temperature of treatment with molecular oxygen-containing gas will generally be in the range of about 1000 to 1800° F. but below a temperature where the catalyst undergoes any substantial deleterious change in its physical or chemical characteristics, preferably a temperature of about 1150 to 1350° or even as high as 1600° F. The duration of the oxygen treatment and the amount of vanadium prepared by the treatment for subsequent removal is dependent upon the temperature and the characteristics of the equipment used. If any significant amount of carbon is present in the catalyst at the start of this high-temperature treatment, the essential oxygen contact is that continued after carbon removal, which may vary from the short time necessary to produce an observable effect in the later treatment, say, a quarter of an hour, to a time just long enough not to damage the catalyst. In any event, after carbon

removal, the oxygen treatment of the essentially carbon-free catalyst is at least long enough to stabilize a substantial amount of vanadium in its highest valence state, as evidenced by a significant increase, say at least about 10%, preferably at least about 100%, in the vanadium removal in subsequent stages of the process. This increase is over and above that which would have been obtained by the other metals removal steps without the oxygen treatment. The maximum practical time of treatment will vary from about 4 to 24 hours, depending on the type of equipment used. The oxygen-containing gas used in the treatment contains molecular oxygen as the essential active ingredient and there is little significant consumption of oxygen in the treatment. The gas may be oxygen, or a mixture of oxygen with inert gas, such as air or oxygen-enriched air, containing at least about 1%, preferably at least about 10% O₂. The partial pressure of oxygen in the treating gas may range widely, for example, from about 0.1 to 30 atmospheres, but rarely will the total gas pressure exceed about 25 atmospheres.

The catalyst may pass directly from the oxygen treatment to a vanadium removal treatment especially where this is the only important contaminant, as may be the case when a feed is derived, for example, from Venezuelan crude. Such treatment may be a basic aqueous wash such as described in copending patent applications Serial No. 767,794, and Serial No. 39,810. Alternatively vanadium may be removed by a chlorination procedure as described in copending application Serial No. 849,199.

Vanadium may be removed from the catalyst after the high temperature treatment with molecular oxygen-containing gas by washing it with a basic aqueous solution. The pH is frequently greater than about 7.5 and preferably the solution contains ammonium ions which may be in the form of NH₄⁺ ions or organic-substituted NH₄⁺ ions such as methyl ammonium and quaternary hydrocarbon radical ammoniums. The amount of ammonium ion in the solution is sufficient to give the desired vanadium removal and will often be in the range of about 1 to 25 or more pounds per ton of catalyst treated. The temperature of the wash solution may vary within wide limits: room temperature or below, or higher. Temperatures above 215° F. require pressurized equipment, the cost of which does not appear to be justified. Very short contact times, for example, about a minute, are satisfactory, while the time of washing may last 2 to 5 hours or longer. After the ammonium wash the catalyst slurry can be filtered to give a cake which may be reslurried with water or rinsed in other ways, such as, for example, by a water wash on the filter, and the rinsing may be repeated, if desired, several times.

Alternatively, after the high temperature treatment with oxygen-containing gas, treatment of a metals contaminated catalyst with a chlorinating agent at a moderately elevated temperature up to about 1000° F. is of value in removing vanadium contaminants from the catalyst as volatile chlorides. This treatment is described in copending application Serial No. 849,199. The chlorination takes place at a temperature of at least about 300° F., preferably about 550 to 650° F. with optimum results usually being obtained near 600° F. The chlorinating agent is essentially anhydrous, that is, if changed to the liquid state no separate aqueous phase would be observed in the reagent.

The chlorinating reagent is a vapor which contains chlorine or sometimes HCl, preferably in combination with carbon or sulfur. Such reagents include molecular chlorine but preferably are mixtures of chlorine with, for example, a chlorine substituted light hydrocarbon, such as carbon tetrachloride, which may be used as such or formed in-situ by the use of, for example, a vaporous mixture of chlorine gas with low molecular weight hydrocarbons such as methane, n-pentane, etc. About 1-40 percent active chlorinating agent based on the weight of

the catalyst is generally used. The carbon or sulfur compound promoter is generally used in the amount of about 1-5 or 10 percent or more, preferably about 2-3 percent, based on the weight of the catalyst for good metals removal; however, even if less than this amount is used, a considerable improvement in metals conversion is obtained over that which is possible at the same temperature using chlorine alone. The chlorine and promoter may be supplied individually or as a mixture to a poisoned catalyst. Such a mixture may contain about 0.1 to 50 parts chlorine per part of promoter, preferably about 1-10 parts per part of promoter. A chlorinating gas comprising about 1-30 weight percent chlorine, based on the catalyst, together with one percent or more S_2Cl_2 gives good results. Preferably, such a gas provides 1-10 percent Cl_2 and about 1.5 percent S_2Cl_2 , based on the catalyst. A "saturated" mixture of CCl_4 and Cl_2 or HCl can be made by bubbling chlorine or hydrogen chloride gas at room temperature through a vessel containing CCl_4 ; such a mixture generally contains about 1 part CCl_4 /5-10 parts Cl_2 or HCl . Conveniently, a pressure of about 0-100 or more p.s.i.g. preferably about 0-15 p.s.i.g. may be maintained in chlorination. The chlorination may take about 5 to 120 minutes, more usually about 20 to 60 minutes, but shorter or longer reaction periods may be possible or needed, for instance, depending on the linear velocity of the chlorinating and purging vapors.

The demetallization procedure employed in this invention may be directed toward nickel removal from the catalyst, generally in conjunction with vanadium removal. Nickel removal may be accomplished by removing nickel compounds directly from the catalyst for example, by dissolving, and/or by converting the nickel compounds to volatile materials such as nickel carbonyl and/or materials soluble or dispersible in an aqueous medium, e.g. water or dilute acid. The water-dispersible form may be one which decomposes in water to produce water-soluble products. The removal procedure for the converted metal may be based on the form to which the metal is converted. The mechanism of the washing steps may be one of simultaneous conversion of nickel and/or vanadium to removable form and removal by the aqueous wash; however, this invention is not to be limited by such a theory.

Conversion of some of the metal poisons, especially nickel, to the sulfate or other water-dispersible form as described in copending application Serial No. 758,681 comprises subjecting the catalyst to a sulfating gas, that is SO_2 , SO_3 or a mixture of SO_2 and O_2 , at an elevated temperature. Sulfur oxide contact is usually performed at a temperature of about 500 to 1200° F. and frequently it is advantageous to include some free oxygen in the treating gas. Another procedure described in copending applications Serial Nos. 763,834, and 842,618 includes sulfiding the catalyst and performing an oxidation process, after which metal contaminants in water-dispersible form, preferably prior to an ammonium wash may be removed from the catalyst by an aqueous medium.

The sulfiding step can be performed by contacting the poisoned catalyst with elemental sulfur vapors, or more conveniently by contacting the poisoned catalyst with a volatile sulfide, such as H_2S , CS_2 or a mercaptan. The contact with the sulfur-containing vapor can be performed at an elevated temperature generally in the range of about 500 to 1500° F., preferably about 800 to 1300° F. Other treating conditions can include a sulfur-containing vapor partial pressure of about 0.1 to 30 atmospheres or more, preferably about 0.5 to 25 atmospheres. Hydrogen sulfide is the preferred sulfiding agent. Pressures below atmospheric can be obtained either by using a partial vacuum or by diluting the vapor with gas such as nitrogen or hydrogen. The time of contact may vary on the basis of the temperature and pressure chosen and other factors such as the amount of metal to be removed. The sulfiding may run for, say, up to about 20 hours or more depending on these conditions and the severity of the poisoning.

Temperatures of about 900 to 1200° F. and pressures approximating 1 atmosphere or less seem near optimum for sulfiding and this treatment often continues for at least 1 or 2 hours but the time, of course, can depend upon the manner of contacting the catalyst and sulfiding agent and the nature of the treating system, e.g. batch or continuous, as well as the rate of diffusion within the catalyst matrix. The sulfiding step performs the function not only of supplying a sulfur-containing metal compound which may be easily converted to a water-dispersible form but also appears to concentrate some metal poisons, especially nickel, at the surface of the catalyst particle.

Oxidation after sulfiding may be performed by a gaseous oxidizing agent to provide metal poisons in a dispersible form. Gaseous oxygen, or mixtures of gaseous oxygen with inert gases such as nitrogen, may be brought into contact with the sulfided catalyst at an oxygen partial pressure of about 0.2 atmosphere and upward, temperatures upward of room temperature and usually not above about 1300° F., and times dependent on temperature and oxygen partial pressure. Gaseous oxidation is best carried out near 900° F., about one atmosphere O_2 and at very brief contact times.

The metal sulfide may be rendered water-dispersible by a liquid aqueous oxidizing agent such as a dilute hydrogen peroxide or hypochlorous acid water solution, as described in copending application Serial No. 842,618. The inclusion in the liquid aqueous oxidizing solution of sulfuric acid or nitric acid has been found greatly to reduce the consumption of peroxide. In addition, the inclusion of nitric acid in the oxidizing solution provides for increased vanadium removal. Useful proportions of acid to peroxide to catalyst generally include about 2 to 25 pounds acid (on a 100% basis) to about 1 to 30 pounds or more H_2O_2 (also on a 100% basis) in a very dilute aqueous solution, to about one ton of catalyst. A 30% H_2O_2 solution in water seems to be an advantageous raw material for preparing the aqueous oxidizing solution. Sodium peroxide or potassium peroxide may be used in place of hydrogen peroxide and in such circumstances, extra sulfuric or nitric acid may be used.

Another highly advantageous oxidizing medium is an aerated dilute nitric acid solution in water. Such a solution may be provided by continuously bubbling air into a slurry of the catalyst in very dilute nitric acid. Other oxygen-containing gases may be substituted for air. Varying oxygen partial pressure in the range of about 0.2 to 1.0 atmosphere appears to have no effect in time required for oxidation, which is generally at least about 7 to 8 minutes. The oxidizing slurry may contain about 20% solids and provide about five pounds of nitric acid per ton of catalyst. Studies have shown a greater concentration of HNO_3 to be of no significant advantage. Other oxidizing agents, such as chromic acid where a small residual Cr_2O_3 content in the catalyst is not significant, and similar aqueous oxidizing solutions such as water solutions of manganates and permanganates, chlorites, chlorates and perchlorates, bromites, bromates and perbromates, iodites, iodates and periodates, are also useful. Bromine or iodine water, or aerated, ozonated or oxygenated water, with or without acid also will provide a dispersible form. The conditions of oxidation can be selected as desired. The temperature can conveniently range up to about 220° F. with temperatures of above about 150° F. being preferred. Temperatures above about 220° F. necessitate the use of superatmospheric pressures and no need for such has been found.

After conversion of nickel sulfide to a dispersible form, the catalyst is washed with an aqueous medium to remove the metal compound. This aqueous medium, for best removal of nickel, is generally somewhat acidic, and this condition may be brought about, at least initially, by the presence of an acid-acting salt or some entrained acidic oxidizing agent on the catalyst. The aqueous medium can contain extraneous ingredients in trace amounts, so

long as the medium is essentially water and the extraneous ingredients do not interfere with demetallization or adversely affect the properties of the catalyst. Ambient temperatures can be used in the wash but temperatures of about 150° F. to the boiling point of water are sometimes helpful. Pressures above atmospheric may be used but the results usually do not justify the additional equipment. Where an aqueous oxidizing solution is used, the solution may perform part or all of the metal compound removal simultaneously with the oxidation. In order to avoid undue solution of alumina from a chlorinated catalyst, contact time in this stage is preferably held to about 3 to 5 minutes which is sufficient for nickel removal. Also, since a slightly acidic solution is desirable for nickel removal, this wash preferably takes place before the ammonium wash.

Alternative to the removal of poisoning metals by procedures involving contact of the sulfided or sulfated catalyst with aqueous media, nickel poison may be removed through conversion of the nickel sulfide to the volatile nickel carbonyl by treatment with carbon monoxide, as described in copending application Serial No. 47,598. In such a procedure the catalyst is treated with hydrogen at an elevated temperature during which nickel contaminant is reduced to the elemental state, then treated, preferably under elevated pressure and at a lower temperature with carbon monoxide, during which nickel carbonyl is formed and flushed off the catalyst surface. Hydrogenation takes place at a temperature of about 800 to 1600° F., at a pressure from atmospheric or less up to about 1000 p.s.i.g. with a vapor containing 10 to 100% hydrogen. Preferred conditions are a pressure up to about 15 p.s.i.g. and a temperature of about 1100 to 1300° F. and a hydrogen content greater than about 80 mole percent. The hydrogenation is continued until surface accumulations of poisoning metals, particularly nickel, are substantially reduced to the elemental state. Carbonylation takes place at a temperature substantially lower than the hydrogenation, from about ambient temperature to 300° F. maximum and at a pressure up to about 2000 p.s.i.g. with a gas containing about 50–100 mole percent CO. Preferred conditions include greater than about 90 mole percent CO, a pressure of up to about 800 p.s.i.g. and a temperature of about 100–180° F. The CO treatment serves generally both to convert the elemental metals, especially nickel, to volatile carbonyl and to remove the carbonyl.

After the ammonium wash, or after the final treatment which may be used in the catalyst demetallization procedure, the catalyst is conducted back to the cracking system. Where a small amount of the catalyst inventory is demetallized, the catalyst may be returned to the cracking system, preferably to the regenerator standpipe, as a slurry in its final aqueous treating medium. Where a large amount of catalyst inventory is treated, lest the water put out the fire or unduly lower the temperature in the regenerator, it may be desirable first to dry a wet catalyst filter cake or filter cake slurry at say about 250 to 450° F. and also, prior to reusing the catalyst in the cracking operation it can be calcined, say at temperatures usually in the range of about 700 to 1300° F. Prolonged calcination of the catalyst at above about 1100° F. may sometimes be disadvantageous. Calcination removes free water, if any is present, and perhaps some but not all of the combined water, and leaves the catalyst in an active state without undue sintering of its surface. Inert gases such as nitrogen frequently may be employed after contact with reactive vapors to remove any of these vapors entrained in the catalyst or to purge the catalyst of reaction products.

The demetallization procedure of this invention has been found to be highly successful when used in conjunction with fluidized catalytic cracking systems to control the amount of metal poisons on the catalyst. When such catalysts are processed, a fluidized solids technique is

recommended for these vapor contact demetallization procedures as a way to shorten the time requirements. Any given step in the demetallization treatment is usually continued for a time sufficient to effect a substantial conversion or removal of poisoning metal and ultimately results in a substantial increase in metals removal compared with that which would have been removed if the particular step had not been performed. After the available catalytically active poisoning metal has been removed, in any removal procedure, further reaction time may have relatively little effect on the catalytic activity of the depoisoned catalyst, although further metals content may be removed by repeated or other treatments.

The following is illustrative of a practice of this invention. A Mid-Continent vacuum asphalt having an initial boiling point above about 650° F. and having the following inspection

Specific gravity, 60° F./60° F.	0.997
Penetration at 77° F.	199
Carbon residue (Conradson)	19.2
Viscosity:	
FV/350° F.	—
FV/275° F.	100
FV/210° F.	675
Ring and ball softening point, ° F.	105
Pentane insolubles, wt. percent	13.98
Benzene insolubles, wt. percent	0.25
Sulfur, wt. percent	0.97
Extraction sediment, wt. percent	0.007
NiO, p.p.m.	60.7
V ₂ O ₅ , p.p.m.	61.7

is charged to a vis-breaker with an outlet temperature within the range of about 925–975° F. and a tower pressure of about 25–75 p.s.i.g. The resulting viscosity-broken vacuum asphalt is introduced into a fractionator where the visbroken products are distilled at about atmospheric pressure, and which yields about 10 weight percent of gasoline and gas, which are drawn off from the system. The gas oil recovered in the fractionator amounts to 20.9 volume percent and has a boiling range of about 400 to 900° F. and analyzes 2.3 p.p.m. nickel as NiO and 3.6 p.p.m. vanadium as V₂O₅. This fraction is passed to the catalytic cracking unit. The fractionator bottoms which amounts to about 69.3 volume percent, has a gravity of about 5.8 API. It is introduced into a vacuum flash tower operated at about 15 to 30 mm. Hg. and a temperature of about 600 to 700° F. There is recovered in the overhead from the vacuum tower a gas oil fraction, amounting to about 27.6 percent by volume of the charge to the visbreaker, which has a boiling range of about 400 to 1100–1200° F., and of which about 65% by volume has a boiling point in the range of 900 to 1200° F. There is also recovered from the vacuum tower a heavy bottoms fraction having a boiling point of greater than about 1100–1200° F. and amounting to about 41.7% by volume, on the basis of the vacuum asphalt charge to the vis-breaker. These vacuum tower bottoms, having a gravity of about —2.1° API, specific gravity 60° F./60° F. of 1.0935, penetration at 77° F. of about 1, and Conradson carbon residue of about 27.6%, are removed from the system for blending and subsequent use as a residual fuel oil. The following are typical of the yields from the vis-breaking operation:

Dry gas, wt. percent	2.2
i-C ₄ , vol. percent	0.2
n-C ₄ , vol. percent	0.7
C ₄ =, vol. percent	0.5
C ₅ –, 430° F. EP, vol. percent	9.6
Gas oil, vol. percent	48.5
Vacuum stripper bottoms, vol. percent	41.7

The gas oil fraction from the vacuum flash tower, having a boiling point range of about 400 to 1100–1200° F., analyzing 6.3 p.p.m. nickel oxide and 9.5 p.p.m. vanadi-

um pentoxide, is combined with the gas oil fraction from the fractionator, resulting in a cracker feed with an overall metals level of 4.5 p.p.m. nickel as the oxide and 6.9 p.p.m. vanadium as the pentoxide. This feedstock is sent to a catalytic cracking unit having a synthetic silica-alumina gel catalyst containing about 25% alumina and the remainder essentially silica, wherein a temperature of about 875-975° F. is maintained under a pressure of about 5 to 35 p.s.i.g., at a weight hourly space velocity of about 0.25 to 25, and a catalyst-to-oil ratio of about 5 to 15. The resulting cracked products are fractionated to recover a distillate gasoline of 430° F. end boiling point and cycle oils having a boiling point of about 430-900° F. The bottoms are tapped from the lower portion of the fractionator and removed from the system.

The catalyst is continually sent to a regenerator where it is contacted with air at a temperature of about 1000-1200° F. to burn off the carbon. The catalyst, whose carbon content is reduced from 0.76% to 0.36%, analyzing 325 p.p.m. nickel oxide, and 1265 p.p.m. vanadium pentoxide is continuously removed from the regenerator at a daily inventory rate of about 45% and sent to a zone where it is held for about an hour in contact with air at about 1300° F. and then sent to a sulfiding zone where it is fluidized with H₂S gas at a temperature of about 1100° F. for about an hour. The catalyst is then cooled and purged with inert gas and chlorinated in a chlorination zone with an equimolar mixture of Cl₂ and CCl₄ at about 600° F. After about an hour no trace of vanadium chloride can be found in the chlorination effluent and the catalyst is quickly washed with water. A pH of about 2.5 is imparted to this wash medium by chlorine entrained in the catalyst and the wash serves to remove nickel chloride.

The catalyst, substantially reduced in nickel and vanadium content, is filtered from the wash slurry, dried at about 350° F. and returned to the regenerator. The treated catalyst is analyzed and shows a metal content of 130 p.p.m. nickel, 949 p.p.m. vanadium, a reduction of about 60% in nickel and about 25% in vanadium.

It is claimed:

1. A process for treating a residual hydrocarbon oil boiling above the gasoline range and containing more than about 25 to about 500 p.p.m. nickel and more than about 50 to about 1000 p.p.m. vanadium which comprises treating said hydrocarbon oil at an elevated temperature under visbreaking conditions, fractionating the resulting visbroken oil to yield a gas oil fraction containing at least about 0.8 to less than about 25 p.p.m. nickel and at least about 1.5 to less than about 50 p.p.m. vanadium, said gas oil fraction having about 40 to 85% of its volume boiling primarily in the range of about 900° F. to 1200° F., subjecting said gas oil fraction to catalytic cracking, said gas oil being present in the cracking feedstock in an amount to supply at least about 1 p.p.m. nickel and at least about 1 p.p.m. vanadium and said feedstock containing less than about 10 p.p.m. nickel and less than about 20 p.p.m. vanadium, regenerating the catalyst, removing a portion of metal contaminated catalyst from the cracking system, the removed catalyst containing more than about 200 p.p.m. nickel and more than about 500 p.p.m. vanadium, demetallizing said metal contaminated catalyst to remove at least 50% of the nickel and at least 15% of the vanadium from the catalyst, and returning resulting demetallized catalyst to said cracking system and recovering gasoline from said catalytic cracking, said metal contents being calculated as the metal oxides.

2. The process of claim 1 wherein the cracking catalyst is a synthetic gel silica-based cracking catalyst.

3. The process of claim 2 wherein the visbreaking temperature is about 800 to 1000° F.

4. The process of claim 2 in which the cracking catalyst is silica-alumina.

5. A process for treating an asphaltic residual hydrocarbon oil having an initial boiling point greater than

about 550° F. and containing more than about 25 to about 500 p.p.m. nickel and more than about 50 to about 1000 p.p.m. vanadium which comprises treating said hydrocarbon oil at an elevated temperature of about 800 to 1000° F. under visbreaking conditions, fractionating the resulting visbroken oil to yield a first gas oil fraction boiling primarily in the range of about 400 to 900° F. and a first bottoms fraction, said first gas oil fraction containing at least about 0.8 p.p.m. to less than about 25 p.p.m. nickel and at least about 1.5 to less than about 50 p.p.m. vanadium, fractionating said first bottoms fraction under reduced pressure to produce a second gas oil fraction boiling primarily in the range of about 900 to 1200° F., combining said first gas oil fraction with said second gas oil fraction resulting in a combined gas oil fraction, subjecting said combined gas oil fraction to catalytic cracking, said combined gas oil being present in the cracking feedstock in an amount to supply at least about 1 p.p.m. nickel and at least about 1 p.p.m. vanadium and said feedstock containing less than about 10 p.p.m. nickel and less than about 20 p.p.m. vanadium, regenerating the catalyst, removing a portion of metal contaminated catalyst from the cracking system, the removed catalyst containing more than about 200 p.p.m. nickel and more than about 500 p.p.m. vanadium, demetallizing said metal contaminated catalyst to remove at least 50% of the nickel and at least 15% of the vanadium from the catalyst, and returning resulting demetallized catalyst to said cracking system and recovering gasoline from said catalytic cracking, said metal contents being calculated as the metal oxides.

6. The process of claim 5 wherein the cracking catalyst is a synthetic gel silica-based cracking catalyst.

7. The process of claim 6 wherein the catalyst is silica-alumina.

8. The process of claim 5 wherein the first gas oil fraction, boiling primarily in the range of about 400 to 900° F., amounts to about 15 to 35% by volume of the visbreaker feed.

9. The process of claim 5 wherein the second gas oil fraction, boiling primarily in the range of about 900 to 1200° F., amounts to about 40 to 45% by volume of the first bottoms fraction.

10. The process of claim 1 wherein the contaminated catalyst is demetallized at a rate of about 5 to 50% of the total catalyst inventory in the system per day.

11. A process for treating an asphaltic residual hydrocarbon oil having an initial boiling point greater than about 550° F. and containing more than about 25 to about 500 p.p.m. nickel and more than about 50 to about 1000 p.p.m. vanadium which comprises treating said hydrocarbon oil at an elevated temperature of about 800 to 1000° F. under visbreaking conditions, fractionating the resulting visbroken oil to yield a first gas oil fraction amounting to about 15 to 35% by volume of the visbreaker feed and boiling primarily in the range of about 400 to 900° F. and a first bottoms fraction, said first gas oil containing at least about 0.8 to less than about 25 p.p.m. nickel and at least about 1.5 to less than about 50 p.p.m. vanadium, fractionating said first bottoms fraction under reduced pressure to produce a second gas oil fraction amounting to about 40 to 45% by volume of the first bottoms fraction and boiling primarily in the range of about 900 to 1200° F., combining said first gas oil fraction with said second gas oil fraction resulting in a combined gas oil fraction, subjecting said combined gas oil fraction to catalytic cracking, said combined gas oil being present in the cracking feedstock in an amount to supply at least about 1 p.p.m. nickel and at least about 1 p.p.m. vanadium and said feedstock containing less than about 10 p.p.m. nickel and less than about 20 p.p.m. vanadium, regenerating the catalyst, removing a portion of the regenerated, metal contaminated catalyst containing at least about 200 parts per million nickel and 500 parts per million vanadium from the hydrocarbon cracking system, contacting the regenerated catalyst with a

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molecular oxygen containing gas at a temperature of about 1000 to about 1800° F. to enhance subsequent vanadium removal, sulfiding the poisoning metal containing component on the catalyst by contact with a sulfiding agent at a temperature of about 500 to 1500° F. to enhance subsequent nickel removal, chlorinating poisoning metal containing component on the sulfided catalyst by contact with an essentially anhydrous chlorinating agent at a temperature of about 300 to 1000° F., contacting the chlorinating agent-treated catalyst with a liquid, essentially aqueous medium to remove soluble metal components from the catalyst, the resulting catalyst being demetallized to an extent of at least 50% of the nickel and at least 15% of the vanadium based on the catalyst removed for demetallization, conducting the demetallized catalyst to said hydrocarbon cracking system and recovering gasoline from said catalytic cracking, said metal contents being calculated as the metal oxides.

12. The method of claim 11 wherein the cracking catalyst is a synthetic gel silica-based cracking catalyst.

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13. The method of claim 12 in which the sulfiding is performed by contact with H_2S at a temperature of about 800 to 1300° F.

14. The method of claim 13 in which the chlorinating is performed with an equimolar mixture of Cl_2 and CCl_4 at a temperature of about 300 to 650° F.

15. The method of claim 11 wherein the contaminated catalyst is demetallized at a rate of about 5 to 50% of the total catalyst inventory in the system per day.

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