

Nov. 21, 1950

L. P. EVANS

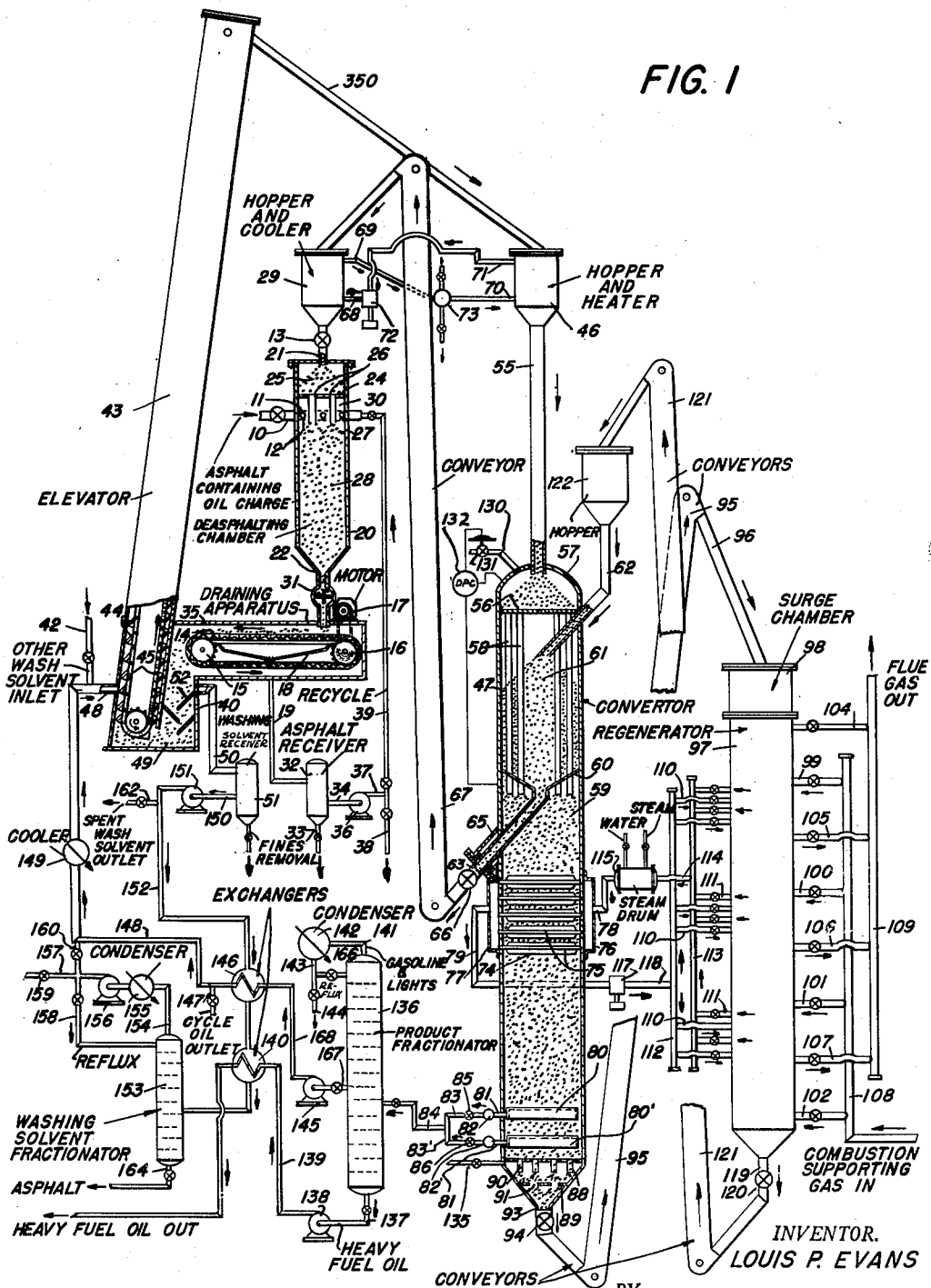
2,531,356

HYDROCARBON CONVERSION PROCESS

Filed Sept. 27, 1947

3 Sheets-Sheet 1

FIG. 1



INVENTOR.
LOUIS P. EVANS
BY *John A. Crowley, Jr.*
AGENT OR ATTORNEY

Nov. 21, 1950

L. P. EVANS

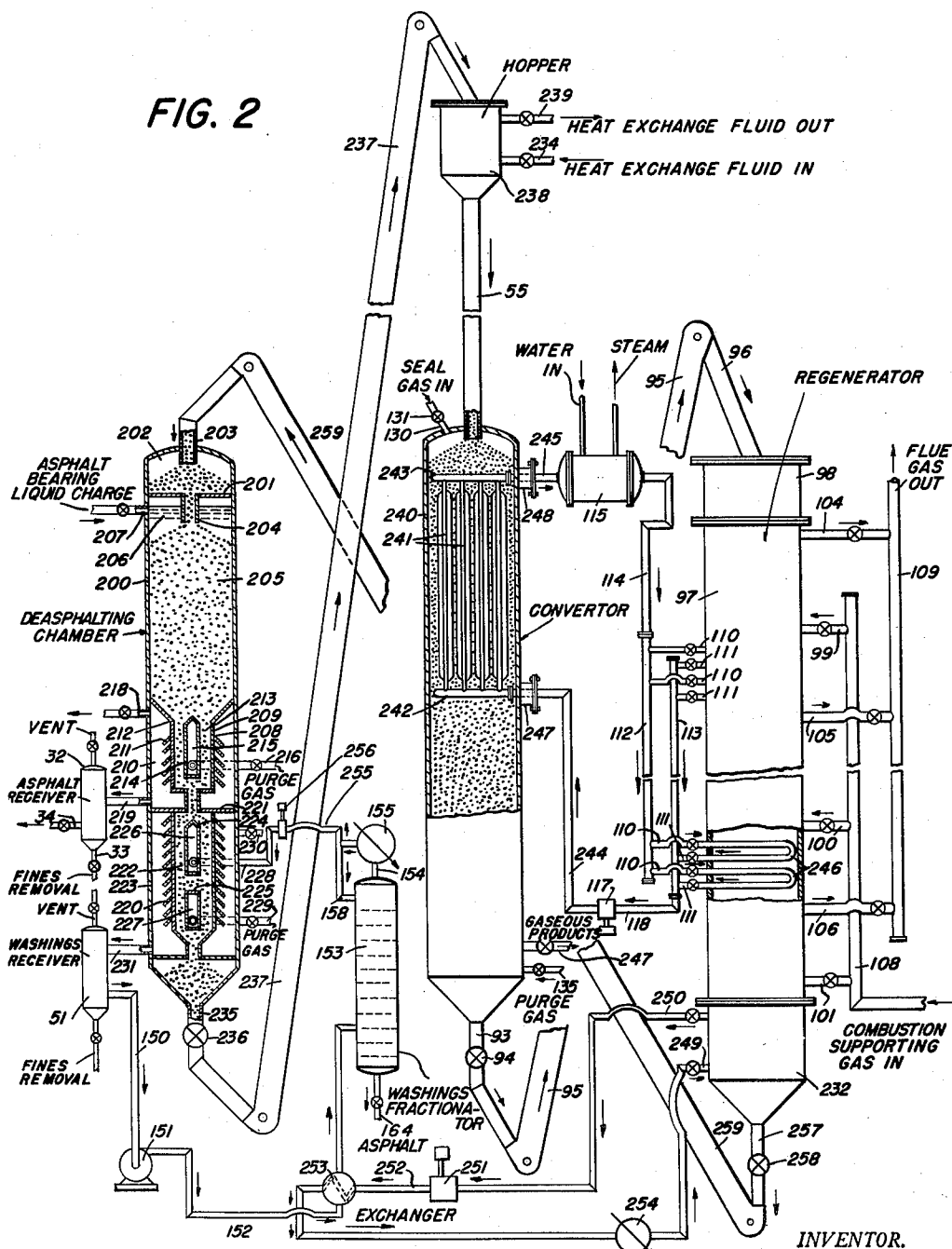
2,531,356

HYDROCARBON CONVERSION PROCESS

Filed Sept. 27, 1947

3 Sheets-Sheet 2

FIG. 2



INVENTOR.

LOUIS P. EVANS

BY

John A. Crowley, Jr.

AGENT OR ATTORNEY

Nov. 21, 1950

L. P. EVANS

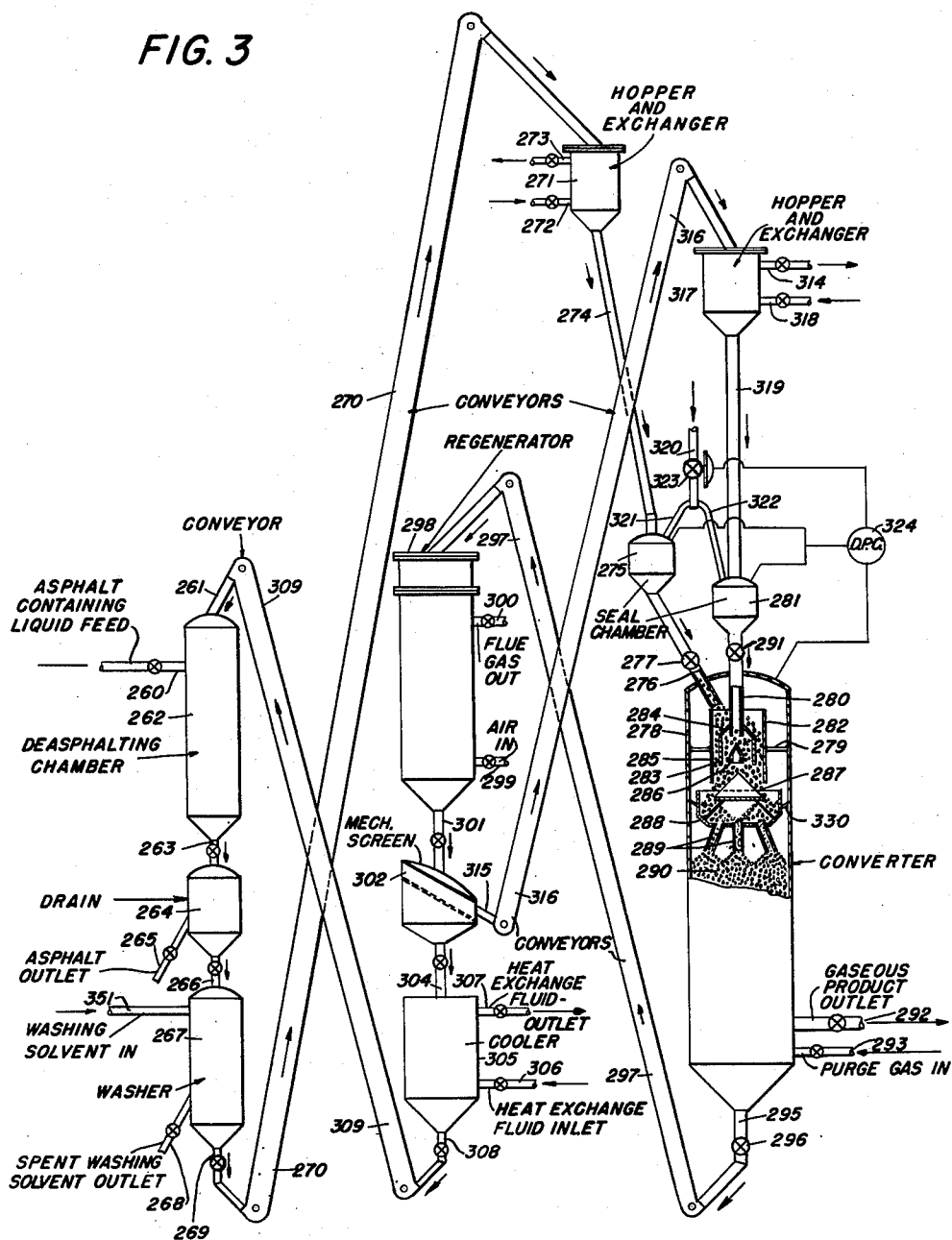
2,531,356

HYDROCARBON CONVERSION PROCESS

Filed Sept. 27, 1947

3 Sheets-Sheet 3

FIG. 3



INVENTOR.

LOUIS P. EVANS

BY

John A. Crowley, Jr.

AGENT OR ATTORNEY

UNITED STATES PATENT OFFICE

2,531,356

HYDROCARBON CONVERSION PROCESS

Louis P. Evans, Woodbury, N. J., assignor to Socony-Vacuum Oil Company, Incorporated, a corporation of New York

Application September 27, 1947, Serial No. 776,472

20 Claims. (Cl. 196—52)

1

This invention pertains to a process for conversion of high boiling hydrocarbons at controlled elevated temperatures in the presence of a particle-form contact mass material. This invention is particularly concerned with a process for the conversion of hydrocarbon feed stocks which contain both asphaltic and oily constituents.

Such conversion processes may involve treating, reforming, polymerization, oxidation, desulfurization, cracking, etc., of the hydrocarbons. A particularly important process is the catalytic cracking conversion of hydrocarbons, it being well known, for example, that hydrocarbon fractions boiling above the gasoline boiling range may be converted to lower boiling gasoline containing hydrocarbons upon being subjected to contact with a suitable solid porous catalyst at temperatures of the order of 800° F. and upwards and at pressures usually above atmospheric.

Heretofore, such conversion processes have been limited to the conversion of relatively light, clean, substantially tar or asphalt free petroleum feed stocks because of the tendency of the asphalt containing stocks to cause the formation of excessive deposits of coky contaminants on the catalyst which deposits cannot be economically removed. In order to avoid these heavy coke deposits which render the cracking process unfeasible, it has been the wide refinery practice to subject some high boiling petroleum feed stocks (when available with a broad boiling range) to a preliminary tar separation step, separate an easily vaporizable fraction from a liquid fraction which bears the asphaltic constituents and to subject only the vaporizable fraction to catalytic cracking while discarding the liquid tar separator bottoms. Since this discarded fraction may be made up of a large proportion of valuable oily constituents and a smaller proportion of asphaltic constituents, it is obvious that a large quantity of otherwise acceptable catalytic cracking feed stock is lost and unavailable as such in the prior art tar separator operation. When the crude residuum is not of such boiling range and does not contain substantial amounts of vaporizable gas oil, it has been considered in practice as being unsuitable as such for a cracking charge stock. The problem is becoming increasingly serious due to the fact that relatively low boiling petroleum crudes are becoming less plentiful and the crudes which are most readily available are high boiling crudes in which the oily constituents boil so high as to prevent their separation from asphaltic constituents by distillation process without subjecting them to temperatures at which undesirable thermal cracking and excessive coking occur. As a result, in order to use such high boiling stocks at all, it is necessary first to subject them to a preliminary thermal coking step to provide some lower

2

boiling oily fractions for a subsequent catalytic cracking operation. By-products from the coking process are a heavy liquid cut which may contain a substantial amount of oily constituents as well as asphaltic constituents and a very large amount of petroleum coke, the disposal of which often creates a serious refinery problem.

A major object of this invention is the provision of a process for conversion of high boiling asphalt bearing hydrocarbon fractions which process avoids the above described difficulties of the prior art.

Another object is the provision of a practical method for catalytically converting the oily constituents in high boiling petroleum residuums without the formation of prohibitive amounts of coke during such conversion.

Another object of this invention is the provision of a practical continuous cyclic process for the catalytic cracking conversion of petroleum residuums.

A specific object of this invention is the provision of a combination petroleum residuum desasphalting and conversion process.

These and other objects of this invention will become apparent from the following discussion.

The process of this invention is broadly one wherein the hydrocarbon feed fraction bearing asphalt and oily constituents is contacted under suitable sorption conditions with a particle-form porous contact material which is suitable for sorbing the oily constituents of the feed in the pores of the contact material while leaving substantially unsorbed the asphaltic constituents of the liquid feed. A substantial separation of unsorbed asphaltic constituents from the contact material bearing sorbed oily constituents is then effected. The separated contact material bearing sorbed oily constituents is then heated to a temperature suitable for effecting the desired conversion of the sorbed oily constituents.

It has long been known that when porous adsorbents such as bauxites and natural and treated clays are contacted with liquid petroleum fractions, the asphaltic constituents may be adsorbed on the clay and thus removed from the oily constituents. Such a process is commercially employed for the decolorizing of mineral oils by percolation of the oils through clay-type adsorbents. The present process is the opposite of the so-called percolation and contact filtration processes for oil refining in that, by the present process, it is the oily constituent and not the asphaltic constituent which is sorbed by the contact material. This fundamental difference makes possible the combination cracking process of this invention and permits the elimination of the asphalt materials without contamination of the catalyst thereby. It has been found that porous

contact materials, having a structure corresponding to that of an inorganic oxide gel having a substantially uniform porosity of low macropore volume with an average pore diameter not exceeding about 125 angstrom units and a particle size preferably not smaller than about 30 mesh for most operations, have the ability to sorb the oily constituents of a liquid hydrocarbon fraction while leaving substantially unsorbed the asphaltic constituents. Natural and treated clays and bauxites such as are employed in oil filtering and decolorizing processes do not appear to have this property. The macropore volume of the contact material employed in the present invention should be relatively low so that the pore volume is mostly that of micropores. In general, the volume of macropores, that is, those pores having radii larger than 100 angstrom units, should constitute less than about 30 per cent of the total pore volume and preferably 10 per cent or less. The measurement of pore size and pore size distribution in various porous materials is discussed in detail by L. C. Drake and H. L. Ritter in *Industrial and Engineering Chemistry, Analytical Edition*, volume 17, pages 782-791, 1945. The methods described there were essentially those employed in determining the bulk densities, average pore diameters, and other pore measurements of the adsorbents employed in the present invention.

The size of the sorbent particles employed in the process of this invention is to some extent dependent upon the variables involved in any particular application of the process. These important variables are time of contact between the liquid asphalt bearing charge and the sorbent in the sorption zone, temperature in the sorption zone, viscosity of the liquid charge, and to a lesser extent the ratio of liquid oil to sorbent charged to the sorption zone. Increasing time of contact and increasing temperature result in a decrease in the efficiency of separation of asphaltic and oily constituents. Decreasing viscosity of the liquid charge has the same effect. On the other hand increasing temperature and decreasing viscosity both result in more rapid sorption of the liquid oily constituents by the sorbent. If the ratio of sorbent to liquid charge is excessive some loss in separation efficiency results. By proper control of these variables some latitude in the average diameter of the sorbent employed may be provided. However, when the diameter of the particles becomes too small, the sorbent preferentially adsorbs the asphaltic constituents from the liquid charge in the same manner as well known oil filtering clays. This is shown in Table I below in which is tabulated the deasphalting results obtained on mid-continent residuums using a silica-alumina gel type sorbent having a bulk density in the 4-8 mesh size range of about 0.7.

Table I

Experiment Number.....	1	4	5	6	7	2	3
Charge Viscosity, S. U. V.....	116.9	116.9	81.8	81.8	81.8	81.8	340
Charge, Ramsbottom Carbon.....			2.3	2.3	2.3	2.3	5.1
Mesh Size of Sorbent (Tyler).....	4-8	30-60	30-60	60-80	30-60	4-8	4-8
Sorption Zone Contact Time.....	24 hrs.	24 hrs.	2 min.	2 min.	2 hrs.	72 hrs.	4 hrs.
Sorption Zone Temperature, °F.....	150	150	150	150	150	75	275
Weight Ratio of Sorbent to Liquid Charge.....	1	1	1	1	1	1	2.2
Properties of Oily Constituents Retained by Sorbent: S. U. V. @ 210° F. Sec. Ramsbottom Carbon, Percent.....	69.7	129.2	75.2	81.7	115.4	49.7	151
			1.8	2.3	3.1		2.4
Properties of Materials Washed from Sorbent Surface: S. U. V. @ 210° F. Sec. Ramsbottom Carbon, Percent.....	164	100.1	85.9	80.5	76.0	139.2	650
			2.4	2.2	2.0	3.5	6.7

It will be apparent from the above Table I that when the gel type sorbent particles were greater than 30 mesh size that even at relatively high temperatures and long contact periods the oily constituents of low viscosity and carbon residue were sorbed in the pores of the sorbent while the asphaltic constituents could be washed away with a suitable washing solvent, in this case benzol. On the other hand, in the case of sorbent particles ranging from 30-60 mesh size, when the contact period was 24 hours (Experiment 4) or even 2 hours (Experiment 7), the sorbent acted similar to a normal filtering clay and preferentially adsorbed the asphaltic constituents. But when the contact time was reduced to two minutes (Experiment 5), the 30-60 mesh sorbent exhibited a preference for the oily constituents over the asphaltic constituents. When the particle size was reduced below 60 mesh, the sorbent preferentially adsorbed the asphaltic constituents even at very low contact periods (Experiment 6).

The effect of contact time and temperature is shown in Table II below in which the deasphalting results on an East Texas residuum having an original Saybolt Universal viscosity of 512 seconds at 210° F. and a Ramsbottom carbon residue of 11.1. In this experiment a silica-alumina gel type sorbent of 4-8 mesh size and 0.48 bulk density was employed.

Table II

Experiment No.....	1	2	3
Sorption Zone Contact Time, Hrs.....	4	4	2
Sorption Zone Contact Temp, °F.....	275	300	300
Sorbent to Oil Weight Ratio.....	1.6	1.4	1.5
Ramsbottom Carbon Residue, per cent of sorbed oily constituents.....	1.9	2.6	2.0

In general it may be said that the particle size of the sorbent material particularly in the case of inorganic oxide gel type sorbents should be greater than about 60 mesh Tyler and preferably within the range about 0.022 to 1.0 inch average diameter. The best results may be obtained by limiting the sorbents within the range 0.03 to 0.20 inch average diameter and of reasonably uniform size. It is pointed out, however, that by proper control of the variables discussed hereinabove and also of the average pore diameter of the sorbent, operation according to the method of this invention may be obtained on sorbent particles outside the size ranges given although the results will be less satisfactory. It is contemplated that in its broader aspects this invention covers these latter operations as well as the operations within the specified preferred limits.

The porosity of the gel particles employed in the process of this invention is of fundamental importance. The degree of porosity is generally re-

flected in the bulk density of the gel composite used; the lower the bulk density, the greater being the degree of porosity. For the purposes of the present process, porous sorbent particles having bulk densities of between about 0.4 and 1.1 grams per cubic centimeter are preferred. The bulk densities indicated correspond to an average pore diameter of between about 20 and about 125 angstrom units. Preferably, the sorbent used will have a bulk density between about 0.6 and about 0.8 gram per cubic centimeter. Gel particles having a bulk density greater than about 0.8 have been found to have excellent selectivity but poor sorbing capacity, while particles with a bulk density less than about 0.6 have relatively poor selectivity. However, since the selectivity of the deasphalting process improves with a decrease in temperature, particles with a bulk density less than 0.6 would be satisfactory for deasphalting stocks which can be processed at low temperatures.

The degree of porosity of a synthetic inorganic oxide gel will, in general, depend on the conditions under which it is prepared and allowed to set to gelation. A particularly convenient method of preparing gel particles used in the process of this invention is described in U. S. 2,384,946, issued September 18, 1945, to Milton M. Marisic. It is there disclosed that spheroidal particles of inorganic oxide gel may be prepared by mixing an acidic stream with a stream of sodium silicate and allowing the resulting sol to be ejected from a nozzle into an oil column, where the gel sets in the form of bead-like spheroids. The resulting gel spheres, after washing, drying and tempering, were of a size varying between about 4 and about 20 mesh. The gel beads so produced had a bulk density of between about 0.4 and about 1.1 and an average pore diameter of between about 20 and about 125 angstrom units. They proved to be excellent selective absorbents for use in the process of this invention.

Likewise, irregularly shaped porous absorbent fragments or particles having the structure of inorganic oxide gels may be used. However, in general, spheroidal particles are to be preferred, since attrition losses are then at a minimum and contamination with gel fines of the asphalt-bearing stock is substantially eliminated.

In general, siliceous gel particles will be used in the process of this invention, such as silica gel, silica-alumina gel, silica-zirconia gel, silica-thoria gel and the like. Porous sorptive silica glasses having a structure approaching that of a siliceous gel likewise are contemplated for use in the process described herein, it being necessary, however, that the porous glasses employed have an average pore diameter less than about 125 angstrom units, and a macropore volume of less than about 30 per cent of the total pore volume. The size of the porous glass particles must also be carefully controlled so as to obtain preferential sorption of the oily constituents. Usually particles of less than 60 mesh size are undesirable. It is also contemplated that within the scope of this invention other porous materials not of the inorganic oxide gel composition which have structures approaching that of a siliceous gel and are within the above specified pore size and particle size limits may be employed within the scope of this invention.

Typical of the porous glasses used are those described in U. S. 2,106,744, issued February 1, 1938, to Hood et al. There it is disclosed that a silica-alkali-boric oxide glass of suitable composi-

tion is prepared by a fusion process. Heat treatment of this glass results in separation of the glass into two phases; one phase is rich in alkali-boric oxide and is soluble in acids, while the other phase, which is insoluble in acid, consists of silica with a small amount of boric oxide. Extraction of this heat treated glass with acid results in a porous silica glass which can be employed as a porous absorbent separating medium in accordance with the present invention.

The invention may be most readily understood by reference to the drawings, attached hereto of which:

Figure 1 is a schematic arrangement of the system of this invention in which some of the apparatus is shown partially in section;

Figure 2 is a similar view of a modified arrangement; and,

Figure 3 is a diagrammatic flow sketch of still another modified arrangement.

All of these drawings are highly diagrammatic in form.

Turning now to Figure 1, for a study of the process of this invention, vessel 20 is a deasphalting chamber which may be of rectangular or any other desired cross-sectional shape. A partition 24 across the upper section of chamber 20 defines a solid inlet surge chamber 25 in its upper end. Tubes 26 depend from partition 24, flow of contact material from chamber 25 onto the surface of the substantially compact contact material column maintained in the sorption section 28 of the deasphalting vessel. Particle form contact material having a catalytic activity for the desired conversion and being suitable for sorbing the oily constituents of a liquid feed while leaving substantially unsorbed the asphalt constituents thereof is cooled to a suitable temperature in hopper 29 positioned above vessel 20 and then passed via conduit 21 into vessel 20 to keep replenished the column of such material in section 28 of vessel 20. A hydrocarbon feed stock which contains both asphaltic and oily constituents, for example, a heavy petroleum residuum fraction or a tar separator bottoms fraction, is introduced into chamber 20 from manifold 10 via headers 11, closed on their ends, which extend into space 30 and nozzles 12 which are spaced along headers 11. The liquid charge distributes itself over the surface 27 of the contact material column and percolates downwardly within the column, whereby the oily constituents become sorbed in the pores of the contact material and the asphalt constituents remain substantially unsorbed. The contact material bearing sorbed oily constituents and the unsorbed liquid are withdrawn together from the bottom of vessel 20 through duct 22 at a suitable rate controlled by the valve 31.

The mixed liquid and solid material are directed by duct 22 onto an endless foraminous moving belt 14 supported over horizontally spaced pulleys 15 and 16, the latter of which is rotated by means of drive motor 17. The drain duct 22 and valve 31 therein may extend horizontally substantially the width of belt 14 so as to uniformly distribute solid material and liquid across the belt. Suitable guards (not shown) may be provided within chamber 35 along the opposite sides of the belt 14 to prevent solid particles from falling off the sides. A drain pan 18 is supported on its opposite sides from the wall of chamber 35 between the pulleys 15 and 16 and below the belt 14 so as to receive liquid which drains therethrough. The drained liquid con-

taining the asphalt constituents is withdrawn from pan 18 via conduit 19 to the asphalt receiver 32. Entrained solid fines may be removed from the bottom of receiver 32 by means of outlet 33 and asphalt may be withdrawn via conduit 34 to pump 36. The asphalt containing liquid then may be entirely pumped from the system via conduits 37 and 38 or in part recycled via conduits 37 and 39 to inlet manifold 10 feeding the deasphalting chamber. In some operations such recycling is desirable in order to reduce the amount of oily material in the finally discarded asphalt constituents to a minimum.

The contact material is carried along on belt 14 in the direction of the flow arrows and the contact material from which most of the un-sorbed liquid has been separated by draining is discharged from the belt 14 onto the washing chamber 40. The chamber 40 communicates on its lower end with the boot section of a bucket elevator 43. In elevator 43 buckets 44 having perforated bottoms are moved upwardly and downwardly on endless chain 45 so as to transfer the washed contact material from the elevator boot section upwardly to duct 350 feeding supply hopper 46 which in turn feeds the hydrocarbon convertor 47. The bottoms of the elevator buckets 44 are perforated, the perforations being of such size as to retain the contact material particles while permitting liquid to pass therethrough. The elevator casing is inclined and the buckets are so shaped that liquid which drains from any given upwardly moving bucket does not fall into the bucket moving upwardly therebelow, but is delivered back to the elevator boot section. A suitable washing solvent such as a naphtha, kerosene, benzol or light gas oil fraction may be introduced from an outside source through conduit 42 into conduit 48 through which it passes into the elevator boot section. The solvent passes from the elevator boot section into the lower section of chamber 40 via passage 49 and then passes upwardly through the washing chamber to be withdrawn from the upper portion thereof through conduit 50 to a washing solvent receiver 51. Baffles 52 provide a zig-zag passage in chamber 40 through which the contact material passes as it descends through the bath of upwardly moving washing solvent. The solid particles are in this manner subjected to a quick wash under conditions so controlled as to accomplish the removal of asphalt containing liquid adhering to the outer surfaces of the contact material particles without substantial separation of the sorbed oily constituents from the contact material. A relatively small amount of washing solvent may also be sorbed by the contact material during the washing operation. The washed contact material may thus contain a substantial amount of sorbed oily constituents from the original feed, a relatively small amount of washing solvent (and in some cases practically no washing solvent) and in some instances small amounts of asphalt constituents from the feed. It should be understood that while the gel type contact material particles of the type described have the unusual characteristic of sorbing oily constituents rather than asphalt constituents from high boiling feeds, nevertheless, in the case of some feed fractions the gel type catalyst will also sorb relatively small amounts of asphalt materials. It has been found that this relatively small amount of sorbed asphaltic materials will not increase the coke deposits on the catalyst to

prohibitive levels. It should be understood that in claiming this invention in the expressions "while leaving the asphalt constituents substantially unsorbed"; or contact material suitable for sorbing "substantially only the oily constituents of the liquid feed" and in like expressions the word "substantially" is intended to allow for these relatively small amounts of asphalt constituents which may in some operations be sorbed along with the much larger amount of oily constituents in the contact material pores.

The washed contact material bearing sorbed oily constituents may be passed from the convertor supply hopper 46 into the upper end of convertor 47 as a substantially compact, elongated gravity feed leg flowing downwardly in conduit 55. Within the upper section of convertor 47 a horizontal partition 56 is positioned so as to define a seal chamber 57 in the upper end of the convertor. It is into this seal chamber 57 that the contact material feed is delivered.

A suitable inert seal gas such as steam or flue gas may be introduced into seal chamber 57 at a rate sufficient to maintain a gaseous pressure therein above that in the conversion section of vessel 47. Conduit 130, diaphragm valve 131 and differential pressure control instrument 132 are provided for this purpose. A plurality of uniformly spaced vertical conduits 58 serve as a passage for solid flow from seal chamber 57 onto the column 59 of contact material maintained in a lower section of the convertor. A second partition 60 positioned near and above the lower ends of conduits 58 provides a chamber 61 surrounding the conduits 58 and within the vessel 47 which chamber is sealed from the seal chamber 57 and from the column of contact material 59 by partitions 56 and 60 respectively. An inlet conduit 62 for hot regenerated contact material extends into the upper section of chamber 61 and an outlet conduit 63 for discharge of that contact material is connected into partition 60. A packing gland 65 is provided to permit expansion of conduit 63 through the wall of vessel 47 while preventing the escape of vapor. The partition 60 may be of such shape as to form a tapered bottom for chamber 61 so that contact material may be easily withdrawn therefrom via conduit 63. The arrangement is such that the relatively cool contact material bearing sorbed oily constituents which enters seal chamber 57 and then passes downwardly through conduits 58 may be heated by indirect heat transfer with a hot regenerated contact material which is introduced into chamber 61 through conduit 62 and withdrawn through conduit 63 at a rate controlled by valve 66. The regenerated contact material is thereby partially cooled and is transferred by means of a suitable conveyor 67 to the combined hopper and cooler 29 from which it passes into the deasphalting chamber 20 as the contact material supply thereto. The regenerated contact material in hopper 29 is cooled to a temperature suitable for its introduction into deasphalting chamber 20 by means of a suitable heat exchange fluid introduced at 68 and removed at 69. If desired, heat transfer tubes may be provided in both hoppers 29 and 46; and the heat exchange fluid withdrawn from the heat transfer tubes in hopper 29 via conduit 69 may be introduced into the tubes in hopper 46 through conduit 70. The heat recovered from the final cooling of the regenerated contact material may thereby be utilized for partially heating the cooler, oily constituent bearing contact material in hopper 46. The heat ex-

change fluid, relieved of its heat in hopper 46 may be withdrawn from the tubes therein through conduit 71 and reintroduced into the tubes in hopper 29 through conduit 68. A pump 72 may be provided to cyclically circulate the heat exchange fluid and an exchanger 73 may be provided to permit any heat adjustments that may be required by the desired contact material outlet temperature from hoppers 29 and 46. Heat may either be added or withdrawn by means of exchanger 73 as the particular operation involved requires. Considering again the converter 47, the partially heated oil bearing contact material from conduits 58 replenishes the column 59 and is finally heated to a temperature suitable for effecting the desired conversion of the sorbed oily constituents by means of heat supplied by indirect heat transfer with a suitable heat exchange fluid passing through the heat transfer tubes 75. The tubes 75 extend in spaced rows horizontally across vessel 47 below the lower ends of conduits 58 and are provided with attached fins 74 to enhance their surface area for heat transfer. An inlet manifold box 76 is provided on one side of the vessel to supply heat exchange fluid to the tubes 75 and an outlet manifold box 77 is provided on the opposite side of vessel 47. Heat exchange fluid enters box 76 through inlet conduit 78 and leaves box 77 through conduit 79. Any suitable heat exchange fluid such as superheated steam, flue gas or molten metallic alloys, lead or inorganic salts, etc. may be employed. As will be shown hereinafter a preferable source of the heat is the contact material regenerator. After being heated to a suitable conversion temperature the oily constituents are catalytically converted to the desired gaseous products which are withdrawn from the lower section of vessel 47 by means of spaced rows of inverted collecting troughs 80 and 80' provided with outlet pipes 81 and 81'. The pipes 81 and 81' connect into manifolds 82 and 82' respectively from which the gaseous products are withdrawn through conduits 83 and 83' respectively which merge into a single outlet conduit 84. Valves 85 and 86 are provided on conduits 83 and 83' respectively to permit control of the amount of the rate of gas withdrawal at each level of collectors. In the lower section of vessel 47, there are provided two horizontal, vertically spaced partitions 88 and 89. A plurality of uniformly distributed tubes 90 depend from partition 88 and a smaller plurality of orifices 91 are provided in partition 89. The orifices 91 are horizontally offset with respect to tubes 90 so as to proportionately receive streams of contact material therefrom and to cause them to merge into a smaller plurality of streams which in turn merge into a single outlet stream in outlet conduit 93. The arrangement is such as to provide for uniform withdrawal of contact material from all portions of the horizontal cross sectional area of vessel 47 through the outlet 93. This arrangement is fully described and claimed in United States application Serial Number 473,861, filed January 28, 1943 in which the present applicant was one of the applicants, and which issued as Patent No. 2,412,136 on December 3, 1946.

A suitable purge gas such as steam or flue gas may be introduced into the lower section of vessel 47 through conduit 135 in order to purge the outflowing used contact material substantially free of the lower boiling conversion products.

It will be noted that in the operation described thus far the inorganic gel type contact material particles serve the dual function of serving as

an unusual sorbent permitting separation of asphaltic constituents from the oily constituents of the original feed fraction and also as a catalyst to promote the conversion of the oily constituents in vessel 47 once a suitable conversion temperature has been reached.

The used contact material which is withdrawn from vessel 47, substantially separately of the gaseous conversion products, through conduit 93 and throttle valve 94 thereon has lost a substantial part of its catalytic effectiveness due to deposition of a carbonaceous contaminant thereon. The used contact material is, therefore, transferred by conveyor 95 to chute 96 feeding the regenerator 97. A surge chamber 98 is provided in the upper end of regenerator 97 to receive the used contact material. The regenerator shown in Figure 1 is of the multi-stage variety which is described and claimed in application Serial Number 447,432, filed in the United States Patent Office June 17, 1942 and application Serial Number 447,433, filed in the United States Patent Office June 17, 1942 in which applications the present applicant is one of the applicants, and which issued as Patent Nos. 2,417,399 and 2,436,780, respectively. In general the regenerator 97 is divided into a vertical series of alternating burning and cooling stages. Separate gas inlets 99, 100, 101 and 102 and separate gas outlets 104-107 inclusive spaced vertically from the inlets, are provided for the burning stages. The gas inlets are supplied by a combustion supporting gas such as oxygen, air or mixtures of air and flue gas, from inlet manifold 108. Flue gas passes from the burning stages through outlets 104-107 and is manifolded into outlet flue 109. Heat transfer tubes or coils may be suitably spaced within the cooling stages. Pipes 110 are inlets to these tubes and pipes 111 are outlets therefrom. The inlet pipes 110 connect into an inlet manifold 112 and the outlet pipes connect into an outlet manifold 113. As pointed out hereinabove the excess heat released by burning the carbonaceous contaminant from the contact material may be carried by a suitable heat exchange fluid passing from outlet manifold 113 through conduit 114 and steam drum 115 into conduit 78 and the manifold box 76 supplying the heat transfer tubes 75 in converter 47. The heat exchange fluid after giving up its heat to the contact material in vessel 47 may then pass via manifold box 77, conduit 79, pump 117 and conduit 118 into the inlet manifold 112 which supplies the heat transfer tubes in the regenerator cooling stages through pipes 110. Any excess heat liberated by the contaminant burning over that required for the final heating of the contact material and oily constituents in converter 47 may be removed by the evaporation of water to provide high pressure steam in drum 115. The heat exchange fluid may take any of a number of forms such as a suitable gas under pressure or fused metallic oxides or mixtures of certain fused inorganic salts.

Hot regenerated contact material is withdrawn from the lower end of regenerator 97 through outlet 119 at the desired rate as controlled by throttle valve 120. The hot regenerated contact material is then transferred by conveyor 121 to hopper 122 from which it passes via conduit 62 into the chamber 61 in vessel 47. As described hereinabove the regenerated contact material is partially cooled in chamber 61 by indirect heat transfer with cooler oil bearing

contact material flowing within tubes 58, and is then passed to hopper 29 where it is finally cooled to a temperature at which it may be re-used in the deasphalting operation. It will be noted that by virtue of heat exchange between the contact material in chamber 61 and that in conduits 58 and by virtue of the exchange of the heat between the contact material in hoppers 29 and 46 as described hereinabove, a large portion of the heat removed from the hot regenerated contact material to adapt it for the deasphalting operation is recovered and used for preheating the contact material to a temperature suitable for conversion of the oily constituents. Moreover, any residual heat required for the heating of the oily constituent bearing contact material is obtained from the contaminant combustion reaction and transferred to the contact material by a heat exchange fluid passing through heat transfer tubes 75. It will be understood that the heat thus obtained from the contaminant burning not only serves to raise the contact material and oil temperature in vessel 47 but also serves to supply the endothermic reaction heat required for the conversion of the oily constituents to the desired products.

Considering again the gaseous products obtained from converter 47 it is pointed out that the term "gaseous" as used herein in describing and in claiming this invention is intended in the sense of covering materials which are in the gaseous phase under the particular operating conditions involved regardless of the normal phase of those materials under atmospheric conditions. For example, gaseous conversion products leaving the converter through conduit 84 at a temperature of the order of 800° F. to 950° F. and say 10 pounds gauge pressure may exist substantially entirely in the gaseous phase under these conditions although gasoline, gas oil and heavy fuel oil constituents may be present which are ordinarily liquids under atmospheric conditions. The gaseous conversion products are directed by conduit 84 into a fractionator 136 which may be of the type conventionally used for this purpose. A heavy cycle or fuel oil fraction may be withdrawn from the bottom of the fractionator 136 through conduit 137. The fuel oil may be pumped by pump 138 through conduit 139 and through exchanger 140 whereby it is cooled. The cooled fuel oil may be withdrawn from the system or it may be recycled as part of the heavy liquid hydrocarbon feed to the deasphalting chamber 20. Gasoline and light products may be withdrawn from the top of fractionator 136 through conduit 141 through which it passes to condenser 142. Part of the condensed material may be refluxed via pipes 143 and 146 and part withdrawn via pipes 143 and 144 in order to be further treated and fractionated to provide a finished gasoline product. An intermediate boiling fraction or a light cycle oil boiling, for example, within the broad range about 400° F. to 800° F. may be withdrawn from an intermediate point along the fractionator 136 via conduit 167. This cycle oil may be pumped by pump 145 through conduit 168 to exchanger 146 wherein it is partially cooled. All or a portion of the cycle oil may then be withdrawn from the system through conduit 147. It has been found desirable to employ at least a portion of this cycle oil as the washing solvent for washing asphaltic material from the outer surface of the contact material particles in washing chamber 40. In case of such operation the cycle oil from exchanger 146 passes via conduit

148 through cooler 149, wherein it is adjusted to a suitable temperature for the washing operation and then into the boot section of elevator 43 via conduit 48. The cycle oil may entirely replace or merely supplement washing solvent from an external source introduced via conduit 42. The used washing solvent collected in receiver 51 may be passed therefrom through conduit 150 to pump 151 and then via conduit 152 through exchangers 146 and 140 into a suitable solvent fractionator 153. In exchangers 146 and 140 the solvent is vaporized and heated to a suitable flash temperature for introduction into the fractionator 153. In fractionator 153 the washing solvent (i. e. cycle oil) is distilled from the asphaltic and high boiling material removed from the contact material in chamber 40. The asphalt containing liquid is withdrawn from the bottom of fractionator 153 through conduit 164 and the recovered solvent vapor is withdrawn from the top of fractionator 153 through conduit 154. The cycle oil vapors are condensed in condenser 155 and passed to pump 156. The condensate may in part be pumped through conduits 157 and 158 back to tower 153 as reflux, and part through conduits 157 and 159 to an outside storage. Alternatively part of the condensate may be passed through conduits 157 and 160 to conduit 148 to be reused as washing solvent.

Alternatively in some operations, the fractionator 153 may be eliminated and the used washing solvent containing asphaltic constituents may be withdrawn from the system through conduit 162 to be employed as a cutting stock in preparing refinery fuel blends and the like. This latter alternative is particularly feasible when a cycle gas oil is employed as the washing solvent. On the other hand, when an outside solvent such as a naphtha fraction is employed as the washing solvent, it is usually desirable to recover the solvent by fractionation.

While the system described hereinabove is one of the preferred forms of this invention, it should be understood that the various elements making up the particular combined system described are shown in highly diagrammatic form in Figure 1 and that the invention is not intended to be limited to the particular detailed construction of the various elements as shown. For example, while it is preferred to percolate the liquid charge downwardly through a column of the gel particles in the deasphalting chamber, nevertheless it is contemplated that within the scope of this invention the contacting of the gel particles and the liquid charge may be accomplished in a number of other ways and any method which permits the desired contacting is considered to be within the scope of this invention. For example, the liquid charge and the gel particles might be merely charged to a batch type mixer provided with suitable mechanical mixing devices and after suitable mixing has been accomplished, the material may then be discharged from the mixer to a suitable liquid solid separator. Likewise, other methods and apparatus than that described hereinabove may be employed to effect separation of unsorbed liquid material from the contact material bearing sorbed oily constituents. For example, a rotary type filter provided with suitable means for accomplishing both filtering off of unsorbed liquid and washing of the contact material may be employed. In some operations the washing step may be eliminated entirely and the combination of draining and purging of the contact material

with a suitable purging gas may be relied upon to separate the contact material from unsorbed asphalt containing liquid. Moreover, while in the system described hereinabove the washed contact material was partially heated and then recharged through a gravity feed leg to the converter, it is contemplated that the preliminary partial heating step may be eliminated and all of the heating accomplished within the converter. Also suitable forced feed devices may be substituted for the gravity feed leg in less preferred forms of the invention as means of introducing the contact material bearing sorbed oily constituents into the converter. It is also contemplated that the converter and regenerator construction may be materially different from that shown in Figure 1. Other suitable means for removal of gaseous products from the conversion zone may be employed where desired and in some operations the contact material and conversion products may be withdrawn together and then separated. The regenerator may be of the single stage type and also of the other types which will be described hereinafter, if desired.

Since the inorganic oxide gel type contact material involved is preferably substantially of 30 mesh size and larger it is more practical and desirable in order to prevent undue attrition of the contact material to handle the contact material as a substantially compact moving bed or column in the converter and regenerator and to convey it between vessels by continuous bucket elevators. However, within the broader scope of this invention it is contemplated that the contact material may move in suspension in a suitable gaseous stream or as a fluidized mass within the conversion and regeneration vessels; and that means other than bucket elevators may be employed for transferring the contact material from one zone to another. It is further contemplated that within its broader scope the method of this invention may involve a substantially "in situ" process wherein the contact material remains permanently in one or more vessels. For example, the deasphalting, draining, washing, heating conversion and catalyst regeneration and cooling steps may be conducted in proper cycle in a single chamber in which the contact material particles remain as a fixed bed. A batch type operation wherein the contact material is moved periodically, batchwise from zone to zone is also contemplated. It should also be understood that within the scope of this invention it is contemplated that the contact material bearing sorbed oily constituents after separation of unsorbed liquid may be heated to the temperature suitable for effecting the desired conversion of the oily constituents either by indirect or by direct heat transfer with suitable fluid heat exchange mediums, by indirect heat transfer from a hot particle form solid which may or may not be regenerated contact material and by the mixing of hot particles of substantially inert heat carrying material with the oily constituent bearing contact material.

It will be understood that the desirable conditions of operation during the deasphalting, washing, conversion and catalyst regeneration and cooling steps will vary depending upon the particular liquid charge stock involved and the conversion reaction involved and the particular conversion products desired. Certain general conditions of operation must, however, be observed. As regards the deasphalting operations the temperature at which the sorption of oily constituents by

the particle-form gel type contact material is conducted should be high enough to give the oil sufficient fluidity to permit rapid sorption of the oily constituents but low enough to permit the contact material to function selectively. The maximum temperature maintained in the sorption zone is dependent on the viscosity of the stock being treated. The sorption of oily constituents becomes less selective as the viscosity decreases. The desirable sorption temperature has been found to vary from below room temperature to about 500° F. depending on the liquid fraction treated. The temperature of the hydrocarbon liquid charged into the sorption zone and the contact material supplied thereto should be both adjusted to provide the desired sorption temperature. The contact material should not be permitted to contact the asphalt containing liquid feed at temperature at which substantial thermal cooking of the liquid fraction would take place. This means that in general the contact material should be cooled in hopper 29 of Figure 1 for example, to a temperature which is at least below about 750° F. The pressure in the sorption zone may conveniently be within the order of atmospheric to 50# per square inch. The residence time of the contact material within section 28 of chamber 20, i. e. the sorption zone, may vary from about 1-10 hours depending upon the liquid fraction involved, the temperature and the ratio of the contact material to the liquid charge. In many operations it is desirable to control the residence time of the contact material in chamber 20 by means of valve 31 such as will permit substantial saturation of the contact material with sorbed oily constituents.

The ratio of contact material to liquid charge to the deasphalting chamber may vary from about 0.5 to 20 parts by weight of contact material per part of liquid asphalt bearing charge and preferably from about 2 to 6 parts of contact material per part of liquid charge.

The amount of solvent employed in the washing operation may vary depending upon the characteristics of the solvent and of the unsorbed liquid involved. In general the contact material washing should be a relatively "quick wash" so controlled as to prevent removal by the solvent of substantial amounts of sorbed oily constituents from the contact material. The amount of solvent employed may be of the order of 0.25 to 2.0 volumes of solvent per volume of contact material. In some operations the purging step following the washing step may be omitted but when this step is employed the purging gas employed should be a gas which is not apt to cause oxidation of the oily constituents during the conversion, unless of course, the conversion process involved is a partial oxidation process. Steam, nitrogen, flue gas and low molecular weight hydrocarbon gases are suitable purging gases for most operations.

When the contact material bearing sorbed oily constituents is partially heated before introduction to the conversion zone as shown in Figure 1, it should be heated only to a temperature which is substantially below the desired conversion temperature. Usually a temperature of the order of 750° F. is the maximum temperature to which the contact material should be heated in hopper 29 of Figure 1. As has been pointed out, the contact material introduced to chamber 20 should be below about 750° F. so that regenerated contact material in hopper 29 of Figure 1 should be cooled to a level at least below about 750° F.

The operating conditions within the convertor 47 will vary depending upon the activity of the catalyst employed, the particular petroleum charge involved, the reaction involved and the products desired. In general it has been found desirable to maintain the pressures within a range varying from sub-atmospheric to about 200 pounds per square inch. Pressures of the order of 5 to 50 pounds per square inch gauge are preferred. The temperature for the conversion for cracking operations may vary from about 750° F. to 1100° F., temperatures of the order of 850 to 1000° F. being preferred where gasoline is the desired product. Where non-condensable gases are the principal desired product somewhat higher temperatures may be employed. The ratio of contact material to hydrocarbon throughput may vary from about 1.0 to 40 parts by weight of contact material per part of hydrocarbon charge. In the operation of the system shown in Figure 1, the contact material bearing oily constituents may be heated to a temperature just below the desired conversion temperature by the time it discharges from conduits 58 and is then heated by means of tubes 75 to a temperature sufficiently above the desired average conversion temperature to supply the endothermic heat of hydrocarbon conversion and to insure the desired average conversion temperature. For example, contact material heated to about 400° F. in hopper 46 may be further heated to about 800° F. by the time it reaches the column 59 in convertor 47, whereupon it may be heated by tubes 75 to about 950° F. The contact material may then cool to about 850° F. before reaching the discharge conduit 93 thereby giving an average conversion temperature of about 900° F.

In alternative operations, the heat transfer effected from chamber 61 may be sufficient, in combination with partial preheating in hopper 46 to provide all the contact material heating required in which case the tubes 75 may be omitted.

In still another alternative operation the tubes 75 may be so spaced and positioned as to provide indirect heat transfer all along the length of the conversion zone so as to permit maintenance of the contact material substantially at the desired conversion temperature all during the conversion of the oily constituents. In a preferred form of this alternative operation the regeneration and conversion zones may themselves be positioned in intimate heat transfer relationship with each other along their lengths so as to permit heat transfer from the moving catalyst undergoing regeneration through the walls of the regeneration zone into the reaction zone. In this manner, the heat of hydrocarbon conversion is supplied directly from the regeneration zone and the catalyst in the regeneration zone is cooled sufficiently to prevent its temperature from rising to heat damaging levels.

In the contact material regenerator, pressures of the order of atmospheric to about 100 pounds per square inch may be employed, pressures around atmospheric being preferred. The contact material temperature should be controlled below a heat damaging level by removal of heat therefrom during the course of the contaminant burning. The heat damaging level is that level at which and above which the contact material suffers permanent loss in catalytic effectiveness for the conversion involved or loss in sorptive efficiency. The heat damaging temperature may vary from temperatures above about 1150° F. to temperatures above about 1450° F. depending

upon the particular gel type catalyst involved.

A modified system for conducting the process of this invention is shown in Figure 2. Many of the elements in Figures 1 and 2 are substantially identical and these elements bear like numerals in both drawings and need not be further discussed in detail. In the arrangement shown in Figure 2 the deasphalting, draining, washing and purging steps are all conducted within a single vessel 200. A partition 201 across the upper section of the vessel 200 provides in the upper end thereof a contact material surge chamber 202 into which regenerated contact material is introduced at a suitable temperature through conduit 203. A conduit 204 depending from partition 201 serves as a passageway for contact material from surge chamber 202 into sorption zone 205, and also to provide a liquid distributing space 206 above the contact material column in zone 205. High boiling liquid hydrocarbon charge containing asphaltic and oily constituents is fed through conduit 207 into space 206 at a sufficient rate to maintain a pool of liquid therein over the surface of the contact material column. The liquid percolates downwardly through the column of downwardly moving gel type contact material particles in zone 205 whereby the oily constituents are sorbed and the asphalt constituents remain unsorbed. The liquid containing asphalt constituents upon reaching the lower section of zone 205 drains off from the contact material through the openings 208 in partition 209. The partition 209 is adapted to retain and direct the contact material flow from zone 205 into a central portion of the horizontal cross section of vessel 200 so as to provide between the partition and the vessel wall a liquid collecting space 210 from which solid flow is excluded. Downwardly sloping drip baffles 211 are connected along the outer side of partition 209 below the openings 208. A second baffle structure 212 which may be in the form of a hollow cylinder closed on top and bottom is positioned centrally within the passage for solid flow 213 defined by partition 209 so as to cause the solid to flow through an annular passageway between the baffle structure 212 and partition 209. Openings 214 also adapted to permit passage of gas or liquid therethrough while preventing solid flow therethrough are provided in the vertical walls of baffle structure 212. A suitable purge gas such as steam or flue gas is introduced into the distributing space 215 provided by structure 213 through conduit 216. This purge gas passes horizontally across the contact material column within passage 213 and through the openings 208 in partition 209 thereby serving to sweep unsorbed liquid from the contact material into collecting space 210. The purging gas may be withdrawn from space 210 through conduit 218 near its upper end and the drained liquid containing asphalt constituents may be withdrawn from collecting space 210 through conduit 219 near its lower end to the asphalt receiver 32. Horizontal partitions 221 and vertical foraminated baffle 220 which may be cylindrical in form provide below the draining section in vessel 200 a washing and purging section. The baffle 220 serves to define within the lower section of vessel 47 and within the central portion of its horizontal cross-section a passage for solid flow 222, and an outer collecting space 223. Vertically spaced baffle arrangements 224 and 225, similar in construction to baffle structure 212 provide a washing solvent distri-

buting zone 226 and a purge gas distributing zone 227 respectively centrally and longitudinally disposed of the passage 222. Washing solvent is introduced into zone 226 through conduit 228 and passes horizontally across the solid column and then through the openings in partition 220 into the collecting space 223. Purge gas is introduced into zone 227 through conduit 229 and then passes horizontally across the contact material column and through the openings in partition 220 into the collecting space 223. Purge gas may be withdrawn from space 223 through conduit 230 near its upper end and used washing solvent containing asphaltic material may be withdrawn from the lower section of space 223 to receiver 51 via conduit 231. By the arrangement hereinabove described the contact material passes as a continuous substantially compact column slowly downwardly through the sorption zone 205, then through a drain zone where unsorbed liquid is drained and purged therefrom, then through a washing zone wherein liquid asphaltic material adhering to the outer surfaces of the solid particles is washed away, then through a purging zone wherein washing solvent is removed and finally is discharged from the bottom of vessel 200 through conduit 235 at a rate controlled by throttle valve 236. The contact material bearing sorbed oily constituents is then conducted by a suitable conveyor 237 to hopper 238 wherein it may be partially heated by means of a suitable heat exchange fluid introduced at 234 and removed at 239. This partial preheating step may, if desired, be omitted. The contact material then passes downwardly through gravity feed leg 55 into the upper end of convertor 240. An inert seal gas is introduced into the upper end of vessel 240 through conduit 130 to maintain a seal gas blanket adjacent the lower end of feed leg 55 thereby preventing the escape of hydrocarbon reactant vapors therethrough. A plurality of spaced, vertical, finned heat transfer tubes 241 are positioned between suitable headers 242 and 243 within an upper portion of convertor 240. Heat exchange fluid from the cooling stages of a regenerator 97 similar to the one shown in Figure 1 may be pumped by pump 117 through conduit 244 feeding inlet header 242 and thence through tubes 241 to outlet manifold 243 from which it is withdrawn through conduit 245 to steam exchanger 115 and thence through conduit 114 back to the cooling coils 246 in regenerator 97. Stuffing boxes 247 and 248 are provided at the points of passage through the shell of conduits 244 and 245 respectively. The contact material bearing sorbed oily constituents passes downwardly as a substantially compact column through convertor 240, being heated by the heat released by contaminant burning in regenerator 97 transferred to the convertor by the heat exchange fluid passing through tubes 241. The contact material is heated by tubes 241 to a temperature suitable for conversion of the oily constituents to the desired gaseous products. The gaseous products are withdrawn from the lower section of the convertor 240 through conduit 247 and the catalyst after being purged by a suitable inert gas introduced into vessel 240 at 135 is withdrawn from the bottom of the convertor through conduit 93 at the desired rate as controlled by throttling valve 94. The used contact material is transferred by conveyor 95 to the regenerator 97 wherein it is regenerated in the manner discussed hereinbefore. Below the lowest burning stage in regenerator 97, there is

provided a cooling stage 232 wherein the contact material is cooled to a suitable temperature for reuse in the deasphalting operation. For this purpose heat transfer tubes (not shown) may be provided within stage 232 and a heat exchange fluid may be introduced therein through inlet conduit 249 and withdrawn therefrom through outlet conduit 250. The hot heat exchange fluid withdrawn from stage 232 may be pumped by pump 251 through conduit 252 and exchanger 253 wherein it gives up its heat to used washing solvent pumped by pump 151 from receiver 51 through conduit 152 and through exchanger 253 into a washing solvent fractionator 153. The cooled heat exchange fluid from exchanger 253 may be further cooled by cooler 254 and then returned to the heat transfer tubes in cooling stage 232 via conduit 249. In this manner the heat recovered from cooling of the hot regenerated catalyst in stage 232 is utilized for vaporizing and heating used washing solvent to a suitable temperature for its fractionation in fractionator 153. The recovered solvent, separated from asphaltic constituents is removed from the top of fractionator 153 via conduit 154 to condenser 155 from which it passes in part through conduit 158 as reflux to the fractionator and in part through conduit 255 to pump 256 by which it is pumped through conduit 228 back to the washing section of vessel 200. Cooled regenerated contact material is withdrawn from the bottom of cooling stage 232 through conduit 257 at a suitable rate controlled by throttle valve 258 and is transferred by conveyor 259 back to conduit 283 supplying the vessel 200.

In another modification of this invention the oily constituent bearing catalyst may be heated by mixing it with a hot inert heat carrying material which has previously been heated in the catalyst regenerator. Such a system is shown in Figure 3. In Figure 3, the liquid feed fraction introduced at 260 and the regenerated catalyst introduced at 261 are contacted in deasphalting chamber 262. The catalyst bearing sorbed oily constituents and the unsorbed liquid pass from chamber 262 via conduit 263 to drain chamber 264 wherein the liquid is drained off, being withdrawn at 265. The catalyst then passes via conduit 266 to washing chamber 267 wherein it is washed by suitable washing solvent introduced at 261. The used washing solvent is withdrawn at 268. The washed catalyst passes from chamber 268 via conduit 269 to conveyor 270 by which it is transferred to hopper 271 wherein it may be heated somewhat by heat exchange fluid introduced at 272 and withdrawn at 273. If desired, the catalyst may pass directly from hopper 271, without heating through gravity feed leg 274 to the seal chamber 275. The catalyst then passes from seal chamber 275 through conduit 276 at a suitable rate controlled by valve 277 into the upper section of convertor 278. Within the upper section of the convertor there is provided an arrangement of baffles adapted to cause the thorough mixing of the catalyst stream entering via conduit 276 and of a stream of particle-form hot inert heat carrying material entering through conduit 280 from a second seal chamber 281. The mixing device consists of a vertical, hollow cylinder 282 open on either end supported by rods 279 centrally of the vessel cross-section and surrounding the lower end of inert material inlet conduit 280. A smaller cylindrical shield 283 is connected by tapered connecting piece 284 to the lower end of conduit 280 so as to provide an an-

nular passage 285 for catalyst flow. Catalyst is directed into the annular passage from conduit 276. Hot heat carrying material particles pass into the space enclosed by shield 283 and are caused to flow around a small centrally placed baffle 286 positioned directly below the outlet of conduit 280. The inert solids stream from under shield 283 mixes with the catalyst stream from annular passage 285 and the combined streams flow onto a conical baffle 287 by which they are further mixed and then pass onto an accumulation of the mixed solids in a basin 288. The basin 288, supported by rods 330, is of smaller diameter than the vessel 278 but is of such diameter and so positioned with respect to the lower end of the cylindrical baffle 282 as to prevent the overflow of solids over the edge of the basin 288. The mixed contact material is distributed onto the surface 290 of the column of mixed material in the vessel therebelow by means of the spaced apart basin drain tubes 289. The rates of catalyst introduction and inert solids introduction into the convertor are controlled by valves 277 and 291 on conduits 276 and 280 respectively in such a manner as to accomplish the heating of the catalyst bearing sorbed oily constituents to a suitable conversion temperature for the oily constituents. The gaseous conversion products are withdrawn from the lower section of convertor through outlet 292 and the mixed spent catalyst and heat carrying material after being purged by a suitable purge gas entering the vessel at 293 are withdrawn from the bottom of vessel 278 through conduit 295. The rate of solid material withdrawal is controlled by valve 296 on conduit 295. The mixed solids are then transferred by conveyor 297 to the regenerator 298. The mixed solids pass downwardly through regenerator 298 being contacted with air introduced into the lower section of vessel 298 through conduit 299. Flue gas resulting from the burning off of the carbonaceous contaminants from the solid particles is withdrawn from the upper section of the regenerator through conduit 300. The excess heat released by the contaminant combustion is absorbed as increased sensible heat by the solid heat carrying particles thereby preventing overheating of the catalyst without the requirement for heat transfer tubes within the regenerator. The hot regenerated catalyst and hot inert heat carrying material are withdrawn together from the regenerator 298 through conduit 301 and then separated in a suitable separator such as a mechanical screen 302. The separated catalyst passes via conduit 304 to cooler 305 wherein it is cooled to a suitable temperature for reuse in the deasphalting operation by means of a heat exchange fluid introduced at 306 and withdrawn at 307. If desired, heat transfer tubes within cooler 305 may be dispensed with and the cooling may be accomplished by passing a cold gas such as air directly through the bed of catalyst in cooler 305. The cooled catalyst passes from cooler 305 through conduit 308 to conveyor 309 by which it is transferred to deasphalting chamber 262. The hot inert heat carrying material separated from the catalyst by screen 302 passes via conduit 315 to conveyor 316 by which it is transferred to the hopper and exchanger 317. In exchanger 317 the temperature of the inert material may be upwardly or downwardly adjusted by hot or cold gas introduced to exchanger 317 at 318, depending upon the thermal requirements of the system. The heat exchange gas is withdrawn from exchanger and hopper 317

through conduit 314. The hot inert heat carrying material then passes downwardly through gravity feed leg 319 to seal chamber 281 from which it is introduced to the convertor 278 via conduit 280. An inert seal gas such as steam or flue gas is introduced from conduit 320 to seal chambers 275 and 281 via conduits 321 and 322 respectively at a rate so controlled by diaphragm operated valve 323 and differential pressure control instrument 324 as to maintain an inert gaseous pressure in seal chambers 275 and 281 slightly above that in the upper section of convertor 278. For example, the pressure in seal chambers 275 and 281 may be maintained about $\frac{1}{4}$ to 1 pound per square inch above that in the upper section of convertor 278 thereby preventing escape of reactants through the solid feed system.

In order to permit the separation of hot regenerated catalyst from the inert heat carrying particles the heat carrying material should consist of particles either smaller or larger in diameter than the catalyst or of a substantially different density or both. For example, where a 4 to 16 mesh siliceous gel spherical (bead) catalyst is employed, the inert heat carrying particles may be of the order of 0.3 to 0.5 inch average diameter or of the order of .01 to .05 inch average diameter. The system shown in Figure 3 has the advantage of permitting the use of very simple and economical regenerator construction and of permitting the elimination of heat transfer tubes in both the regenerator and reactor. Where the heat carrying material is of substantially different density than the catalyst, it may be separated therefrom by a suitable conventional method and apparatus adapted for separating solids of different densities. The system may be very easily and economically maintained in thermal balance by means of direct heat transfer between the inert solid material and a suitable gas in exchanger and hopper 317. If the heat balance conditions in the system require addition of heat to the system this may be easily accomplished either by the introduction of a heated gas into the direct contact exchanger 317 through conduit 318 or by the introduction of air and a suitable fuel gas which may be burned in the bed of inert material within exchanger 317.

In an alternative form of operation the hot inert material may be separated from the used catalyst discharged from convertor 278, recycled directly to combined hopper and exchanger 317, heated therein either by hot gases or by burning a fuel gas, and passed back to the convertor. In such an operation the regenerator may be provided with heat transfer tubes in order to permit control of the catalyst temperature during the contaminant burning.

As an example of the result obtainable by the method of this invention the treatment of an East Texas crude bottoms fraction having an A. P. I. gravity of 15.0 at 60° F., a Saybolt Universal viscosity of 512 seconds at 210° F., a pour point above 115° F., and a Conradson carbon residue of 11.1 percent may be considered. The vacuum assay distillation of this feed fraction was as follows:

	°F.
I. B. P.-----	880
10% -----	964
30% -----	1026
40% -----	1054
47% -----	1082

This feed fraction was contacted in a suitable confined chamber with a silica-alumina, spe-

roidal gel catalyst prepared by the method described in United States Patent 2,384,946 issued September 18, 1945 to Milton Marisic. The catalyst unpacked density was about 44 pounds per cubic foot and consisted of particles falling within the range 4 to 16 mesh by Tyler Standard Screen Analysis. The catalyst has been regenerated until the residual carbon thereon was below 0.5% by weight. During the operation the temperature was maintained at about 275° F. and the pressure was substantially atmospheric. The ratio of liquid to catalyst charge to the sorption zone was about 3.2 parts by weight of catalyst per part by weight of liquid charge. The residence time within the sorption zone was about 240 minutes. The unsorbed liquid was recycled until substantially all of the oily constituents had been removed therefrom. Finally a tar fraction amounting to about 30 percent by weight of the liquid charge was separated from the catalyst bearing sorbed oily constituents and the catalyst was washed with about half of its weight of Stoddard Solvent, the residence time of the catalyst in the washing operation being limited to about 3 minutes. The catalyst after washing contained about 22 percent of its original weight of sorbed oily constituents which represented about 70 percent by weight of the original liquid charge. The catalyst bearing oily constituents was then heated to a temperature suitable for the cracking conversion of the sorbed oily constituents in a confined conversion zone. An analysis of the sorbed oily constituents before conversion was as follows:

A. P. I. gravity 17.1; viscosity (kv.) at 210° F.—46; pour point above 120° F., and Conradson carbon residue 5.7% by weight.

The conditions in the conversion zone were as follows:

Average temperature—890° F.

Pressure @ 0 #/in.² gauge

Residence time—10 minutes

The following conversion yields were obtained:

Gasoline (410° F. E.P.)—41% by weight of the sorbed oily constituents

Cycle oil—44% by weight of the sorbed oily constituents

Coke on catalyst—10% by weight of sorbed oily constituents

Gas—5% by weight of sorbed oily constituents

The coke deposited on the used catalyst was about 2.6% by weight of the catalyst and was readily removed by burning at temperatures within the range 800° F. to 1100° F.

In the above described example a light cycle stock of 32 A. P. I. gravity and boiling within the range about 400° F. to 675° F. by A. S. T. M. distillation was substituted for the Stoddard Solvent in the washing step without any material change in the washing and final conversion results.

It should be understood that the details of apparatus construction and arrangement, of operating conditions, and of applications of the process of this invention given hereinabove are intended merely as illustrative and it is not intended that the scope of this invention should be limited thereto or limited otherwise except as it may be limited in the following claims.

This application is a continuation-in-part of application Serial Number 720,271 filed in the United States Patent Office January 4, 1947, now abandoned.

I claim:

1. A method for conversion of asphalt con-

taining liquid hydrocarbon feeds at elevated temperatures which comprises: contacting the asphalt containing feed with a porous particle-form contact material having the structure of an inorganic oxide gel, in which the total macropore volume is less than about 30 per cent of the total pore volume and in which the particles are substantially all larger than about 30 mesh, at a temperature below about 500° F., whereby the oily constituents of said feed are sorbed in the pores of said contact material while the asphalt constituents remain substantially unsorbed; effecting a substantial separation of the contact material bearing sorbed oily constituents from the unsorbed material and heating said contact material to a temperature suitable for the desired conversion of said oily constituents.

2. A process for the conversion of the high boiling oily constituents present in high boiling petroleum feed fractions containing asphaltic and oily constituents to lower boiling gaseous gasoline containing products which comprises: subjecting the feed fraction in a confined zone to contact with a porous inorganic oxide gel-type contact material consisting of particles having a greater average diameter than about .022 inch and having less than 30 per cent of its pore volume taken up by macropores, the remaining pore volume being taken up by smaller pores, at a temperature below about 500° F., whereby the oily constituents of said feed fraction are substantially sorbed by said contact material and the asphalt constituents remain substantially unsorbed, effecting a substantial separation of unsorbed liquid from said contact material bearing sorbed oily constituents, passing said contact material downwardly through a confined conversion zone as a substantially compact column while heating it to a temperature above about 750° F. which is suitable for conversion of said oily constituents to gaseous gasoline containing products, withdrawing said gaseous products from the lower section of said conversion zone, withdrawing used contact material bearing carbonaceous contaminant deposits from the lower end of said conversion zone substantially separately of said gaseous products, passing said used contact material through a confined regeneration zone while maintaining its temperature above the minimum level required for rapid burning of said deposits but below a heat damaging level, passing a combustion supporting gas into contact with said contact material in said regeneration zone to burn said deposits, withdrawing the regenerated contact material from said regeneration zone, cooling said contact material to a suitable temperature below about 750° F. and reusing at least a portion of said contact material for contacting petroleum feed fraction as aforesaid.

3. A process for conversion of the oily constituents in high boiling liquid hydrocarbon feeds containing asphaltic constituents to gaseous, gasoline containing products which comprises: maintaining within a confined desasphalting zone a substantially compact column of contact material in the form of spheroidal siliceous gel particles characterized in that it consists substantially entirely of spheroidal contact material particles having an average diameter greater than about .022 inch and having less than 30 per cent of its pore volume devoted to macropores, the remaining pore volume being devoted to smaller pores, distributing said liquid feed onto said column adjacent its upper end and

causing said liquid to pass downwardly within said column, while maintaining the temperature of said column below about 500° F., whereby oily constituents of said feed are sorbed by said contact material and the asphaltic constituents remain substantially unsorbed, withdrawing the contact material and unsorbed liquid from said deasphalting zone, draining the liquid from said contact material, subjecting the contact material to a quick wash with a suitable hydrocarbon solvent to wash from its outer surface adhering asphalt containing liquid, subjecting the washed contact material to purging with a suitable non-oxidizing purge gas to remove adhering wash solvent from the outer surface of the contact material particles, passing the purged contact material into a confined zone and heating it therein to a temperature above about 750° F. which is suitable for conversion of the sorbed oily constituents to gaseous gasoline containing products, maintaining said oily constituents in contact with said heated contact material a sufficient time to effect said conversion, effecting separation of said gaseous products from the used contact material upon which a carbonaceous contaminant has been deposited during said conversion, contacting the contact material at suitable elevated regeneration temperatures with a combustion supporting gas to burn off said contaminant deposit, cooling the contact material to a temperature suitable for introduction into said deasphalting zone and passing the cooled contact material into the upper section of said deasphalting zone to replenish said column therein.

4. A process for conversion of the high boiling oily constituents in asphalt bearing hydrocarbon liquid feeds to lower boiling products which comprises: contacting said liquid feed for a suitable time and at a suitable temperature with a porous particle-form inorganic oxide gel-type contact material, in which most of the pores are micropores and the volume of macropores is less than about 30 per cent of the total pore volume and in which the particles are greater than about 30 mesh size, to effect the sorption of the oily constituents of said feed in the pores of said contact material while leaving the asphalt constituents substantially unsorbed, effecting a substantial separation of the unsorbed liquid from the contact material which bears the sorbed oily constituents, and heating said contact material in a confined zone by indirect heat transfer to a temperature suitable for converting said oily constituents to lower boiling products, maintaining the oily constituents in contact with the heated contact material for sufficient time to effect said conversion and effecting separation of the resulting lower boiling products from said contact material.

5. A process for conversion of the high boiling oily constituents in asphalt bearing hydrocarbon liquid feeds to lower boiling products which comprises: contacting said liquid feed for a suitable time and at a suitable temperature with a porous particle-form inorganic oxide gel-type contact material, in which most of the pores are micropores and the volume of macropores is less than about 30 per cent of the total pore volume and in which the particles are greater than about 60 mesh size, to effect the sorption of the oily constituents of said feed in the pores of said contact material while leaving the asphalt constituents substantially unsorbed; effecting a substantial separation of the unsorbed liquid from the contact material which bears the sorbed oily constituents;

subjecting said contact material bearing sorbed oily constituents to indirect heat transfer from a heated particle-form solid material to heat said contact material and the oily constituents to a temperature suitable for the conversion of said oily constituents to lower boiling gaseous products; maintaining the heated oily constituents in contact with said heated contact material for sufficient time to effect said conversion; and effecting separation of said gaseous products from said contact material.

6. A process for conversion of the oily constituents present in a liquid hydrocarbon feed containing both oily and asphaltic constituents at elevated temperatures which process comprises the steps: contacting said liquid feed in a confined zone with a porous particle-form inorganic oxide gel-type contact material, in which most of the pores are micropores and the volume of macropores is less than about 30 per cent of the total pore volume controlling the relative relationship of particle size, and contacting period and temperature to effect the sorption of the oily constituents of said feed in the pores of said contact material while leaving the asphalt constituents substantially unsorbed, the size of the particles employed being larger for longer contact periods and higher contact temperature; effecting a substantial separation of the unsorbed liquid from the contact material which bears the sorbed oily constituents; and mixing sufficient heated substantially inert particle-form solid heat carrying material with the separated contact material bearing the sorbed oily constituents to heat said contact material to a temperature suitable for effecting the desired conversion of said oily constituents.

7. A process for conversion of the oily constituents present in a liquid hydrocarbon feed containing both oily and asphaltic constituents at elevated temperatures which process comprises the steps: contacting said liquid feed in a confined zone with a porous particle-form inorganic oxide gel-type contact material of greater particle size than about 60 mesh Tyler, in which most of the pores are micropores and the volume of macropores is less than about 30 per cent of the total pore volume, controlling the relationships of contacting time and temperature and contact material average particle diameter to effect the sorption of the oily constituents of said feed in the pores of said contact material while leaving the asphalt constituents substantially unsorbed, effecting a substantial separation of the unsorbed liquid from the contact material which bears the sorbed oily constituents, passing said contact material bearing sorbed oily constituents through a confined conversion zone to effect conversion of said oily constituents to lower boiling products, effecting separation of said lower boiling products from the used contact material upon which a carbonaceous contaminant has been deposited during said conversion, passing the used contact material through a confined regeneration zone and contacting it therein with a combustion supporting gas to burn off said contaminant and effecting the transfer by indirect heat transfer of a sufficient portion of the excess heat liberated by burning said contaminant in said regeneration zone to said conversion zone to heat the oily constituents bearing contact material passing there-through to a temperature suitable for effecting said conversion of said oily constituents.

8. A process for conversion of the oily constituents present in a liquid hydrocarbon feed stock

containing both oily and asphaltic constituents at elevated temperatures in the presence of a particle-form contact mass material which process comprises: contacting the liquid charging stock in a confined deasphalting zone with a particle-form porous contact material having the pore structure of an inorganic oxide gel in which the total pore volume is taken up mostly by micropores, there being less than about 30 per cent macropores, the contact material being made up substantially of particles larger than about 30 mesh size, controlling the temperature during the contacting at a level suitable for the sorption of oily constituents in the pores of the contact material and below that which would cause substantial coking of the asphalt constituents, which constituents remain substantially unsorted in the pores of said contact material, removing contact material and unsorted liquid from the deasphalting zone and drawing off the unsorted liquid, washing the contact material with a suitable hydrocarbon solvent to remove asphalt containing liquid adhering to the outer surface of the solid particles, passing the washed contact material bearing sorbed oily constituents through a confined conversion zone while heating it to a temperature suitable for conversion of said oily constituents to valuable lower boiling products, separating said lower boiling products from the used contact material upon which a carbonaceous contaminant has been deposited during said conversion, passing the used contact material through a confined regeneration zone while controlling its temperature at a level suitable for rapid burning of said contaminant but below a level which would cause substantial permanent heat damage to said contact material, passing a combustion supporting gas into contact with said contact material in said regeneration zone to burn off said contaminant, withdrawing regenerated contact material from said regeneration zone, passing the used washing solvent from washing said contact material from said deasphalting zone in indirect heat transfer relationship with said regenerated contact material to help cool the contact material to a temperature suitable for its use in contacting liquid asphalt bearing hydrocarbon feeds as aforesaid and to heat said solvent to a suitable distillation temperature, and passing the heated solvent to a suitable distillation zone to effect the separation of solvent from the asphaltic materials washed from the contact material.

9. A process for conversion of the oily constituents present in a liquid hydrocarbon feed stock containing both oily and asphaltic constituents at elevated temperatures in the presence of a particle-form contact mass material which process comprises: contacting the liquid charging stock in a confined deasphalting zone with a particle-form porous contact material having the pore structure of an inorganic oxide gel in which the total pore volume is taken up mostly by micropores, there being less than about 30 per cent macropores, the contact material being made up substantially of particles larger than about 30 mesh size, controlling the temperature during the contacting at a level suitable for the sorption of oily constituents in the pores of the contact material and below that which would cause substantial coking of the asphalt constituents, which constituents remain substantially unsorted in the pores of said contact material, removing the contact material and unsorted liquid from the deasphalting zone and drawing off the unsorted

liquid, washing the contact material with a suitable hydrocarbon solvent to remove asphalt containing liquid adhering to the outer surface of the solid particles, heating the washed contact material to a temperature substantially above the temperature of the washing but below about 750° F., passing the heated contact material downwardly as a substantially compact column through a confined conversion zone while further heating it therein to a temperature suitable for effecting the conversion of said sorbed oily constituents to lower boiling gaseous products, maintaining the oily constituents within said conversion zone for a sufficient time to effect said conversion, withdrawing said gaseous products from the lower section of said conversion zone and substantially separately withdrawing the used contact material.

10. A process for conversion of the oily constituents present in a liquid hydrocarbon feed stock containing both oily and asphaltic constituents at elevated temperatures in the presence of a particle-form contact mass material which process comprises: contacting the liquid charging stock in a confined deasphalting zone with a particle-form porous contact material having the pore structure of an inorganic oxide gel in which the total pore volume is taken up mostly by micropores, there being less than about 30 per cent macropores, the contact material being made up substantially of particles larger than about 30 mesh size; controlling the temperature during the contacting at a level suitable for the sorption of oily constituents in the pores of the contact material and below that which would cause substantial coking of the asphalt constituents, which constituents remain substantially unsorted in the pores of said contact material; effecting separation of the contact material bearing sorbed oily constituents from the unsorted constituents of said hydrocarbon feed stock; passing the separated contact material bearing sorbed oily constituents downwardly as a substantially compact column through an elongated, confined substantially vertical conversion zone to effect conversion of said oily constituents to lower boiling gaseous products; withdrawing gaseous products near the lower end of said conversion zone; withdrawing used contact material from the lower end of said conversion zone substantially separately of said conversion products the used contact material having deposited thereon a carbonaceous contaminant; passing the used contact material through a confined regeneration zone; passing a combustion supporting gas into contact with said contact material in said regeneration zone to burn said contaminant; withdrawing hot regenerated contact material from said regeneration zone; passing said hot regenerated contact material in indirect heat transfer relationship with an upper portion of said column of oily constituents bearing contact material in the upper section of said conversion zone to cool said regenerated contact material and to partially heat said oily constituent bearing contact material; passing the cooled regenerated contact material to said deasphalting zone as the supply thereto; passing a fluid heat exchange medium in indirect heat transfer relationship with said contact material in said regeneration zone to control the contact material temperature below a heat damaging level; and passing at least part of the heat exchange fluid from the regeneration zone in in-

direct heat transfer relationship with the column of contact material in said conversion zone below that portion of the column devoted to indirect heat transfer with hot regenerated contact material so as to further heat said oily constituent bearing contact material to a temperature suitable for effecting said conversion of said oily constituents.

11. A process for conversion of the oily constituents present in a liquid hydrocarbon feed stock containing both oily and asphaltic constituents at elevated temperatures in the presence of a particle-form contact mass material which process comprises: contacting the liquid charging stock in a confined deasphalting zone with a particle-form porous contact material having the pore structure of an inorganic oxide gel in which the total pore volume is taken up mostly by micropores, there being less than about 30 per cent macropores, the contact material being made up substantially of particles larger than about 30 mesh size, controlling the temperature during the contacting at a level suitable for the sorption of oily constituents in the pores of the contact material and below that which would cause substantial coking of the asphalt constituents, which constituents remain substantially unsorbed in the pores of said contact material, removing the contact material and unsorbed liquid from the deasphalting zone and drawing off the unsorbed liquid, washing the contact material with a suitable hydrocarbon solvent to remove asphalt containing liquid adhering to the outer surface of the solid particles, passing the washed contact material through a partial heating zone, passing the partially heated contact material as a substantially compact column through a confined conversion zone and heating it therein to a temperature suitable for effecting conversion of said oily constituents to gaseous hydrocarbon products, separating the gaseous products from the used contact material upon which a carbonaceous contaminant has been deposited during said conversion, passing the used contact material through a confined regeneration zone while controlling its temperature at a level suitable for rapid burning of said contaminant but below a level which would cause substantial permanent heat damage to said contact material, passing a combustion supporting gas into contact with said contact material in said regeneration zone to burn off said contaminant, withdrawing hot regenerated contact material from said regeneration zone, cyclically passing a suitable heat exchange fluid in indirect heat transfer relationship with said hot regenerated contact material to cool the same to a temperature suitable for its introduction into said deasphalting zone and in indirect heat transfer relationship with the washed contact material in said partial heating zone to partially heat said washed contact material.

12. A process for conversion of the oily constituents present in a liquid hydrocarbon feed stock containing both oily and asphaltic constituents at elevated temperatures in the presence of a particle-form contact mass material which process comprises: contacting the liquid charging stock in a confined deasphalting zone with a particle-form porous contact material having the pore structure of an inorganic oxide gel in which the total pore volume is taken up mostly by micropores, there being less than about 30 per cent macropores, the contact material being made

up substantially of particles larger than about 60 mesh size, controlling the temperature during the contacting at a level suitable for the sorption of oily constituents in the pores of the contact material and below that which would cause substantial coking of the asphalt constituents, which constituents remain substantially unsorbed in the pores of said contact material, removing the contact material and unsorbed liquid from the deasphalting zone and drawing off the unsorbed liquid, washing the contact material with a cycle oil boiling above the boiling range of motor gasoline to remove asphalt containing liquid adhering to the outer surface of the solid particles, passing the washed contact material bearing sorbed oily constituents downwardly through a confined conversion zone as a substantially compact column while heating it to a temperature suitable for effecting conversion of said oily constituents to gaseous gasoline containing products, withdrawing the contact material from the lower section of said conversion zone, withdrawing said gaseous products from said conversion zone separately of said contact material, subjecting said gaseous products to fractionation to separate light and heavy cycle oils boiling above motor gasoline from the other products, and utilizing at least a portion of said light cycle oil for washing the contact material from said deasphalting zone as aforesaid.

13. A process for conversion of the oily constituents present in a liquid hydrocarbon feed containing both oily and asphaltic constituents at elevated temperatures which process comprises the steps: contacting said liquid feed in a confined zone for a suitable time and at a suitable temperature with a porous particle-form inorganic oxide gel-type contact material, in which most of the pores are micropores and the volume of macropores is less than about 30 per cent of the total pore volume and in which the particles are greater than about 60 mesh size, to effect the sorption of the oily constituents of said feed in the pores of said contact material while leaving the asphalt constituents substantially unsorbed, effecting a substantial separation of the unsorbed liquid from the contact material which bears the sorbed oily constituents; passing said contact material bearing sorbed oily constituents through a confined conversion zone in admixture with a sufficient amount of hot, substantially inert, particle-form solid heat carrying material to heat said contact material and the oily constituents to a temperature suitable for accomplishing the conversion of said oily constituents to lower boiling products, said inert solid material consisting of particles of substantially different size than said contact material; effecting a separation of said lower boiling hydrocarbon products from the mixed contact material and inert solid heat carrying material; passing the mixed inert solid material and said used contact material which bears a carbonaceous contaminant deposit through a confined regeneration zone; passing an oxygen containing gas into contact with said contact material in said regeneration zone to burn off said contaminant withdrawing hot regenerated contact material and the inert solid heat carrying material from said regeneration zone; separating the hot inert solid heat carrying material from the regenerated contact material; reusing hot heat carrying material for admixture with said oily bearing contact material for passage through said conversion zone as aforesaid; cooling the regener-

ated contact material to a temperature suitable for contacting said liquid feed and reusing the cooled contact material for contacting the asphalt and oily constituent bearing liquid feed in said confined zone as aforesaid.

14. The continuous cyclic process for conversion of the oily constituents in high boiling liquid petroleum fractions bearing asphalt and oily constituents to lower boiling gasoline containing products in the presence of a particle-form catalyst which process comprises: introducing said liquid feed fraction into a confined deasphalting zone to contact at a temperature below about 500° F. a particle-form porous inorganic oxide gel catalyst made up of particles having an average diameter greater than about .022 inch, in which the pore volume is taken up mostly by micropores and the amount of the total pore space which is taken up by macropores being less than 30 per cent by volume, whereby the oily constituents of said liquid feed fraction are sorbed in the pores of said catalyst and the asphalt constituents remain substantially unsorbed, effecting a substantial separation of the unsorbed asphalt constituents from the catalyst bearing sorbed oily constituents, passing the separated catalyst bearing sorbed oily constituents onto an accumulation of said catalyst in a confined seal zone, passing a stream of said catalyst from said seal zone downwardly into the upper section of a confined, elongated conversion zone, mixing the catalyst in the upper section of said conversion zone with a stream of hot inert solid heat carrying material in such proportions as to heat the catalyst to a temperature suitable for effecting conversion of said sorbed oily constituents to lower boiling gaseous, gasoline containing products, passing the mixed contact material and inert heat carrying material downwardly through a lower section of said conversion zone as a substantially compact column to effect said conversion of said oily constituents, withdrawing said gaseous products from the lower section of said conversion zone, withdrawing the mixed used catalyst and heat carrying material from the lower section of said conversion zone substantially independently of said gaseous products, the catalyst now having a carbonaceous contaminant deposited thereon, passing the mixed used catalyst and heat carrying material through a confined regeneration zone while contacting it with an oxygen containing gas to burn the contaminant from said catalyst, the heat carrying material serving to absorb the excess heat released by the contaminant burning so as to prevent the catalyst temperature from rising to a heat damaging level, effecting the separation of the hot heat carrying material from the hot regenerated catalyst, cooling the regenerated catalyst and returning it to said deasphalting zone as the catalyst supply thereto, passing the separated hot heat carrying material onto an accumulation thereof in a confined seal zone, passing a stream of said hot heat carrying material from said seal zone into the upper section of said conversion zone to mix with said oily constituent bearing catalyst as aforesaid, and maintaining an inert gaseous pressure in both of said seal zones above the gaseous pressure in the upper section of said conversion zone.

15. A process for conversion of oily constituents present in liquid fractions containing oily and asphalt constituents at elevated temperatures which comprises: sorbing said oily constituents from the liquid hydrocarbon fraction onto a por-

ous siliceous gel contact material in the form of spheroidal particles having average diameters within the range .022 to 1.0 inch and characterized by a substantial absence of macropores, whereby oily constituents from said liquid fraction are sorbed and asphalt constituents remain substantially unsorbed, effecting a substantial separation of unsorbed asphalt constituents from the contact material bearing sorbed oily constituents and heating the separated contact material bearing sorbed oily constituents to a temperature suitable for effecting the desired conversion of said oily constituents.

16. A process for obtaining gasoline containing products from high boiling asphalt bearing hydrocarbon feeds which comprises, contacting said liquid feed with a solid inorganic sorbent material in which the pores are mostly micropores and the volume of pores having radii greater than about 100 angstrom units is less than about 30 percent of the total pore volume, controlling the relative relationships of contact time, temperature, and sorbent particle size to effect sorption of the oily constituents of said feed into the pores of the sorbent while leaving substantially unsorbed the asphalt constituents, the size of particles employed being larger for longer contact periods and higher contact temperatures, separating the sorbent bearing oily constituents from the unsorbed asphalt constituents and heating said sorbent to a temperature suitable for the desired conversion of said oily constituents.

17. A process for conversion of oily constituents in asphalt bearing hydrocarbon liquid feeds which comprises, contacting the hydrocarbon fraction with a porous solid inorganic contact material having most of its pore volume devoted to micropores and having less than about 30 percent by volume of its pore volume devoted to pores of greater than about 100 angstrom unit radius and made up of particles of greater size than about 60 mesh Tyler until the oily constituents of said fraction are sorbed into the sorbent pores and the asphalt constituents are left substantially unsorbed, effecting substantial separation of the sorbent material bearing sorbed oily constituents from the unsorbed asphalt constituents, heating the sorbent material and sorbed oily constituents to a temperature suitable for the desired conversion of said oily constituents, and separating the conversion products from the sorbent material.

18. A process for conversion of high boiling liquid asphalt containing hydrocarbon fractions to lower boiling products which comprises, contacting said liquid fraction for a suitable time and at a suitable temperature for oily constituent sorption with a porous inorganic oxide contact material of greater particle size than about 60 mesh Tyler in which most of the pores are micropores and the volume of macropores is less than about 30 percent of the total pore volume while leaving substantially unsorbed the asphalt constituents, effecting a substantial separation of the unsorbed liquid from the contact material which bears the sorbed oily constituents, passing the separated contact material through a confined zone while heating it therein to a temperature suitable for effecting the conversion of said oily constituents to lower boiling products, effecting a substantial separation of said lower boiling products from the used contact material which bears a carbonaceous contaminant deposit, effecting the removal of said contaminant deposit from the contact material and reusing

the contact material after removal of said contaminant deposit for contacting liquid asphalt bearing fraction as aforesaid.

19. A process for obtaining gasoline containing products from high boiling asphalt bearing hydrocarbon feeds which comprises, contacting said liquid feed with a solid inorganic sorbent material in which the pores are mostly micropores and the volume of pores having radii greater than about 100 angstrom units is less than about 30 percent of the total pore volume, controlling the relative relationships of contact time, temperature, and sorbent particle size to effect sorption of the oily constituents of said feed into the pores of the sorbent while leaving substantially unsorted the asphalt constituents, the size of particles employed being larger for longer contact periods and higher contact temperatures, separating the sorbent bearing oily constituents from the unsorted asphalt constituents, and passing a suitable heat exchange fluid in indirect heat transfer relationship with the sorbent bearing sorbed oily constituents to heat said sorbent and said oily constituents to a temperature suitable for effecting the desired conversion of said oily constituents.

20. A process for conversion of oily constituents in asphalt bearing hydrocarbon fractions which comprises, contacting the hydrocarbon fraction with a porous inorganic oxide solid sorbent made up of particles of greater than about 60 mesh Tyler particle size and having most of its pore volume devoted to micropores and hav-

ing less than about 30 percent by volume of its pores devoted to pores of greater than about 100 angstrom unit radius to effect sorption of liquid hydrocarbons onto said sorbent under controlled contacting conditions, washing asphaltic constituents off of said sorbent and heating said sorbent bearing oily constituents but free of at least most of the asphaltic constituents to a temperature suitable for the desired conversion of said oily constituents.

LOUIS P. EVANS.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
226,001	Riebeck	Mar. 30, 1880
1,278,023	Rosenbaum	Sept. 3, 1918
1,447,297	Day	Mar. 6, 1923
1,568,018	Forrest et al.	Dec. 29, 1925
2,188,007	Kistler	Jan. 23, 1940
2,354,355	Abrams et al.	July 25, 1944
2,382,755	Tyson	Aug. 14, 1945
2,487,795	Evans	Nov. 15, 1949

OTHER REFERENCES

Allibone "Journal of the Institute of Petroleum," vol. 27, pages 94-108 (1941).

A New Type of Silica Gel; by Holmes et al., Industrial & Eng. Chem., vol. 17, No. 3, pages 280-287.

Certificate of Correction

Patent No. 2,531,356

November 21, 1950

LOUIS P. EVANS

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 3, line 17, for the word "ores" read *pores*; line 27, for "htose" read *those*; column 14, line 20, for "cooking" read *coking*; column 24, lines 70 and 71 and column 26, line 62, for "constituents" read *constituent*;

and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 15th day of May, A. D. 1951.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.