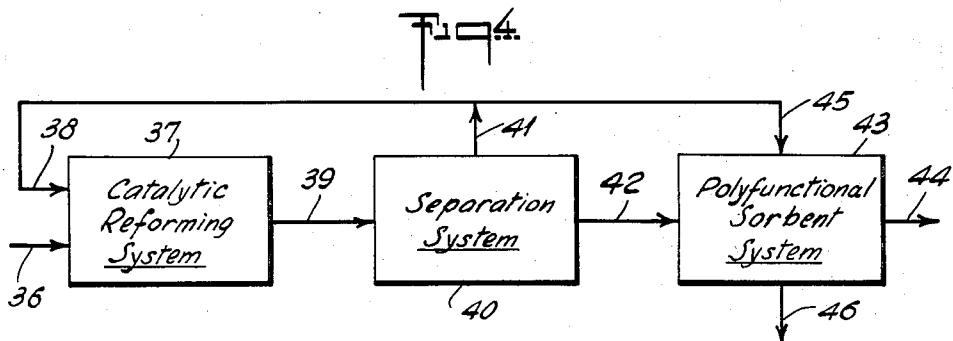
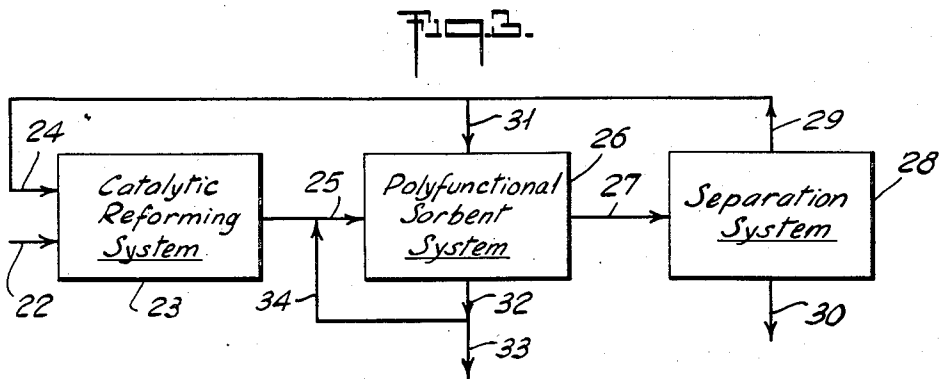
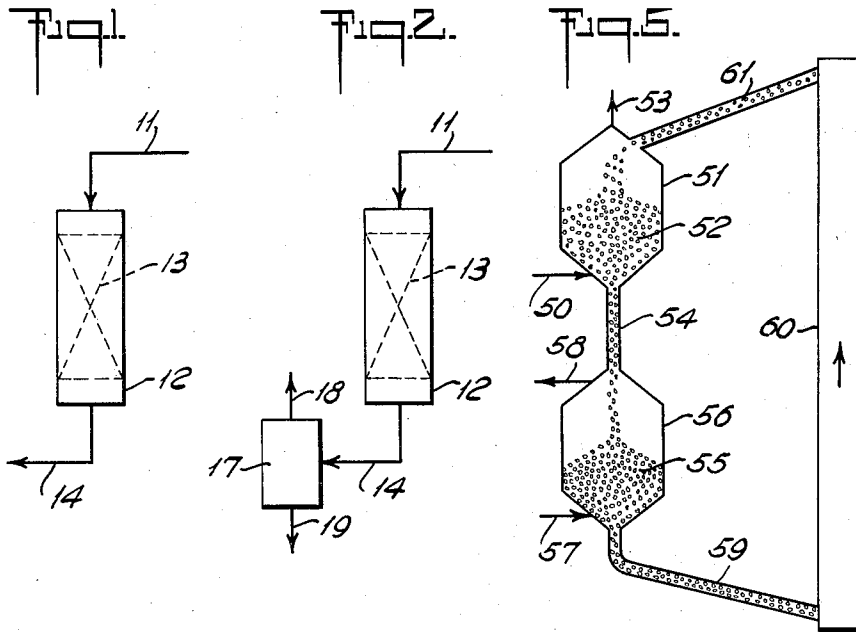


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POLYFUNCTIONAL SOLID SORBENTS

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POLYFUNCTIONAL SOLID SORBENTS

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This invention relates to a polyfunctional solid sorbent useful for treating hydrocarbon fractions such as petroleum fractions and hydrocarbon synthesis (Fischer-Tropsch) fractions, process for producing such polyfunctional sorbent, and methods of treating a hydrocarbon stream with such polyfunctional sorbent.

Broadly, our polyfunctional solid sorbent comprises about 0.1 to 20 weight percent metalliferous catalytic agent for reforming hydrocarbons supported on and integral with mineral sorbent selective for straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons in a mixture thereof.

Our process for producing the polyfunctional sorbents of this invention comprises depositing, from an inert dispersion in a liquid vehicle onto mineral sorbent selective for straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons in a mixture thereof, metalliferous reforming catalyst-providing material equivalent to about 0.1–20 percent metalliferous reforming catalyst based on the weight of finished polyfunctional sorbent; and converting deposited metalliferous catalyst-providing material on said mineral sorbent into metalliferous catalytic reforming agent.

When a hydrocarbon stream containing straight chain hydrocarbons and non-straight chain hydrocarbons is contacted with the polyfunctional solid sorbents of this invention under conditions hereinafter described, a hydrocarbon effluent having a reduced amount of straight chain hydrocarbons is produced. Upon recovery of sorbed hydrocarbons from the polyfunctional sorbent under reforming conditions a hydrocarbon mixture having largely non-straight chain character is collected; simultaneously the sorbing capacity of the sorbent is reconstituted for another cycle of operation. We have found that maintenance of not more than 20 weight percent metalliferous catalytic reforming agent (based on weight of finished polyfunctional sorbent) integral with the mineral sorbent does not impair the sorbing capacity of the original mineral sorbent to any great extent, e.g., not more than about 1/3 and usually not more than about 10–20%.

The drawings are process flow diagrams showing employment of our novel polyfunctional sorbents in the treatment of hydrocarbon fractions.

By straight chain hydrocarbons is meant any aliphatic or acyclic or open chain hydrocarbon which does not possess side chain branching. Representative straight chain hydrocarbons are the normal paraffins and the normal olefins, mono or polyolefins, or straight chain acetylenic hydrocarbons. The non-straight chain hydrocarbons comprise the aromatic and naphthenic hydrocarbons as well as the isoparaffins, isoolefinic hydrocarbons and the like. Straight chain hydrocarbon-containing mixtures which are suitably treated in accordance with this invention include mixed butanes, mixtures of normal alkanes and their isomers, and various petroleum fractions such as a naphtha fraction, a gasoline fraction, a diesel oil fraction, a kerosene fraction, a gas oil fraction and the

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like. Particularly suitable for treatment in accordance with this invention are straight chain hydrocarbon-containing fractions having a boiling point or a boiling range in the range of 40–550° F. and containing a substantial amount of straight chain hydrocarbons, e.g., 2–35% by volume. More particularly, a petroleum fraction suitable for use in practice of this invention could have an initial boiling point in the range of 40–300° F. and an end point in the range of 150–550° F. A petroleum fraction for use in the practice of this invention must contain both straight chain and non-straight chain hydrocarbons as demonstrated by the following composition:

Hydrocarbon Type	Percent by Volume
Naphthenes.....	0–75
Aromatics.....	0–50
Acyclic Saturates (including normal paraffins and iso-paraffins.....	2–90
Acyclic Unsaturates (including normal olefins and isoolefins.....	0–50

Typical refinery stocks or fractions which are applicable to the practice of this invention are a wide boiling straight run naphtha, a light straight run naphtha, a heavy straight run naphtha, a catalytically cracked naphtha, a thermally cracked or thermally reformed naphtha, a catalytically reformed naphtha and the like. By the term “motor naphtha” used herein we mean a naphtha fraction suitable as a base for conventional automobile fuel and containing no additives, as to be distinguished from gasoline which can contain various additives of specialized function, e.g., tetraethyl lead.

Any solid selective sorbent which selectively sorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons is suitable material for the polyfunctional sorbents of our invention and herein will be called a “mineral sorbent” for convenience. It is preferred, however, to employ as the selective sorbent certain natural or synthetic zeolites or aluminosilicates, such as a calcium aluminosilicate, which exhibit the property of a molecular sieve, that is, matter made up of porous crystals wherein the pores of the crystals are of molecular dimension and are of substantially uniform size. A particularly suitable solid mineral sorbent for straight chain hydrocarbons is a calcium aluminosilicate, apparently actually a sodium calcium aluminosilicate, manufactured by Linde Air Products Company and designated in the trade as Linde Type 5A molecular sieve, and its particular zeolitic structure has been nominated as “Type A” for ease of reference. The crystals of this particular calcium aluminosilicate have a pore size or diameter of about 5 Angstrom units, such pore size being sufficiently large to admit straight chain hydrocarbons such as the normal paraffins and normal olefins to the substantial exclusion of the non-straight chain naphthenic, aromatic, isoparaffinic and isoolefinic hydrocarbons. This particular mineral sorbent is available in various sizes, e.g., a finely divided powder having a particle size in the range of 0.5–5.0 microns, exhibiting a bulk density in lbs. per cubic foot of 33, and a particle density in grams per cc. of 1.6. Another form of the above-mentioned selective sorbent consists of a multiplicity of small sieve particles aggregated, extruded in cylindrical form, and cut into short lengths.

The polyfunctional sorbent of our invention can be in a number of forms, e.g., the metalliferous catalyst can be impregnated or otherwise coated upon fine mineral sorbent particles; or the fine mineral sorbent particles can be formed with adhesives such as starch and higher molecular weight fatty acids into larger bodies, e.g., by extrusion or pelleting. In the latter case the catalytic

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agent can be deposited on the body of mineral sorbent particles essentially in the form of a coating with only incidental metalliferous catalyst penetration into the body of sorbent particles. Alternatively, the catalytic agent can be substantially uniformly diffused throughout an agglomerated body of fine mineral sorbent particles by forming into larger bodies a plurality of finely divided sorbent particles which have been impregnated or otherwise coated with the metalliferous catalytic agent. As a practical matter, the most generally useful polyfunctional sorbents of our invention are those made in the form of cylindrical pellets, spheres, beads or irregular shapes from about $\frac{1}{16}$ " to $\frac{5}{8}$ " diameter in the upper size range down to 100–300 mesh sieve size (U.S. Standard) in the lower size range, but it is obvious to one skilled in the art that many other shapes and sizes can be made without departing from the spirit or scope of this invention. For fixed bed or moving bed use the larger sized polyfunctional sorbents are preferred, and, for fluidized bed work, sizes in the screen range of 100 to 300 mesh are preferred.

The two principal types of the agglomerated polyfunctional sorbents of this invention, i.e., the type having a coating of metalliferous catalytic agent and the one having the metalliferous catalytic agent substantially uniformly diffused throughout the body of agglomerated particles, have distinct and particular advantages for use in the treatment of hydrocarbons. The coated agglomerate is particularly well suited for fixed bed operations because the catalytic coating will wear off first and thus protect the base mineral sorbent. When the coating is depleted, it can be recovered, e.g., from the base of the vessel containing the sorbent and reapplied to the partially denuded sorbent without removing this material from the reactor.

The sorbent having the metalliferous catalytic agent substantially uniformly diffused throughout the body of fine particles can be made quite rugged. The metalliferous catalyst in this case appears to serve as a bonding agent between individual coated particles, thus, acting not only catalytically but as a cement. Agglomerated particles of this type are eminently suitable, not only for fixed bed operations, but also for moving and/or fluidized bed operations. Surprisingly, the sorptive capacity of this type of polyfunctional sorbent for straight chain hydrocarbons is not significantly different from the coated variety, and in neither variety of polyfunctional sorbent is the capacity of the mineral sorbent markedly impaired when the proportion of metalliferous catalytic agent is limited to 20 weight percent.

A wide variety of individual metalliferous catalysts for hydrocarbon reforming and their combinations, previously proposed for application to alumina, silica-alumina and like supports in the reforming field, can be used, e.g., platinum-containing deposits such as are used on the "Platforming" or "Sovaforming" catalyst, cobalt molybdate catalyst such as is employed in the so-called "Hyperforming" catalyst, chromia which can be identified as a component of "Thermofor Catalytic Reforming" catalyst, molybdena catalyst as is identified with "Hydroforming" or "Orthoforming" catalyst, and vanadium oxide. The metal component or components of such metalliferous catalysts are from groups 5b, 6b and 8b of the periodic table and are used to obtain a variety of hydrocarbon reactions along with or exclusive from purely cracking of the molecule. Accordingly, by the term "metalliferous hydrocarbon reforming catalyst" we mean one composed of one or more of such metals, the catalytic metal or metals being in the elemental state and/or in a combined form. It is, of course, possible to incorporate with the catalytic metal a minor portion of promotor elements, e.g., copper, beryllium, and the like.

As the presently most appealing application of our polyfunctional sorbents is in the upgrading of motor naphtha stocks (increasing octane rating of various com-

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ponents of the stock or the whole stock), advantageously the metalliferous catalytic agent of the polyfunctional sorbent is a naphtha reforming catalyst selected from the group consisting of catalytic metals and metal oxides of groups 6 and 8 of the periodic table, e.g., oxides of chromium, molybdenum, tungsten, and metallic platinum, iridium, palladium, rhodium, cobalt, nickel and ruthenium, or mixtures of such naphtha reforming catalysts. We have found chromia and platinum to be specially advantageous in this connection.

The sorbed straight chain hydrocarbons recovered from our polyfunctional sorbent appear to be reformed by a number of reactions including isomerization, dehydrogenation, aromatization or dehydrocyclization, some cracking, and disproportionation and the like, depending on the composition of the sorbed hydrocarbons and the particular desorbing conditions. During the sorbing operation temperature used can be as high as about 550° F. Generally it will be between about 100° and 500° F. and is preferably about 375–475° F. Pressure can range from atmospheric or below up to about 1000 p.s.i.g. or even higher. Sorbing can be conducted with part or all of the feed in liquid phase during part or all of the operation, but vapor phase operation is preferred and the pressures, advantageously atmospheric to about 800 p.s.i.g., employed are controlled relative to the operating temperature for maintaining the feed in vapor form.

Desorption temperature is selected in the range of about 600° to about 1000° F. Below 600° F. the desorbed material is only incidentally reformed, and at about 1100° F. and above the mineral sorbent structure can be adversely affected. Desorbing temperatures toward the lower end of the range favor isomerization of sorbed hydrocarbons, while aromatization and dehydrogenation is favored at the upper end of the range. In the processing of naphthas with our polyfunctional sorbent we prefer to use temperatures of about 850–950° F., preferably about 900° F. Pressure of the desorbing operation can be from atmospheric or below up to about 1000 p.s.i.g. or higher. For efficiency and economy the pressure is usually the same or lower than the one in the desorbing operation, preferably below 800 p.s.i.g. and particularly about atmospheric to about 500 p.s.i.g. In some cases, however, use of a higher desorbing pressure can save recompression costs if the hydrocarbon-laden desorbing medium is being fed to a subsequent operation maintained at elevated pressure.

In our process for producing the polyfunctional solid sorbent it is especially important to use a dispersion of metalliferous catalyst-providing material for coating the mineral sorbent particles or agglomeration thereof which is essentially inert towards said mineral particles or agglomeration. The dispersion can be a true solution, e.g., hydrated chromium nitrate in water, or a colloidal dispersion, e.g., a chloride of platinum treated with ethylene oxide or H₂S. Such dispersion must not have any substantial effect on the mineral sorbent. The dispersion can have pH broadly in the range of about 5 to 10 and preferably is of practically neutral pH (7); furthermore the dispersion advantageously should not contain appreciable amounts of alkali or alkaline earth metal compounds lest base exchange occur between the metal moiety of such alkali and the materials making up a fraction of the mineral sorbent. The metalliferous catalyst-providing material used should be one convertible to metalliferous catalytic reforming agent, e.g., by heat, hydrogenation, calcining in the presence of air or oxygen, or a combination of such conversion treatments. To remove sorbed water from the finished sorbent calcining in the presence of a sweeping gas, e.g., air, or under decreased pressure appears the most effective.

Suitable catalyst-providing materials are compounds such as the nitrate, acetate, sulfate, oxalate, lactate, alcoholate, sulfonate, naphthenate, or various chelate

salts such as the acetylacetonate of the metal being deposited. Calcination in the presence of air, followed by hydrogenation, is the preferred method for converting the catalyst-providing material to a metalliferous catalytic reforming agent for naphtha. For efficiency and economy we prefer to use, in the case of making a catalytic metal oxide-bearing polyfunctional sorbent, the nitrate such as chromium nitrate; and in the case of making a catalytic noble metal-bearing polyfunctional sorbent such as a platinum-bearing sorbent, a chloride of the metal buffered with ammonia to have pH between about 7.5 and about 9. Suitable liquid vehicles for depositing the catalyst-providing material onto mineral sorbent particles are: water, a lower aliphatic alcohol of 1 to 4 carbon atoms, a lower aliphatic ester capable of being made from a lower aliphatic alcohol of 1-4 carbon atoms and a carboxylic acid of 1-4 carbon atoms, pyridine, substituted pyridines, phenol, and substituted phenols. Water is preferred liquid vehicle for efficiency and economy in the practice of our process, but a liquid vehicle which does not create much ionization of the catalyst-providing material is also attractive because there is less likelihood of blocking the fine pores of the mineral sorbent with a dispersion of catalyst-providing material in the manufacturing operation. Solutions of non-ionizing or only weakly ionizing metalliferous catalytic agent, or colloidal dispersions of the agent are also appealing for the same reason.

The amount of catalyst-providing material so deposited on mineral sorbent is controlled to be equivalent to 0.1-20 percent by weight metalliferous catalytic reforming agent based on the weight of finished polyfunctional sorbent. Polyfunctional sorbent containing less than about 0.1 percent by weight metalliferous catalyst is ordinarily impractical as it has insufficient reforming effect on the sorbed hydrocarbons to be of substantial commercial value; polyfunctional sorbent containing substantially more than about 20 weight percent of metalliferous catalytic reforming agent has sharply impaired sorptive capacity for straight chain hydrocarbons. Preferably the metalliferous reforming catalyst fraction of the finished polyfunctional sorbent is controlled between about 0.3 and about 15 weight percent, nearer the lower limit range of this range when producing the polyfunctional solid sorbent containing an expensive noble metal such as platinum, and in the upper two-thirds of this range when producing the polyfunctional sorbent containing a metal oxide such as chromia.

A particular embodiment of our process for producing polyfunctional solid sorbent is the sorption of a straight chain hydrocarbon, e.g., a lower alkane of 5 to 8 carbon atoms such as n-heptane or n-hexane, on the mineral sorbent preparatory to depositing thereon the metalliferous catalyst-providing material. By such treatment it is believed that the pores of the mineral sorbent are at least partially blocked with hydrocarbon of the nature to be later sorbed; thereby the chance of plugging the pores with catalyst-providing material during the deposition is lessened. Sufficient of the lower alkane is then expelled, e.g., by air drying and/or gentle heating, to make the coated sorbent safe from fire, explosion, or carbonization in the conversion step to follow. The catalyst-providing material is then converted to the desired catalytic agent, e.g., by calcining and hydrogenation, leaving the finished polyfunctional sorbent receptive for straight chain hydrocarbons.

Treatment of hydrocarbons with our polyfunctional sorbent can be better understood by reference to the accompanying drawings. Figures 1 and 2 show the use of a simple fixed bed system of the polyfunctional sorbent such as can be used to evaluate the effectiveness thereof. In Figure 1 a raw vaporized mixture of straight chain and non-straight chain hydrocarbons, e.g., a naphtha, is passed through inlet 11 of vessel 12 downwardly in vapor phase through fresh polyfunctional sorbent 13, and out outlet 14, thereby emerging as a treated

naphtha vapor product having a reduced amount of straight chain hydrocarbons in comparison to non-straight chain hydrocarbons. Pressure in vessel 12 can be from about atmospheric or below up to about 1000 p.s.i.g., and temperature between about 100° and about 550° F. Advantageously, flow of the hydrocarbon therethrough is maintained between 0.2 and 3.0 liquid volumes of hydrocarbon per volume of polyfunctional sorbent per hour, and preferably between about 0.5 and 1.5 liquid volumes per volume per hour. When the sorptive capacity of bed 13 is substantially depleted by the passage of raw naphtha (as can be noted by change in octane rating, refractive index, or A.P.I. gravity of the treated product emerging from outlet 14) the desorbing operation is conducted as shown in Figure 2. Here, flowing at 25 to 200 volumes per hour per volume of polyfunctional sorbent, a gasiform desorbing medium, e.g., nitrogen, hydrogen, carbon dioxide, flue gas essentially devoid of H₂S and CO, methane, natural gas preponderantly composed of methane, lighter hydrocarbons up to C₄ hydrocarbons, or mixtures of such desorbing media, is passed through inlet 11 into vessel 12 wherein temperature is maintained from about 600° to 1000° F. and pressure from about 0 to about 1000 p.s.i.g. These conditions of desorbing medium flow, temperature and pressure will be termed herein, for brevity, "reforming conditions" with respect to our desorbing operation. It is generally desirable to carry out the desorption operation at a pressure substantially lower than the sorption operation to enhance stripping effect of the desorbing medium but this is not necessary. Preferred reforming conditions are temperature from about 850-950° F., pressure below about 500 p.s.i.g., and 40 to 100 volumes of gasiform desorbing medium per hour per volume of polyfunctional sorbent. The desorbing medium passes downwardly through bed 13 and outlet 14 bearing with it catalytically reformed hydrocarbons produced from the sorbed straight chain hydrocarbons originally present in the raw naphtha feed. The laden desorbing medium stream is then separated in separator 17 into denuded desorbing medium which is withdrawn through outlet 18 and a recovered reformed hydrocarbon fraction of high value which is withdrawn through outlet 19. Separation is conveniently accomplished by condensing the reformed hydrocarbons, e.g., by cooling and/or compression of the laden desorbing stream, adsorption of these hydrocarbons on activated charcoal or the like from which they can be stripped, or a combination of such techniques. A similar sorbing and desorbing operation can be conducted in practically any direction through a bed of the polyfunctional sorbent, and this invention is not restricted to a particular flow direction through a moving, fluidized or static bed or mass of polyfunctional sorbent.

The preferred desorbing medium for use in the practice of our naphtha treating process is a gas having atomic number below 8, i.e., hydrogen, helium or nitrogen, since carbon deposition on the polyfunctional sorbent is minimized if not practically entirely prevented by using such gaseous desorbents. Preferably, the desorbing medium used is hydrogen, i.e., substantially pure hydrogen or hydrogen obtained from conventional naphtha reforming operations such as a "Platforming" operation. Such hydrogen streams can contain up to 25 volume percent light hydrocarbons such as methane and ethane without substantially affecting the efficiency of the invention process.

Figure 3 shows one way of upgrading a naphtha fraction employing our polyfunctional sorbing system in combination with a conventional reforming operation, e.g., Platforming, Hyperforming or Thermoform Catalytic Reforming. Raw naphtha vapor to be upgraded is fed through inlet 22 into conventional reforming system 23 along with a recycle flow of hydrogen entering inlet 24. A series of fixed bed reactors or moving bed reactors or fluidized bed reactors can be used in the reforming sys-

tem. Temperature in such reforming system can be between 600° and 1000° F., generally rising in a series of reactors from about 875° to 975° F. Pressure in such reforming system is maintained broadly between 50 and 1000 p.s.i.g., generally between about 500 and 800 p.s.i.g. Hourly space velocity of the naphtha feed is between about 0.5 and 10 volumes of naphtha liquid per volume of catalyst per hour, and the hydrogen:naphtha mol ratio is maintained between about 0.5 and 10 in the reforming vessel. The catalyst used can be, for example, a conventional platinum-containing catalyst, a conventional cobalt molybdate catalyst, a conventional chromia-alumina catalyst or a conventional molybdena-alumina catalyst. Motor naphtha of enhanced octane rating and hydrogen are withdrawn from the reforming system by line 25 and fed as a mixture into polyfunctional sorbent system 26 which can be a single vessel or a plurality of vessels connected in series or in parallel. The polyfunctional sorbent of our invention can be maintained in one or more of the vessels in a fixed bed, a moving bed, or a fluidized bed of solids or in any desirable combination of such beds.

During the sorbing operation temperature of the polyfunctional sorbent bed or beds on such service is maintained between about 100° to about 550° F. and pressure therein is maintained between 0 and 1000 p.s.i.g. A stream of hydrogen and treated naphtha having a reduced amount of straight chain hydrocarbons is withdrawn from sorbent system 26 by outlet 27 and passed into a separating system 28 wherein temperature and pressure are maintained so that the upgraded naphtha is condensed, recovered and withdrawn from outlet 30 while part of the separated hydrogen is recycled from outlet 29 into inlet 24 of reforming system 23.

Periodically one or more vessels in the sorbent system are stripped of sorbed hydrocarbons by another portion of separated hydrogen withdrawn from outlet 29 and passed into the sorbent system through inlet 31. During desorption a sorbent bed is maintained between 600° and 1000° F. and atmospheric to 1000 p.s.i.g. pressure whereby the hydrogen flow entering line 31 strips the bed and is withdrawn laden with catalytically reformed hydrocarbons through outlet 32. Advantageously the hydrogen is preheated for desorbing, say to 600–900° F. At this juncture practically all or a lesser part of the stripped catalytically reformed hydrocarbons, produced from straight chain hydrocarbon originally present in the motor naphtha fed from system 23, can be separated from the laden hydrogen stream and withdrawn at outlet 33. The separated hydrogen can be recycled through line 34 into line 25 carrying motor naphtha and hydrogen from reforming system 23 to polyfunctional sorbent system 26. If it is desired, all of the stripped, recovered, reformed hydrocarbons from the sorbent system can be recycled for reprocessing with the hydrogen in line 34.

Figure 4 shows another process for upgrading a naphtha fraction employing our polyfunctional sorbent in combination with a conventional reforming operation as hereinbefore described. In this case a vaporized raw naphtha fraction is passed through inlet 36 into conventional reforming system 37 along with a recycle flow of hydrogen entering inlet 38. Hydrogen and motor naphtha of enhanced octane rating are withdrawn from reforming system 37 and passed into separation system 40 by conduit 39. In separation system 40, operated as hereinbefore described, the motor naphtha and hydrogen are separated. Hydrogen is withdrawn from outlet 41. Part of it is recycled into reforming system 37 at inlet 38. Separated motor naphtha containing both straight and non-straight chain hydrocarbons is passed through inlet 42 into polyfunctional sorbent system 43 operated as hereinbefore described. From outlet 46 there is withdrawn a treated motor naphtha effluent having a reduced amount of straight chain hydrocarbons by virtue of one action of our polyfunctional sorbent. When one or more

beds of the polyfunctional sorbent becomes saturated with straight chain hydrocarbons, such bed or beds are then desorbed with a flow of separated hydrogen withdrawn from outlet 41, entering inlet 45, passing through the bed or beds to be desorbed, and issuing from outlet 46. Such hydrogen carries with it stripped, catalytically reformed hydrocarbons produced from sorbed straight chain hydrocarbons originally present in the motor naphtha fed to polyfunctional sorbent system 42. These stripped hydrocarbons are separated from the hydrogen desorbing medium and recovered. Separated hydrogen desorbing medium can be recycled for use in later desorbing and/or in the conventional reforming as is desired.

In some cases it can be desirable first to pass the raw naphtha through our polyfunctional sorbent system, thence to a conventional reforming operation, particularly when only a very minor portion of the raw naphtha is composed of straight chain hydrocarbons. The recovered, desorbed, catalytically reformed hydrocarbons from such treatment can be fed into the first or subsequent stage of a conventional catalytic reforming operation to augment its feed or directly added to the conventionally reformed product. We have, for example, recovered a hydrocarbon mixture by desorbing our polyfunctional sorbent which mixture analyzed, in volume percent, 43% aromatics, 2% olefins, and 55% mixed saturates, e.g., aliphatic and naphthenic hydrocarbons.

Figure 5 shows a moving bed operation employing our polyfunctional sorbent. Sorption and desorption pressures and temperatures are maintained as described hereinbefore. In such system use of a rugged polyfunctional sorbent containing the catalytic agent substantially uniformly diffused throughout an agglomerated body of fine mineral sorbent particles is advisable so that attrition of the sorbent is minimized. A hydrocarbon vapor stream containing straight chain and non-straight chain hydrocarbons is passed through inlet 50 into vessel 51 containing a bed of fresh polyfunctional sorbent. Herein straight chain hydrocarbons are sorbed on the fresh bed and treated hydrocarbon effluent having a reduced amount of straight chain hydrocarbons is withdrawn from outlet 53. Bed 52 is being constantly replenished by a supply of desorbed polyfunctional sorbent particles entering from inlet 61 and is maintained at substantially constant volume by withdrawal of laden polyfunctional sorbent down outlet 54, through a star feeder or similar mechanism whereby the laden sorbent is passed into the top of desorbing bed 55 maintained in vessel 56. Gasiform desorbing medium, e.g., hydrogen, is passed into the base of vessel 56 through inlet 57 and withdrawn near the top of vessel 56 through outlet 58. The desorbent stream contains stripped catalytically reformed hydrocarbons produced from the sorbed straight chain hydrocarbons originally present in the hydrocarbon stream fed to vessel 51. The stripped hydrocarbons can be recovered as hereinbefore described. Bed 55 is maintained at substantially constant volume by withdrawal of desorbed polyfunctional sorbent through outlet 59 and passed into elevator means 60. Vessels 51 and 56 are sized to give sufficient residence time for economical hydrocarbon and desorption with polyfunctional sorbent. Elevator 60, which can be, for example, a gas lift, a screw, or a bucket elevator, passes desorbed polyfunctional sorbent up to inlet 61 which feeds vessel 51. Make-up polyfunctional sorbent can be added to the system at any convenient point, e.g., outlet 59, elevator 60, inlet 61 or vessel 51.

Carbon deposition or "coking" of the polyfunctional sorbents can occur after repeated sorbing and desorbing cycles. This will decrease sorptive capacity of the sorbent. We have found that controlled combustion of coke on the sorbent with an oxygen-containing gas at temperature not higher than 1100° F. will regenerate the sorption capacity of the sorbent for continued use. Preferably,

when oxidatively regenerating elemental metal-containing, e.g., platinum-containing polyfunctional sorbent the temperature is maintained below about 975° F. and the oxygen concentration of the gas is maintained low, e.g., 2-5%, while the metal oxide-containing sorbents such as chromia can stand more vigorous combustion conditions, e.g., 1000+° F. and air feed.

While not intending to be bound by any theory as to exactly why the materials of our invention are so significantly effective, it appears to us that the combination of the selective sorbing structure of the mineral base and the substantially unhindering catalytic metalliferous surfaces proximate thereto is especially favorable for production of valuable isomeric and cyclic materials from straight chain hydrocarbon components.

The following examples show several ways in which our invention has been practiced but are not to be construed as limiting the same. Herein gas flows are referred to standard conditions of temperature and pressure, i.e., 60° F. and 760 mm. Hg. Except as otherwise indicated percentages in the examples are weight percentages.

Example 1.—Polyfunctional sorbent, designed to contain 10 percent chromia impregnated essentially as a surface coating on $\frac{3}{16}$ " by $\frac{1}{8}$ " extruded pellets of agglomerated Linde 5A molecular sieve, was made as follows: A solution of 1270 grams of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 1600 ml. of water was thoroughly mixed at room temperature and allowed to stand overnight with 2070 grams of the mineral sorbent pellets, which had been dried previously for three hours at 900° F. The chromium nitrate deposited principally as a crust over the mineral sorbent pellets. The encrusted pellets were dried in a flask and calcined in the presence of oxygen at 900° F. for three hours, thereby converting deposited chromium nitrate into a dark green chromia coating.

Example 2.—Polyfunctional sorbent consisting of 10 percent chromia substantially uniformly diffused throughout an agglomerated body of fine mineral sorbent particles was prepared as follows: 2070 grams of dried Linde 5A molecular sieve powder having size grading between about 2 and about 4 microns was mixed thoroughly with 2500 ml. of n-heptane and allowed to stand for four hours with occasional stirring. The so-treated sieve powder was then mixed thoroughly with a solution of 1210 grams of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 1600 ml. of water and allowed to stand overnight. The resulting material, a hard solid, was ground to powder and subjected to a vacuum of 29 inches of mercury while being heated on a steam plate overnight, thereby freeing the powder of practically all heptane. This powder was pelleted in a confining die with 4 percent starch and 2 percent stearic acid into cylinders about $\frac{3}{16}$ " diameter by $\frac{1}{8}$ " high, then calcined in the presence of oxygen at about 1000° F. for 6 hours whereby chromium nitrate was converted to chromia. The product was a batch of hard pellets.

Example 3.—Polyfunctional sorbent containing 0.5 percent platinum impregnated on agglomerated mineral sorbent particles was prepared as follows: 2070 grams of dried Linde 5A molecular sieve $\frac{1}{16}$ " extruded pellets were soaked in 2500 ml. n-heptane for 4 hours. The excess heptane liquid was removed. 27.7 grams of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ was heated at 275° F. for 2 hours and then dissolved in 1600 ml. of water. Aqueous ammonia was added to this solution to bring pH to 8.83. This platinum solution, a chloride of platinum, was mixed with the heptane-treated pellets of mineral sorbent. The mixture was allowed to stand overnight, then was dried and tested for the presence of flammable material. None was found. The pellets impregnated with platinum-providing material were calcined at 900° F. for 3 hours. They emerged brown in color and were suitable for hydrocarbon treating after hydrogen treatment, as shown hereinafter.

Example 4.—Table I, following, shows the superior

strength of random samples of solid sorbent made in accordance with invention principles over random samples of conventional fine mineral sorbent particles pelleted in the same conventional machinery with and without chromia powder, and a random sample of conventional mineral sorbent extruded agglomerates. Sample V was of compressed pellets $\frac{3}{32}$ " diameter x $\frac{1}{4}$ " high made essentially as described in Example 2; sample W was of dried Linde 5A molecular sieve powder of 2-4 micron size which had been pelleted like sample V; sample X was of Linde 5A sieve powder and about 10% fine chromium oxide which was mixed dry, then pelleted like sample V; sample Y was of $\frac{1}{16}$ " diameter by about $\frac{1}{8}$ " long extruded Linde 5A agglomerates as received from the manufacturer; and sample Z was the same kind of agglomerate as sample Y except that they had been saturated with n-heptane, then impregnated with chromium nitrate solution to obtain about 10% by weight chromia on the finished sorbent, dried and calcined essentially as shown in Example 1.

Table I

Sample—Designation	Crushing Strength, Grams	
	Average	Range
V.....	3,604	2,630-4,450
W.....	2,238	1,423-2,710
X.....	986	402-2,025
Y.....	3,664	2,831-4,724
Z.....	4,932	3,799-5,688

Example 5. Table II, following, shows the superior abrasion resistance of a random sample of polyfunctional sorbent from the same batch as sample V over random samples of sorbents corresponding to samples W and X of preceding Table I. These data were obtained by tumbling 70 grams of the sorbents in a rotating drum equipped with internal flights. The drum was rotated for two hours at about 17 r.p.m. with each sample. Each sample was then sieved for 15 minutes on a mechanical sieve equipped with a 16 and a 60 mesh screen.

Table II

Sample—Designation	Weight Percent		
	retained on 16 mesh	passing 16 mesh	passing 60 mesh
V.....	92.9	7.1	2.9
W.....	88.6	11.4	7.2
X.....	61.5	38.5	17.2

Example 6.—A series of runs was made treating motor naphtha with a variety of polyfunctional sorbents prepared as previously described in Examples 1, 2, and 3. The motor naphtha used in each run was the product of a commercial refinery "Patforming" operation using a platinum-on-alumina catalyst procured from the Universal Oil Products Company. Characteristics of the motor naphtha used were: A.P.I. gravity, 48.8°; refractive index

(20° C.)
(4° C.)

about 1.444; A.S.T.M. distillation I.B.P., 126° F.; and end point, 377° F.; and A.T.S.M. research clear octane rating, 87.1.

The sorbent treating operations were conducted in a vertical cylindrical reactor 31" tall and 1.94" I.D. containing a 1500 ml. bed of the particular polyfunctional sorbent under test, a control sample of conventional sorbent was tested in the same apparatus under the same conditions. Preparatory to each initial test run the reactor was purged with nitrogen and hydrogen, the tem-

perature was raised to 900° F., and the sorbent reduced for one hour using a stream of 5 s.c.f.h. of hydrogen. Sorbing operations were conducted as follows: reacting temperature was 450° F. $\pm$ 5° F., and the motor naphtha was charged to the top of the reactor under substantially atmospheric pressure at the rate of 1500 ml./hr. (metered as a liquid) whereby it contacted the sorbent in vapor form, was withdrawn from the bottom of the reactor as product vapor, and was condensed with water-cooled condenser. Periodic product samples were taken. Motor naphtha feed to the reactor was terminated after 1.0 to 1.25 hours of sorption when the value of refractive index or A.P.I. gravity of the product stream approached the value of the feed.

Reactor temperature was then raised to 900° F. $\pm$ 5° F. at atmospheric pressure as 5 s.c.f.h. of gasiform desorbing medium was passed through the reactor from the top to the bottom for stripping sorbed hydrocarbons from the solid sorbent. The laden desorbing medium was then vented through a water-cooled condenser and a trap refrigerated with Dry Ice to separate the desorbing medium from desorbed hydrocarbons (for convenience herein called "desorbate"). When hydrocarbon separation from the chilled desorbing medium flow had virtually ceased the sorbent was considered reconstituted for another cycle of sorption, and the desorbing operation was terminated. Table III below, summarizes results obtained by the foregoing procedure using a conventional sorbent (dried Linde 5A molecular sieve $\frac{1}{16}$ " diameter by about $\frac{3}{16}$ " long extruded pellets), and using repetitively in two or more cycles our polyfunctional solid sorbents compounded as described in Examples 1, 2 and 3, above, designated in Table III, below, as polyfunctional sorbents A, B and C, respectively. The desorbing medium used with the conventional sorbent and sorbent A was nitrogen; with sorbents B and C it was hydrogen.

Octane rating of the product naphtha treated with the above sorbents was measured clear or with addition of 3 cc. of tetraethyl lead per gallon by the A.S.T.M. research method. Octane of the desorbate was measured in a similar manner but on a micro scale, using a 100 ml. sample of fuel. Description of such micro octane rating test is given in the section entitled "Proposed Method of Test for Motor and Research Octane Number of Small Samples," page 727, Appendix VI, September 1951, A.S.T.M. Standards, published by the American Society for Testing Materials, Philadelphia, Pa.

Table III

Type of Sorbent Used	Linde 5A Molecular Sieve	Polyfunctional Sorbents						
		A		B			C	
		1st Cycle	2nd Cycle	1st Cycle	2nd Cycle	3rd Cycle	3rd Cycle	4th Cycle
Product:								
Recovery, Wt. Percent of Charge	92.5	91.3	95.3	93.6	93.5	92.7	92.5	93.6
Octane rating, clear	92.4	189	189.2	88.4	88.8	88.4	92.2	91.7
+3 cc.T.E.L. per gal.	99.7	198.3	198.1	97.8	97.9	97.9	100.0	99.3
Desorbate:								
Recovery, Wt. Percent of Charge	6.6	8.4	4.4	5.9	5.3	5.6	5.4	4.7
Octane Rating, clear	25.5	276.6				68.2	45.1	45.1
+3 cc.T.E.L. per gal.	60.3			85.5	86.3	85.6	72.1	72.1

¹ Average of product samples.

² Octane rating tested on combined desorbate samples.

Example 7.—After a series of sorbing and desorbing operations done in the manner described in Example 6 carbon deposition occurred on a polyfunctional sorbent bed and reduced its sorptive capacity. This polyfunctional sorbent was made originally in the manner of Example 1 except that the pellets of mineral sorbent were soaked in n-heptane before treating with chromium nitrate. The desorbed "coked" polyfunctional sorbent was

heated for 12 hours at 1000° F. in a muffle furnace in the presence of air to burn off carbon, then reused for treatment of motor naphtha of the same kind as and in the same manner as is described in Example 6, using hydrogen as the desorbing medium. Very little change was observed between the performance of the sorbent as originally made and after regeneration. Table IV, below, summarizes results obtained with the regenerated sorbent for treatment of the motor naphtha.

Table IV

	1st cycle	2nd cycle
Product:		
Recovery, wt. percent of charge	95.6	95.6
Octane rating clear	88.6	88.7
+3 cc.T.E.L./gal.	97.6	97.6
Desorbate:		
Recovery, wt. percent of charge	3.3	4.4
Octane Rating with 3 cc.T.E.L./gal.	186.9	

¹ Octane rating tested on combined desorbate samples.

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

We claim:

1. A polyfunctional solid sorbent comprising 0.1 to 20 weight percent of at least one metalliferous catalytic reforming agent selected from the group consisting of metals and metal oxides of groups 6 and 8 of the periodic table supported on and integral with Type A zeolite selective for straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons in a mixture thereof.
2. The polyfunctional sorbent of claim 1 wherein the catalytic agent is essentially in the form of a coating on a body of agglomerated fine Type A zeolite particles.
3. The polyfunctional sorbent of claim 1 wherein the catalytic agent is substantially uniformly diffused throughout an agglomerated body of fine Type A zeolite particles.
4. The polyfunctional sorbent of claim 1 wherein the catalytic agent consists essentially of chromia.
5. The polyfunctional sorbent of claim 1 wherein the catalytic agent consists essentially of platinum.
6. The polyfunctional solid sorbent of claim 1, which

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forming catalyst selected from the group consisting of metals and metal oxides of groups 6 and 8 of the periodic table; forming the resulting zeolite particles into an agglomerate; and converting deposited catalyst-providing material in said agglomerate into metalliferous catalytic reforming agent.

7. The polyfunctional solid sorbent of claim 1, which sorbent is the product of depositing, from an inert dispersion in a liquid vehicle onto an agglomerate of fine particles of Type A zeolite selective for straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons, metalliferous reforming catalyst-providing material equivalent to 0.1-20% metalliferous catalytic reforming agent based on the weight of finished polyfunctional sorbent, said catalytic agent being at least one reforming catalyst selected from the group consisting of metals and metal oxides of groups 6 and 8 of the periodic table; and converting deposited metalliferous catalyst-providing material on said agglomerate into metalliferous catalytic reforming agent.

8. The polyfunctional solid sorbent of claim 1, which sorbent is a product of impregnating with at least one straight chain hydrocarbon Type A zeolite selective for straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons; depositing, from an inert dispersion in a liquid vehicle onto said impregnated zeolite particle, metalliferous reforming catalyst-provid-

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ing material equivalent to 0.1-20% metalliferous catalytic reforming agent based on the weight of finished polyfunctional sorbent, said metalliferous catalytic reforming agent being at least one reforming catalyst selected from the group consisting of metals and metal oxides of groups 6 and 8 of the periodic table; removing at least part of the straight chain hydrocarbons in said impregnated zeolite particle; and converting deposited metalliferous catalyst-providing material on said particle into catalytic reforming agent.

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UNITED STATES PATENT OFFICE
CERTIFICATION OF CORRECTION

Patent No. 2,970,968

February 7, 1961

Michael D. Riordan et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 10, Table I, third column thereof, under the heading "Range", fourth line, for "2,83-4,724" read -- 2,836-4,724 --; column 12, line 71, for "chin" read -- chain --.

Signed and sealed this 20th day of June 1961.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

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Commissioner of Patents