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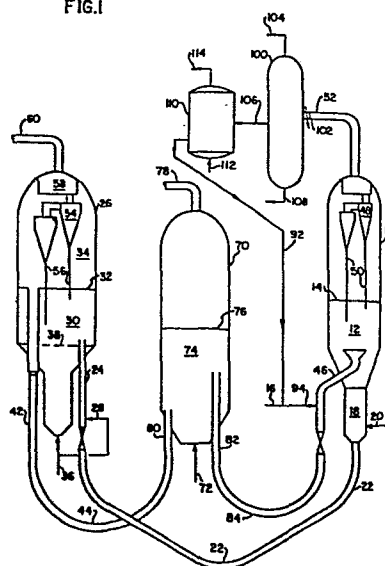
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54 **Method of reducing coke formation in heavy hydrocarbon feed catalytic cracking.**

57 A method for decreasing the amount of coke produced during the cracking of hydrocarbon feedstock to lower molecular weight products in a reaction zone (10), where the feedstock contains at least two metal contaminants selected from nickel, vanadium and iron, and where these contaminants become deposited on the catalyst, comprises passing the catalyst through a reduction zone (70) maintained at an elevated temperature for a time sufficient to at least partially passivate the catalyst before the catalyst enters the reaction zone (10). The amount of coke may be decreased still further by the addition to reaction zone (10) of a hydrogen donor material which may be, e.g. a hydrogenated fraction (92) of the cracked product (52).

FIG.1



1 BACKGROUND OF THE INVENTION

2 This invention relates to a method for
3 decreasing the catalytic activity of metal contam-
4 inants on cracking catalysts and for decreasing the
5 hydrogen and coke formation on cracking catalysts.
6 More specifically, this invention is directed to a
7 method for reducing the coke and hydrogen formation
8 caused by metal contaminants, such as nickel, vana-
9 dium and/or iron, which have become deposited upon
10 cracking catalysts from feedstock containing same.

11 In the catalytic cracking of hydrocarbon
12 feedstocks, particularly heavy feedstocks, vanadium,
13 nickel and/or iron present in the feedstock becomes
14 deposited on the cracking catalyst promoting exces-
15 sive hydrogen and coke makes. These metal contamin-
16 ants are not removed during conventional catalyst
17 regeneration operations during which coke deposits on
18 the catalyst are converted to CO and CO₂. As used
19 hereinafter the term "passivation" is defined as a
20 method for decreasing the detrimental catalytic
21 effects of metal contaminants such as nickel, vana-
22 dium and iron which become deposited on catalyst.

23 U.S. Patent Nos. 3,711,422; 4,025,545;
24 4,031,002; 4,111,845; 4,141,858; 4,148,712; 4,148,714
25 and 4,166,806 all are directed to the contacting of
26 the cracking catalyst with antimony compounds to
27 passivate the catalytic activity of the iron, nickel
28 and vanadium contaminants deposited on the catalyst.
29 However, antimony compounds, alone, may not passivate
30 the metal contaminants to sufficiently low levels
31 particularly where the metal contaminant concentra-
32 tion on the catalyst is relatively high. U.S.
33 Patent No. 4,176,084 is directed to the passivation
34 of metals contaminated catalyst in a regeneration

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1 zone operated for incomplete combustion of the coke
2 to CO₂ by periodically increasing the oxygen con-
3 centration above that required for complete combus-
4 tion of the coke and by maintaining the temperature
5 above 1300°F. This patent does not disclose a
6 method for passivating metals-contaminated catalyst
7 in a system where the regeneration zone is routinely
8 operated for complete combustion of the coke.

9 U.S. Patent No. 4,162,213 is directed at
10 decreasing the catalytic activity of metal contamin-
11 ants present in cracking catalyst by regenerating the
12 catalyst at temperatures of 1300-1400°F in such a
13 manner as to leave less than 0.10 wt. % residual
14 carbon on the catalyst.

15 Cimbalo, Foster and Wachtel in an article
16 entitled "Deposited Metals Poison FCC Catalyst"
17 published at pp 112-122 of the May 15, 1972 issue of
18 Oil and Gas Journal disclose that the catalytic
19 activity of metal contaminants decrease with repeated
20 oxidation and reduction cycles.

21 U.S. Patent No. 3,718,553 is directed at
22 the use of a cracking catalyst impregnated with
23 100-1000 parts per million by weight (WPPM) of iron,
24 nickel or vanadium or a combination of these metals
25 to increase the octane number of the cracked hydro-
26 carbon products. This reference does not recognize
27 that use of certain of these metals may adversely
28 affect the catalyst selectivity or activity.

29 U.S. Patent Nos. 3,479,279 and 4,035,285
30 disclose hydrotreating of catalytic cracker product
31 cuts and recirculating this product to the catalytic
32 cracker. Related U.S. Patent Nos. 3,413,212 and
33 3,533,936 disclose the use of hydrogen donor mate-
34 rials for decreasing the rate of coke formation on
35 cracking catalyst. These patents each disclose in

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1 Table V that hydrotreating a fraction from a cata-
2 lytic cracking zone and returning the hydrotreated
3 material with the cat cracker feed decreases the coke
4 make in the catalytic cracking zone. These patents
5 also disclose that the hydrotreated material prefer-
6 ably is a hydrogen donor material which releases
7 hydrogen to unsaturated olefinic hydrocarbons in a
8 cracking zone without dehydrogenative action. Suit-
9 able materials disclosed are hydroaromatic, naphthene
10 aromatic and naphthenic compounds. Preferred mate-
11 rials are compounds having at least one and prefer-
12 ably 2, 3 or 4 aromatic nuclei, partially hydro-
13 genated and containing olefinic bonds. The hydrogen
14 donor material was hydrogenated by contacting the
15 donor material with hydrogen over a suitable hydro-
16 genation catalyst at hydrogenation conditions.

17 The subject invention is directed at the
18 addition of hydrogen donor material to a catalytic
19 cracking zone in which the metals contaminated
20 cracking catalyst has been passivated by passing the
21 catalyst through a reduction zone maintained at
22 an elevated temperature. The addition of hydrogen
23 donor material and passivation of the cracking
24 catalyst operate to decrease the coke makes on the
25 cracking catalyst.

26 SUMMARY OF THE INVENTION

27 This invention is directed at a method for
28 reducing the rate of coke production from a hydro-
29 carbon feedstock cracked to lower molecular weight
30 products in a reaction zone containing cracking
31 catalyst where the feedstock contains at least two
32 metals selected from the class consisting of nickel,
33 vanadium and iron and where at least some of the
34 metal contaminants become deposited on the catalyst.
35 The method comprises passing the catalyst after

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1 regeneration from the reaction zone through a
2 reduction zone maintained at an elevated temperature
3 for a time sufficient to at least partially passivate
4 the metal contaminants on the catalyst, a reducing
5 environment maintained in the reduction zone by the
6 addition to the reduction zone of a material selected
7 from the class consisting of hydrogen, carbon monox-
8 ide and mixtures thereof, said passivated catalyst
9 thereafter passing to the reaction zone without
10 further processing. The metal contaminants may be
11 further passivated by the addition to the reaction
12 zone of a hydrogen donor material which transfers
13 hydrogen to the hydrocarbon feedstock and/or to the
14 cracked lower molecular weight products. The metal
15 contaminants may be passivated still further by
16 monitoring the concentration of each metal con-
17 taminant on the catalyst and adding predetermined
18 amounts of selected metal contaminants to the system.
19 The catalyst may be still further passivated by the
20 addition of known passivation agents to the system.
21 The temperature of the reduction zone preferably is
22 maintained above about 600°C. The hydrogen donor
23 material added to the reaction zone preferably has a
24 boiling point between about 200°C and about 500°C.
25 In a preferred embodiment, the hydrogen donor
26 material is obtained by fractionating the cracked
27 molecular products from the reaction zone, passing
28 the desired fraction through a hydrogenation zone and
29 then recirculating the material to the reaction
30 zone.

31 BRIEF DESCRIPTION OF THE DRAWING

32 The Figure is a flow diagram of a fluidized
33 catalytic cracking unit employing the subject inven-
34 tion.

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1 DETAILED DESCRIPTION OF THE INVENTION

2 Referring to the Figure, the present inven-
3 tion is shown as applied to a typical fluid catalytic
4 cracking process. Various items such as pumps, com-
5 pressors, steam lines, instrumentation and other
6 process equipment has been omitted to simplify the
7 drawing. Reaction or cracking zone 10 is shown
8 containing a fluidized catalyst bed 12 having a
9 level at 14 in which a hydrocarbon feedstock is
10 introduced into the fluidized bed through lines 16
11 and 94 for catalytic cracking. The hydrocarbon
12 feedstock may comprise naphthas, light gas oils,
13 heavy gas oils, residual fractions, reduced crude
14 oils, cycle oils derived from any of these, as well
15 as suitable fractions derived from shale oil kerogen,
16 tar sands, bitumen processing, synthetic oils, coal
17 hydrogenation, and the like. Such feedstocks may
18 be employed singly, separately in parallel reaction
19 zones, or in any desired combination. Typically,
20 these feedstocks will contain metal contaminants
21 such as nickel, vanadium and/or iron. Heavy feed-
22 stocks typically contain relatively high concentra-
23 tions of vanadium and/or nickel as well as coke
24 precursors, such as Conradson carbon materials.
25 The determination of the amount of Conradson car-
26 bon material present may be determined by ASTM
27 test D189-65, which is incorporated herein by refer-
28 ence. Hydrocarbon gas and vapors passing through
29 fluidized bed 12 maintain the bed in a dense tur-
30 bulent fluidized condition. Preferably hydrogen
31 donor material passes through line 92 for preblend-
32 ing with cat cracker feedstock in line 16 prior
33 to entering fluidized catalyst bed 12 through line
34 94. Alternatively the hydrogen donor material may be
35 added directly to reaction zone 10 in close proximity

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1 to the point where the cat cracker feedstock enters
2 reaction zone 10. Typically, the hydrogen donor
3 material will comprise between about 5 and about 100
4 wt. % of the hydrocarbon feedstock to be cracked.

5 In reaction zone 10, the cracking catalyst
6 becomes spent during contact with the hydrocarbon
7 feedstock due to the deposition of coke thereon.
8 Thus, the terms "spent" or "coke contaminated"
9 catalyst as used herein generally refer to catalyst
10 which has passed through a reaction zone and which
11 contains a sufficient quantity of coke thereon to
12 cause activity loss, thereby requiring regeneration.
13 Generally, the coke content of spent catalyst can
14 vary anywhere from about 0.5 to about 5 wt. % or
15 more. Typically, spent catalyst coke contents vary
16 from about 0.5 to about 1.5 wt. %.

17 Prior to actual regeneration, the spent
18 catalyst is usually passed from reaction zone 10 into
19 a stripping zone 18 and contacted therein with a
20 stripping gas, which is introduced into the lower
21 portion of zone 18 via line 20. The stripping gas,
22 which is usually introduced at a pressure of from
23 about 10 to about 50 psig, serves to remove most of
24 the volatile hydrocarbons from the spent catalyst. A
25 preferred stripping gas is steam, although nitrogen,
26 other inert gases or flue gas may be employed.
27 Normally, the stripping zone is maintained at essen-
28 tially the same temperature as the reaction zone,
29 i.e. from about 450°C to about 600°C. Stripped
30 spent catalyst from which most of the volatile
31 hydrocarbons have been removed, is then passed from
32 the bottom of stripping zone 18, through U-bend 22
33 and into a connecting vertical riser 24 which extends
34 into the lower portion of regeneration zone 26. Air

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1 is added to riser 24 via line 28 in an amount suffic-
2 ient to reduce the density of the catalyst flowing
3 therein, thus causing the catalyst to flow upward
4 into regeneration zone 26 by simple hydraulic balance.

5 In the particular configuration shown, the
6 regeneration zone is a separate vessel (arranged at
7 approximately the same level as reaction zone 10)
8 containing a dense phase catalyst bed 30 having a
9 level indicated at 32, which is undergoing regenera-
10 tion to burn-off coke deposits formed in the reaction
11 zone during the cracking reaction, above which is a
12 dilute catalyst phase 34. An oxygen-containing
13 regeneration gas enters the lower portion of regenera-
14 tion zone 26 via line 36 and passes up through a
15 grid 38 and the dense phase catalyst bed 30, main-
16 taining said bed in a turbulent fluidized condition
17 similar to that present in reaction zone 10. Oxygen-
18 containing regeneration gases which may be employed
19 in the process of the present invention are those
20 gases which contain molecular oxygen in admixture
21 with a substantial portion of an inert diluent gas.
22 Air is a particularly suitable regeneration gas. An
23 additional gas which may be employed is air enriched
24 with oxygen. Additionally, if desired, steam may
25 be added to the dense phase bed along with the
26 regeneration gas or separately therefrom to provide
27 additional inert diluents and/or fluidization gas.
28 Typically, the specific vapor velocity of the regen-
29 eration gas will be in the range of from about 0.8 to
30 about 6.0 feet/sec., preferably from about 1.5 to
31 about 4 feet/sec.

32 Regenerated catalyst from the dense phase
33 catalyst bed 30 in the regeneration zone 26 flows
34 downward through standpipe 42 and passes through

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1 U-bend 44, and line 80 into reduction zone 70 main-
2 tained at a temperature above 500°C preferably
3 above about 600°C having a reducing agent such as
4 hydrogen or carbon monoxide, entering through line 72
5 to maintain a reducing environment in the reduction
6 zone to passivate the contaminants as described in
7 more detail hereinafter. The regenerated and passi-
8 vated catalyst then passes from reduction zone 70
9 through line 82 and U-bend 84 into the reaction zone
10 10 by way of transfer line 46 which joins U-bend 84
11 near the level of the oil injection line 16 and
12 hydrogen donor line 92.

13 By regenerated catalyst is meant catalyst
14 leaving the regeneration zone which has contacted an
15 oxygen-containing gas causing at least a portion,
16 preferably a substantial portion, of the coke present
17 on the catalyst to be removed. More specifically,
18 the carbon content of the regenerated catalyst can
19 vary anywhere from about 0.01 to about 0.2 wt. %, but
20 preferably is from about 0.01 to about 0.1 wt. %.
21 Predetermined quantities of selected metals or con-
22 ventional passivation promoters may be added to
23 the hydrocarbon feedstock through lines 16 and/or 94,
24 if desired, as described more fully hereinafter. The
25 hydrocarbon feedstock for the cracking process,
26 containing minor amounts of iron, nickel and/or
27 vanadium contaminants is injected into line 46
28 through line 94 to form an oil and catalyst mixture
29 which is passed into fluid bed 12 within reaction
30 zone 10. The metal contaminants and the passivation
31 promoter, if any, become deposited on the cracking
32 catalyst. Product vapors containing entrained
33 catalyst particles pass overhead from fluid bed 12
34 into a gas-solid separation means 48 wherein the
35 entrained catalyst particles are separated therefrom

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1 and returned through diplegs 50 leading back into
2 fluid bed 12. The product vapors are then conveyed
3 through line 52 and condenser 102 into fractionation
4 zone 100, wherein the product stream is separated
5 into two or more fractions. Fractionation zone 100
6 may comprise any means for separating the product
7 into fractions having different boiling ranges.
8 Typically, zone 100 may comprise a plate or packed
9 column of conventional design. In the embodiment
10 shown the product is separated into an overhead
11 stream exiting through line 104, comprising light
12 boiling materials, i.e. compounds boiling below about
13 200°C, a middle cut boiling in the range of about
14 200 to 370°C exiting through line 106 and a bottoms
15 stream boiling above about 370°C exiting through
16 line 108. At least a fraction of the product in line
17 106, preferably a major fraction, passes into hydro-
18 genation zone 110 maintained under hydrogenating
19 conditions where the product contacts hydrogen enter-
20 ing zone 110 through line 112. A gaseous stream may
21 pass from zone 110 through line 114 for removal of
22 any undesired by-products. Zone 110 typically will
23 contain a conventional hydrogenating catalyst as,
24 for example, a molybdenum salt such as molybdenum
25 oxide or molybdenum sulfide, and a nickel or cobalt
26 salt, such as nickel or cobalt oxides and/or sul-
27 fides. These salts typically are deposited on a
28 support material such as alumina and/or silica
29 stabilized alumina. Hydrogenation catalysts which
30 are particularly suitable are described in U.S.
31 Patent No. 3,509,044, the disclosure of which is
32 incorporated herein by reference. Zone 110 will be
33 maintained at a temperature ranging between about 350
34 and 400°C and a pressure ranging between about 600
35 and 3000 psi. A vapor stream exits zone 110 for

1 recycling and a further processing (not shown).
2 The at least partially hydrogenated stream exiting
3 zone 110, also referred to as the hydrogen donor
4 material, is recycled to the reaction zone through
5 line 92.

6 In regeneration zone 26, flue gases formed
7 during regeneration of the spent catalyst pass from
8 the dense phase catalyst bed 30 into the dilute
9 catalyst phase 34 along with entrained catalyst
10 particles. The catalyst particles are separated from
11 the flue gas by a suitable gas-solid separation means
12 54 and returned to the dense phase catalyst bed 30
13 via diplegs 56. The substantially catalyst-free flue
14 gas then passes into a plenum chamber 58 prior to
15 discharge from the regeneration zone 26 through line
16 60. Where the regeneration zone is operated for
17 substantially complete combustion of the coke, the
18 flue gas typically will contain less than about 0.2,
19 preferably less than 0.1 and more preferably less
20 than 0.05 volume % carbon monoxide. The oxygen
21 content usually will vary from about 0.4 to about 7
22 vol. %, preferably from about 0.8 to about 5 vol. %,
23 more preferably from about 1 to about 3 vol. %, most
24 preferably from about 1.0 to about 2 vol. %.

25 Reduction zone 70 may be any vessel provid-
26 ing suitable contacting of the catalyst with a reduc-
27 ing environment at elevated temperatures. The shape
28 of reduction zone 70 is not critical. In the embodi-
29 ment shown, reduction zone 70 comprises a treater
30 vessel having a shape generally similar to that of
31 regeneration zone 26, with the reducing environment
32 maintained, and catalyst fluidized by, reducing agent
33 entering through line 72 and exiting through line 78.
34 The volume of dense phase 74 having a level at 76
35 is dependent on the required residence time. The

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1 residence time of the catalyst in reduction zone 70
2 is not critical as long as it is sufficient to effect
3 the passivation. The residence time will range from
4 about 5 sec. to about 30 min., typically from about
5 2 to 5 minutes. The pressure in this zone is not
6 critical and generally will be a function of the
7 location of reduction zone 70 in the system and the
8 pressure in the adjacent regeneration and reaction
9 zones. In the embodiment shown, the pressure in zone
10 70 will be maintained in the range of about 5 to 50
11 psia, although the reduction zone preferably should
12 be designed to withstand pressures of 100 psia. The
13 temperature in reduction zone 70 should be above
14 about 500°C preferably above 600°C, but below the
15 temperature at which the catalyst sinters or de-
16 grades. A preferred temperature range is about
17 600-850°C, with the more preferred temperature range
18 being 650-750°C. The reduction zone 70 can be
19 located either before or after regeneration zone
20 26, with the preferred location being after the
21 regeneration zone, so that the heat imparted to the
22 catalyst by the regeneration obviates or minimizes
23 the need for additional catalyst heating. The
24 reducing agent utilized in the reduction zone 70 is
25 not critical, although hydrogen and carbon monoxide
26 are the preferred reducing agents. Other reducing
27 agents including light hydrocarbons, such as C₃
28 hydrocarbons, may also be satisfactory.

29 Reduction zone 70 can be constructed of any
30 chemically resistant material sufficiently able to
31 withstand the relatively high temperatures involved
32 and the high attrition conditions which are inherent
33 in systems wherein fluidized catalyst is transported.
34 Specifically, metals are contemplated which may or
35 may not be lined. More specifically, ceramic liners
36 are contemplated within any and all portions of the

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1 reduction zone together with alloy use and structural
2 designs in order to withstand the maximum contemplated
3 operating temperatures.

4 The reducing agent utilized in all but one
5 of the following tests was high purity grade hydrogen,
6 comprising 99.9% hydrogen. In the remaining test,
7 shown in Table VIII a reducing agent comprising 99.3%
8 CO was utilized. It is expected that commercial
9 grade hydrogen, commercial grade CO, and process gas
10 streams containing H₂ and/or CO can be utilized.
11 Examples include cat cracker tail gas, catalytic
12 reformer off-gas, spent hydrogen streams from cata-
13 lytic hydroprocessing, synthesis gas, and flue
14 gases. The rate of consumption of the reducing agent
15 in reducing zone 70 will, of course, be dependent on
16 the amount of reducible material entering the
17 reducing zone. In a typical fluidized catalytic
18 cracking unit it is anticipated that about 10 to 100
19 scf of hydrogen or about 10 to 100 scf of CO gas
20 would be required for each ton of catalyst passed
21 through reduction zone 70.

22 If the reducing agent entering through line
23 72 is circulated through reduction zone 70 and thence
24 into other units, a gas-solids separation means may
25 be required for use in connection with the reduction
26 zone. If the reducing agent exiting from zone 70 is
27 circulated back into the reduction zone, a gas-solids
28 separation means may not be necessary. Preferred
29 separation means for zones 10, 26 and 70 will be
30 cyclone separators, multiclones or the like whose
31 design and construction are well known in the art.
32 In the case of cyclone separators, a single cyclone
33 may be used, but preferably, more than one cyclone
34 will be used in parallel or in series flow to effect
35 the desired degree of separation.

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1 The construction of regeneration zone 26
2 can be made with any material sufficiently able to
3 withstand the relatively high temperatures involved
4 when afterburning is encountered within the vessel
5 and the high attrition conditions which are inherent
6 in systems wherein fluidized catalyst is regenerated
7 and transported. Specifically, metals are contem-
8 plated which may or may not be lined. More specif-
9 ically, ceramic liners are contemplated within
10 any and all portions of the regeneration zone
11 together with alloy use and structural designs in
12 order to withstand temperatures of about 760°C and,
13 for reasonably short periods of time, temperatures
14 which may be as high as 1000°C.

15 The pressure in the regeneration zone is
16 usually maintained in a range from about atmospheric
17 to about 50 psig., preferably from about 10 to 50
18 psig. It is preferred, however, to design the
19 regeneration zone to withstand pressures of up to
20 about 100 psig. Operation of the regeneration zone
21 at increased pressure has the effect of promoting the
22 conversion of carbon monoxide to carbon dioxide and
23 reducing the temperature level within the dense bed
24 phase at which the substantially complete combustion
25 of carbon monoxide can be accomplished. The higher
26 pressure also lowers the equilibrium level of carbon
27 on regenerated catalyst at a given regeneration
28 temperature.

29 The residence time of the spent catalyst in
30 the regeneration zone is not critical so long as the
31 carbon on the catalyst is reduced to an acceptable
32 level. In general, it can vary from about 1 to
33 30 minutes. The contact time or residence time of
34 the flue gas in the dilute catalyst phase establishes
35 the extent to which the combustion reaction can reach

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1 equilibrium. The residence time of the flue gas may
2 vary from about 10 to about 60 seconds in the regen-
3 eration zone and from about 2 to about 30 seconds in
4 the dense bed phase. Preferably, the residence time
5 of the flue gas varies from about 15 to about 20
6 seconds in the dense bed.

7 The present invention may be applied
8 beneficially to any type of fluid cat cracking unit
9 without limitation as to the spatial arrangement of
10 the reaction, stripping, and regeneration zones, with
11 only the addition of reduction zone 70 and related
12 elements. In general, any commercial catalytic
13 cracking catalyst designed for high thermal stability
14 could be suitably employed in the present invention.
15 Such catalysts include those containing silica and/or
16 alumina. Catalysts containing combustion promoters
17 such as platinum can be used. Other refractory metal
18 oxides such as magnesia or zirconia may be employed
19 and are limited only by their ability to be effec-
20 tively regenerated under the selected conditions.
21 With particular regard to catalytic cracking, pre-
22 ferred catalysts include the combinations of silica
23 and alumina, containing 10 to 50 wt. % alumina, and
24 particularly their admixtures with molecular sieves
25 or crystalline aluminosilicates. Suitable molecular
26 sieves include both naturally occurring and synthetic
27 aluminosilicate materials, such as faujasite, cha-
28 bazite, X-type and Y-type aluminosilicate materials
29 and ultra stable, large pore crystalline alumino-
30 silicate materials. When admixed with, for example,
31 silica-alumina to provide a petroleum cracking
32 catalyst, the molecular sieve content of the fresh
33 finished catalyst particles is suitably within
34 the range from 5-35 wt. %, preferably 8-20 wt. %. An
35 equilibrium molecular sieve cracking catalyst may

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1 contain as little as about 1 wt. % crystalline
2 material. Admixtures of clay-extended aluminas may
3 also be employed. Such catalysts may be prepared in
4 any suitable method such as by impregnation, milling,
5 co-gelling, and the like, subject only to the provi-
6 sion that the finished catalyst be in a physical
7 form capable of fluidization. In the following tests
8 a commercially available silica alumina zeolite
9 catalyst sold under the tradename CBZ-1, manufactured
10 by Davison Division, W. R. Grace & Company was used
11 after steaming to simulate the approximate equilib-
12 rium activity of the catalyst.

13 Fractionation zone 100, of conventional
14 design, typically is maintained at a top pressure
15 ranging between about 10 and 20 psi and a bottoms
16 temperature ranging up to about 400°C. The specific
17 conditions will be a function of many variables
18 including inlet product composition, inlet feed rates
19 and desired compositions in the overhead, middle
20 cut and bottoms. The middle cut fed to hydrogenation
21 zone 110 preferably has a boiling range of about 200
22 to about 370°C and is frequently referred to as a
23 light cat cycle oil. The feed to the hydrogenation
24 zone, preferably light cat cycle oil, should include
25 compounds which will accept hydrogen in zone 110 and
26 readily release the hydrogen in reaction zone 10
27 without dehydrogenative action. Preferred hydrogen
28 donor compounds include two ring naphthenic compounds
29 such as decahydronaphthalene (decalin) and two ring
30 hydroaromatic compounds such as tetrahydronaphthalene
31 (tetralin).

32 Hydrogenation zone 110 may be of conven-
33 tional design. Typical hydrogenation catalysts
34 include molybdenum salts and nickel and/or cobalt
35 salts deposited on a support material. The residence

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1 time of the middle cut from zone 100 in the hydrogen-
2 ation zone may range from about 10 to about 240
3 minutes, depending on the hydrogen donor, hydrogenation
4 catalyst, operating conditions and the desired
5 degree of hydrogenation.

6 As shown by the data in Tables I-IX the
7 incorporation of a reduction zone 70 is not effective
8 for passivating a metal contaminated catalyst unless:

9 A. a temperature in excess of about 500°C
10 is used; and

11 B. at least two metals selected from the
12 group consisting of nickel, iron and vanadium are
13 utilized.

14 The data in Table X shows that use of a
15 hydrogen donor also decreases hydrogen and coke
16 makes. When the use of a hydrogen donor is combined
17 with the previously described passivation process,
18 this results in still lower coke makes.

19 Unless otherwise noted the following test
20 conditions were used. The CBZ-1 catalyst utilized
21 was first steamed at 760°C for 16 hours after
22 which the catalyst was contaminated with the indi-
23 cated metals by laboratory impregnation followed by
24 calcining in air at about 540°C for four hours.
25 The catalyst was then subjected to the indicated
26 number of redox cycles. Each cycle consisted of a
27 five-minute residence in a hydrogen atmosphere,
28 a five-minute nitrogen flush and then a five-minute
29 residence in an air atmosphere at the indicated
30 temperatures. Following the redox cycles the cata-
31 lyst was utilized in a microcatalytic cracking (MCC)
32 unit. The MCC unit comprises a captive fluidized bed
33 of catalyst kept at a cracking zone temperature of
34 500°C. Tests were run by passing a vacuum gas
35 oil having a minimum boiling point of about 340°C

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1 and a maximum boiling point of about 565°C through
2 the reactor for two minutes and analyzing for hydro-
3 gen and coke production. In Table I data is pre-
4 sented illustrating that the incorporation of a
5 reduction step followed by an oxidation step (redox)
6 significantly decreased the hydrogen and coke makes.

TABLE I

	Wt. % Metal on Catalyst			Treatment Prior to Cracking	Yields Wt. % on Feed	
	Ni	V	Fe		H ₂	Coke
12	0.16	0.18		Calined	0.86	7.82
13	0.16	0.18		Redox 650°C	0.62	6.04
14	0.12	0.12		Calined	0.53	5.49
15	0.12	0.12		Redox 650°C	0.34	4.15
16	0.15	0.19	0.35	Calined	1.16	10.61
17	0.15	0.19	0.35	Redox 650°C	0.79	7.48

18 Table II illustrates that hydrogen and coke make
19 reductions similar to that shown in Table I also were
20 obtained on a metals contaminated catalyst wherein
21 the metals had been deposited by the processing of
22 heavy metal containing feeds rather than by labora-
23 tory impregnation.

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TABLE II

	Wt. % Metal on Catalyst			Treatment	Yields Wt. % on Feed	
	Ni	V	Fe		H ₂	Coke
5	0.28	0.31	0.57	510°C	1.13	9.11
6				Cracking		
7				620°C		
8				Regen.		
9				(Many cycles)		
10	0.28	0.31	0.57	Redox 650°C	0.75	5.41
11				4 cycles		
12	0.26	0.29	0.36	510°C Cracking	0.73	6.05
13				707°C Regen.		
14				(Many cycles)		
15	0.26	0.29	0.36	Redox 650°C	0.53	3.94
16				4 cycles		

Table III illustrates that the degree of passivation is a function of the reduction zone temperature. It can be seen that the adverse catalytic effects of the metal contaminants are only slightly reduced over that of untreated catalyst, where the temperature in reduction zone 70 is only 500°C. As the reduction zone temperature is increased, it can be seen that the degree of passivation increases.

TABLE III

	Wt. % Metal on Catalyst	Redox Treatment Temp. °C	Yields Wt. % On Feed	
			H ₂	Coke
29	0.28Ni, 0.31V, 0.57Fe	No Redox Treatment	1.13	9.11
30		500	1.10	8.55
31		600	0.99	7.94
32		625	0.98	7.33
33		650	0.75	5.41
34		700	0.59	4.80
35		750	0.50	4.11

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1 Based on this data, it is believed that the reduction
2 step decreases the hydrogen and coke makes and that
3 the reduction must be performed at a temperature in
4 excess of 500°C.

5 Table IV, illustrates that where only one
6 of the metal contaminants is present, the redox step
7 at 650°C is not effective in reducing the hydrogen
8 and coke makes.

9	<u>TABLE IV</u>			
10		Treatment	Yields, Wt. %	
11		Prior To	on Feed	
12	<u>Wt. % Metal on Catalyst</u>	<u>Cracking</u>	<u>H₂</u>	<u>Coke</u>
13	0.21 Ni	Calcined	0.80	8.10
14	0.21 Ni	Redox 650°C	0.72	7.96
15		4 cycles		
16	0.29 V	Calcined	0.38	3.88
17	0.29 V	Redox 650°C	0.36	4.20
18		4 cycles		

19 Thus, to passivate the metal contaminants
20 on a catalyst, where at least a major portion i.e.,
21 at least 50 wt. % of the total of the metal contamin-
22 ants comprises nickel, vanadium or iron, it may be
23 necessary to add predetermined quantities of either
24 of the other two contaminants. Typically, crude oil
25 will not contain relative high concentrations of
26 iron. Vanadium and nickel, however, typically are
27 found in many crudes, with the relative amounts
28 varying with the type of crude. For example, cer-
29 tain Venezuelan crudes have relatively high vanadium
30 and relatively low nickel concentrations, while the
31 converse is true for certain domestic crudes. In
32 addition, certain hydrotreated residual oils and
33 hydrotreated gas oils may have relatively high nickel

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1 and relatively low vanadium concentrations, since
 2 hydrotreating removes vanadium more effectively than
 3 nickel. A catalyst could have substantial iron
 4 depositions where the iron oxide scale on process
 5 equipment upstream of the catalyst breaks off and
 6 is transported through the system by the feedstock.
 7 The relative catalytic activity of the individual
 8 metal contaminants nickel, vanadium and iron for the
 9 formation of hydrogen and coke are approximately 10:
 10 2.5: 1. Based on this, iron preferably should be
 11 added to passivate catalyst contaminated only with
 12 nickel, or vanadium. Table V illustrates the passi-
 13 vation that is achieved by adding quantities of
 14 iron to catalyst comprising only vanadium or only
 15 nickel.

TABLE V

17		Treatment	Yield, Wt. %	
18		Prior to	on Feed	
19	<u>Wt. % Metal on Catalyst</u>	<u>Cracking</u>	<u>H₂</u>	<u>Coke</u>
20	0.17 Ni	Calcined	0.76	7.30
21	0.17 Ni, 0.23 Fe	Redox 650°C	0.51	5.27
22		4 cycles		
23	0.29 V	Calcined	0.38	3.88
24	0.29 V, 0.13 Fe	Redox 650°C	0.30	3.72
25		4 cycles		

26 Table VI illustrates the passivation
 27 achieved by adding varying weights of vanadium to
 28 catalyst comprising only the nickel contaminant.
 29 Attention is directed to the fact that the addition
 30 of 0.02 wt. % vanadium followed by redox partially
 31 passivated the catalyst. Combination of the nickel
 32 contaminated catalyst with 0.12 wt. % vanadium
 33 followed by redox further passivated the catalyst.
 34 However, combination of the nickel contaminated

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1 catalyst with 0.50 wt. % vanadium resulted in an
 2 increase in undesired catalytic activity over that of
 3 the catalyst containing only 0.12 wt. % nickel.
 4 Thus, there appears to be a level of addition of the
 5 second metal component, above which the effectiveness
 6 of the passivation decreases. The exact amount of
 7 nickel, vanadium or iron which should be added to a
 8 metal-contaminated catalyst has not been determined.

9 TABLE VI

	Wt. % Metal on Catalyst		Treatment Prior To Cracking	Yields, Wt. % on Feed	
	Ni	V		H ₂	Coke
13	0.12		Calcined	0.60	5.65
14	0.12		Redox 650°C	0.44	4.78
15			4 cycles		
16	0.12	0.02	Redox 650°C	0.39	4.53
17			4 cycles		
18	0.12	0.12	Redox 650°C	0.34	4.15
19			4 cycles		
20	0.12	0.50	Calcined	1.17	11.08
21	0.12	0.50	Redox 650°C	0.72	6.86
22			4 cycles		

23 Table VII illustrates passivation of a
 24 catalyst impregnated with equal weight percentages of
 25 nickel and vanadium. It should be noted that the
 26 redox at 650°C resulted in a significant decrease
 27 in hydrogen and coke makes, but that, here also, the
 28 further addition of passivating metal in the form of
 29 iron actually increased the undesired catalytic
 30 activity of the metal contaminants slightly.

TABLE VII

2	Wt. % Metal			Treatment	Yields, Wt. % on Feed	
3	on Catalyst			Prior To		
4	Ni	V	Fe	Cracking	H ₂	Coke
5	0.12	0.12		Calcined	0.53	5.49
6	0.12	0.12		Redox 650°C	0.34	4.15
7				4 cycles		
8	0.12	0.12	0.26	Redox 650°C	0.37	4.50
9				4 cycles		

Table VIII illustrates that metals-contaminated catalyst also can be passivated by the use of carbon monoxide rather than hydrogen as the reducing agent. In one run CP* grade CO containing 99.3% CO by volume was utilized in the previously described passivation process while reagent grade hydrogen was used in the comparative run. It can be seen that both reducing agents passivated the catalyst to about the same extent.

TABLE VIII

	Wt. % Metal on Catalyst			Treatment Prior To Cracking	Yields, Wt. % on Feed	
	Ni	V	Fe		H ₂	Coke
20						
21						
22						
23	0.28	0.31	0.57	Calcined	1.13	9.11
24				Redox 650°C	0.75	5.41
25				4 cycles, H ₂		
26				Redox 650°C	0.73	5.83
27				4 cycles, CO		

28 . As shown by the data of Table IX, the
29 addition of iron or antimony followed by high temper-
30 ature redox, reduced the rate of hydrogen and coke
31 formation. The addition of both iron and antimony
32 followed by high temperature redox leads to a still ^{greater}
33 decrease in hydrogen and coke makes.

* Chemically Pure

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TABLE IX

Wt. % Metal on Catalyst	Treatment Prior To Cracking	Yields, Wt. % on Feed	
		H ₂	Coke
0.17 Ni	Calcined	0.76	7.30
0.17 Ni, 0.23 Fe	Redox 650°C 4 cycles	0.51	5.27
0.27 Ni	Calcined	0.83	8.40
0.27 Ni, 0.52 Sb	Redox 650°C 4 cycles	0.59	6.03
0.27 Ni, 0.52 Sb, 0.34 Fe	Redox 650°C 4 cycles	0.54	5.31

In addition to antimony, it is believed that other known passivation agents such as tin, bismuth and manganese in place of the antimony also would decrease the hydrogen and coke makes.

It has been found that one passage through the reaction and regeneration zones reduces the effectiveness of the reduction zone passivation. Thus, at least a portion of the catalyst preferably is passed through reduction zone 70 on every catalyst regeneration cycle.

The quantity of metal contaminant, or passivation promoter, if any, that should be added to the system may be determined preferably by monitoring the hydrogen and coke makes in the reaction zone or by analyzing the metal contaminant concentration either in the hydrocarbon feed or on the catalyst. Where additional iron, vanadium or nickel is to be added to the system to reduce the hydrogen and coke makes, it is believed that the additional quantities of these metals should be added to the feed, rather than impregnated onto the catalyst prior to use. Impregnation of an excess of these metals onto the catalyst prior to use in the cracking operation may lead to higher initial hydrogen and coke makes.

1 Moreover, where passivation promoters having rela-
2 tively high vapor pressures, such as antimony, are
3 used, some of the passivation promoter may be lost
4 to the atmosphere if it is impregnated onto the
5 catalyst. It has been found that the passivation
6 efficiency of antimony is higher when the antimony
7 is incorporated into the hydrocarbon feedstock than
8 when it is impregnated onto the catalyst.

9 Table X shows that the addition of a
10 hydrogen donor to the reaction zone reduces the
11 hydrogen and coke makes. When this is combined
12 with the previously described passivation process,
13 still lower coke makes result. In Table X the feed
14 for all tests was 60% vacuum gas oil (VGO), and 40%
15 light cat cycle oil (LCCO). The vacuum gas oil had
16 a minimum boiling point of about 340°C and a maxi-
17 mum boiling point of about 565°C as in the previous
18 tests. The light cat cycle oil had a minimum boiling
19 point of about 200°C and a maximum boiling point of
20 about 325°C. In the first test shown in Table X
21 the LCCO was not hydrogenated and the metals contam-
22 inated catalyst was not passivated. In the second
23 test the LCCO fraction of the feed was hydrogenated
24 by passing the LCCO through a hydrogenation zone
25 maintained at a temperature of about 371°C and
26 2000 psig, comprising a nickel-molybdenum sulfided
27 catalyst in a carbonaceous matrix to increase the
28 hydrogen content of the LCCO fraction from 10.51 wt.
29 % hydrogen to 12.10 wt. % hydrogen. The average
30 residence time of the LCCO in the hydrogenation zone
31 was about 180 minutes. In the third test, the LCCO
32 fraction of the feed was not hydrogenated, but the
33 catalyst was passivated by subjecting the catalyst to
34 4 redox cycles in a hydrogen atmosphere as previously
35 described. In the fourth test the LCCO fraction of

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1 the feed was hydrogenated as in test 2, and the
 2 catalyst was passivated as in test 3. It may be seen
 3 that the coke make in test 4 was substantially lower
 4 than that in tests 1, 2 or 3, thus demonstrating
 5 that use of a hydrogen donor material in the feed
 6 combined with catalyst passivation decreases the coke
 7 make more than either process alone.

TABLE X

Feed Composition-40% LCCO:60%VGO

	Wt. % Metal on Catalyst			Test No.	Treatment Prior To Cracking	Yields, Wt. % on Feed	
	Ni	V	Fe			H ₂	Coke
13	0.48	0.61	0.61	1	No LCCO	1.10	10.10
14					hydrogena-		
15					tion. No		
16					catalyst		
17					passivation		
18				2	LCCO hydro-	1.02	8.16
19					genated. No		
20					catalyst		
21					passivation		
22				3	No LCCO	0.76	6.67
23					hydrogena-		
24					tion.		
25					Catalyst		
26					passivated.		
27					Redox 750°C		
28					4 cycles, H ₂		
29				4	LCCO hydro-	0.75	4.60
30					genated.		
31					Catalyst		
32					passivated.		
33					Redox 750°C		
34					4 Cycles, H ₂		

35 Although the subject process has been
 36 described with reference to a specific embodiment, it
 37 will be understood that it is capable of further
 38 modification. Any variations, uses or adaptations of

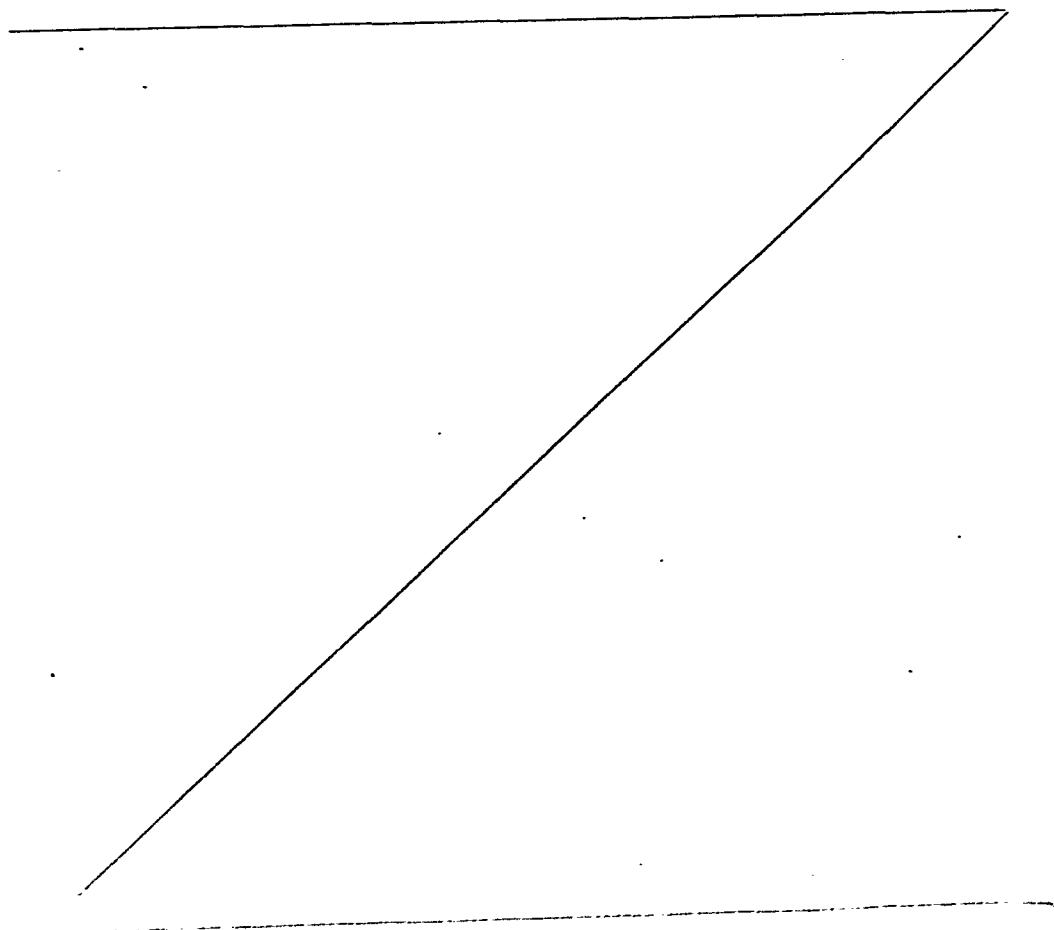
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1 the invention following, in general, the principles
2 of the invention are intended to be covered, includ-
3 ing such departures from the present disclosure
4 as come within known or customary practice in the art
5 to which the invention pertains and as may be applied
6 to the essential features hereinbefore set forth, and
7 as fall within the scope of the invention.

In this patent specification, "psi" designates "pounds per square inch" and is converted to the equivalent pressure in kg/cm^2 by multiplying by 0.07031. "SCF" designates "standard cubic feet", and is converted to litres by multiplying by 28.316.

Velocities in "feet/sec" are converted to cms/sec by multiplying by 30.48, and weights expressed in "tons" are converted to tonnes by multiplying by 0.9072.

Temperatures in $^{\circ}\text{F}$ are converted to $^{\circ}\text{C}$ by subtracting 32 and then dividing by 1.8.



CLAIMS

1. A method of reducing the rate of coke production from a hydrocarbon feedstock (16) which is cracked to lower molecular weight products (52) by contact (10) with a cracking catalyst where the feedstock contains at least two metals selected from nickel, vanadium and iron and where at least some of the said metals become deposited on the catalyst as contaminants and where the catalyst is periodically subjected to a regeneration treatment (26) in the absence of hydrocarbon feedstock, characterized in that after the regeneration treatment (26) and before contact (10) with hydrocarbon feedstock (16), the catalyst is subjected to a reduction treatment (70) at an elevated temperature for a time which is sufficient to at least partially passivate the metal contaminants on the catalyst.

2. The method of claim 1 in which the reduction treatment (70) is performed at a temperature above 600°C.

3. The method of either claim 1 or claim 2 in which at least 50 weight percent of the total of said metal contaminants deposited on the catalyst comprises only one of said metal contaminants.

4. The method of any one of claims 1 to 3 comprising the steps of:

(a) monitoring the composition of the metal contaminant deposited on the catalyst; and

(b) adding an effective amount of one of said metal contaminants not present as the major contaminant on the catalyst.

5. The method of any one of claims 1 to 4 in which the catalyst is subjected to the reduction treatment (70) for a time or an average time in the range of from 10 to 240 minutes.

6. The method of any one of claims 1 to 5 in which the contacting (10) of the hydrocarbon feedstock with the cracking catalyst is effected in the presence of added hydrogen donor material (92) whereby at least a portion of the hydrogen donor material transfers hydrogen to the hydrocarbon feedstock and/or to cracked lower molecular weight products.

7. The method of claim 6 in which the added hydrogen donor material (92) has a boiling point in the range between 200°C and 500°C.

8. The method of claim 6 or claim 7 in which the hydrogen donor material is obtained by:

(a) fractionating (100) the cracked lower molecular weight products (52); and

(b) at least partially hydrogenating (110) the fractionated product (106).

9. The method of any one of claims 6, 7 or 8 in which the added hydrogen donor material (92) comprises from 5 to 100 wt.% of the hydrocarbon feedstock to be cracked.

10. The method of any one of claims 1 to 9 in which there is added a passivation agent selected from antimony, tin, bismuth and manganese to further passivate the catalyst.

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European Patent
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EUROPEAN SEARCH REPORT

Application number

EP 81 30 2405

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
Y	US - A - 4 013 546 (SUGGIT) * Abstract; column 2, line 51 - column 3, line 60; column 5, line 1 - column 6, line 67; claims 1-14 * --	1,2,3	C 10 G 11/02 11/18
A	US - A - 4 264 433 (McKAY) * Abstract; column 2, line 28 - column 5, line 2; claims 1-4 * --	1,2,5, 10	TECHNICAL FIELDS SEARCHED (Int.Cl. ³)
Y	US - A - 4 183 803 (McKAY) * Abstract; column 1, line 35 - column 3, line 2; column 3, lines 56-65; column 4, line 11 - line 65; claims 1-16 * --	1,2,3, 5,10	C 10 G
A	CA - A - 729 167 (SHELL) * Page 2, line 3 - page 6, line 25; claims 1-6 * --	1	
A	US - A - 4 263 172 (McKAY) * Abstract; column 3, line 47 - column 4, line 56; claims 1-7 * --	10	CATEGORY OF CITED DOCUMENTS
A	US - A - 4 257 919 (ROBERTS) * Column 2, line 20 - column 4, line 33; claims 1-20 * -- ./.	10	X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons &: member of the same patent family, corresponding document
/ The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 09-02-1982	Examiner LO CONTE

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
DA	<u>US - A - 4 031 002</u> (McKAY)		
DA	<u>US - A - 3 479 279</u> (POHLENZ)		
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A	<u>US - A - 3 224 961</u> (ERICKSON)		
A	<u>US - A - 4 244 810</u> (YOUNG BLOOD)		
A	<u>US - A - 2 575 258</u> (CORNEIL)		

			TECHNICAL FIELDS SEARCHED (Int. Cl. ³)