



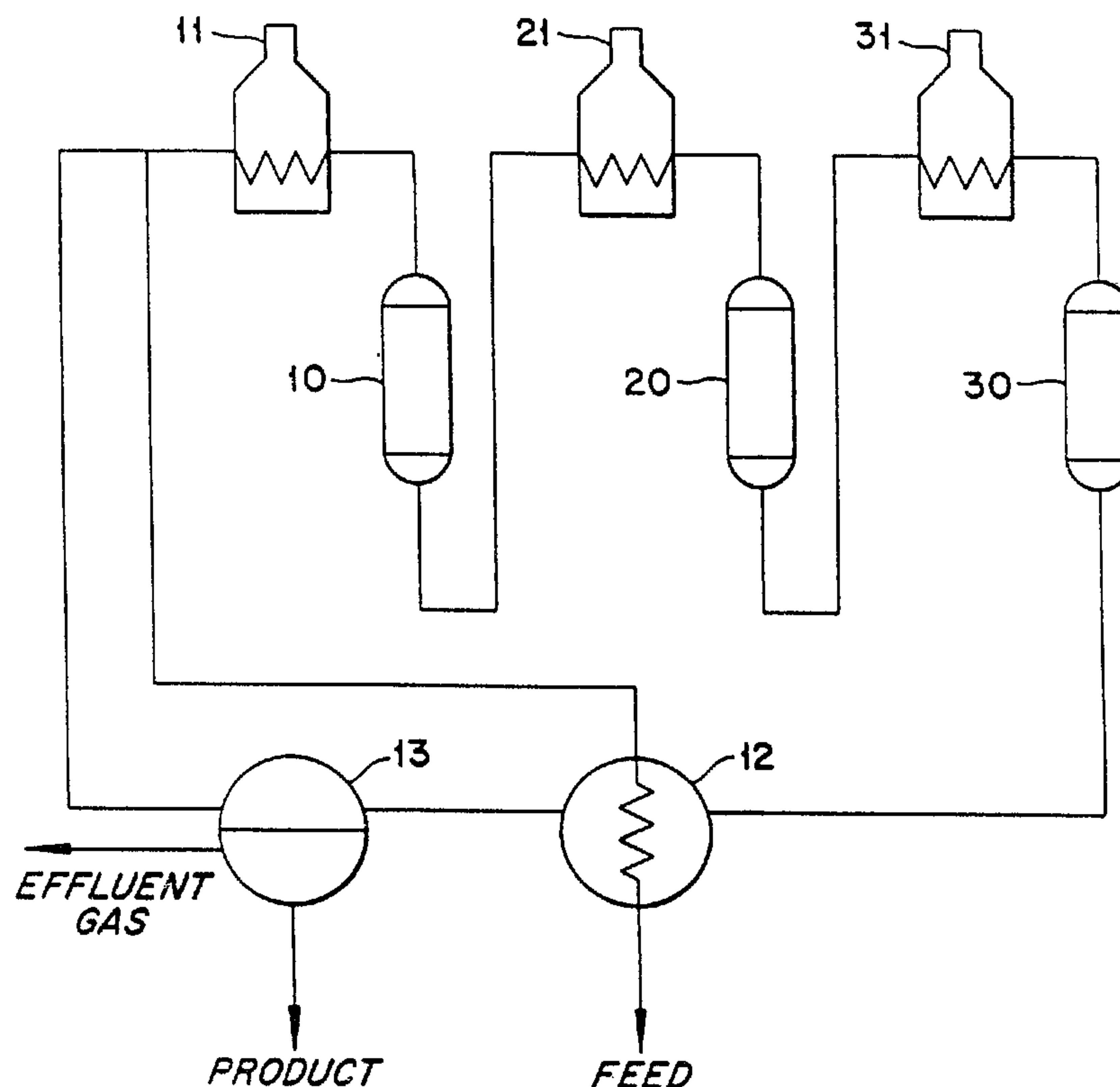
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(54) Titre : PROCÉDES DE REFORMAGE A FAIBLE TENEUR EN SOUFRE
(54) Title: LOW-SULFUR REFORMING PROCESSES



(57) Abrégé/Abstract:

Disclosed is a method for reforming hydrocarbons comprising contacting the hydrocarbons with a catalyst in a reactor system (10, 20, 30) of improved resistance to carburization and metal dusting under conditions of low sulfur.

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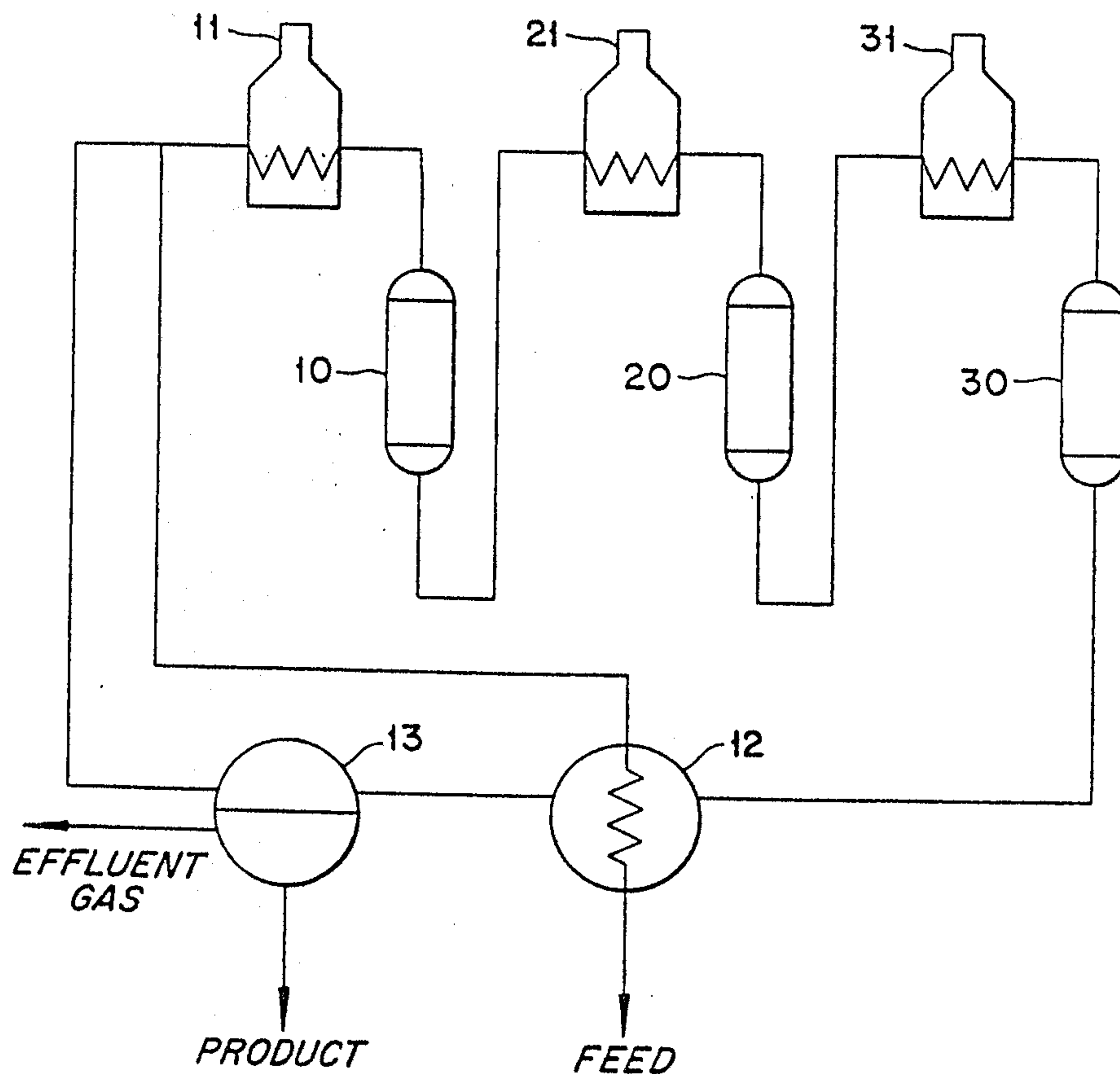
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(54) Title: LOW-SULFUR REFORMING PROCESSES



(57) Abstract

Disclosed is a method for reforming hydrocarbons comprising contacting the hydrocarbons with a catalyst in a reactor system (10, 20, 30) of improved resistance to carburization and metal dusting under conditions of low sulfur.

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1 LOW-SULFUR REFORMING PROCESSES

2

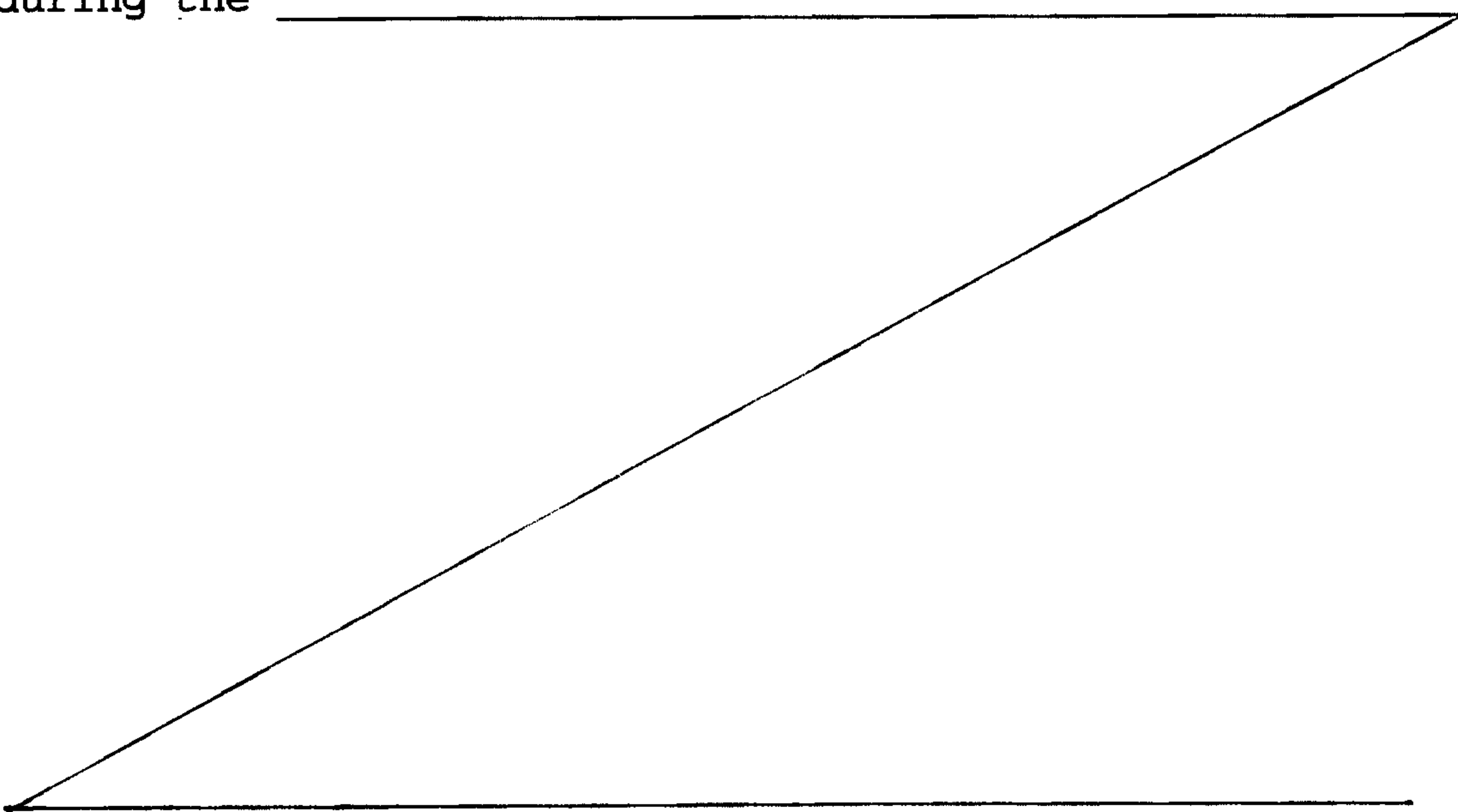
3 BACKGROUND OF THE INVENTION

4

5 The present invention relates to improved techniques
6 for catalytic reforming, particularly, catalytic
7 reforming under low-sulfur, and low-sulfur and low-water
8 conditions. More specifically, the invention relates to
9 the discovery and control of problems particularly acute
10 with low-sulfur, and low-sulfur and low-water reforming
11 processes.

12

13 Catalytic reforming is well known in the petroleum
14 industry and involves the treatment of naphtha fractions
15 to improve octane rating by the production of aromatics.
16 The more important hydrocarbon reactions which occur
17 during the _____



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1 reforming operation include the dehydrogenation of
2 cyclohexanes to aromatics, dehydroisomerization of
3 alkylcyclopentanes to aromatics, and
4 dehydrocyclization of acyclic hydrocarbons to
5 aromatics. A number of other reactions also occur,
6 including the dealkylation of alkylbenzenes,
7 isomerization of paraffins, and hydrocracking
8 reactions which produce light gaseous hydrocarbons,
9 e.g., methane, ethane, propane and butane. It is
10 important to minimize hydrocracking reactions during
11 reforming as they decrease the yield of gasoline
12 boiling products and hydrogen.

13
14 Because there is a demand for high octane
15 gasoline, extensive research has been devoted to the
16 development of improved reforming catalysts and
17 catalytic reforming processes. Catalysts for
18 successful reforming processes must possess good
19 selectivity. That is, they should be effective for
20 producing high yields of liquid products in the
21 gasoline boiling range containing large
22 concentrations of high octane number aromatic
23 hydrocarbons. Likewise, there should be a low yield
24 of light gaseous hydrocarbons. The catalysts should
25 possess good activity to minimize excessively high
26 temperatures for producing a certain quality of

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1 products. It is also necessary for the catalysts to
2 either possess good stability in order that the
3 activity and selectivity characteristics can be
4 retained during prolonged periods of operation; or be
5 sufficiently regenerable to allow frequent
6 regeneration without loss of performance.

7
8 Catalytic reforming is also an important process
9 for the chemical industry. There is an increasingly
10 larger demand for aromatic hydrocarbons for use in
11 the manufacture of various chemical products such as
12 synthetic fibers, insecticides, adhesives,
13 detergents, plastics, synthetic rubbers,
14 pharmaceutical products, high octane gasoline,
15 perfumes, drying oils, ion-exchange resins, and
16 various other products well known to those skilled in
17 the art.

18
19 An important technological advance in catalytic
20 reforming has recently emerged which involves the use
21 of large-pore zeolite catalysts. These catalysts are
22 further characterized by the presence of an alkali or
23 alkaline earth metal and are charged with one or more
24 Group VIII metals. This type of catalyst has been
25 found to advantageously provide higher selectivity
26 and longer catalytic life than those previously used.

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1 Having discovered selective catalysts with
2 acceptable cycle lives, successful commercialization
3 seemed inevitable. Unfortunately, it was
4 subsequently discovered that the highly selective,
5 large pore zeolite catalysts containing a Group VIII
6 metal were unusually susceptible to sulfur poisoning.
7 See U.S. Patent No. 4,456,527. Ultimately, it was
8 found that to effectively address this problem,
9 sulfur in the hydrocarbon feed should be at ultra-low
10 levels, preferably less than 100 parts per billion
11 (ppb), more preferably less than 50 ppb to achieve an
12 acceptable stability and activity level for the
13 catalysts.

14

15 After recognizing the sulfur sensitivity
16 associated with these new catalysts and determining
17 the necessary and acceptable levels of process
18 sulfur, successful commercialization reappeared on
19 the horizon; only to vanish with the emergence of
20 another associated problem. It was found that
21 certain large pore zeolite catalysts are also
22 adversely sensitive to the presence of water under
23 typical reaction conditions. Particularly, water was
24 found to greatly accelerate the rate of catalyst
25 deactivation.

26

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1 Water sensitivity was found to be a serious
2 drawback which was difficult to effectively address.
3 Water is produced at the beginning of each process
4 cycle when the catalyst is reduced with hydrogen.
5 And, water can be produced during process upsets when
6 water leaks into the reformer feed, or when the feed
7 becomes contaminated with an oxygen-containing
8 compound. Eventually, technologies were also
9 developed to protect the catalysts from water.

10

11 Again commercialization seemed practical with
12 the development of various low-sulfur, low-water
13 systems for catalytic reforming using highly
14 selective large-pore zeolite catalysts with long
15 catalytic lives. While low-sulfur/low-water systems
16 were initially effective, it was discovered that a
17 shut down of the reactor system can be necessary
18 after only a matter of weeks. The reactor system of
19 one test plant had regularly become plugged after
20 only such brief operating periods. The plugs were
21 found to be those associated with coking. However,
22 although coking within catalyst particles is a common
23 problem in hydrocarbon processing, the extent and
24 rate of coke plug formation exterior to the catalyst
25 particles associated with this particular system far
26 exceeded any expectation.

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SUMMARY OF THE INVENTION

1
2 Accordingly, one object of the invention is to
3 provide a method for reforming hydrocarbons under
4 conditions of low sulfur which avoids the
5 aforementioned problems found to be associated with
6 low-sulfur processes, such as brief operating
7 periods.

8
9 It is another object of the invention to provide
10 a reactor system for reforming hydrocarbons under
11 conditions of low sulfur which permits longer
12 operating periods.

13
14 After a detailed analysis and investigation of
15 the coke plugs of low-sulfur reactor systems, it was
16 surprisingly found that they contained particles and
17 droplets of metal; the droplets ranging in size of up
18 to a few microns. This observation led to the
19 startling realization that there are new, profoundly
20 serious, problems which were not of concern with
21 conventional reforming techniques where process
22 sulfur and water levels were significantly higher.
23 More particularly, it was discovered that problems
24 existed which threatened the effective and economic
25 operability of the systems, and the physical
26 integrity of the equipment as well. It was also

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1 discovered that these problems emerged due to the
2 low-sulfur conditions, and to some extent, the low
3 levels of water.
4

5 For the last forty years, catalytic reforming
6 reactor systems have been constructed of ordinary
7 mild steel (e.g., 2½ Cr 1 Mo). Over time, experience
8 has shown that the systems can operate successfully
9 for about twenty years without significant loss of
10 physical strength. However, the discovery of the
11 metal particles and droplets in the coke plugs
12 eventually lead to an investigation of the physical
13 characteristics of the reactor system. Quite
14 surprisingly, conditions were discovered which are
15 symptomatic of a potentially severe physical
16 degradation of the entire reactor system, including
17 the furnace tubes, piping, reactor walls and other
18 environments such as catalysts that contain iron and
19 metal screens in the reactors. Ultimately, it was
20 discovered that this problem is associated with the
21 excessive carburization of the steel which causes an
22 embrittlement of the steel due to injection of
23 process carbon into the metal. Conceivably, a
24 catastrophic physical failure of the reactor system
25 could result.
26

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1 With conventional reforming techniques
2 carburization simply was not a problem or concern;
3 nor was it expected to be in contemporary low-
4 sulfur/low-water systems. And, it was assumed that
5 conventional process equipment could be used.
6 Apparently, however, the sulfur present in
7 conventional systems effectively inhibits
8 carburization. Somehow in conventional processes the
9 process sulfur interferes with the carburization
10 reaction. But with extremely low-sulfur systems,
11 this inherent protection no longer exists.

12
13 Figure 1A is a photomicrograph of a portion of
14 the inside (process side) of a mild steel furnace
15 tube from a commercial reformer. The tube had been
16 exposed to conventional reforming conditions for
17 about 19 years. This photograph shows that the
18 surface of the tube has remained essentially
19 unaltered with the texture of the tube remaining
20 normal after long exposure to hydrocarbons at high
21 temperatures (the black portion of the photograph is
22 background).

23
24 Figure 1B is a photomicrograph of a portion of a
25 mild steel coupon sample which was placed inside a
26 reactor of a low-sulfur/low-water demonstration plant

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1 for only 13 weeks. The photograph shows the eroded
2 surface of the sample (contrasted against a black
3 background) from which metal dusting has occurred.
4 The dark grey-like veins indicate the environmental
5 carburization of the steel, which was carburized and
6 embrittled more than 1 mm in depth.

7
8 Of course, the problems associated with
9 carburization only begin with carburization of the
10 physical system. The carburization of the steel
11 walls leads to "metal dusting"; a release of
12 catalytically active particles and melt droplets of
13 metal due to erosion of the metal.

14
15 The active metal particulates provide additional
16 sites for coke formation in the system. While
17 catalyst deactivation from coking is generally a
18 problem which must be addressed in reforming, this
19 new significant source of coke formation leads to a
20 new problem of coke plugs which excessively
21 aggravates the problem. In fact, it was found that
22 the mobile active metal particulates and coke
23 particles metastasize coking generally throughout the
24 system. The active metal particulates actually
25 induce coke formation on themselves and anywhere that
26 the particles accumulate in the system resulting in

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1 coke plugs and hot regions of exothermic
2 demethanation reactions. As a result, an
3 unmanageable and premature coke-plugging of the
4 reactor system occurs which can lead to a system
5 shut-down within weeks of start-up. Use of the
6 process and reactor system of the present invention,
7 however, overcomes these problems.

8
9 Therefore, a first aspect of the invention
10 relates to a method for reforming hydrocarbons
11 comprising contacting the hydrocarbons with a
12 reforming catalyst, preferably a large-pore zeolite
13 catalyst including an alkali or alkaline earth metal
14 and charged with one or more Group VIII metals, in a
15 reactor system having a resistance to carburization
16 and metal dusting which is an improvement over
17 conventional mild steel reactor systems under
18 conditions of low sulfur and often low sulfur and low
19 water, and upon reforming the resistance being such
20 that embrittlement from carburization will be less
21 than about 2.5 mm/year, preferably less than 1.5
22 mm/year, more preferably less than 1 mm/year, and
23 most preferably less than 0.1 mm/year. Preventing
24 embrittlement to such an extent will significantly
25 reduce metal dusting and coking in the reactor

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1 system, and permits operation for longer periods of
2 time.

3
4 And, another aspect of the invention relates to
5 a reactor system including means for providing a
6 resistance to carburization and metal dusting which
7 is an improvement over conventional mild steel
8 systems in a method for reforming hydrocarbons using
9 a reforming catalyst such as a large-pore zeolite
10 catalyst including an alkaline earth metal and
11 charged with one or more Group VIII metals under
12 conditions of low sulfur, the resistance being such
13 that embrittlement will be less than about 2.5
14 mm/year, preferably less than 1.5 mm/year, more
15 preferably less than 1 mm/year, and most preferably
16 less than 0.1 mm/year.

17
18 Thus, among other factors, the present invention
19 is based on the discovery that in low-sulfur, and
20 low-sulfur and low-water reforming processes there
21 exist significant carburization, metal dusting and
22 coking problems, which problems do not exist to any
23 significant extent in conventional reforming
24 processes where higher levels of sulfur are present.
25 This discovery has led to intensive work and
26 development of solutions to the problems, which

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1 solutions are novel to low-sulfur reforming and are
2 directed to the identification and selection of
3 resistant materials for low-sulfur reforming systems,
4 ways to effectively utilize and apply the resistant
5 materials, additives (other than sulfur) for reducing
6 carburization, metal dusting and coking, various
7 process modifications and configurations, and
8 combinations thereof, which effectively address the
9 problems.

10

11 More particularly, the discovery has led to the
12 search for, identification of, and selection of
13 resistant materials for low-sulfur reforming systems,
14 preferably the reactor walls, furnace tubes and
15 screens thereof, which were previously unnecessary in
16 conventional reforming systems such as certain alloy
17 and stainless steels, aluminized and chromized
18 materials, and certain ceramic materials. Also, it
19 was discovered that other specific materials, applied
20 as a plating, cladding, paint, etc., can be
21 effectively resistant. These materials include
22 copper, tin, arsenic, antimony, brass, lead bismuth
23 chromium, intermetallic compounds thereof, and alloys
24 thereof, as well as silica and silicon based
25 coatings. In one preferred embodiment of the

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1 invention there is provided a novel and resistant tin-
2 containing paint.
3

4 Furthermore, the discovery led to the development of
5 certain additives, hereinafter referred to as
6 anticarburizing and anticoking agents, which out of
7 necessity are essentially sulfur free, preferably
8 completely sulfur free, which are novel to reforming.
9 Such additives include organo-tin compounds, organo-
10 antimony compounds, organo-bismuth compounds, organo-
11 arsenic compounds and organo-lead compounds.
12

13 Also, the problems associated with low-sulfur
14 reforming has lead to the development of certain process
15 modifications and configurations previously unnecessary
16 in conventional reforming. These include certain
17 temperature control techniques, the use of superheated
18 hydrogen between reactors, more frequent catalyst
19 regenerations, the use of staged heaters and tubes, the
20 use of staged temperature zones, the use of superheated
21 raw materials, and the use of larger tube diameters
22 and/or higher tube velocities.
23

24 According to one aspect of the invention, there is
25 provided an improved method for catalytically reforming a
26 hydrocarbon, comprising the step of contacting, under
27 conditions of low sulfur, a sulfur-sensitive zeolite
28 reforming catalyst with a hydrocarbon in a reactor system
29 having a plurality of furnace tubes, wherein a portion of

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1 said reactor system has a resistance to carburization and
2 metal dusting under low sulfur reforming conditions at
3 least as great as that of stainless steel.
4

5 According to another aspect of the invention, there
6 is provided a method for the catalytic reforming of a
7 hydrocarbon stream to produce an aromatic compound using
8 a reactor system, having a sulfur-sensitive reforming
9 catalyst charged with at least one Group VIII metal, over
10 a prolonged period of operation without significant coke-
11 plugging, comprising the steps of:

12 providing a low sulfur hydrocarbon-containing stream
13 prepared by reducing the sulfur content of said
14 hydrocarbon-containing stream to less than 50 ppb sulfur;

15 providing a reforming reactor system of improved
16 resistance to carburization and metal dusting upon
17 reforming said hydrocarbon-containing stream, said
18 reactor system having at least one furnace to heat said
19 hydrocarbon-containing stream to catalytic reforming
20 temperatures, said furnace having, in contact with said
21 hydrocarbon-containing stream, a plurality of furnace
22 tubes having a resistance to carburization and metal
23 dusting at least as great as that of 347 stainless steel;
24 and

25 passing said hydrocarbon-containing stream through
26 said reactor system to contact said hydrocarbon-
27 containing stream with said reforming catalyst to produce
28 an aromatic.

- 13b -

1 According to a further aspect of the invention,
2 there is provided a method for improving the
3 carburization resistance of at least a portion of an
4 apparatus for hydrocarbon conversion, comprising the
5 steps of:

6 applying a reducible, tin-containing paint to a
7 portion of an apparatus for hydrocarbon conversion; and
8 heating said reducible paint under reducing
9 conditions to form a protective layer which provides
10 improved carburization resistance.

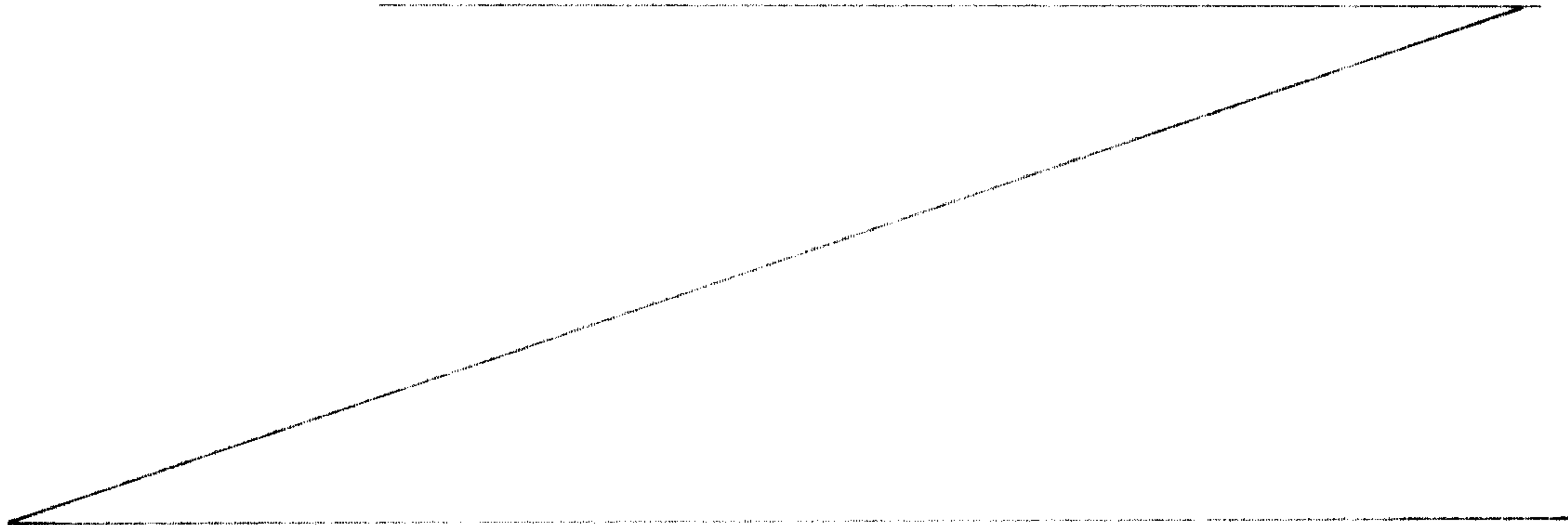
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12 According to another aspect of the invention, there
13 is provided a catalytic reforming reactor system for
14 catalytically reforming hydrocarbons under low sulfur
15 conditions, comprising:

16 a furnace having a plurality of furnace tubes;

17 a reforming reactor having a catalyst bed containing
18 a sulfur-sensitive catalyst; and

19 wherein a portion of said catalytic reforming
20 reactor system, which contacts a low-sulfur stream
21 containing a hydrocarbon, has an improved resistance to
22 carburization.



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1 BRIEF DESCRIPTION OF THE DRAWING

2 As noted above, Figure 1A is a photomicrograph
3 of a portion of the inside (process side) of a mild
4 steel furnace tube from a commercial reformer which
5 had been in use about 19 years; and as also noted
6 above,

7
8 Figure 1B is a photomicrograph of a portion of a
9 mild steel coupon sample which was placed inside a
10 reactor of a low-sulfur/low-water demonstration plant
11 for only 13 weeks.

12
13 Figure 2 is an illustration of a suitable
14 reforming reactor system for use in the present
15 invention.

16
17 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

18 The metallurgical terms used herein are to be
19 given their common metallurgical meanings as set
20 forth in THE METALS HANDBOOK of the American Society
21 of Metals. For example, "carbon steels" are those
22 steels having no specified minimum quantity for any
23 alloying element (other than the commonly accepted
24 amounts of manganese, silicon and copper) and
25 containing only an incidental amount of any element
26 other than carbon, silicon, manganese, copper, sulfur

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1 and phosphorus. "Mild steels" are those carbon
2 steels with a maximum of about 0.25% carbon. Alloy
3 steels are those steels containing specified
4 quantities of alloying elements (other than carbon
5 and the commonly accepted amounts of manganese,
6 copper, silicon, sulfur and phosphorus) within the
7 limits recognized for constructional alloy steels,
8 added to effect changes in mechanical or physical
9 properties. Alloy steels will contain less than 10%
10 chromium. Stainless steels are any of several steels
11 containing at least 10, preferably 12 to 30%,
12 chromium as the principal alloying element.

13

14 Generally, therefore, one focus of the invention
15 is to provide an improved method for reforming
16 hydrocarbons using a reforming catalyst, particularly
17 a large pore zeolite catalyst including an alkali or
18 alkaline earth metal and charged with one or more
19 Group VIII metals which is sulfur sensitive, under
20 conditions of low sulfur. Such a process, of course,
21 must demonstrate better resistance to carburization
22 than conventional low-sulfur reforming techniques.

23

24 One solution for the problem addressed by the
25 present invention is to provide a novel reactor
26 system which can include one or more various means

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1 for improving resistance to carburization and metal
2 dusting during reforming using a reforming catalyst
3 such as the aforementioned sulfur sensitive large-
4 pore zeolite catalyst under conditions of low sulfur.
5

6 By "reactor system" as used herein there is
7 intended at least one reforming reactor and its
8 corresponding furnace means and piping. Figure 2
9 illustrates a typical reforming reactor system
10 suitable for practice of the present invention. It
11 can include a plurality of reforming reactors (10),
12 (20) and (30). Each reactor contains a catalyst bed.
13 The system also includes a plurality of furnaces
14 (11), (21) and (31); heat exchanger (12); and
15 separator (13).
16

17 Through research associated with the present
18 invention, it was discovered that the aforementioned
19 problems with low-sulfur reforming can be effectively
20 addressed by a selection of an appropriate reactor
21 system material for contact with the hydrocarbons
22 during processing. Typically, reforming reactor
23 systems have been constructed of mild steels, or
24 alloy steels such as typical chromium steels, with
25 insignificant carburization and dusting. For
26 example, under conditions of standard reforming, 2½

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1 Cr furnace tubes can last twenty years. However, it
2 was found that these steels are unsuitable under low-
3 sulfur reforming conditions. They rapidly become
4 embrittled by carburization within about one year. For
5 example, it was found that 2½ Cr 1 Mo steel carburized
6 and embrittled more than 1 mm/year.

7
8 Furthermore, it was found that materials considered
9 under standard metallurgical practice to be resistant to
10 coking and carburization are not necessarily resistant
11 under low-sulfur reforming conditions. For example,
12 nickel-rich alloys such as Incoloy 800™ and 825; Inconel
13 600™; Marcel and Haynes 230™, are unacceptable as they
14 exhibit excessive coking and dusting.

15
16 However, 300 series stainless steels, preferably
17 304, 316, 321 and 347, are acceptable as materials for at
18 least portions of the reactor system according to the
19 present invention which contact the hydrocarbons. They
20 have been found to have a resistance to carburization
21 greater than mild steels and nickel-rich alloys.

22
23 Initially it was believed that aluminized materials
24 such as those sold by Alon Corporation _____

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1 ("Alonized Steels") would not provide adequate
2 protection against carburization in the reforming
3 reactor system and process of the invention. It has
4 since been discovered, however, that the application
5 of thin aluminum or alumina films to metal surfaces
6 of the reforming reactor system, or simply the use of
7 Alonized Steels during construction, can provide
8 surfaces which are sufficiently resistant to
9 carburization and metal dusting under the low-sulfur
10 reforming conditions. However, such materials are
11 relatively expensive, and while resistant to
12 carburization and metal dusting, tend to crack, and
13 show substantial reductions in tensile strengths.
14 Cracks expose the underlying base metal rendering it
15 susceptible to carburization and metal dusting under
16 low sulfur reforming conditions.

17
18 While aluminized materials have been used to
19 prevent carburization in ethylene steam cracking
20 processes, such processes are operated at
21 significantly higher temperatures than reforming;
22 temperatures where carburization would be expected.
23 Carburization and metal dusting simply have not been
24 problems in prior reforming processes.

25

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1 Therefore, another solution to the problems of
2 carburization and metal dusting involves the
3 application of thin aluminum or alumina films on, or
4 the use of aluminized materials as, at least a
5 portion of the metal surfaces in the reactor system.
6 In fact, the metal surfaces particularly susceptible
7 to carburization and metal dusting can be provided in
8 that manner. Such metal surfaces include but are not
9 limited to, the reactor walls, furnace tubes, and
10 furnace liners.

11
12 When applying an aluminum or alumina film, it is
13 preferable that the film have a thermal expansivity
14 that is similar to that of the metal surface to which
15 it is applied (such as a mild steel) in order to
16 withstand thermal shocks and repeated temperature
17 cycling which occur during reforming. This prevents
18 cracking or spalling of the film which could expose
19 the underlying metal surface to the carburization
20 inducing hydrocarbon environment.

21
22 Additionally, the film should have a thermal
23 conductivity similar to that of, or exceeding, those
24 of metals conventionally used in the construction of
25 reforming reactor systems. Furthermore, the aluminum
26 or alumina film should not degrade in the reforming

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1 environment, or in the oxidizing environment
2 associated with catalyst regeneration, nor should it
3 result in the degradation of the hydrocarbons in the
4 reactor system.

5
6 Suitable methods for applying aluminum or
7 alumina films to metal surfaces such as mild steels
8 include well known deposition techniques. Preferred
9 processes include powder and vapor diffusion
10 processes such as the "Alonizing" process, which has
11 been commercialized by Alon Processing, Inc.,
12 Terrytown, Pa.

13
14 Essentially, "Alonizing" is a high temperature
15 diffusion process which alloys aluminum into the
16 surface of a treated metal, such as e.g., a
17 commercial grade mild steel. In this process, the
18 metal (e.g., a mild steel) is positioned in a retort
19 and surrounded with a mixture of blended aluminum
20 powders. The retort is then hermetically sealed and
21 placed in an atmosphere-controlled furnace. At
22 elevated temperatures, the aluminum deeply diffuses
23 into the treated metal resulting in an alloy. After
24 furnace cooling, the substrate is taken out of the
25 retort and excess powder is removed. Straightening,
26 trimming, beveling and other secondary operations can

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1 then be performed as required. This process can
2 render the treated ("alozined") metal resistant to
3 carburization and metal dusting under low-sulfur
4 reforming conditions according to the invention.
5

6 Thin chromium or chromium oxide films can also
7 be applied to metal surfaces of the reactor system to
8 render the surfaces resistant to carburization and
9 metal dusting under low-sulfur reforming conditions.
10 Like the use of alumina and aluminum films, and
11 aluminized materials, chromium or chromium oxide
12 coated metal surfaces have not been used to address
13 carburization problems under low-sulfur reforming
14 conditions.
15

16 The chromium or chromium oxide can also be
17 applied to carburization and metal dusting
18 susceptible metal surfaces such as the reactor walls,
19 furnace liners, and furnace tubes. However, any
20 surface in the system which would show signs of
21 carburization and metal dusting under low-sulfur
22 reforming conditions would benefit from the
23 application of a thin chromium or chromium oxide
24 film.
25

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1 When applying the chromium or chromium oxide
2 film, it is preferable that the chromium or chromium
3 oxide film have a thermal expansivity similar to that
4 of the metal to which it is applied. Additionally,
5 the chromium or chromium oxide film should be able to
6 withstand thermal shocks and repeated temperature
7 cycling which are common during reforming. This
8 avoids cracking or spalling of the chromium or
9 chromium oxide film which could potentially expose
10 the underlying metal surfaces to carburization
11 inducing environments. Furthermore, the chromium or
12 chromium oxide film should have a thermal
13 conductivity similar to or exceeding those materials
14 conventionally used in reforming reactor systems (in
15 particular mild steels) in order to maintain
16 efficient heat transfer. The chromium or chromium
17 oxide film also should not degrade in the reforming
18 environment or in the oxidizing environment
19 associated with catalyst regeneration, nor should it
20 induce degradation of the hydrocarbons in the reactor
21 system.

22
23 Suitable methods for applying chromium or
24 chromium oxide films to surfaces such as e.g., mild
25 steels, include well known deposition techniques.
26 Preferred processes include powder-pack and vapor

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1 diffusion processes such as the "chromizing" process,
2 which is commercialized by Alloy Surfaces, Inc., of
3 Wilmington, Delaware.

4
5 The "chromizing" process is essentially a vapor
6 diffusion process for application of chromium to a
7 metal surface (similar to the above described
8 "Alonizing process"). The process involves
9 contacting the metal to be coated with a powder of
10 chromium, followed by a thermal diffusion step.
11 This, in effect, creates an alloy of the chromium
12 with the treated metal and renders the surface
13 extremely resistant to carburization and metal
14 dusting under low-sulfur reforming conditions.

15
16 In some areas of the reactor systems, localized
17 temperatures can become excessively high during
18 reforming (e.g., 900-1250°F). This is particularly
19 the case in furnace tubes, and in catalyst beds where
20 exothermic demethanation reactions occur within
21 normally occurring coke balls causing localized hot
22 regions. While still preferred to mild steels and
23 nickel-rich alloys, the 300 series stainless steels
24 do exhibit some coking and dusting at around 1000°F.
25 Thus, while useful, the 300 series stainless steels

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1 are not the most preferred material for use in the
2 present invention.

3
4 Chromium-rich stainless steels such as 446 and
5 430 are even more resistant to carburization than 300
6 series stainless steels. However, these steels are
7 not as desirable for heat resisting properties (they
8 tend to become brittle).

9
10 Resistant materials which are preferred over the
11 300 series stainless steels for use in the present
12 invention include copper, tin, arsenic, antimony,
13 bismuth, chromium and brass, and intermetallic
14 compounds and alloys thereof (e.g., Cu-Sn alloys, Cu-
15 Sb alloys, stannides, antimonides, bismuthides,
16 etc.). Steels and even nickel-rich alloys containing
17 these metals can also show reduced carburization. In
18 a preferred embodiment, these materials are provided
19 as a plating, cladding, paint (e.g., oxide paints) or
20 other coating to a base construction material. This
21 is particularly advantageous since conventional
22 construction materials such as mild steels can still
23 be used with only the surface contacting the
24 hydrocarbons being treated. Of these, tin is
25 especially preferred as it reacts with the surface to
26 provide a coating having excellent carburization

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1 resistance at higher temperatures, and which resists
2 peeling and flaking of the coating. Also, it is
3 believed that a tin containing layer can be as thin
4 as 1/10 micron and still prevent carburization.
5

6 Where practical, it is preferred that the
7 resistant materials be applied in a paint-like
8 formulation (hereinafter "paint") to a new or
9 existing reactor system. Such a paint can be
10 sprayed, brushed, pigged, etc. on reactor system
11 surfaces such as mild steels or stainless steels. It
12 is most preferred that such a paint be a
13 decomposable, reactive, tin-containing paint which
14 reduces to a reactive tin and forms metallic
15 stannides (e.g., iron stannides and nickel/iron
16 stannides) upon heating in a reducing atmosphere.
17

18 It is most preferred that the aforementioned
19 paint contain at least four components (or their
20 functional equivalents); (i) a hydrogen decomposable
21 tin compound, (ii) a solvent system, (iii) a finely
22 divided tin metal and (iv) tin oxide as a reducible
23 sponge/dispersing/binding agent. The paint should
24 contain finely divided solids to minimize settling,
25 and should not contain non-reactive materials which

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1 will prevent reaction of reactive tin with surfaces
2 of the reactor system.

3
4 As the hydrogen decomposable tin compound, tin
5 octanoate is particularly useful. Commercial
6 formulations of this compound itself are available
7 and will partially dry to an almost chewing-gum-like
8 layer on a steel surface; a layer which will not
9 crack and/or split. This property is necessary for
10 any coating composition used in this context because
11 it is conceivable that the coated material will be
12 stored for months prior to treatment with hydrogen.
13 Also, if parts are coated prior to assembly they must
14 be resistant to chipping during construction. As
15 noted above, tin octanoate is available commercially.
16 It is reasonably priced, and will decompose smoothly
17 to a reactive tin layer which forms iron stannide in
18 hydrogen at temperatures as low as 600°F.

19
20 Tin octanoate should not be used alone in a
21 paint, however. It is not sufficiently viscous.
22 Even when the solvent is evaporated therefrom, the
23 remaining liquid will drip and run on the coated
24 surface. In practice, for example, if such were used
25 to coat a horizontal furnace tube, it would pool at
26 the bottom of the tube.

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1 Component (iv), the tin oxide
2 sponge/dispersing/binding agent, is a porous tin-
3 containing compound which can sponge-up an organo-
4 metallic tin compound, yet still be reduced to active
5 tin in the reducing atmosphere. In addition, tin
6 oxide can be processed through a colloid mill to
7 produce very fine particles which resist rapid
8 settling. The addition of tin oxide will provide a
9 paint which becomes dry to the touch, and resists
10 running.

11
12 Unlike typical paint thickeners, component (iv)
13 is selected such that it becomes a reactive part of
14 the coating when reduced. It is not inert like
15 formed silica; a typical paint thickener which would
16 leave an unreactive surface coating after treatment.

17
18 Finely divided tin metal, component (iii), is
19 added to insure that metallic tin is available to
20 react with the surface to be coated at as low a
21 temperature as possible, even in a non-reducing
22 atmosphere. The particle size of the tin is
23 preferably one to five microns which allows excellent
24 coverage of the surface to be coated with tin metal.
25 Non-reducing conditions can occur during drying of
26 the paint and welding of pipe joints. The presence

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1 of metallic tin ensures that even when part of the
2 coating is not completely reduced, tin metal will be
3 present to react and form the desired stannide layer.

4
5 The solvent should be non-toxic, and effective
6 for rendering the paint sprayable and spreadable when
7 desired. It should also evaporate quickly and have
8 compatible solvent properties for the hydrogen
9 decomposable tin compound. Isopropyl alcohol is most
10 preferred, while hexane and pentane can be useful, if
11 necessary. Acetone, however, tends to precipitate
12 organic tin compounds.

13
14 In one embodiment, there can be used a tin paint
15 of 20 percent Tin Ten-Cem (stannous octanoate in
16 octanoic acid), stannic oxide, tin metal powder and
17 isopropyl alcohol.

18
19 The tin paint can be applied in many ways. For
20 example, furnace tubes of the reactor system can be
21 painted individually or as modules. A reforming
22 reactor system according to the present invention can
23 contain various numbers of furnace tube modules
24 (e.g., about 24 furnace tube modules) of suitable
25 width, length and height (e.g., about 10 feet long,
26 about 4 feet wide, and about 40 feet in height).

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1 Typically, each module will include two headers of
2 suitable diameter, preferably about 2 feet in
3 diameter, which are connected by about four to ten u-
4 tubes of suitable length (e.g., about 42 feet long).
5 Therefore, the total surface area to be painted in
6 the modules can vary widely; for example, in one
7 embodiment it can be about 16,500 ft².

8
9 Painting modules rather than the tubes
10 individually can be advantageous in at least four
11 respects; (i) painting modules rather than individual
12 tubes should avoid heat destruction of the tin paint
13 as the components of the modules are usually heat
14 treated at extremely elevated temperatures during
15 production; (ii) painting modules will likely be
16 quicker and less expensive than painting tubes
17 individually; (iii) painting modules should be more
18 efficient during production scheduling; and (iv)
19 painting of the modules should enable painting of
20 welds.

21

22 However, painting the modules may not enable the
23 tubes to be as completely coated with paint as if the
24 tubes were painted individually. If coating is
25 insufficient, the tubes can be coated individually.

26

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1 It is preferable that the paint be sprayed into
2 the tubes and headers. Sufficient paint should be
3 applied to fully coat the tubes and headers. After a
4 module is sprayed, it should be left to dry for about
5 24 hours followed by application of a slow stream of
6 heated nitrogen (e.g., about 150°F for about 24
7 hours). Thereafter, it is preferable that a second
8 coat of paint be applied and also dried by the
9 procedure described above. After the paint has been
10 applied, the modules should preferably be kept under
11 a slight nitrogen pressure and should not be exposed
12 to temperatures exceeding about 200°F prior to
13 installation, nor should they be exposed to water
14 except during hydrotesting.

15
16 Iron bearing reactive paints are also useful in
17 the present invention. Such an iron bearing reactive
18 paint will preferably contain various tin compounds
19 to which iron has been added in amounts up to one
20 third Fe/Sn by weight.

21
22 The addition of iron can, for example, be in the
23 form of Fe_2O_3 . The addition of iron to a tin
24 containing paint should afford noteworthy advantages;
25 in particular: (i) it should facilitate the
26 reaction of the paint to form iron stannides thereby

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1 acting as a flux; (ii) it should dilute the nickel
2 concentration in the stannide layer thereby providing
3 better protection against coking; and (iii) it
4 should result in a paint which affords the anti-
5 coking protection of iron stannides even if the
6 underlying surface does not react well.

7

8 Yet another means for preventing carburization,
9 coking, and metal dusting in the low-sulfur reactor
10 system comprises the application of a metal coating
11 or cladding to chromium rich steels contained in the
12 reactor system. These metal coatings or claddings
13 may be comprised of tin, antimony, bismuth or
14 arsenic. Tin is especially preferred. These
15 coatings or claddings may be applied by methods
16 including electroplating, vapor depositing, and
17 soaking of the chromium rich steel in a molten metal
18 bath.

19

20 It has been found that in reforming reactor
21 systems where carburization, coking, and metal
22 dusting are particularly problematic that the coating
23 of the chromium-rich, nickel-containing steels with a
24 layer of tin in effect creates a double protective
25 layer. There results an inner chromium rich layer
26 which is resistant to carburization, coking, and

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1 metal dusting and an outer tin layer which is also
2 resistant to carburization, coking and metal dusting.
3 This occurs because when the tin coated chromium rich
4 steel is exposed to typical reforming temperatures,
5 such as about 1200°F, it reacts with the steel to
6 form iron nickel stannides. Thereby, the nickel is
7 preferentially leached from the surface of the steel
8 leaving behind a layer of chromium rich steel. In
9 some instances, it may be desirable to remove the
10 iron nickel stannide layer from the stainless steel
11 to expose the chromium rich steel layer.

12

13 For example, it was found that when a tin
14 cladding was applied to a 304 grade stainless steel
15 and heated at about 1200°F there resulted a chromium
16 rich steel layer containing about 17% chromium and
17 substantially no nickel, comparable to 430 grade
18 stainless steel.

19

20 When applying the tin metal coating or cladding
21 to the chromium rich steel, it may be desirable to
22 vary the thickness of the metal coating or cladding
23 to achieve the desired resistance against
24 carburization, coking, and metal dusting. This can
25 be done by, e.g., adjusting the amount of time the
26 chromium rich steel is soaked in a molten tin bath.

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1 This will also affect the thickness of the resulting
2 chromium rich steel layer. It may also be desirable
3 to vary the operating temperature, or to vary the
4 composition of the chromium rich steel which is
5 coated which in order to control the chromium
6 concentration in the chromium rich steel layer
7 produced.

8
9 It has additionally been found that tin-coated
10 steels can be further protected from carburization,
11 metal dusting, and coking by a post-treatment process
12 which involves application of a thin oxide coating,
13 preferably a chromium oxide, such as Cr_2O_3 . This
14 coating will be thin, as thin as a few μm .
15 Application of such a chromium oxide will protect
16 aluminum as well as tin coated steels, such as
17 Alonized steels, under low-sulfur reforming
18 conditions.

19
20 The chromium oxide layer can be applied by
21 various methods including: application of a chromate
22 or dichromate paint followed by a reduction process;
23 vapor treatment with an organo-chromium compound; or
24 application of a chromium metal plating followed by
25 oxidation of the resulting chromium plated steel.

26

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1 Examination of tin-electroplated steels which
2 have been subjected to low-sulfur reforming
3 conditions for a substantial period of time has shown
4 that when a chromium oxide layer is produced on the
5 surface of the stannide layer or under the stannide
6 layer, the chromium oxide layer does not cause
7 deterioration of the stannide layer, but appears to
8 render the steel further resistant to carburization,
9 coking and metal dusting. Accordingly, application
10 of a chromium oxide layer to either tin or aluminum
11 coated steels will result in steels which are further
12 resistant to carburization and coking under the low-
13 sulfur reforming conditions. This post-treatment
14 process has particular applications for treating tin
15 or aluminum coated steels which, after prolonged
16 exposure to low-sulfur reforming conditions, are in
17 need of repair.

18
19 It has further been found that aluminized, e.g.,
20 "Alonized" steels which are resistant to
21 carburization under the present reforming conditions
22 of low sulfur can be rendered further resistant by
23 post-treatment of the aluminum coated steel with a
24 coating of tin. This results in a steel which is
25 more carburization resistant since there are
26 cumulative effects of carburization resistance

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1 obtained from both the aluminum coating and the tin
2 coating. This post-treatment affords an additional
3 benefit in that it will mend any defects or cracks in
4 the aluminum, e.g., Alonized, coating. Also, such a
5 post-treatment should result in a lower cost since a
6 thinner aluminum coating can be applied to the steel
7 surface which is to be post-treated with the tin
8 coating. Additionally, this post-treatment will
9 protect the underlying steel layer exposed by bending
10 of aluminized steels, which can introduce cracks in
11 the aluminum layer, and expose the steel to
12 carburization induced under reforming conditions.
13 Also, this post-treatment process can prevent coke
14 formation on the treated steel surfaces and also
15 prevent coke formation that occurs on the bottom of
16 cracks which appear on steels which have been
17 aluminized, but not additionally coated with tin.

18

19 Samples of Alonized Steels painted on one side
20 with tin, were found to show a deposit of black coke
21 only on the untreated side under low-sulfur reforming
22 conditions. The coke that forms on an aluminized
23 surface is a benign coke resulting from cracking on
24 acidic alumina sites. It is incapable of inducing
25 additional coke deposition. Accordingly, a post-
26 treatment application of a tin coating to aluminized

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1 steels can provide further minimization of the
2 problems of carburization, coking, and metal dusting,
3 in reactor systems operating under reforming
4 conditions according to the invention.

5
6 While not wishing to be bound by theory, it is
7 believed that the suitability of various materials
8 for the present invention can be selected and
9 classified according to their responses to
10 carburizing atmospheres. For example, iron, cobalt,
11 and nickel form relatively unstable carbides which
12 will subsequently carburize, coke and dust. Elements
13 such as chromium, niobium, vanadium, tungsten,
14 molybdenum, tantalum and zirconium, will form stable
15 carbides which are more resistant to carburization
16 coking and dusting. Elements such as tin, antimony
17 and bismuth do not form carbides or coke. And, these
18 compounds can form stable compounds with many metals
19 such as iron, nickel and copper under reforming
20 conditions. Stannides, antimonides and bismuthides,
21 and compounds of lead, mercury, arsenic, germanium,
22 indium, tellurium, selenium, thallium, sulfur and
23 oxygen are also resistant. A final category of
24 materials include elements such as silver, copper,
25 gold, platinum and refractory oxides such as silica
26 and alumina. These materials are resistant and do

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1 not form carbides, or react with other metals in a
2 carburizing environment under reforming conditions.
3

4 As discussed above, the selection of appropriate
5 metals which are resistant to carburization and metal
6 dusting, and their use as coating materials for metal
7 surfaces in the reactor system is one means for
8 preventing the carburization and metal dusting
9 problem. However, carburization and metal dusting
10 can be prevalent in a wide variety of metals; and
11 carburization resistant metals can be more costly or
12 exotic than conventional materials (e.g., mild
13 steels) used in the construction of reforming reactor
14 systems. Accordingly, it may be desirable in the
15 reactor system of the invention to use ceramic
16 materials which do not form carbides at typical
17 reforming conditions, and thus are not susceptible to
18 carburization, for at least a portion of the metal
19 surfaces in the reactor system. For example, at
20 least a portion of the furnace tubes, or furnace
21 liners or both may be constructed of ceramic
22 materials.
23

24 In choosing the ceramic materials for use in the
25 present invention, it is preferable that the ceramic
26 material have thermal conductivities about that or

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1 exceeding those of materials conventionally used in
2 the construction of reforming reactor systems.
3 Additionally, the ceramic materials should have
4 sufficient structural strengths at the temperatures
5 which occur within the reforming reactor system.
6 Further, the ceramic materials should be able to
7 withstand thermal shocks and repeated temperature
8 cycling which occur during operation of the reactor
9 system. When the ceramic materials are used for
10 constructing the furnace liners, the ceramic
11 materials should have thermal expansivities about
12 that of the metal outer surfaces with which the liner
13 is in intimate contact. This avoids undue stress at
14 the juncture during temperature cycling that occurs
15 during start-up and shut-down. Additionally, the
16 ceramic surface should not be susceptible to
17 degradation in the hydrocarbon environment or in the
18 oxidizing environment which occurs during catalyst
19 regeneration. The selected ceramic material also
20 should not promote the degradation of the
21 hydrocarbons in the reactor system.

22
23 Suitable ceramic materials include, but are not
24 restricted to, materials such as silicon carbides,
25 silicon oxides, silicon nitrides and aluminum
26 nitrides. Of these, silicon carbides and silicon

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1 nitrides are particularly preferred as they appear
2 capable of providing complete protection for the
3 reactor system under low-sulfur reforming conditions.
4

5 At least a portion of the metal surfaces in the
6 reactor system can also be coated with a silicon or
7 silica film. In particular, the metal surfaces which
8 can be coated include, but are not limited to the
9 reactor walls, furnace tubes, and furnace liners.
10 However, any metal surface in the reactor system,
11 which shows signs of carburization and metal dusting
12 under low-sulfur reforming conditions would benefit
13 from the application of a thin silicon or silica
14 film.
15

16 Conventional methods can be used for applying
17 silicon or silica films to coat metal surfaces.
18 Silica or silicon can be applied by electroplating
19 and chemical vapor deposition of an alkoxysilane in a
20 steam carrier gas. It is preferable that the silicon
21 or silica film have a thermal expansivity about that
22 of the metal surface which it coats. Additionally,
23 the silicon or silica film should be able to
24 withstand thermal shocks and repeated temperature
25 cycling that occur during reforming. This avoids
26 cracking or spalling of the silicon or silica film,

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1 and potential exposure of the underlying metal
2 surface to the carburization inducing hydrocarbon
3 environment. Also, the silica or silicon film should
4 have a thermal conductivity approximate to or
5 exceeding that of metals conventionally used in
6 reforming reactor systems so as to maintain efficient
7 heat transfer. The silicon or silica film also
8 should not degrade in the reforming environment or in
9 the oxidizing environment associated with catalyst
10 regeneration; nor should it cause degradation of the
11 hydrocarbons themselves.

12

13 Because different areas of the reactor system of
14 the invention (e.g., different areas in a furnace)
15 can be exposed to a wide range of temperatures, the
16 material selection can be staged, such that those
17 materials providing better carburization resistances
18 are used in those areas of the system experiencing
19 the highest temperatures.

20

21 With regard to materials selection, it was
22 discovered that oxidized Group VIII metal surfaces
23 such as iron, nickel and cobalt are more active in
24 terms of coking and carburization than their
25 unoxidized counterparts. For example, it was found
26 that an air roasted sample of 347 stainless steel was

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1 significantly more active than an unoxidized sample
2 of the same steel. This is believed to be due to a
3 re-reduction of oxidized steels which produces very
4 fine-grained iron and/or nickel metals. Such metals
5 are especially active for carburization and coking.
6 Thus, it is desirable to avoid these materials as
7 much as possible during oxidative regeneration
8 processes, such as those typically used in catalytic
9 reforming. However, it has been found that an air
10 roasted 300 series stainless steel coated with tin
11 can provide similar resistances to coking and
12 carburization as unroasted samples of the same tin
13 coated 300 series stainless steel.

14

15 Furthermore, it will be appreciated that
16 oxidation will be a problem in systems where sulfur
17 sensitivity of the catalyst is not of concern, and
18 sulfur is used to passivate the metal surfaces. If
19 sulfur levels in such systems ever become
20 insufficient, any metal sulfides which have formed on
21 metal surfaces would, after oxidation and reduction,
22 be reduced to fine-grained metal. This metal would
23 be highly reactive for coking and carburization.
24 Potentially, this can cause a catastrophic failure of
25 the metallurgy, or a major coking event.

26

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1 As noted above, excessively high temperatures
2 can occur in the catalyst beds when exothermic
3 demethanation reactions within cokeballs cause
4 localized hot regions. These hot spots also pose a
5 problem in conventional reforming reactor systems (as
6 well as other areas of chemical and petrochemical
7 processing).

8
9 For example, the center pipe screens of
10 reformers have been observed to locally waste away
11 and develop holes; ultimately resulting in catalyst
12 migration. In conventional reforming processes the
13 temperatures within cokeballs during formation and
14 burning are apparently high enough to overcome the
15 ability of process sulfur to poison coking,
16 carburization, and dusting. The metal screens,
17 therefore, carburize and are more sensitive to
18 wasting by intergranular oxidation (a type of
19 corrosion) during regeneration. The screen openings
20 enlarge and holes develop.

21
22 Thus, the teachings of the present invention are
23 applicable to conventional reforming, as well as
24 other areas of chemical and petrochemical processing.
25 For example, the aforementioned platings, claddings
26 and coatings can be used in the preparation of center

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1 pipe screens to avoid excessive hole development and
2 catalyst migration. In addition, the teachings can
3 be applied to any furnace tubes which are subjected
4 to carburization, coking and metal dusting, such as
5 furnace tubes in coker furnaces.

6

7 In addition, since the techniques described
8 herein can be used to control carburization, coking,
9 and metal dusting at excessively high temperatures,
10 they can be used in cracking furnaces operating at
11 from about 1400° to about 1700°F. For example, the
12 deterioration of steel occurring in cracking furnaces
13 operating at those temperatures can be controlled by
14 application of various metal coatings. These metal
15 coatings can be applied by melting, electroplating,
16 and painting. Painting is particularly preferred.

17

18 For example, a coating of antimony applied to
19 iron bearing steels protects these steels from
20 carburization, coking and metal dusting under the
21 described cracking conditions. In fact, an antimony
22 paint applied to iron bearing steels will provide
23 protection against carburization, coking, and metal
24 dusting at 1600°F.

25

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1 A coating of bismuth applied to nickel rich
2 steel alloys (e.g., INCONEL 600) can protect those
3 steels against carburization, coking, and metal
4 dusting under cracking conditions. This has been
5 demonstrated at temperatures of up to 1600°F.
6

7 Bismuth coatings may also be applied to iron
8 bearing steels and provide protection against
9 carburization, metal dusting, and coking under
10 cracking conditions. Also, a metal coating
11 comprising a combination of bismuth, antimony, and/or
12 tin can be used.
13

14 Looking again to low-sulfur reforming, other
15 techniques can also be used to address the problem
16 discovered according to the present invention. They
17 can be used in conjunction with an appropriate
18 material selection for the reactor system, or they
19 can be used alone. Preferred from among the
20 additional techniques is the addition of non-sulfur,
21 anti-carburizing and anti-coking agent(s) during the
22 reforming process. These agents can be added
23 continuously during processing and function to
24 interact with those surfaces of the reactor system
25 which contact the hydrocarbons, or they may be
26 applied as a pretreatment to the reactor system.

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1 While not wishing to bound by theory it is
2 believed that these agents interact with the surfaces
3 of the reactor system by decomposition and surface
4 attack to form iron and/or nickel intermetallic
5 compounds, such as stannides, antimonides,
6 bismuthides, plumbides, arsenides, etc. Such
7 intermetallic compounds are resistant to
8 carburization, coking and dusting and can protect the
9 underlying metallurgy.

10

11 The intermetallic compounds are also believed to
12 be more stable than the metal sulfides which were
13 formed in systems where H_2S was used to passivate the
14 metal. These compounds are not reduced by hydrogen
15 as are metal sulfides. As a result, they are less
16 likely to leave the system than metal sulfides.
17 Therefore, the continuous addition of a carburization
18 inhibitor with the feed can be minimized.

19

20 Preferred non-sulfur anti-carburizing and anti-
21 coking agents include organo-metallic compounds such
22 as organo-tin compounds, organo-antimony compounds,
23 organo-bismuth compounds, organo-arsenic compounds,
24 and organo-lead compounds. Suitable organo-lead
25 compounds include tetraethyl and tetramethyl lead.

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1 Organo-tin compounds such as tetrabutyl tin and
2 trimethyl tin hydride are especially preferred.

3
4 Additional specific organo-metallic compounds
5 include bismuth neodecanoate, chromium octoate,
6 copper naphthenate, manganese carboxylate, palladium
7 neodecanoate, silver neodecanoate,
8 tetrabutylgermanium, tributylantimony,
9 triphenylantimony, triphenylarsine, and zirconium
10 octoate.

11
12 How and where these agents are added to the
13 reactor system is not critical, and will primarily
14 depend on particular process design characteristics.
15 For example, they can be added continuously or
16 discontinuously with the feed.

17
18 However, adding the agents to the feed is not
19 preferred as they would tend to accumulate in the
20 initial portions of the reactor system. This may not
21 provide adequate protection in the other areas of the
22 system.

23
24 It is preferred that the agents be provided as a
25 coating prior to construction, prior to start-up, or
26 in-situ (i.e., in an existing system). If added in-

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1 situ, it should be done right after catalyst
2 regeneration. Very thin coatings can be applied.
3 For example, it is believed that when using organo-
4 tin compounds, iron stannide coatings as thin as 0.1
5 micron can be effective.

6
7 A preferred method of coating the agents on an
8 existing or new reactor surface, or a new or existing
9 furnace tube is to decompose an organometallic
10 compound in a hydrogen atmosphere at temperatures of
11 about 900°F. For organo-tin compounds, for example,
12 this produces reactive metallic tin on the tube
13 surface. At these temperatures the tin will further
14 react with the surface metal to passivate it.

15
16 Optimum coating temperatures will depend on the
17 particular organometallic compound, or the mixtures
18 of compounds if alloys are desired. Typically, an
19 excess of the organometallic coating agent can be
20 pulsed into the tubes at a high hydrogen flow rate so
21 as to carry the coating agent throughout the system
22 in a mist. The flow rate can then be reduced to
23 permit the coating metal mist to coat and react with
24 the furnace tube or reactor surface. Alternatively,
25 the compound can be introduced as a vapor which

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1 decomposes and reacts with the hot walls of the tube
2 or reactor in a reducing atmosphere.

3
4 As discussed above, reforming reactor systems
5 susceptible to carburization, metal dusting and
6 coking can be treated by application of a
7 decomposable coating containing a decomposable
8 organometallic tin compound to those areas of the
9 reactor system most susceptible to carburization.
10 Such an approach works particularly well in a
11 temperature controlled furnace.

12
13 However, such control is not always present.
14 There are "hot spots" which develop in the reactor
15 system, particularly in the furnace tubes, where the
16 organometallic compound can decompose and form
17 deposits. Therefore, another aspect of the invention
18 is a process which avoids such deposition in
19 reforming reactor systems where temperatures are not
20 closely controlled and exhibit areas of high
21 temperature hot spots.

22
23 Such a process involves preheating the entire
24 reactor system to a temperature of from 750 to 1150,
25 preferably 900 to 1100, and most preferably about
26 1050°F, with a hot stream of hydrogen gas. After

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1 preheating, a colder gas stream at a temperature of
2 400 to 800, preferably 500 to 700, and most
3 preferably about 550°F, containing a vaporized
4 organometallic tin compound and hydrogen gas is
5 introduced into the preheated reactor system. This
6 gas mixture is introduced upstream and can provide a
7 decomposition "wave" which travels throughout the
8 entire reactor system.

9
10 Essentially this process works because the hot
11 hydrogen gas produces a uniformly heated surface
12 which will decompose the colder organometallic gas as
13 it travels as a wave throughout the reactor system.
14 The colder gas containing the organometallic tin
15 compound will decompose on the hot surface and coat
16 the surface. The organometallic tin vapor will
17 continue to move as a wave to treat the hotter
18 surfaces downstream in the reactor system. Thereby,
19 the entire reactor system can have a uniform coating
20 of the organometallic tin compound. It may also be
21 desirable to conduct several of these hot-cold
22 temperature cycles to ensure that the entire reactor
23 system has been uniformly coated with the
24 organometallic tin compound.
25

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1 In operation of the reforming reactor system
2 according to the present invention, naphtha will be
3 reformed to form aromatics. The naphtha feed is a
4 light hydrocarbon, preferably boiling in the range of
5 about 70°F to 450°F, more preferably about 100 to
6 350°F. The naphtha feed will contain aliphatic or
7 paraffinic hydrocarbons. These aliphatics are
8 converted, at least in part, to aromatics in the
9 reforming reaction zone.

10

11 In the "low-sulfur" system of the invention, the
12 feed will preferably contain less than 100 ppb
13 sulfur, and more preferably, less than 50 ppb sulfur.
14 If necessary, a sulfur sorber unit can be employed to
15 remove small excesses of sulfur.

16

17 Preferred reforming process conditions include a
18 temperature between 700 and 1050°F, more preferably
19 between 850 and 1025°F; and a pressure between 0 and
20 400 psig, more preferably between 15 and 150 psig; a
21 recycle hydrogen rate sufficient to yield a hydrogen
22 to hydrocarbon mole ratio for the feed to the
23 reforming reaction zone between 0.1 and 20, more
24 preferably between 0.5 and 10; and a liquid hourly
25 space velocity for the hydrocarbon feed over the

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1 reforming catalyst of between 0.1 and 10, more
2 preferably between 0.5 and 5.
3

4 To achieve the suitable reformer temperatures,
5 it is often necessary to heat the furnace tubes to
6 high temperatures. These temperatures can often
7 range from 600 to 1800°F, usually from 850 and
8 1250°F, and more often from 900 and 1200°F.
9

10 As noted above, the problems of carburization,
11 coking and metal dusting in low-sulfur systems have
12 been found to associated with excessively high,
13 localized process temperatures of the reactor system,
14 and are particularly acute in the furnace tubes of
15 the system where particularly high temperatures are
16 characteristic. In conventional reforming techniques
17 where high levels of sulfur are present, furnace tube
18 skin temperatures of up to 1175°F at end of run are
19 typical. Yet, excessive carburization, coking and
20 metal dusting was not observed. In low-sulfur
21 systems, however, it has been discovered that
22 excessive and rapid carburization, coking and metal
23 dusting occurred with CrMo steels at temperatures
24 above 950°F, and stainless steels at temperatures
25 above 1025°F.
26

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1 Accordingly, another aspect of the invention is
2 to lower the temperatures of the metal surfaces
3 inside the furnace tubes, transfer-lines and/or
4 reactors of the reforming system below the
5 aforementioned levels. For example, temperatures can
6 be monitored using thermocouples attached at various
7 locations in the reactor system. In the case of
8 furnace tubes, thermocouples can be attached to the
9 outer walls thereof, preferably at the hottest point
10 of the furnace (usually near the furnace outlet).
11 When necessary, adjustments in process operation can
12 be made to maintain the temperatures at desired
13 levels.

14
15 There are other techniques for reducing exposure
16 of system surfaces to undesirably high temperatures
17 as well. For example, heat transfer areas can be
18 used with resistant (and usually more costly) tubing
19 in the final stage where temperatures are usually the
20 highest.

21
22 In addition, superheated hydrogen can be added
23 between reactors of the reforming system. Also, a
24 larger catalyst charge can be used. And, the
25 catalyst can be regenerated more frequently. In the
26 case of catalyst regeneration, it is best

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1 accomplished using a moving bed process where the
2 catalyst is withdrawn from the final bed,
3 regenerated, and charged to the first bed.
4

5 Carburization and metal dusting can also be
6 minimized in the low-sulfur reforming reactor system
7 of the invention by using certain other novel
8 equipment configurations and process conditions. For
9 example, the reactor system can be constructed with
10 staged heaters and/or tubes. In other words, the
11 heaters or tubes which are subjected to the most
12 extreme temperature conditions in the reactor system
13 can be constructed of materials more resistant to
14 carburization than materials conventionally used in
15 the construction of reforming reactor systems;
16 materials such as those described above. Heaters or
17 tubes which are not subjected to extreme temperatures
18 can continue to be constructed of conventional
19 materials.
20

21 By using such a staged design in the reactor
22 system, it is possible to reduce the overall cost of
23 the system (since carburization resistant materials
24 are generally more expensive than conventional
25 materials) while still providing a reactor system
26 which is sufficiently resistant to carburization and

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1 metal dusting under low-sulfur reforming conditions.
2 Additionally, this should facilitate the retrofitting
3 of existing reforming reactor systems to render them
4 carburization and metal dusting resistant under low-
5 sulfur operating conditions; since a smaller portion
6 of the reactor system would need replacement or
7 modification with a staged design.

8
9 The reactor system can also be operated using at
10 least two temperature zones; at least one of higher
11 and one of lower temperature. This approach is based
12 on the observation that metal dusting has a
13 temperature maximum and minimum, above and below
14 which dusting is minimized. Therefore, by "higher"
15 temperatures, it is meant that the temperatures are
16 higher than those conventionally used in reforming
17 reactor systems and higher than the temperature
18 maximum for dusting. By "lower" temperatures it is
19 meant that the temperature is at or about the
20 temperatures which reforming processes are
21 conventionally conducted, and falls below that in
22 which dusting becomes a problem.

23
24 Operation of portions of the reactor system in
25 different temperature zones should reduce metal
26 dusting as less of the reactor system is at a

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1 temperature conducive for metal dusting. Also, other
2 advantages of such a design include improved heat
3 transfer efficiencies and the ability to reduce
4 equipment size because of the operation of portions
5 of the system at higher temperatures. However,
6 operating portions of the reactor system at levels
7 below and above that conducive for metal dusting
8 would only minimize, not completely avoid, the
9 temperature range at which metal dusting occurs.
10 This is unavoidable because of temperature
11 fluctuations which will occur during day to day
12 operation of the reforming reactor system;
13 particularly fluctuations during shut-down and start-
14 up of the system, temperature fluctuations during
15 cycling, and temperature fluctuations which will
16 occur as the process fluids are heated in the reactor
17 system.

18
19 Another approach to minimizing metal dusting
20 relates to providing heat to the system using
21 superheated raw materials (such as e.g., hydrogen),
22 thereby minimizing the need to heat the hydrocarbons
23 through furnace walls.

24
25 Yet another process design approach involves
26 providing a pre-existing reforming reactor system

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1 with larger tube diameters and/or higher tube
2 velocities. Using larger tube diameters and/or
3 higher tube velocities will minimize the exposure of
4 the heating surfaces in the reactor system to the
5 hydrocarbons.

6
7 As noted above, catalytic reforming is well
8 known in the petroleum industry and involves the
9 treatment of naphtha fractions to improve octane
10 rating by the production of aromatics. The more
11 important hydrocarbon reactions which occur during
12 the reforming operation include the dehydrogenation
13 of cyclohexanes to aromatics, dehydroisomerization of
14 alkylcyclopentanes to aromatics, and
15 dehydrocyclization of acyclic hydrocarbons to
16 aromatics. In addition, a number of other reactions
17 also occur, including the dealkylation of
18 alkylbenzenes, isomerization of paraffins, and
19 hydrocracking reactions which produce light gaseous
20 hydrocarbons, e.g., methane, ethane, propane and
21 butane, which hydrocracking reactions should be
22 minimized during reforming as they decrease the yield
23 of gasoline boiling products and hydrogen. Thus,
24 "reforming" as used herein refers to the treatment of
25 a hydrocarbon feed through the use of one or more
26 aromatics producing reactions in order to provide an

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1 aromatics enriched product (i.e., a product whose
2 aromatics content is greater than in the feed).
3

4 While the present invention is directed
5 primarily to catalytic reforming, it will be useful
6 generally in the production of aromatic hydrocarbons
7 from various hydrocarbon feedstocks under conditions
8 of low sulfur. That is, while catalytic reforming
9 typically refers to the conversion of naphthas, other
10 feedstocks can be treated as well to provide an
11 aromatics enriched product. Therefore, while the
12 conversion of naphthas is a preferred embodiment, the
13 present invention can be useful for the conversion or
14 aromatization of a variety of feedstocks such as
15 paraffin hydrocarbons, olefin hydrocarbons, acetylene
16 hydrocarbons, cyclic paraffin hydrocarbons, cyclic
17 olefin hydrocarbons, and mixtures thereof, and
18 particularly saturated hydrocarbons.
19

20 Examples of paraffin hydrocarbons are those
21 having 6 to 10 carbons such as n-hexane,
22 methylpentane, n-heptane, methylhexane,
23 dimethylpentane and n-octane. Examples of acetylene
24 hydrocarbons are those having 6 to 10 carbon atoms
25 such as hexyne, heptyne and octyne. Examples of
26 acyclic paraffin hydrocarbons are those having 6 to

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1 10 carbon atoms such as methylcyclopentane,
2 cyclohexane, methylcyclohexane and
3 dimethylcyclohexane. Typical examples of cyclic
4 olefin hydrocarbons are those having 6 to 10 carbon
5 atoms such as methylcyclopentene, cyclohexene,
6 methylcyclohexene, and dimethylcyclohexene.

7
8 The present invention will also be useful for
9 reforming under low-sulfur conditions using a variety
10 of different reforming catalysts. Such catalyst
11 include, but are not limited to Noble Group VIII
12 metals on refractory inorganic oxides such as
13 platinum on alumina, Pt/SN on alumina and Pt/Re on
14 alumina; Noble Group VIII metals on a zeolite such as
15 Pt, Pt/SN and Pt/Re on zeolites such as L-zeolites,
16 ZSM-5, silicalite and beta; and Nobel Group VIII
17 metals on alkali- and alkaline-earth exchanged L-
18 zeolites.

19
20 A preferred embodiment of the invention involves
21 the use of a large-pore zeolite catalyst including an
22 alkali or alkaline earth metal and charged with one
23 or more Group VIII metals. Most preferred is the
24 embodiment where such a catalyst is used in reforming
25 a naphtha feed.

26

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1 The term "large-pore zeolite" is indicative
2 generally of a zeolite having an effective pore diameter
3 of 6 to 15 Angstroms. Preferable large pore crystalline
4 zeolites which are useful in the present invention
5 include the type L zeolite, zeolite X, zeolite Y and
6 faujasite. These have apparent pore sizes on the order
7 to 7 to 9 Angstroms. Most preferably the zeolite is a
8 type L zeolite.

9

10 The composition of type L zeolite expressed in terms
11 of mole ratios of oxides, may be represented by the
12 following formula:

13

14 $(0.9-1.3)M_{2/n}O:AL_2O_3(5.2-6.9)SiO_2:yH_2O$
15

16 In the above formula M represents a cation, n
17 represents the valence of M, and y may be any value from
18 0 to about 9. Zeolite L, its X-ray diffraction pattern,
19 its properties, and method for its preparation are
20 described in detail in, for example, U.S. Patent No.
21 3,216,789. The actual formula may vary without changing
22 the crystalline structure. For example, the mole ratio
23 of silicon to aluminum (Si/Al) may vary from 1.0 to 3.5.

24

25 The chemical formula for zeolite Y expressed in
26 terms of mole ratios of oxides may be written as:

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1 (0.7-1.1)Na₂O:Al₂O₃:xSiO₂:yH₂O

2

3 In the above formula, x is a value greater than 3 and up
4 to about 6. y may be a value up to about 9. Zeolite Y
5 has a characteristic X-ray powder diffraction pattern
6 which may be employed with the above formula for
7 identification. Zeolite Y is described in more detail in
8 U.S. Patent No. 3,130,007.

9

10 Zeolite X is a synthetic crystalline zeolitic
11 molecular sieve which may be represented by the formula:

12

13 (0.7-1.1)M_{2/n}O:Al₂O₃:(2.0-3.0)SiO₂:yH₂O

14

15 In the above formula, N represents a metal, particularly
16 alkali and alkaline earth metals, n is the valence of M,
17 and y may have any value up to about 8 depending on the
18 identity of M and the degree of hydration of the
19 crystalline zeolite. Zeolite X, its X-ray diffraction
20 pattern, its properties, and method for its preparation
21 are described in detail in U.S. Patent No. 2,882,244,

22

23 An alkali or alkaline earth metal is preferably
24 present in the large-pore zeolite. That alkaline _____

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1 earth metal may be either barium, strontium or
2 calcium, preferably barium. The alkaline earth metal
3 can be incorporated into the zeolite by synthesis,
4 impregnation or ion exchange. Barium is preferred to
5 the other alkaline earths because it results in a
6 somewhat less acidic catalyst. Strong acidity is
7 undesirable in the catalyst because it promotes
8 cracking, resulting in lower selectivity.

9
10 In another embodiment, at least part of the
11 alkali metal can be exchanged with barium using known
12 techniques for ion exchange of zeolites. This
13 involves contacting the zeolite with a solution
14 containing excess Ba^{++} ions. In this embodiment the
15 barium should preferably constitute from 0.1% to 35%
16 by weight of the zeolite.

17
18 The large-pore zeolitic catalysts used in the
19 invention are charged with one or more Group VIII
20 metals, e.g., nickel, ruthenium, rhodium, palladium,
21 iridium or platinum. The preferred Group VIII metals
22 are iridium and particularly platinum. These are
23 more selective with regard to dehydrocyclization and
24 are also more stable under the dehydrocyclization
25 reaction conditions than other Group VIII metals. If

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1 used, the preferred weight percentage of platinum in
2 the catalyst is between 0.1% and 5%.

3
4 Group VIII metals are introduced into large-pore
5 zeolites by synthesis, impregnation or exchange in an
6 aqueous solution of appropriate salt. When it is
7 desired to introduce two Group VIII metals into the
8 zeolite, the operation may be carried out
9 simultaneously or sequentially.

10
11 To obtain a more complete understanding of the
12 present invention, the following examples
13 illustrating certain aspects of the invention are set
14 forth. It should be understood, however, that the
15 invention is not limited in any way to the specific
16 details set forth therein.

17

18

EXAMPLE 1

19 Tests were run to demonstrate the effect of
20 sulfur and water on carburization in reforming
21 reactors.

22

23 In these tests, eight inch long, $\frac{1}{4}$ inch outside
24 diameter copper tubes were used as a reactor to study
25 the carburization and embrittlement of 347 stainless
26 steel wires. Three of these stainless steel wires

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1 having a diameter of 0.035 inches were inserted into
2 the tube, while a four inch section of the tube was
3 maintained at a uniform temperature of 1250°F by a
4 furnace. The pressure of the system was maintained
5 at 50 psig. Hexane was introduced into the reactor
6 at a rate of 25 microliters/min. (1.5 ml/hr) with a
7 hydrogen rate of about 25 cc/min. (ratio of H₂ to HC
8 being 5:1). Methane in the product effluent was
9 measured to determine the existence of exothermic
10 methane reactions.
11

12 A control run was made using essentially pure
13 hexane containing less than 0.2 ppm sulfur. The tube
14 was found to be completely filled with carbon after
15 only three hours. This not only stopped the flow of
16 the hydrogen and hexane feeds, the growth of carbon
17 actually split the tube and produced a bulge in the
18 reactor. Methane in the product effluent was
19 approaching 60-80 wt% before plugging.
20

21 Another run was conducted using essentially the
22 same conditions except that 10 ppm sulfur was added.
23 The run continued for 50 hours before it was shut
24 down to examine the wires. No increase in methane
25 was noted during the run. It remained steady at
26 about 16 wt% due to thermal cracking. No coke plugs

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1 were found and no carburization of the steel wires
2 was observed.

3

4 Another identical run was made except that only
5 1 ppm sulfur was added (10 times lower than the
6 previous run). This run exhibited little methane
7 formation or plugging after 48 hours. An examination
8 of the steel wires showed a small amount of surface
9 carbon, but no ribbons of carbon.

10

11 Another run was conducted except that 1000 ppm
12 water (0.1%) was added to the hexane as methanol. No
13 sulfur was added. The run lasted for 16 hours and no
14 plugs occurred in the reactor. However, upon
15 splitting the tube it was discovered that about 50
16 percent of the tube was filled with carbon. But the
17 carbon buildup was not nearly as severe as with the
18 control run.

19

20

EXAMPLE 2

21 Tests were conducted to determine suitable
22 materials for use in low-sulfur reforming reactor
23 systems; materials which would exhibit better
24 resistance to carburization than the mild steels
25 conventionally used in low-sulfur reforming
26 techniques.

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1 In these tests there was used an apparatus
2 including a Lindberg alumina tube furnace with
3 temperatures controlled to within one degree with a
4 thermocouple placed on the exterior of the tube in
5 the heated zone. The furnace tube had an internal
6 diameter of 5/8 inches. Several runs were conducted
7 at an applied temperature of 1200°F using a
8 thermocouple suspended within the hot zone (≈2
9 inches) of the tube. The internal thermocouple
10 constantly measured temperatures from 0 to 10°F lower
11 than the external thermocouple.

12
13 Samples of mild steels (C steel and 2½ Cr) and
14 samples of 300 series stainless steels were tested at
15 1100°F, 1150°F and 1200°F for twenty-four hours, and
16 1100°F for ninety hours, under conditions which
17 simulate the exposure of the materials under
18 conditions of low-sulfur reforming. The samples of
19 various materials were placed in an open quartz boat
20 within the hot zone of the furnace tube. The boats
21 were one inch long and ½ inch wide and fit well
22 within the two-inch hot zone of the tube. The boats
23 were attached to silica glass rods for each placement
24 and removal. No internal thermocouple was used when
25 the boats were placed inside the tube.
26

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1 Prior to start up the tube was flushed with
2 nitrogen for a few minutes. A carburizing gas of a
3 commercially bottled mixture of 7% propane in
4 hydrogen was bubbled through a liter flask of toluene
5 at room temperature in order entrain about 1% toluene
6 in the feed gas mix. Gas flows of 25 to 30 cc/min.,
7 and atmospheric pressure, were maintained in the
8 apparatus. The samples were brought to operating
9 temperatures at a rate of 144°F/min.
10

11 After exposing the materials to the carburizing
12 gas for the desired period at the desired
13 temperature, the apparatus was quenched with an air
14 stream applied to the exterior of the tube. When the
15 apparatus was sufficiently cool, the hydrocarbon gas
16 was swept out with nitrogen and the boat was removed
17 for inspection and analysis.
18

19 Prior to start up the test materials were cut to
20 a size and shape suitable for ready-visual
21 identification. After any pretreatment, such as
22 cleaning or roasting, the samples were weighed. Most
23 samples were less than 300 mg. Typically, each run
24 was conducted with three to five samples in a boat.
25 A sample of 347 stainless steel was present with each
26 run as an internal standard.

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1 After completion of each run the condition of
2 the boat and each material was carefully noted.
3 Typically the boat was photographed. Then, each
4 material was weighed to determine changes while
5 taking care to keep any coke deposits with the
6 appropriate substrate material. The samples were
7 then mounted in an epoxy resin, ground and polished
8 in preparation for petrographic and scanning electron
9 microscopy analysis to determine the coking, metal
10 dusting and carburization responses of each material.

11

12 By necessity, the residence time of the
13 carburizing gas used in these tests were considerably
14 higher than in typical commercial operation. Thus,
15 it is believed that the experimental conditions may
16 have been more severe than commercial conditions.
17 Some of the materials which failed in these tests may
18 actually be commercially reliable. Nevertheless, the
19 test provides a reliable indication of the relative
20 resistances of the materials to coking, carburization
21 and metal dusting.

22

23

The results are set forth in the Table below.

Table*

		Wt. % C		
		<u>Gain</u>	<u>Dusting</u>	<u>Composition</u>
1200°F; 24 hours				
C Steel	86	Severe		
2½ Cr	61	Severe		
304	little	No	18 Cr 10 Ni	
347	little	No	18 Cr 10 Ni	
1150°F; 24 hours				
C Steel	63	Severe		
2½ Cr	80	Severe		
304	1	No		
347	1	No		
1100°F; 24 hours				
C Steel Trace		Trace, localized		
2½ Cr	0	No		
304	0	No		
347	0	No		
1100°F; 90 hours				
C Steel	52	Severe		
2½ Cr	62	Severe		
304	5	No		
347	1	No		

* 15% C₇H₈ + 50% C₃H₈ + H₂ (by weight)

Of course, the above results are qualitative and depend on surface morphology, i.e., microscopic roughness of the metals. The carbon weight gain is indicative of surface coking which is autocatalytic.

EXAMPLE 3

The same techniques used above were used again to screen a wide assortment of materials at a temperature of 1200°F for 16 hours. The results are

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1 set forth below. Each group represents a side-by-
2 side comparison in a single boat under identical
3 conditions.

4 TABLE (1)

5		Wt. % C		
6		<u>Gain</u>	<u>Dusting</u>	<u>Composition</u>
7				
8	<u>Group I</u>			
9	Inconel 600	57	Severe	15 Cr 75 Ni
10	347 oxid.(2)	21	Moderate	
11	347 Fresh	4	No	18 Cr 10 Ni
12				
13	<u>Group II</u>			
14	Inconel 600	40	Severe	15 Cr 75 Ni
15	310	8	Mild	25 Cr 20 Ni
16	Incoloy 800	5	Moderate	21 Cr 32 Ni
17	347	1	Trace	
18				
19	<u>Group III</u>			
20	Incoloy 825	<1	Moderate	
21	Haynes 230	2	Mild	22 Cr 64 Ni
22	Alonized 347	3	Trace	
23	347	<1	Trace	
24				
25	<u>Group IV</u>			
26	Ni (Pure)	656	Severe	100 Ni
27	Cu (Pure)	0	No	100 Cu
28	Sn (Fused)	0	No	
29	100 Sn			
30	Tin Can	0	No	
31	Sn + C Steel			

- 32
- 33
- 34
- 35 (1) 15% C₂H₆ + 50% C₃H₈ + H₂ (By Wt.)
- 36
- 37 (2) Roasted in air 2 hours at
- 38 1000°C to produce a thin
- 39 oxide crust.
- 40
- 41
- 42

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1

EXAMPLE 4

2

3

4

5

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26

Additional materials were tested, again using the techniques described in Example 2 (unless stated otherwise).

Samples of 446 stainless steel and 347 stainless steel were placed in a sample boat and tested simultaneously in the carburization apparatus at 1100°F for a total of two weeks. The 446 stainless steel had a thin coating of coke, but no other alteration was detected. The 347 stainless steel, on the other hand, had massive localized coke deposits, and pits more than 4 mils deep from which coke and metal dust had erupted.

Samples were tested of a carbon steel screen electroplated with tin, silver, copper and chromium. the samples had coatings of approximately 0.5 mil. After 16-hour carburization screening tests at 1200°F, no coke had formed on the tin-plated and chromium-plated screens. Coke formed on the silver-plated and copper-plated screens, but only where the platings had peeled. Unplated carbon steel screens run simultaneously with the plated screens, exhibited severe coking carburization, and metal dusting.

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1 Samples were tested of a 304 stainless steel
2 screen; each sample being electroplated with one of
3 tin, silver, copper and chromium. The samples had
4 coatings with thicknesses of approximately 0.5 mil.
5 After 16-hour carburization screening tests at
6 1200°F, no coke had formed on any of the plated
7 screens, except locally on the copper-plated screen
8 where the plating had blistered and peeled. Thin
9 coke coatings were observed on unplated samples of
10 304 stainless steel run simultaneously with the
11 plated screens.

12
13 Samples were tested of a 304 stainless steel
14 screen; each sample being electroplated with one of
15 tin and chromium. These samples were tested along
16 with a sample of 446 stainless steel in a
17 carburization test at 1100°F. The samples were
18 exposed for five weeks. Each week the samples were
19 cooled to room temperature for observation and
20 photographic documentation. They were then re-heated
21 to 1100°F. The tin plated screen was free of coke;
22 the chromium-plated screen was also free of coke,
23 except locally where the chrome plate had peeled; and
24 the piece of 446 stainless steel was uniformly coated
25 with coke.

26

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1 Samples of uncoated Inconel 600 (75% Ni) and
2 tin-coated (electroplated) Inconel 600 (75% Ni) were
3 tested at 1200°F for 16 hours. The tin-plated sample
4 coked and dusted, but not to the extent of the
5 uncoated sample.
6

7 EXAMPLE 5

8 The following experiments were conducted to
9 study the exothermic methanization reaction occurring
10 during the formation and burning of cokeballs during
11 reforming under conditions of low-sulfur. In
12 addition tin, as an additive to reduce methane
13 formation was studied.
14

15 In low-sulfur reforming reactor systems, coke
16 deposits containing molten particles of iron have
17 been found. This formation of molten iron during
18 reforming at temperatures between 900 and 1200°F is
19 believed to be due to very exothermic reactions which
20 occur during reforming. It is believed that the only
21 way to generate such temperatures is through the
22 formation of methane which is very exothermic. The
23 high temperatures are particularly surprising since
24 reforming is generally endothermic in nature and
25 actually tends to cool the reactor system. The high
26 temperatures may be generated inside the well

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1 insulated cokeballs by diffusion of hydrogen into the
2 interior catalytic iron dust sites where they
3 catalyze methane formation from coke and hydrogen.
4

5 In this experiment steel wool was used to study
6 methane formation in a micro pilot plant. A $\frac{1}{4}$ inch
7 stainless steel tube was packed with 0.14 grams of
8 steel wool and placed into a furnace at 1175°F.
9 Hexane and hydrogen were passed over the iron and the
10 exit stream was analyzed for feed and products. The
11 steel wool was pretreated in hydrogen for twenty
12 hours before introduction of the hexane. Then hexane
13 was introduced into the reactor at a rate of 25
14 microliters/min. with a hydrogen rate of about 25
15 cc/min.
16

17 Initially, methane formation was low, but
18 continued to increase as the run progressed; finally
19 reaching 4.5%. Then, 0.1 cc of tetrabutyl tin
20 dissolved in 2 cc of hexane was injected into the
21 purified feed stream ahead of the iron. The methane
22 formation decreased to about 1% and continued to
23 remain at 1% for the next three hours. The data is
24 summarized in the Table below.
25
26

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TABLE

<u>HOURS</u>	<u>CH4</u>	<u>ETHANE</u>	<u>PROPANE</u>	<u>HEXANE</u>
19.2	0.0	0.5	0.3	98.6
20.7	1.06	2.08	1.74	93.4
21.2	2.62	4.55	3.92	85.3
21.5	3.43	4.23	3.83	84.6
21.9	4.45	4.50	4.32	82.0
22	Tetrabutyl Tin Added			
22.6	1.16	3.81	4.12	86.2
23.0	1.16	3.96	4.24	85.9
23.3	1.0	4.56	3.77	87.5
24.3	0.97	3.60	3.76	87.6
25.3	1.0	4.47	3.57	88.0

From the results above it can be seen that the addition of tin to the steel wool stops the acceleration of methane formation, and lowers it to acceptable levels in the product.

EXAMPLE 6

Additional tests were conducted using tetrabutyl tin pre-coated steel wool. In particular, as in Example 5, three injections of 0.1 cc of tetrabutyl tin dissolved in 2 cc of hexane were injected into a $\frac{1}{4}$ inch stainless steel tube containing 0.15 grams of steel wool. The solution was carried over the steel wool in a hydrogen stream of 900°F.

The hydrocarbon feed was then introduced at 1175°F at a hydrocarbon rate of 25 microliters/min

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1 with a hydrogen rate of about 25 cc/min. The exit
2 gas was analyzed for methane and remained below 1%
3 for 24 hours. The reactor was then shut down, and
4 the reactor tube was split open and examined. Very
5 little carburization had occurred on the steel wool.
6

7 In contrast, a control was run without
8 tetrabutyl tin pre-treatment. It was run for one day
9 under the same conditions described above. After 24
10 hours, no hydrogen or feed could be detected at the
11 tube exit. The inlet pressure had risen to 300 lbs.
12 from the original 50 lbs. When the reactor tube was
13 split open and examined, it was found that coke had
14 completely plugged the tube.
15

16 Thus, it can be seen that organo-tin compounds
17 can prevent carburization of steel wool under
18 reforming conditions.
19

20 EXAMPLE 7

21 Another run like the control run of Example 1
22 was conducted to investigate the effect of
23 carburization conditions on vapor tin coated
24 stainless steel wires in a gold plated reactor tube.
25 The only other difference from the control run was
26 that a higher hydrogen rate of 100 ml/min was used.

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1 The run continued for eight hours with no
2 plugging or excessive methane formation. When the
3 tube was split and analyzed, no plugs or carbon
4 ribbons were observed. Only one black streak of
5 carbon appeared on one wire. This was probably due
6 to an improper coating.
7

8 This experiment shows that tin can protect
9 stainless steel from carburization in a manner
10 similar to sulfur. Unlike sulfur, however, it does
11 not have to be continuously injected into the feed.
12 Sulfur must be continuously injected into the feed to
13 maintain the partial pressure of hydrogen sulfide in
14 the system at a sufficient level to maintain a
15 sulfide surface on the steel. Any removal of sulfur
16 from the feedstock will lead to a start of
17 carburization after sulfur is stripped from the
18 reactor system. This usually occurs within 10 hours
19 after cessation of sulfur.
20

21 While the invention has been described above in
22 terms of preferred embodiments, it is to be
23 understood that variations and modifications may be
24 used as will be appreciated by those skilled in the
25 art. For example, portions of steel in the reactor
26 system can be coated with niobium, zirconium, silica

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1 ceramics, tungsten, or chromium (chromizing),
2 although these techniques could be excessively
3 difficult to do or use, or prohibitively expensive.
4 Or, the use of heat exchangers to heat hydrocarbons
5 to reaction temperature could be minimized. The heat
6 could be provided by super-heated hydrogen. Or, the
7 exposure of heating surfaces to hydrocarbons can be
8 reduced by using larger tube diameters and higher
9 tube velocities. Essentially, therefore, there are
10 many variations and modifications to the above
11 preferred embodiments which will be readily evident
12 to those skilled in the art, and which are to be
13 considered within the scope of the invention as
14 defined by the following claims.

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WHAT IS CLAIMED IS:

1. An improved method for catalytically reforming a hydrocarbon, comprising the step of contacting, under conditions of low sulfur, a sulfur-sensitive zeolite reforming catalyst with a hydrocarbon in a reactor system having a plurality of furnace tubes, wherein a portion of said reactor system has a resistance to carburization and metal dusting under low sulfur reforming conditions at least as great as that of stainless steel.
2. The method of claim 1, wherein said sulfur-sensitive zeolite reforming catalyst is an L-zeolite catalyst.
3. The method of claims 1 or 2, wherein said improved resistance to carburization and metal dusting under low sulfur reforming conditions is at least as great as that of 300 series stainless steel.
4. The method of any one of claims 1-3, wherein said improved resistance to carburization and metal dusting under low sulfur reforming conditions is at least as great as that of 347 stainless steel.
5. The method of any one of claims 1-4, wherein said reactor system comprises a fired furnace.
6. The method of claim 5, wherein said plurality of furnace tubes are positioned within a single furnace.

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7. The method of any one of claims 1-6, wherein said portion of said reactor system is at least one of said plurality of furnace tubes.
8. The method of any one of claims 1-7, wherein said portion of said reactor system is a portion of a wall of said reactor system.
9. The method of any one of claims 1-8, wherein said conditions of low sulfur comprise less than about 100 ppb sulfur.
10. The method of any one of claims 1-9, wherein said conditions of low sulfur comprise less than about 50 ppb sulfur.
11. The method of any one of claims 1-10, wherein said contacting step is conducted under conditions of low water content.
12. The method of any one of claims 1-11, wherein said contacting step is conducted under conditions of 1000 ppm of water, or less.
13. The method of any one of claims 1 or 3-12, wherein said sulfur-sensitive reforming catalyst comprises a large-pore zeolite comprising an alkali or alkaline earth metal and at least one Group VIII metal.
14. The method of claim 13, wherein said Group VIII metal comprises platinum.

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15. The method of any one of claims 1-14, wherein said improved resistance to carburization and metal dusting is provided by a cladding, coating, or paint on said portion of said reactor system.
16. The method of claim 15, wherein said paint comprises a reducible paint and further comprising the step of heating said reducible paint under reducing conditions.
17. The method of claim 16, wherein said heating step is conducted in the presence of hydrogen.
18. The method of claims 15 or 16, wherein said paint comprises a tin-containing paint.
19. The method of claim 18, wherein said tin-containing paint further comprises a hydrogen decomposable tin compound, a solvent system, a finely divided tin metal, and a tin oxide.
20. The method of claims 18 or 19, wherein said tin-containing paint further comprises a tin-containing compound and an iron compound, and wherein the iron:tin ratio is less than approximately 1:3 by weight.
21. The method of claims 15 or 16, wherein said paint comprises a metal oxide.
22. The method of claims 15 or 16, wherein said paint comprises a hydrogen decomposable compound.

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23. The method of claim 15, wherein said coating is selected from the group consisting of copper, tin, intermetallic tin compounds, tin alloys, arsenic, antimony, brass, lead, bismuth, chromium, intermetallic compounds thereof, alloys thereof, a copper-tin alloy, a copper-antimony alloy, and mixtures thereof.
24. The method of claim 23, wherein said coating retains said resistance to carburization and metal dusting after oxidation.
25. The method of claim 15, wherein said coating is selected from the group consisting of aluminum, alumina, chromium, chromium oxide, an aluminized material, a chromized material and mixtures thereof.
26. The method of claim 15, wherein said coating comprises a ceramic coating.
27. The method of claim 15, wherein said coating comprises a silica coating.
28. The method of any one of claims 1-14, wherein said resistance to carburization and metal dusting is provided by a layer of a metallic stannide on said portion of said reactor system.
29. The method of any one of claims 1-14, wherein said portion is constructed of a material that provides said resistance to carburization and metal dusting.

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30. The method of claim 29, wherein said portion is 347 stainless steel or has a resistance to carburization and metal dusting at least as good as 347 stainless steel.
31. The method of any one of claims 1-14, wherein said resistance to carburization and metal dusting is provided by the step of implementing a process modification selected from the group consisting of operating said reactor system at a lower reforming temperature, superheating said low-sulfur stream, operating said reactor system with two temperature zones, operating said reactor system with staged heaters or furnace tubes, operating said reactor system with staged heaters and staged furnace tubes, operating said reactor system by minimizing the exposure of the heating surfaces of said reactor system to said hydrocarbon, and combinations thereof, thereby providing said portion of said reactor system with an improved resistance to carburization and metal dusting.
32. The method of any one of claims 1-14, wherein said resistance to carburization and metal dusting is provided by the step of adding a non-sulfur, anti-carburizing, anti-coking agent to said reactor system.
33. The method of claim 32, wherein said non-sulfur, anti-carburizing agent is selected from the group consisting of organo-metallic compounds, organo-tin compound, organo-antimony compounds, organo-bismuth compounds, organo-arsenic compounds, organo-lead

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compounds, tetraethyl lead, tetramethyl lead, tetrabutyl tin, trimethyl tin hydride, bismuth neodecanoate, chromium octoate, copper naphthenate, manganese carboxylate, palladium neodecanoate, silver neodecanoate, tetrabutyl germanium, tributyl antimony, triphenyl antimony, triphenyl arsine, zirconium octoate and combinations thereof.

34. The method of any one of claims 1-33, wherein said reactor system is an existing reactor system.
35. The method of any one of claims 1-33, wherein said reactor system is a new reactor system.
36. The method of any one of claims 1-35, wherein said portion of said reactor system, prior to having an improved resistance to carburization and metal dusting, is oxidized steel.
37. A method for the catalytic reforming of a hydrocarbon stream to produce an aromatic compound using a reactor system, having a sulfur-sensitive reforming catalyst charged with at least one Group VIII metal, over a prolonged period of operation without significant coke-plugging, comprising the steps of:
 - providing a low sulfur hydrocarbon-containing stream prepared by reducing the sulfur content of said hydrocarbon-containing stream to less than 50 ppb sulfur;
 - providing a reforming reactor system of improved resistance to carburization and metal dusting upon reforming said hydrocarbon-containing

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stream, said reactor system having at least one furnace to heat said hydrocarbon-containing stream to catalytic reforming temperatures, said furnace having, in contact with said hydrocarbon-containing stream, a plurality of furnace tubes having a resistance to carburization and metal dusting at least as great as that of 347 stainless steel; and
passing said hydrocarbon-containing stream through said reactor system to contact said hydrocarbon-containing stream with said reforming catalyst to produce an aromatic.

38. The method of claim 37, wherein said sulfur-sensitive reforming catalyst comprises a large-pore zeolite comprising an alkali or alkaline earth metal and at least one Group VIII metal.
39. The method of claims 37 or 38, wherein said sulfur-sensitive zeolite reforming catalyst is an L-zeolite catalyst.
40. A method for improving the carburization resistance of at least a portion of an apparatus for hydrocarbon conversion, comprising the steps of:
applying a reducible, tin-containing paint to a portion of an apparatus for hydrocarbon conversion;
and
heating said reducible paint under reducing conditions to form a protective layer which provides improved carburization resistance.
41. The method of claim 40, wherein said reducible, tin-containing paint comprises a hydrogen decomposable

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tin compound, a solvent system, a finely divided tin metal and a tin oxide.

42. The method of claims 40 or 41, wherein said heating step is conducted in the presence of hydrogen.
43. The method of any one of claims 40-42, wherein said protective layer comprises a metallic stannide.
44. A catalytic reforming reactor system for catalytically reforming hydrocarbons under low sulfur conditions, comprising:
 - a furnace having a plurality of furnace tubes;
 - a reforming reactor having a catalyst bed containing a sulfur-sensitive catalyst; and
 - wherein a portion of said catalytic reforming reactor system, which contacts a low-sulfur stream containing a hydrocarbon, has an improved resistance to carburization.
45. The catalytic reforming reactor system of claim 44, wherein said sulfur-sensitive zeolite reforming catalyst is an L-zeolite catalyst.
46. The catalytic reforming reactor system of claims 44 or 45, wherein said portion of said catalytic reforming reactor system is at least one of said plurality of furnace tubes.
47. The catalytic reforming reactor system of claims 44 or 45, wherein said portion of said catalytic reforming reactor system is a portion of a wall of said catalytic reforming reactor system.

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48. The catalytic reforming reactor system of any one of claims 44-47, wherein said low sulfur stream has less than about 100 ppb sulfur.
49. The catalytic reforming reactor system of any one of claims 44-48, wherein said low sulfur stream has less than about 50 ppb sulfur.
50. The catalytic reforming reactor system of any one of claims 44-49, wherein said sulfur-sensitive catalyst is a large-pore zeolite comprising an alkali or alkaline earth metal and at least one Group VIII metal.
51. The catalytic reforming reactor system of claim 50, wherein said Group VIII metal comprises platinum.
52. The catalytic reforming reactor system of any one of claims 44-51, wherein said improved resistance to carburization is provided by a cladding, a coating or a paint on said portion of said reforming reactor.
53. The catalytic reforming reactor system of claim 52, wherein said paint comprises a reducible paint which has been heated under reducing conditions.
54. The catalytic reforming reactor system of claims 52 or 53, wherein said paint comprises a tin-containing paint.

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55. The catalytic reforming reactor system of claim 54, wherein said tin-containing paint further comprises a hydrogen decomposable tin compound, a solvent system, a finely divided tin metal, and a tin oxide.
56. The catalytic reforming reactor system of claims 52, wherein said coating is selected from the group consisting of copper, tin, intermetallic tin compounds, tin alloys, arsenic, antimony, brass, lead, bismuth, chromium, intermetallic compounds thereof, alloys thereof, a copper-tin alloy, a copper-antimony alloy, and mixtures thereof.
57. The catalytic reforming reactor system of claim 52, wherein said coating is selected from the group consisting of aluminum, alumina, chromium, chromium oxide, an aluminized material, a chromized material and mixtures thereof.
58. The catalytic reforming reactor system of claim 52, wherein said coating comprises a ceramic coating.
59. The catalytic reforming reactor system of claim 52, wherein said coating comprises a silica coating.
60. The catalytic reforming reactor system of any one of claims 44-51, wherein said portion of said catalytic reforming reactor system comprises a protective layer comprising a metallic stannide which provides said improved resistance to carburization.
61. The catalytic reforming reactor system of any one of claims 44-51, wherein said portion is constructed of

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a material that provides said resistance to carburization and metal dusting.

62. The catalytic reforming reactor system of claim 61, wherein said material is 347 stainless steel or has a resistance to carburization and metal dusting at least as good as 347 stainless steel under low sulfur reforming conditions.
63. The catalytic reforming reactor system of any one of claims 44-62, wherein said catalytic reforming reactor system is an existing catalytic reforming reactor system.
64. The catalytic reforming reactor system of any one of claims 44-62, wherein said catalytic reforming reactor system is a new catalytic reforming reactor system.
65. The catalytic reforming reactor system of any one of claims 44-64, wherein said portion of said catalytic reforming reactor system, prior to having an improved resistance to carburization and metal dusting, is oxidized steel.

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Fig. 1A



Fig. 1B

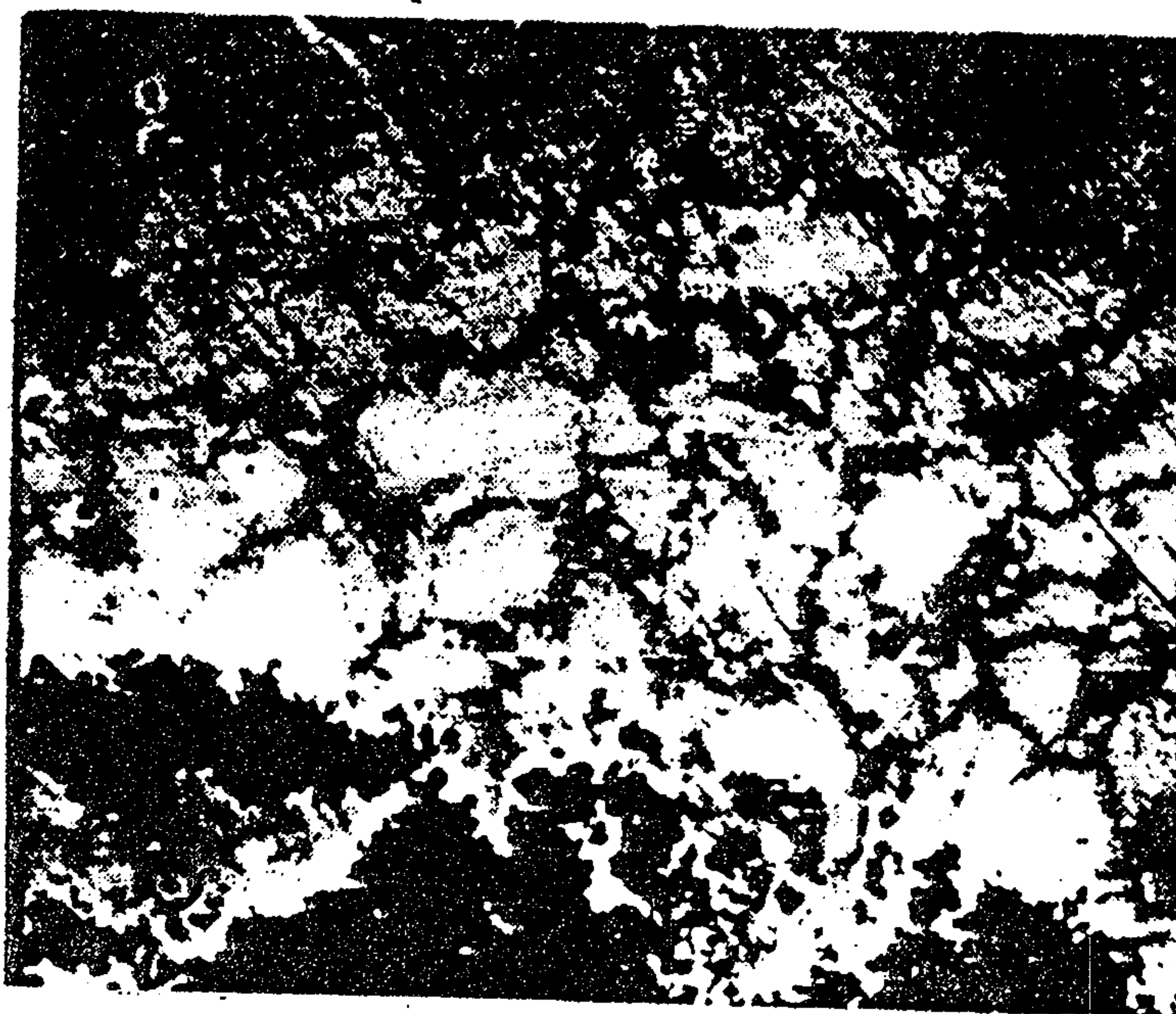


Fig. 2

