

19



Europäisches Patentamt
European Patent Office
Office européen des brevets

11 Publication number:

0 096 483
A1

12

EUROPEAN PATENT APPLICATION

21 Application number: 83302771.7

22 Date of filing: 17.05.83

51 Int. Cl.³: **B 01 J 23/46**
B 01 J 37/00
//C10G35/085

30 Priority: 04.06.82 US 385158

43 Date of publication of application:
21.12.83 Bulletin 83/51

84 Designated Contracting States:
BE DE FR GB IT NL SE

71 Applicant: MOBIL OIL CORPORATION
150 East 42nd Street
New York New York 10017(US)

72 Inventor: Krishnamurthy, Sowmithri
1281 Marlboro Road
Cherry Hill New Jersey 08003(US)

72 Inventor: Landolt, George Robert
108 Tweed Avenue
Audubon New Jersey 08106(US)

72 Inventor: Schoennagel, Hans Juergen
42 Pine Knoll Drive
Lawrenceville New Jersey 08648(US)

74 Representative: West, Alan Harry
Mobil Court 3 Clements Inn
London WC2A 2EB(GB)

54 Pretreatment of a fresh iridium-containing catalyst.

57 In the pretreatment of a fresh iridium-containing reforming catalyst, the catalyst is initially treated at an elevated temperature with oxygen and a hydrogen halide, preferably dry hydrogen chloride. Thereafter the catalyst is treated with a reducing agent at an elevated temperature.

EP 0 096 483 A1

PRETREATMENT OF A FRESH IRIIDIUM-CONTAINING CATALYST

The present invention relates to a method for treating fresh iridium-containing reforming catalysts.

Methods of preparation of metal-containing hydrocarbon conversion catalysts, including iridium-containing reforming catalysts, are well-known in the art. Much of the patent literature in this field relates to the regeneration of spent catalysts to impart a performance similar to that of a fresh or untreated catalyst. U.S. Patent No. 3,998,755 discloses a series of treatment steps which may be performed on either a deactivated catalyst which is being regenerated or a fresh catalyst as part of a pretreatment procedure. The treatment consists basically of a drying step at 200-600°F (93-316°C) for 2 to 24 hours, a calcination step at 700-1100°F (371-593°C) for 5 to 10 hours, and a water-free reduction step at 800-1100°F (427-593°C).

U.S. Patent No. 3,941,682 discloses a method of treating a catalyst which can be applied to either a spent or a fresh catalyst which comprises drying the catalyst at 220-250°F (104-121°C) followed by a calcination step at 500-700°F (260-371°C). This patent notes that calcination temperatures in excess of 700°F (371°C) should be avoided. The drying and calcination steps may be followed by contact with hydrogen chloride or reduction with hydrogen.

The present invention resides in a process for the treatment of a fresh iridium-containing reforming catalyst, comprising subjecting said catalyst to the following steps:

- (1) treatment with oxygen at an elevated temperature,
- (2) treatment with hydrogen halide at an elevated temperature, and
- (3) after steps (1) and (2), treatment with a reducing agent at an elevated temperature.

The oxygen and hydrogen halide treatments of the invention assure that the iridium component of the catalyst is placed in the proper oxidation state prior to final reduction.

The present process is preferably carried out by treating a fresh catalyst prepared from hexachloroiridic acid with an oxygen-containing gas at elevated temperatures. Preferred conditions range from temperatures of 750-1000°F (399-538°C), pressures of 0.1-500 psig (102-3549 kPa) and oxygen concentrations of 0.1-50 wt.% for 0.1 to 24 hours. More preferably, the oxygen treatment step is accomplished by treating the fresh catalyst with 0.1-21 wt.% of oxygen at temperatures of 850-950°F (454-510°C) for 0.25 to 2 hours at atmospheric pressure.

The next step in the treatment sequence involves the addition of a dry hydrogen halide, preferably hydrogen chloride, to the catalyst. The expression "dry hydrogen halide" is intended to mean that water is controlled to a level no greater than 1/30 the concentration of hydrogen halide. Preferably, water is present at a level no greater than 10 ppm. As an example, commercially available hydrogen chloride is suitable as is, i.e. no drying step is necessary. The treatment with dry hydrogen halide is preferably carried out at temperatures ranging from 700-1000°F (371-538°C) and pressures ranging from about 0.1-500 psig (102-3549 kPa) for a period of time ranging from 0.5 to 24 hours utilizing at least 0.1 wt.% of hydrogen halide per weight of catalyst per hour. The amount of hydrogen halide used is generally no greater than 10 wt.% per weight of catalyst per hour since higher amounts, although operable, are not necessary to obtain the desired results. Preferably, hydrogen chloride with a concentration of about 3 vol.% in an inert gas is added at 1.5 wt.% of hydrogen chloride per weight of catalyst per hour at a temperature of 850 to 950°F (454 to 510°C) for about 2 hours at atmospheric pressure.

The oxygen and hydrogen halide treatment steps may also be accomplished simultaneously with the same results.

The final pretreatment step consists of treating the catalyst with a reducing agent, e.g. hydrogen. Suitable conditions include

temperatures ranging from 400-1100°F (204-593°C) for periods of time ranging from 0.1 to 24 hours. Preferably, this procedure is performed at a temperature of 850-950°F (454-510°C) for 0.5 to 2 hours at atmospheric pressure. It is to be understood that this last step, i.e. reduction with hydrogen, can be carried out either as a separate step in the pretreatment procedure or can be carried out as part of the reformer start-up procedure. The hydrogen reduction step should, however, be performed after the oxygen and hydrogen halide treatments.

It is important to note that the presence of water during any of the three pretreatment steps is detrimental to the formation and performance of the catalyst.

In a particularly preferred embodiment, the treatment in step 1 (oxygen) and step 2 (hydrogen halide) is carried out by mixture of the same with an inert diluent such as nitrogen, neon, helium or argon. The amount of inert gas is not critical and can range from 50 to 99.9 vol.% based on oxygen and can range from 90 to 99.9 vol.% based on the dry hydrogen halide.

The iridium-containing catalysts used herein comprise a porous carrier or support material in combination with iridium and other metals such as platinum and rhenium. The support component of the catalyst is preferably a porous, adsorptive material having a surface area, as determined by the Brunauer-Emmit-Teller (BET) method, of 20-800, preferably 100-300 square meters per gram. This support material should be refractory at the temperature and pressure conditions utilized in any given hydrocarbon conversion process. Useful support materials include: (a) silicon-based materials such as silica or silica gel, silicon carbide, clays, natural or synthetic silicates such as kieselguhr, kaolin, china clay or Attapulgius clay; (b) aluminosilicate zeolite materials such as naturally occurring or synthetic erionite, mordenite or faujasite, that may or may not have been previously converted to a hydrogen or ammonium form and reduced in sodium content by virtue of an exchange reaction with various metal cations, including rare earth metal cations; (c) refractory inorganic oxides, including alumina, titanium dioxide, zinc oxide, magnesia,

thoria, chromia, silica-alumina, alumina-titania, silica-zirconia and alumina-chromia; and (d) mixtures of one or more of the materials referred to above.

Refractory inorganic oxide materials are preferred catalyst support materials. In general, superior results are obtained when alumina, in particular the gamma or eta form, is employed. Alumina is the preferred catalyst support material when the catalyst is employed in naphtha reforming operations. The support materials described above are known articles of commerce and can be prepared for use as catalyst constituents by many varied techniques. Typically, the support materials are prepared in the form of spheres, granules, powders, extrudates or pellets. It is possible to have all the metals of the iridium-containing catalyst on the same support in one particle, e.g. platinum and iridium on alumina, or as a mixture of separate particles, e.g. platinum on alumina mixed with iridium on alumina. When mixtures of separate particles are used, the supports can be the same or different.

Where the iridium-containing catalyst is employed in a naphtha reforming, the catalyst preferably contains greater than 0.1 wt.% iridium, based upon the dry weight of the total catalyst. For other types of operation, lesser quantities of iridium may be employed. Specifically, iridium and platinum may each be present on the catalyst in amounts varying from 0.01 to 5.0 wt.%, preferably in amounts varying from 0.1 to 1.0 wt.%, based upon the total weight of the dry catalyst. Iridium/platinum naphtha reforming catalysts having maximum effectiveness normally contain 0.2 to 0.5 wt.% each, of iridium and platinum, based on total catalyst.

The iridium-containing catalysts may be prepared employing simple impregnation techniques well known in the art. Such a catalyst may be prepared by impregnating a support material with a solution of a soluble iridium compound and soluble compounds of any additional metals to be incorporated in the catalyst. Generally, an aqueous solution of the metal compounds is used. The support material may be impregnated with the various metal-containing compounds either sequentially or

simultaneously. The carrier material is impregnated with solutions of appropriate concentration to provide the desired quantity of metals in the finished catalyst. In the case of iridium, compounds suitable for the impregnation onto the carrier include hexachloroiridic acid, iridium tribromide, iridium trichloride, and ammonium chloroiridate, with hexachloroiridic acid being preferred. The preferred catalyst manufacturing technique involves contacting a previously prepared support, such as alumina, with an aqueous solution of hexachloroiridic acid of appropriate concentration to provide the desired quantity of metal in the finished catalyst.

After impregnating the carrier, the composite catalyst is dried at a temperature varying from 220-250°F (104-121°C). The catalyst may be dried in air at the above stated temperatures or may be dried by treating the catalyst in a flowing stream of inert gas, e.g. nitrogen. The fresh catalyst is then subjected to the pretreatment steps described above. Preferably, the catalyst is dried in an oxygen-containing gas at a temperature of from 850°-950°F (454°-510°C) for 0.25 to 2 hours. The drying step is followed by treatment with hydrogen chloride for 2 hours again at a temperature of from 850-950°F (424-510°C). If preferred, the foregoing steps may be accomplished simultaneously. The catalyst is next treated with reducing agent such as hydrogen for 0.5 to 2 hours also at a temperature of 850-950°F (454-510°C).

Iridium-containing reforming catalysts are used to improve the octane quality of naphthas and straight run gasolines. In addition they may be used to promote a wide variety of hydrocarbon conversion reactions such as hydrocracking, isomerization, dehydrogenation and cracking.

In a naphtha hydroforming process (reforming) a substantially sulfur-free naphtha stream that typically contains 15 to 80 volume percent paraffins, 15 to 80 volume percent naphthenes and 2 to 20 percent aromatics and boiling at atmospheric pressure substantially between 80°F and 450°F (27°C and 232°C), preferably between 150°F and 375°F (66°C and 191°C), is contacted with the iridium-containing

catalyst composite in the presence of hydrogen. The reactions typically occur in the vapor phase at a temperature varying from about 650-1000°F (343-538°C), preferably about 750-980°F (399-527°C). Reaction zone pressures may vary from 1 to 50 atmospheres (101 to 5065 kPa), preferably from 5 to 30 atmospheres (507-3039 kPa). The naphtha feed stream is conveniently passed over the catalyst composite at space velocities varying from 0.5 to 20 parts by weight of naphtha per hour per part by weight of catalyst (W/hr/W), preferably from 1 to 10 W/hr/W. The hydrogen to hydrocarbon mole ratio within the reaction zone is conveniently maintained between 0.5 and 20, preferably between 1 and 10. During the reforming process, the hydrogen used may be in admixture with light gaseous hydrocarbons. In a typical operation, the catalyst is maintained as a fixed bed within a series of adiabatically operated reactors. The product stream from each reactor (except the last) in the reactor train is reheated prior to passage to the following reactor. As an alternate to the above-described process, the catalyst may be used in a moving bed in which the naphtha charge stock, hydrogen and catalyst are passed in parallel through the reactor or in a fluidized system wherein the naphtha feed stock is passed upwardly through a turbulent bed of finely divided catalyst particles. Finally, if desired, the catalyst may be simply slurried with the charge stock and the resulting mixture conveyed to the reaction zone for further reaction.

The invention will now be more particularly described with reference to the examples and comparative examples and with reference to the accompanying drawings in which:-

Figure 1 is a graph of inlet temperature versus days on stream for a naphtha reforming operation using a conventional bi-metallic catalyst and a tri-metallic catalyst pretreated according to one example of the invention, and

Figure 2 is a graph similar to Figure 1 but comparing the pretreated catalyst of said one example with a pretreated Pt-Re catalyst mixed with a fresh iridium component.

COMPARATIVE EXAMPLE 1

A deactivated reforming catalyst comprising:

	<u>Wt. %</u>
Iridium	0.3
Platinum	0.3
Rhenium	0.3

was regenerated in the following manner.

1. The spent catalyst was heated to 850°F (454°C) in the presence of 5% oxygen and 3% hydrogen chloride in a nitrogen atmosphere for 8 hours to remove the coke deposits from the catalyst.
2. The product of step 1 was treated with hydrogen for 0.5 hours at a temperature of 850°F (454°C).

All of the catalysts in this and the following examples were examined by Temperature Programmed Desorption (TPD) of hydrogen. TPD of hydrogen is a technique used for estimating metal dispersions on reforming catalysts. The procedure consists of chemisorbing hydrogen on the metals at room temperature and further desorbing it by applying heat at a programmed rate. By collecting the hydrogen desorbed and knowing the hydrogen to metal ratio, the metal dispersion can be calculated. Thus, a dispersion of 0.5 is equivalent to 50% of the total metal being exposed as surface metal. It has been found that a dispersion of at least 0.5 is necessary to effect reforming reactions. Typically, pretreated iridium-containing catalysts have dispersions in the range of 0.6 to 1.0. The nature of the desorption spectrum, which is a plot of the rate of hydrogen release with respect to temperature as a function of temperature, provides additional information on the state of the metals on the support.

The resulting catalyst of Example 1 had a dispersion of less than 0.5. The pretreatment procedure therefore does not work well with a deactivated or spent catalyst.

COMPARATIVE EXAMPLE 2

A fresh reforming catalyst comprising:

	<u>Wt. %</u>
Iridium	0.3
Platinum	0.3

was pretreated in the following manner.

1. The fresh catalyst was heated to a temperature of 850°F (454°C) in the presence of 5% oxygen and 3% hydrogen chloride in nitrogen and water for 2 hours. A water:hydrogen chloride molar ratio of 5.6:1 was maintained during this period.
2. The product of step 1 was treated in hydrogen under dry conditions for 0.5 hours at a temperature of 850°F (454°C).

The resulting catalyst had a dispersion of less than 0.5. Therefore the presence of water is detrimental to the pretreatment procedure.

EXAMPLE 1

A fresh reforming catalyst comprising:

	<u>Wt. %</u>
Iridium	0.3
Platinum	0.3
Rhenium	0.3

was pretreated in the following manner.

1. The fresh catalyst was heated at a temperature of 950°F (510°C) in 5% oxygen in a nitrogen atmosphere for 0.5 hours.
2. The product of step 1 was further treated in 3.09% hydrogen chloride in nitrogen at 1.5 wt.% hydrogen chloride per weight of catalyst per hour for 2 hours at 950°F (510°C).
3. The product of step 2 was treated with hydrogen for 1 hour at a temperature of 950°F (510°C).

The resulting catalyst had a dispersion of greater than 0.5 which indicates that the pretreatment was successful.

COMPARATIVE EXAMPLE 3

A fresh reforming catalyst comprising:

	<u>Wt. %</u>
Iridium	0.3
Platinum	0.3
Rhenium	0.3

was pretreated in the following manner.

1. The fresh catalyst was heated at a temperature of 850°F (454°C) in nitrogen for 0.5 hours.
2. The product of step 1 was treated with 3.09% hydrogen chloride in nitrogen at 1.5 wt.% hydrogen chloride per weight of catalyst per hour for 2 hours at a temperature of 850°F (454°C).
3. The product of step 2 was treated with hydrogen for 1 hour at a temperature of 850°F (454°C).

The resulting catalyst had a dispersion of less than 0.5. The low dispersion clearly indicates the necessity of oxygen to effect the pretreatment.

COMPARATIVE EXAMPLE 4

The catalyst of Comparative Example 3 was treated in the same manner as Comparative Example 3 with the exceptions of substituting temperatures of 900°F (488°C) and 950°C (510°C) in steps 1-3.

The resulting catalysts also had a dispersion of less than 0.5 which indicates the necessity of oxygen to effect the pretreatment.

COMPARATIVE EXAMPLE 5

A fresh reforming catalyst comprising:

	<u>Wt. %</u>
Iridium	0.3
Platinum	0.3
Rhenium	0.3

was pretreated in the following manner.

1. The catalyst was heated to a temperature of 950°F (510°C) in the presence of 3.09% hydrogen chloride in nitrogen at 1.5 wt.% hydrogen chloride per weight of catalyst per hour.
 2. The product of step 1 was treated with hydrogen for one hour at a temperature of 950°F (510°C).
- The resulting catalyst again had a dispersion of less than 0.5.

EXAMPLE 2

A fresh reforming catalyst comprising:

	<u>Wt. %</u>
Iridium	0.3
Platinum	0.3
Rhenium	0.3

was pretreated in the following manner.

1. The fresh catalyst was heated to a temperature of 850°F (454°C) in the presence of 5% oxygen in a nitrogen atmosphere and 1.5 wt.% of 3.09% hydrogen chloride per weight of catalyst per hour for 2 hours.
2. The product of step 1 was treated with hydrogen for 1 hour at a temperature of 850°F (454°C).

The resulting catalyst had a dispersion of greater than 0.5. Therefore steps 1 and 2 of the pretreatment procedure can be accomplished sequentially (Example 1) or simultaneously.

EXAMPLE 3

A fresh reforming catalyst comprising:

	<u>Wt. %</u>
Iridium	0.3
Platinum	0.3
Rhenium	0.3

was pretreated as in Example 2 resulting in a dispersion of greater than 0.5 as determined by hydrogen chemisorption.

A commercial platinum-rhenium reforming catalyst (E603) having a composition of 0.35% platinum, and 0.35% rhenium was pretreated in a conventional manner using 5% oxygen in a nitrogen atmosphere for 2 hours at a temperature of 950°F (510°C) and subsequently treated with hydrogen for 1 hour at a temperature of 950°F (510°C). The pretreated bi-metallic and tri-metallic catalysts were then evaluated at an octane severity of 98 R+0 for the reforming of a C₆-350°F (177°C) Arabian Light Naphtha having the following properties:

	<u>Volume %</u>
Paraffins	71.4
Naphthenes	17.5
Aromatics	11.1
Sp. Gr.	0.7324
Sulfur, ppm	0.2
Nitrogen, ppm	0.2

The reaction conditions were 250 psig (1825 kPa), 2 WHSV and a total molar recycle ratio of 7. A comparison of the inlet temperatures versus days on stream is shown in Figure 1. As can be seen, the pretreated tri-metallic catalyst had improved stability as compared with the conventional bi-metallic catalyst.

EXAMPLE 4

A fresh reforming catalyst comprising:

	<u>Wt. %</u>
Iridium	0.3
Platinum	0.3
Rhenium	0.3

was pretreated in accordance with Example 2.

A platinum-rhenium catalyst was pretreated with 1.93% chlorine in nitrogen at 1.5 wt.% chlorine per weight of catalyst per hour for 2

F-1518

-12-

hours at a temperature of 900°F (482°C). The iridium component was then added and the composite was treated in hydrogen for 1 hour at a temperature of 850°F (454°C).

The pretreated platinum-rhenium/fresh iridium catalyst and the platinum-rhenium/iridium catalyst pretreated in accordance with this invention were evaluated at an octane severity of 98 R+0 for the reforming of C₆-350°F (177°C) Arabian Light Naphtha having the following properties.

	<u>Volume %</u>
Paraffins	71.4
Naphthenes	17.5
Aromatics	11.1
Sp. Gr.	0.7324
Sulfur, ppm	0.2
Nitrogen, ppm	0.2

The reaction conditions were 250 psig (1825 kPa), 2 WHSV and a total molar recycle ratio of 7. A comparison of the inlet temperature versus days on stream is shown in Figure 2. As can be seen, the pretreated catalyst according to this invention had an octane advantage of 10°F (6°C) after 40 days on the stream.

EXAMPLE 5

A bi-metallic catalyst comprising:

	<u>Wt. %</u>
Iridium	0.3
Platinum	0.3

was pretreated in accordance with Example 2.

The pretreated catalyst had a dispersion of greater than 0.5 which indicates that the pretreatment procedure was successful.

EXAMPLE 6

A commercial bi-metallic catalyst designated KX-130 having a composition comprising:

	<u>Wt. %</u>
Iridium	0.3
Platinum	0.3

was pretreated in accordance with Example 2 with the exception of the temperature which was maintained at a temperature of 850°F (454°C) in all steps.

The pretreated catalyst had a dispersion of greater than 0.5 which indicates that the pretreatment procedure was successful.

COMPARATIVE EXAMPLE 6

A fresh reforming catalyst comprising:

Platinum	0.3 wt. %
Iridium	0.3 wt. %
Rhenium	0.3 wt. %

was pretreated according to the procedure in Example 2 with the exception that the fresh catalyst was first reduced in hydrogen for 1 hour at 450°C. The resulting catalyst had a dispersion less than 0.5 as determined by hydrogen chemisorption. Therefore, the prescribed pretreatment procedure is ineffective on a previously reduced reforming catalyst.

EXAMPLE 7

A fresh reforming catalyst comprising:

Platinum	0.3 wt. %
Iridium	0.3 wt. %

was pretreated according to the procedure in Example 2 resulting in a dispersion of greater than 0.5 (0.7) as determined by hydrogen chemisorption. The reduced catalyst was again subjected to the

pretreatment procedure of Example 2. The resulting catalyst had a dispersion of greater than 0.5 (0.8), which indicates the effectiveness of the multiple use of this procedure.

COMPARATIVE EXAMPLE 7

A fresh reforming catalyst comprising:

Platinum	0.3 wt.%
Iridium	0.3 wt.%
Rhenium	0.3 wt.%

was pretreated according to the procedure in Example 2 with the exception that oxygen-chlorine was used instead of oxygen/hydrogen chloride in step 1. The resulting catalyst had a dispersion less than 0.5 as determined by hydrogen chemisorption which indicates the necessity of the presence of oxygen with a hydrogen halide to effect successful pretreatment.

CLAIMS:

1. A process for the treatment of a fresh iridium-containing reforming catalyst, comprising subjecting said catalyst to the following steps:

- (1) treatment with oxygen at an elevated temperature,
- (2) treatment with hydrogen halide at an elevated temperature, and
- (3) after steps (1) and (2), treatment with a reducing agent at an elevated temperature.

2. The process of claim 1 wherein said treatment with oxygen and hydrogen halide are combined into a single step.

3. The process of claim 1 or claim 2 wherein said oxygen treatment step comprises treating the catalyst with 0.1-50 wt.% of oxygen at a temperature of 750-1000°F (399-538°C) for 0.1 to 24 hours and at a pressure of 0.1-500 psig (102-3549 kPa).

4. The process of claim 1 or claim 2 wherein said oxygen treatment step comprises treating said catalyst with from 0.1 to 21 wt.% of oxygen at a temperature of from 850-950°F (454-510°C) for 0.25 to 2 hours.

5. The process of any preceding claim wherein said hydrogen halide treatment step comprises treating said catalyst with 0.1-10 wt.% of hydrogen halide per weight of said catalyst per hour for 0.5 to 24 hours at a temperature of 700-1000°F (371-538°C).

6. The process of any preceding claim wherein the hydrogen halide is hydrogen chloride.

F-1518

-16-

7. The process of any preceding claim wherein said catalyst is treated with a reducing agent at a temperature of 400-1000°F (204-593°C) for 0.1 to 24 hours.

8. The process of any preceding claim wherein the catalyst is treated with a reducing agent at a temperature of 850-950°F (454-510°C) for 0.5 to 2 hours.

9. The process of any preceding claim wherein said reducing agent is hydrogen.

10. The process of any preceding claim wherein said catalyst also contains platinum or platinum and rhenium.

2379n

1/2

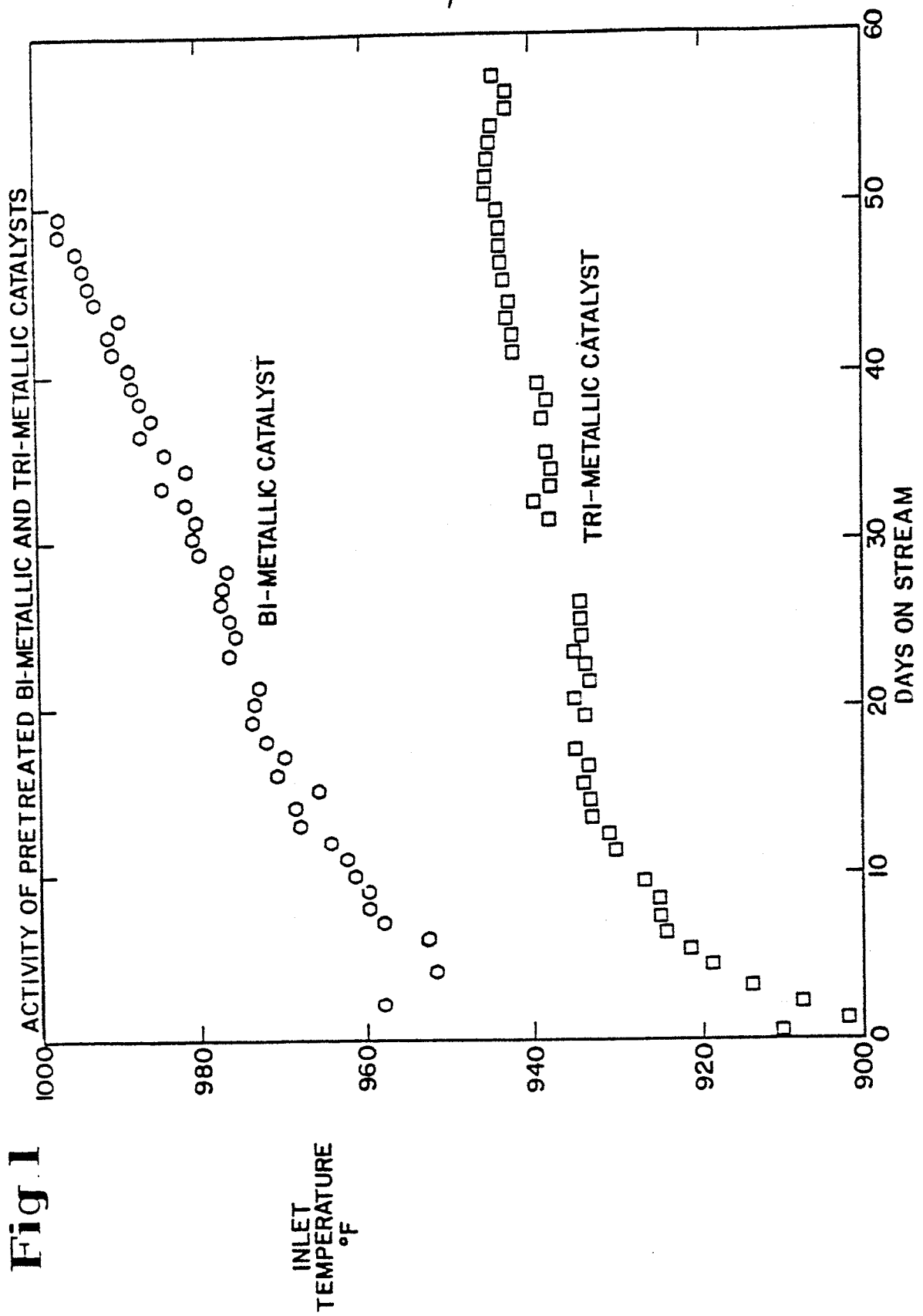
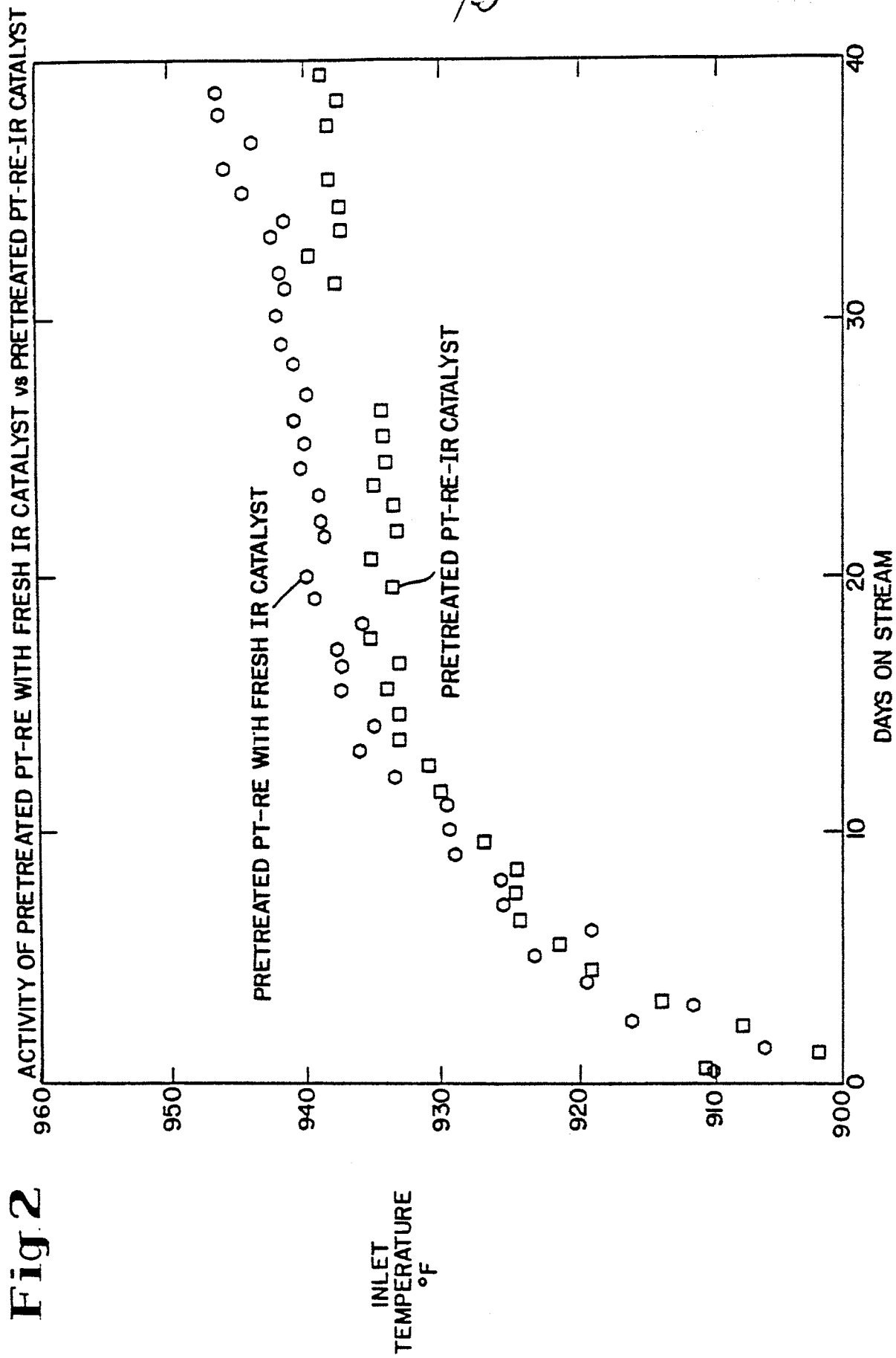


Fig 2



0096483

75/2



DOCUMENTS CONSIDERED TO BE RELEVANT			EP 83302771.7
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
A	<p><u>EP - A1 - 0 009 309</u> (MOBIL OIL CORPORATION)</p> <p>* Pages 6,7; claims *</p> <p>--</p>	1,6,7-10	<p>B 01 J 23/46</p> <p>B 01 J 37/00</p> <p>//C 10 G 35/085</p>
D,A	<p><u>US - A - 3 998 755</u> (HAYES)</p> <p>* Columns 4,5; column 8, lines 21-64; claims *</p> <p>--</p>	1-10	
A	<p><u>GB - A - 2 020 993</u> (EXXON RE-SEARCH)</p> <p>* Pages 2,3; claims *</p> <p>----</p>	1,3,7-10	
The present search report has been drawn up for all claims			<p>TECHNICAL FIELDS SEARCHED (Int. Cl. 3)</p> <p>B 01 J</p>
Place of search		Date of completion of the search	Examiner
VIENNA		31-08-1983	TENGLER
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone</p> <p>Y : particularly relevant if combined with another document of the same category</p> <p>A : technological background</p> <p>O : non-written disclosure</p> <p>P : intermediate document</p> <p>T : theory or principle underlying the invention</p> <p>E : earlier patent document, but published on, or after the filing date</p> <p>D : document cited in the application</p> <p>L : document cited for other reasons</p> <p>& : member of the same patent family, corresponding document</p>			