May 5, 1959 W. F. JOHNSTON, JR 2,885,351

PRETREATMENT OF HYDROFORMING CATALYSTS

Filed March 9, 1954

2 Sheets-Sheet 1

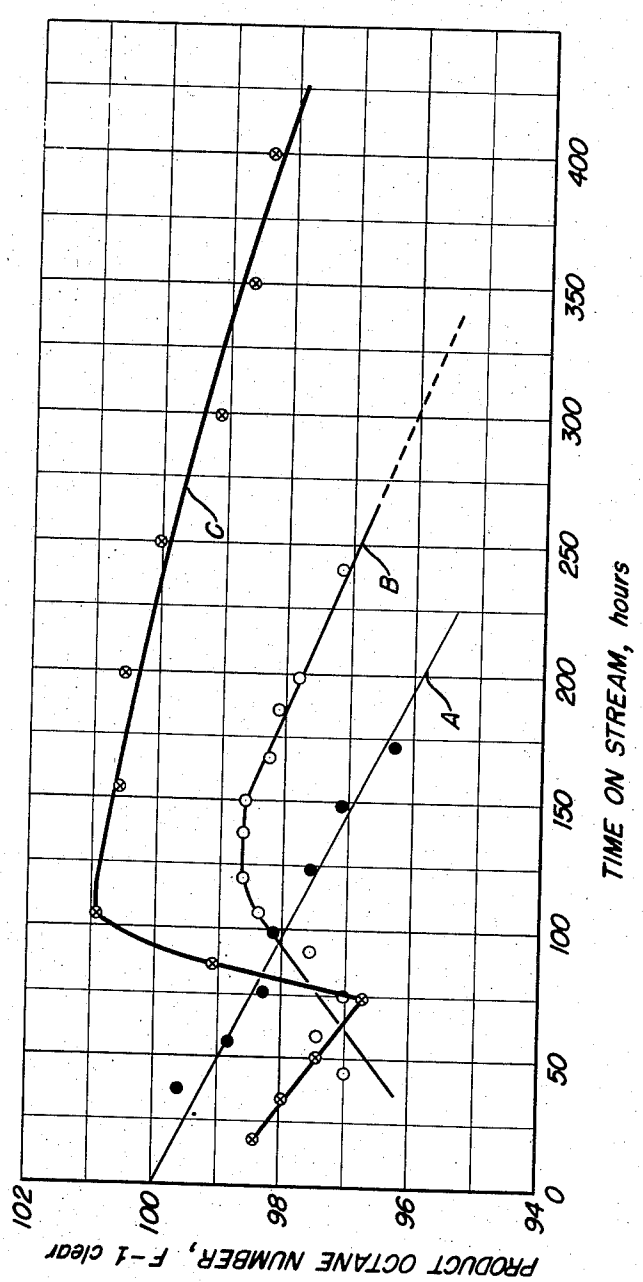


Fig. 1

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2 Sheets-Sheet 2

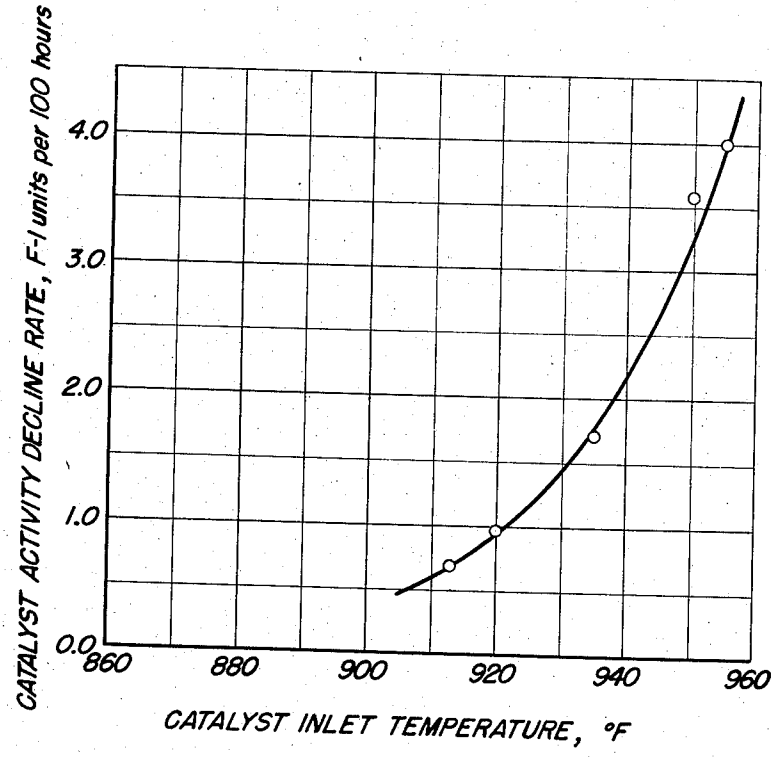


Fig. 2

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2,885,351

PRETREATMENT OF HYDROFORMING CATALYSTS

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Application March 9, 1954, Serial No. 414,954

7 Claims. (Cl. 208—138)

This invention relates to the reforming of hydrocarbons. More particularly, it relates to the hydroforming of petroleum naphthas in the presence of an alumina-supported platinum catalyst.

Within recent years, platinum-alumina catalysts have been adopted widely for upgrading petroleum naphthas into gasoline products of high octane number and improved performance characteristics, and for this purpose such catalysts have a number of properties which have made them outstandingly successful. They are capable of producing a product of high octane number and desirable volatility characteristics in excellent yield over a long period of time, when employed with due regard to the well known sensitivity of platinum metals to poisoning by various trace components in the charging stocks. It is normal for such catalysts to produce a product of very high octane number during the initial hours of operation, but the octane number ordinarily undergoes a more or less steady decline, depending upon a number of the operating variables, primarily the temperature, pressure, charging stock end-point, and concentration of deleterious substances such as sulfur, arsenic, and the like in the charging stock. It has been observed, moreover, that at the high hydroforming temperatures which are normally required to obtain gasolines of premium octane number, all of the various deleterious effects are emphasized, producing a higher rate of octane decline and making it correspondingly difficult to produce a reformate pool having the desired octane level. To avoid this difficulty, I have now discovered a technique of operation whereby the octane number decline rate for platinum-alumina catalysts can be substantially lowered during operation at higher octane levels. It is accordingly an object of my invention to improve the reforming of hydrocarbons, in particular the hydroforming of petroleum naphthas in the presence of alumina-supported platinum catalysts. A further object is to increase the reformate pool octane number obtainable with platinum-alumina catalysts. Another object is to extend the effective life of platinum-alumina hydroforming catalysts. These and other objects of my invention will be apparent from the appended description and claims.

I have discovered that the overall performance of a platinum-alumina catalyst in a hydroforming process for producing a premium-grade gasoline can be greatly improved by subjecting the catalyst to a preliminary conditioning for a period of around 10 to 100 hours or more in a hydroforming operation at a lower temperature from about 15 to 75° F., preferably from 25 to 50° F., below the temperature level initially to be employed to reach the desired octane level, the other operating conditions being within the conventional ranges. Following the said preconditioning period, the catalyst-zone temperature is raised directly to the desired hydroforming level, and the catalyst is then found to be substantially improved in activity maintenance, exhibiting a rate of decline in product octane number materially below the decline rate of untreated catalysts.

My invention is especially useful in connection with the treatment of naphthenic-type naphthas to produce gasoline products having F–1 octane numbers in the range of 90 to 100 or higher. In order to reach this level of product quality, the hydroforming operation is best carried out at a pressure within the range of about 100 to 500 pounds per square inch gage, a temperature between about 875 and 1000° F., preferably between about 940 and 975° F., an hourly weight space velocity between about 0.5 and 5, and a hydrogen input rate between about 2000 and 10,000 standard cubic feet per barrel of charging stock. I have succeeded in maintaining the product pool octane level around 95 during an extended period of operation by subjecting the catalyst to a preliminary exposure to a hydrocarbon stock under the defined conditions with the exception that a lower temperature is employed which initially yields a hydroformate quality from 2 to 10 F–1 octane units below the maximum level thereafter afforded by the catalyst. The pretreatment is preferably carried out at a substantially constant temperature ranging between about 800 and 950° F., and preferably under temperature conditions which do not produce a rise in product octane level during the pretreating operation.

The hydrocarbon stock employed in my catalyst pretreating step can suitably be the petroleum naphtha subsequently to be employed in the hydroforming operation. Alternatively it can be another petroleum fraction of naphtha boiling range or a fraction thereof, or a hydroformed naphtha or a fraction thereof, or a mixture of such materials. The charging stock should have an ASTM boiling range end point below about 425° F., preferably below about 375° F., and should be low in sulfur (less than about 0.05 weight-percent) and other contaminants. Paraffin and aromatic hydrocarbon diluents can be added if desired.

The application of my new technique is conveniently illustrated in connection with the treatment of a conventional naphthenic naphtha containing 40 to 60% naphthenes. When such a naphtha is hydroformed over a 0.6% platinum-on-alumina catalyst, a temperature of about 955° F. is initially required at a pressure of 300 p.s.i.g. and an hourly weight space velocity around 1.5 to produce a reformate having a clear F–1 octane number around 100, and at this temperature the catalyst normally declines in activity at the rate of 4 octane numbers per 100 hours on stream. By pretreating the catalyst in the said hydroforming operation at a lower temperature around 920° F. for 80 hours, and thereafter raising the temperature directly to the desired level of 955° F., the activity decline of the catalyst during the subsequent operation is reduced to only 1.0 octane number per 100 hours. As a result, even after allowance for the comparatively low octane number of the product obtained during the pretreatment period, the total product output has a substantially higher average octane level than is obtainable with any of the processes of the prior art.

The effectiveness of my new technique will be apparent by inspection of the attached graphs.

Figure 1 contains three curves, in which hydroformer product F–1 clear octane number is plotted against on-stream time, the data having been obtained from three platinum hydroforming tests under comparable conditions which differed significantly only with respect to the temperature cycle. All of the tests were carried out at 300 pounds per square inch gage reactor pressure and a hydrogen input rate of 5,000 standard cubic feet per barrel of feed over a 0.6% platinum-on-alumina catalyst. The charging stock was a paraffinic heavy naphtha having an ASTM distillation range of 232–392° F., an API gravity of 50.8 degrees, a Reid vapor pressure of 1.0

pound per square inch, and an F–1 clear octane number of 44.8.

Curve A represents a "first start-up" hydroforming operation of the conventional type in a two-bed reaction system having an impressed temperature gradient in each of the catalyst zones, simulating adiabatic operation. At the beginning of the test, an average catalyst temperature of 950° F. was established in the two zones, and the charging stock was introduced at an hourly weight space velocity of 1.0. Within five hours, a 100° F. temperature gradient had been established in each of the two zones, with catalyst inlet and outlet temperatures of 970 and 870° F. respectively. Under these conditions, it was observed that the product octane number dropped off at the rate of 2 units per 100 hours.

Curve B represents a "slow start-up" hydroforming operation in which the hydroforming was begun at a low temperature and the temperature was gradually raised to the desired operating level. This procedure of raising the reactor temperature to compensate for loss in activity by the catalyst is typical of the prior art, and is based on the well-known observation that the hydroforming effectiveness of a platinum-alumina catalyst, measured in terms of reformate octane number, increases as the hydroforming temperature is raised. The test to which curve B relates was also carried out in a two-bed impressed-gradient reaction system. The flow of charging stock was started at an hourly weight space velocity of 1.5 and with catalyst inlet and outlet temperatures of 800 and 700° F. respectively in each of the two beds. The temperatures in both beds were raised 5° F. per hour until inlet and outlet temperatures of 950 and 850° F. were reached. The space velocity was then reduced to 1.0 after a total of 40 hours on stream. Temperatures were thereafter raised gradually until the 100-octane level was reached at inlet and outlet temperatures of 970 and 870° F. after a total of 110 hours on stream. At this point the temperature was held constant, and it was observed that the product quality declined at the rate of 1.7 octane numbers per 100 hours.

Curve C represents the results of a test on my new process in a single-bed quasi-isothermal reactor, operating at an hourly weight space velocity of 1.5. The catalyst inlet temperature was maintained at about 920° F. for the first 80 hours on stream, and was thereafter raised quickly to 970° F. (equivalent to an integrated average temperature of 955° F. over the length of the catalyst bed), where it was held constant. During the initial low-temperature period, the activity decline rate was 2.5 octane numbers per 100 hours, but in the subsequent higher-temperature operation, the decline rate was only 0.8 unit per 100 hours, and was maintained at this level over an extended period of operation.

For further comparison, Figure 2 is a correlation of catalyst activity decline rate against catalyst inlet temperature in a fixed-temperature hydroforming operation of the prior-art type, employing a 0.6% platinum-on-alumina catalyst in the treatment of a paraffinic heavy naphtha at 300 pounds per square inch gage, an hourly weight space velocity of 1.5, and a hydrogen input rate of 5,000 standard cubic feet per barrel of feed. The catalyst activity decline rate, it will be observed, increases very rapidly with the temperature in the usual operating range; and in all cases, it is substantially greater than the rates obtainable by means of my invention. For instance, Figure 2 indicates that a decline rate of 4.0 F–1 units per 100 hours would normally be expected under the defined conditions at a catalyst inlet temperature of 955° F., whereas I have observed a decline rate of only 1.0 unit per 100 hours in an operation initiated at a relatively low temperature level according to my new technique.

In designating the temperature of a fixed-bed or moving-bed hydroformer catalyst zone, it is necessary to take into consideration the nature of the reactions involved in the hydroforming process. The most common and desirable charging stocks are rich in naphthenes, which undergo dehydrogenation to aromatics, a highly endothermic reaction. At the opposite extreme are the low-naphthene, paraffin-rich stocks, in which exothermic hydrocracking reactions may predominate. As a result it is seldom that the combined reactions are isenthalpic, and it is ordinarily found that a temperature gradient of some magnitude exists in nonfluidized catalyst beds, even in reactors equipped with internal heat-exchange means. In adiabatic-type reactors, a temperature drop of 100 to 150° F. through a single catalyst bed is commonly encountered when processing naphthenic stocks. For this reason, it is necessary to employ a consistent basis in designating the temperatures employed in the catalyst pretreating step of my invention and in the subsequent hydroforming step at higher temperature. Thus, it is satisfactory to choose the catalyst inlet temperature, or in general the temperature of any point within the catalyst bed, provided that the same reference point is used in each step. It is also satisfactory to employ an average catalyst temperature, preferably an integrated average temperature over the entire length of the catalyst bed.

Advantageous results are in general obtained from the pretreating step of my invention without regard to the temperature pattern in the catalyst zone. It will be apparent, however, that in zones having a steep temperature drop, the parts of the catalyst bed having abnormally low temperatures (i.e., below about 800° F.) during the pretreating operation will receive less than the optimum degree of preconditioning. For this reason, it is desirable to minimize the temperature gradient, at least to the point of maintaining a minimum temperature in the catalyst bed of at least about 800° F. Best results are obtained by maintaining the catalyst zone at a uniform temperature throughout.

A convenient technique for minimizing the catalyst-zone temperature gradient in my pretreating step, and thereby improving the effectiveness of the catalyst preconditioning, lies in choosing the charging stock and/or adjusting the charging-stock composition to hold the heat effects during the said step at as low a level as possible. In the temperature range employed, exothermic reactions such as hydrocracking do not take place to any important extent. The observed heat effects are largely caused by the highly endothermic dehydrogenation of naphthenes to aromatics. It is accordingly advantageous to employ as the charging stock in the pretreating step a stock low in naphthenes, such as a paraffinic naphtha, containing 20 percent or less of naphthenes, or to dilute the regular hydroformer charging stock with 50 percent or more of such a naphtha. We prefer to carry out the catalyst preconditioning with hydroformate (i.e., a stock which has already been hydroformed and which consequently shows little or no thermal effect), or with a regular charging stock diluted with 50 to 90 percent of hydroformate. It will be apparent that different charging stocks may be used in the pretreating and hydroforming operations.

My process is suitable for use with any of the alumina-supported platinum hydroforming catalysts described in the prior art, including unpromoted platinum-on-alumina, as well as platinum-alumina catalysts which contain a promoting additive such as vanadia, chromia, titania, iridium, rhodium, an oxide of phosphorus, or the like, or a mild cracking adjuvant, such as boria, silica, fluorine, chlorine, or the like. The catalysts commonly contain platinum in a proportion between 0.05 and 1 percent by weight, based on dry Al_2O_3. Third components are usually present in a proportion between about 0.1 and 10% by weight.

The following specific examples will more fully illustrate my invention.

Example 1

A Mid-Continent virgin naphtha was subjected to a quasi-iso-thermal hydroforming operation in accordance with my new technique at a pressure of 300 pounds per square inch gage, an hourly weight space velocity of 1.0,

and a hydrogen input of 5,000 standard cubic feet per barrel. The charging stock had an ASTM boiling range of 200–360° F., an F–1 octane number of 44, and a sulfur content of 0.03%, and contained 41.5% naphthenes, 50% paraffins, and 8.5% aromatics. The catalyst was cogelled platinum-on-alumina containing 0.6% by weight of platinum. During the first 80 hours of operation, the reaction zone was maintained at a temperature of 920° F., and the F–1 octane number of the unstabilized reformate declined from an initial level of 98.0 to a final level of 96.0, corresponding to a decline rate of 2.5 units per 100 hours. The temperature was thereupon raised to 955° F., where it was maintained for 40 hours. During this time the octane number of the unstabilized reformate ranged between 100.3 and 100.6 with no marked decline. At the end of this time, the temperature was lowered to 949° F. and maintained for 128 hours, during which time the product octane number declined from an initial level of 99.7 at the rate of 0.8 unit per 100 hours.

Example 2

A paraffinic heavy naphtha charge containing 37% paraffins, 50% naphthenes, and 13% aromatics, and having a final boiling point of 353° F. was subjected to hydroforming in an isothermal-type reaction zone at a pressure of 300 pounds per square inch gage, an hourly weight space velocity of 1.5, and a hydrogen input rate of 5,000 standard cubic feet per barrel. The catalyst was cogelled platinum-on-alumina containing 0.6% by weight of platinum. During the first 80 hours of operation, the catalyst temperature was held at 920° F. and an unstabilized product was obtained having an initial F–1 octane number of 98.5 and declining at the rate of 1.4 units per 100 hours. The temperature was then raised to 955° F., as a result of which the octane level rose to 100.8 at 140 hours on stream and declined to only 98.3 at 376 hours on stream, equivalent to an activity decline rate of 1.0 unit per 100 hours.

While I have described my invention with reference to certain specific examples, it is to be understood that such examples are illustrative only and not by way of limitation. Numerous alternative charging stocks, catalysts, manipulative steps, operating conditions, and other process details will be apparent from the above description to those skilled in the art.

In accordance with the foregoing description, I claim as my invention:

1. In a method for hydroforming a petroleum naphtha in the presence of an alumina-supported platinum catalyst at a hydroforming temperature between about 875 and 1000° F. and obtaining therefrom a gasoline having an F–1 octane number above about 90, the improvement which comprises preconditioning the said catalyst prior to said hydroforming operation by exposing the said catalyst for a period of more than about 10 hours to contact with a hydrocarbon stock of naphtha boiling range under hydroforming conditions, including an hourly weight space velocity between about 0.5 and 5.0, at a temperature from 15 to 75° F. below the initial temperature to be employed in the ensuing hydroforming operation, and thereafter directly raising the temperature of the said catalyst to said initial hydroforming level, whereby the activity maintenance of the said catalyst in the ensuing hydroforming operation is substantially improved.

2. In a method for hydroforming a petroleum naphtha in the presence of an alumina-supported platinum catalyst at a hydroforming temperature sufficient to obtain therefrom a gasoline having an F–1 octane number above about 90, the improvement which comprises preconditioning the said catalyst prior to said hydroforming operation by exposing the said catalyst for a period of more than about 10 hours to contact with a petroleum naphtha under hydroforming conditions, including an hourly weight space velocity between about 0.5 and 5.0, at a substantially constant temperature between about 800 and 950° F.

and from 15 to 75° F. below the initial temperature to be employed in the ensuing hydroforming operation, and thereafter directly raising the temperature of the said catalyst to said initial hydroforming level, whereby the rate of decline in activity of the said catalyst in the ensuing hydroforming operation is substantially reduced.

3. In a method for hydroforming a petroleum naphtha in the presence of an alumina-supported platinum catalyst at a hydroforming temperature between about 875 and 1000° F. and obtaining therefrom a gasoline having an F–1 octane number above about 90, the improvement which comprises preconditioning the said catalyst prior to said hydroforming operation by exposing the said catalyst for a period of more than about 10 hours to contact with said petroleum naphtha under hydroforming conditions, including an hourly weight space velocity between about 0.5 and 5.0, at a temperature between about 800 and 950° F. and from 15 to 75° F. below the initial temperature to be employed in the ensuing hydroforming operation, at which temperature a hydroformate is obtained of an anti-knock quality from 2 to 10 F–1 octane units below the maximum level afforded by the said catalyst in the ensuing hydroforming operation, and thereafter directly raising the temperature of the said catalyst to said initial hydroforming level, whereby the activity maintenance of the said catalyst in the ensuing hydroforming operation is substantially improved.

4. In a method for hydroforming a petroleum naptha in the presence of an alumina-supported platinum catalyst at a hydroforming temperature between about 875 and 1000° F. and a pressure between about 100 and 500 pounds per square inch gage and obtaining therefrom a gasoline having an F–1 octane number above about 90, the improvement which comprises preconditioning the said catalyst prior to said hydroforming operation by exposing the said catalyst for a period of around 10 to 100 hours to contact with a petroleum naphtha under hydroforming conditions, including an hourly weight space velocity between about 0.5 and 5.0, at a pressure within the said range and at a temperature from 25 to 50° F., below the initial temperature to be employed in the ensuing hydroforming operation, and thereafter directly raising the temperature of the said catalyst to said initial hydroforming level, whereby the rate of decline in activity of the said catalyst in the ensuing hydroforming operation is substantially reduced.

5. In a method for hydroforming a petroleum naptha in the presence of an alumina-supported platinum catalyst at a hydroforming temperature between about 875 and 1000° F. and a pressure between about 100 and 500 pounds per square inch gage and obtaining therefrom a gasoline having an F–1 octane number above about 90, the improvement which comprises preconditioning the said catalyst prior to said hydroforming operation by exposing the said catalyst for a period of around 10 to 100 hours to contact with said petroleum naptha under hydroforming conditions, including an hourly weight space velocity between about 0.5 and 5.0, at a pressure within the said range and at a temperature from 25 to 50° F., below the initial temperature to be employed in the ensuing hydroforming operation, and thereafter directly raising the temperature of the said catalyst to said initial hydroforming level, whereby the rate of decline in activity of said catalyst in the ensuing hydroforming operation is substantially reduced.

6. In a method for hydroforming a petroleum naptha in the presence of a fixed-bed catalyst consisting essentially of alumina and between about 0.05 and 1 percent by weight of platinum, based on dry Al_2O_3, at a pressure between about 100 and 500 pounds per square inch gage and a hydroforming temperature between about 875 and 1000° F. sufficient to obtain therefrom a gasoline having an F–1 octane number between about 90 and 100, the improvement which comprises preconditioning the said catalyst prior to said hydroforming operation by expos-

ing the said catalyst for a period of between about 10 and 100 hours to contact with said petroleum naptha under hydroforming conditions, including an hourly weight space velocity between about 0.5 and 5.0, at a pressure within the said range and at a substantially constant temperature from 15 to 75° F. below the initial temperature to be employed in the ensuing hydroforming operation, and thereafter directly raising the temperature of the said catalyst to said initial hydroforming level, whereby the activity maintenance of the said catalyst in the ensuing hydroforming operation is substantially improved.

7. In a method for hydroforming a naphthenic petroleum naphtha in the presence of a fixed-bed catalyst consisting essentially of alumina and between about 0.05 and 1 percent by weight of platinum, based on dry Al_2O_3, at a pressure between about 100 and 500 pounds per square inch gage and a hydroforming temperature between about 875 and 1000° F. sufficient to obtain therefrom a gasoline having an F–1 octane number between about 90 and 100, the improvement which comprises preconditioning the said catalyst prior to said hydroforming operation by exposing the said catalyst for a period of between about 10 and 100 hours to contact with a hydroformed petroleum naphtha under hydroforming conditions, including an hourly weight space velocity between about 0.5 and 5.0, at a pressure within the said range and at a temperature from 25 to 50° F. below the initial temperature to be employed in the ensuing hydroforming operation, and thereafter directly raising the temperature of the said catalyst to said initial hydroforming level, whereby the activity maintenance of the said catalyst in the ensuing hydroforming operation is substantially improved.

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CERTIFICATE OF CORRECTION

Patent No. 2,885,351 May 5, 1959

Walker F. Johnston, Jr.

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

In the grant, line 2, for "assignor to The American Oil Company," read -- assignor to The American Oil Company, a corporation of Texas, --; in the heading to the printed specification, line 5, for "The American Oil Company" read -- assignor to The American Oil Company, a corporation of Texas --.

Signed and sealed this 29th day of March, 1960.

(SEAL)
Attest:
KARL H. AXLINE

Attesting Officer

ROBERT C. WATSON
Commissioner of Patents