

[54]	LUBRICATING OIL PRODUCTION UTILIZING HYDROGEN IN TWO CATALYTIC STAGES	3,159,568	12/1964	Price et al.....	208/89
		3,494,854	2/1970	Gallagher et al.	208/89
		3,506,568	4/1970	Annesser et al.	208/89
		3,528,908	9/1970	Bowles et al.....	208/89

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 5,963, Jan. 26,
1970, abandoned.

[52] U.S. Cl..... 208/210; 208/89

[51] Int. Cl.²..... C10G 23/04; C10G 23/02

[58] Field of Search 208/89, 212, 210, 59

[56] **References Cited**

UNITED STATES PATENTS

3,140,253	7/1964	Plank et al.	252/455 Z
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[57] **ABSTRACT**

Lubricating oil of increased viscosity index and reduced aromatic hydrocarbon content is prepared by contacting a heavy lubricating oil fraction with hydrogen in the presence of a sulfur-resistant catalyst (e.g., nickel molybdate on alumina) to form an effluent oil and further contacting the effluent oil with hydrogen in the presence of a hydrogen- or rare-earth-exchanged, faujasite catalyst containing a platinum group metal to produce a product from which a lubricating oil having a reduced aromatic hydrocarbon content relative to the feedstock can be recovered.

11 Claims, No Drawings

LUBRICATING OIL PRODUCTION UTILIZING HYDROGEN IN TWO CATALYTIC STAGES

This application is a continuation-in-part of application Ser. No. 5,963, filed Jan. 26, 1970, now abandoned.

This invention relates to a process employing two distinct catalyst types to produce high quality lubricating oil stocks from raw, mineral lubricating oil fractions. More particularly, this invention concerns a catalytic hydroconversion process for the production of a refined mineral lubricating oil having an increased viscosity index and a reduced content of aromatic hydrocarbons.

Raw heavy lubricating oil fractions often require additional refining for quality improvement. It is often desirable to increase the viscosity index of such raw fractions, as well as to reduce the aromatic hydrocarbon content of these materials. However, since these raw lubricating oil fractions are valuable, it is also desirable to increase the viscosity index and reduce the aromatic hydrocarbon content while minimizing the losses of lubricating oil to, for example, lower boiling components.

Therefore, one of the objects of the present invention is to provide a method for producing a lubricating oil having an increased viscosity index from a raw, mineral lubricating oil fraction.

Another object of the present invention is to provide a process for producing a lubricating oil having a reduced aromatic hydrocarbon content from a raw, mineral lubricating oil fraction.

A still further object of the present invention is to provide a process for producing a lubricating oil having an increased viscosity index and a reduced aromatic hydrocarbon content from a raw, mineral lubricating oil fraction while minimizing the loss of this fraction to lower boiling hydrocarbon components. Other objects and advantages of the present invention will become apparent hereinafter.

An improved process has now been discovered using a raw, mineral lubricating oil feedstock to produce a lubricating oil with an increased viscosity index and a reduced content of aromatic hydrocarbons, relative to the feedstock, without undue cracking and yield loss of the feedstock to lighter materials, such as gasoline, i.e., less than about 20%, preferably less than about 15%, by weight of the feedstock is converted to material boiling lower than 400°F. The raw, mineral lubricating oil feedstock is derived from a waxy mineral crude oil and contains at least about 0.3% by weight of sulfur and at least about 1000 ppm. by weight of nitrogen. The present improvement comprises first contacting this raw feedstock with hydrogen in the presence of a sulfur-resistant hydrogenation catalyst at a temperature of from about 600°F. to about 800°F. to form an effluent oil and second contacting this effluent oil with hydrogen in the presence of a second catalyst at a temperature of from about 500°F. to about 800°F. to improve the viscosity index of the effluent oil. The second catalyst comprises (1) a major amount, preferably at least about 70% by weight, of a faujasite in which at least 50% of the cations are selected from the group consisting of hydrogen ion, rare earth ion and mixtures thereof and the faujasite has a silica-to-alumina mole ratio of greater than about 3:1; (2) a minor, catalytically-effective amount of at least one platinum group metal; and (3) a minor amount of at least one refractory inor-

ganic oxide effective to improve the mechanical strength of the second catalyst. The first and second contactings described above are carried out at conditions so that less than about 20%, preferably less than about 15%, by weight of the feedstock is converted by hydrogen materials boiling below 400°F. The first and second contactings of the present invention can be conducted either with or, preferably without, intermediate processing, for example, separation of gases, e.g., H₂S and NH₃, from the effluent oil prior to the second contacting. The material obtained from the second contacting may be further processed using conventional methods, e.g., flashing distillation, and the like, to obtain a lubricating oil having increased viscosity index and reduced aromatic hydrocarbon content relative to the raw mineral lubricating oil feedstock. In addition, at least a portion of the material obtained from the second contacting step may be dewaxed, as by solvent dewaxing, to remove any wax present.

The raw, mineral lubricating oil fractions or feedstocks suitable in the process of the instant invention are typically heavy lubricating oil fractions, such as deasphalted residual lubricating oil fractions having a 5% boiling point of greater than about 800°F. Such heavy lubricating oil fractions can be deasphalted, for instance, by distillation or by a solvent treatment of the residual fraction obtained from the vacuum distillation of a waxy mineral crude oil. These raw, mineral lubricating oil feedstocks often possess a viscosity of equal to or greater than about 25 K.V. at 120°F., for example, from about 30 K.V. to about 50 K.V. at 120°F. These feedstocks typically contain small amounts of sulfur and nitrogen, e.g., at least about 0.3%, often from about 0.3% to about 1%, by weight of sulfur, and at least about 1000 ppm. (parts per million), often from about 1000 ppm. to about 2000 ppm. by weight of nitrogen. These raw, mineral oil feedstocks also contain aromatic compounds, for example, in an amount such that the feedstock has a specific dispersion of at least about 110, preferably at least about 130.

The first contacting step of the present process is conducted at temperatures from about 600°F. to about 800°F., preferably from about 675°F. to about 775°F. The other first contacting conditions preferably include pressures of from about 500 psig., to about 5000 psig., more preferably from about 1000 psig.; to about 3000 psig.; weight hourly space velocities (WHSV) of from about 0.1 to about 2, preferably from about 0.25 to about 1; and molecular hydrogen to feedstock ratios of from about 5,000 SCF/B (i.e., standard cubic feet of hydrogen per barrel of feedstock) to about 20,000 SCF/B, more preferably, from about 10,000 SCF/B to about 15,000 SCF/B. This first contacting step functions to produce an effluent oil. At least a portion, preferably at least a major portion, of both the sulfur and the nitrogen contained in the raw, mineral lubricating oil feedstock is chemically converted to H₂S and NH₃, respectively, in this first contacting step.

The effluent oil from the first contacting step is subjected to a second contacting step wherein a substantially hydrocarbon product is produced. The catalyst in the second contacting step is especially chosen to effect selective aromatic hydrocarbon hydrogenation and hydrocracking. This second contacting step occurs at conditions, e.g., temperature, so as to provide a substantially hydrocarbon product from which lubricating oil having an increased viscosity index and reduced ar-

omatic hydrocarbon content relative to the raw mineral lubricating oil feedstock without undue cracking and loss to lighter materials can be recovered. Temperatures in the second contacting step can range, for example, from about 500°F. to about 800°F., with temperatures of from about 600°F. to about 750°F. being preferred. Other second contacting conditions preferably include pressures of from about 500 psig. to about 5000 psig., more preferably from about 1000 psig. to about 3000 psig.; weight hourly space velocities of from about 0.1 to about 2, preferably from about 0.25 to about 1; and molecular hydrogen to effluent oil ratios of from about 5,000 SCF/B to about 20,000 SCF/B, more preferably, from about 10,000 SCF/B to about 15,000 SCF/B.

The catalyst used in the first contacting step of the present process can be any of the sulfur-resistant or sulfur-active, non-precious metal hydrogenation catalyst, such as those conventionally employed in the hydrogenation of heavy mineral oils. Examples of suitable catalytic ingredients are tin, vanadium, members of Group VIB in the Periodic Table, i.e., chromium, molybdenum and tungsten, and metals of the iron group, i.e., iron cobalt and nickel, metals of Group VIII in the Periodic Table. These metals are present in catalytically-effective amounts, for instance, from about 2% to about 30% by weight, and may be present in the elemental form or in combined form such as the oxides or sulfides, with the sulfide form being preferred. Mixtures of these metals can be employed, for example, mixtures of the iron group metal oxides or sulfides with the oxides or sulfides of Group VIB providing very satisfactory catalysts. Examples of such mixtures are nickel molybdate, tungstate or chromate (or thiomolybdate, thiotungstate or thiochromate) or mixtures of nickel or cobalt oxides with molybdenum, tungsten or chromium oxides. As the art is aware, and as the specific examples below illustrate, these catalytic ingredients are generally employed while disposed on a suitable carrier of the solid metal oxide type, e.g., a predominantly calcined or activated alumina. Commonly employed catalysts have about 1% to about 10% by weight of an iron group metal (calculated as the elemental metal) and about 5% to about 25% by weight of a Group VIB metal (calculated as the oxide). Advantageously, the catalyst is sulfided nickel-molybdena supported on alumina. Such preferred catalysts can be prepared by the method described in U.S. Pat. No. 2,938,002.

The catalyst employed in the second contacting step of the present invention comprises: (1) a major amount, preferably at least about 70%, by weight (based on the total catalyst) of a faujasite in which at least about 50%, preferably at least about 70%, of the cations are selected from the group consisting of hydrogen ion, rare earth ion and mixtures thereof; (2) a minor, catalytically-effective amount, preferably from about 0.1% to about 5% and more preferably, from about 0.3% to about 2%, by weight (based on the total catalyst) of at least one platinum group metal; and (3) a minor amount, preferably from about 5% to about 25% by weight (based on the total catalyst) of at least one refractory inorganic oxide effective to improve the mechanical strength of the catalyst. In certain instances, during activation and/or use of the catalyst employed in the second contacting step, at least a portion of the hydrogen cations of the faujasite are removed.

The remaining faujasite thus includes cation vacancies and may be termed a "decaionized" faujasite. Such decaionized faujasites are, by definition, within the class of faujasites suitable for use in the catalyst of the second contacting step provided that they are derived from faujasites in which at least 50%, preferably at least 70%, of the cations are hydrogen ion.

The faujasite component of the catalyst in the second contacting step may be synthetic or naturally-occurring. This component has pore openings of from about 8A to about 15A in diameter, preferably from about 10A to about 14A. Usually, with a given material, the pores are relatively uniform in size. Suitable faujasites have silica-to-alumina mole ratios of greater than about 3:1, usually not above about 12:1. In a preferred embodiment, the faujasite component has a silica-to-alumina mole ratio of from about 4:1 to about 6:1. The faujasite is at least about 50%, preferably at least about 70%, hydrogen- or rare-earth-exchanged. That is, at least about 50% of the cations present in the faujasite are hydrogen or one or more of the rare-earth metals or mixtures thereof. Included among the suitable rare-earth metals are cerium, lanthanum, neodymium and the like. Hydrogen exchange often is carried out by exchange of the cations of the synthetic or naturally-occurring faujasites with ammonium ions, for instance, through contact with an aqueous solution of ammonium chloride or other water soluble ammonium compound and subsequently calcining the faujasite, for instance at a temperature of about 500°F. to about 1500°F., preferably from about 700°F. to about 1100°F. Similarly, rare-earth metal exchange is commonly carried out by exchange of the cations with a water-soluble rare-earth metal compound followed by calcination.

The platinum group metals of the catalyst of the second contacting step include such Group VIII metals as, for example, platinum, palladium, ruthenium, osmium, rhodium and iridium. The platinum group metal, preferably platinum, palladium and mixtures thereof, more preferably platinum, may be present in the metallic form or as a sulfide, oxide or other combined form. The metal may interact with other constituents of the catalyst, but, if during use, the platinum group metal is present in metallic form, then it is preferred that it be so finely divided that it is not detectable by X-ray diffraction means, i.e., that it exist as crystallites of less than about 50A in size. The platinum group metal may be combined with the faujasite before or after the calcination of the hydrogen- or rare-earth metal-exchanged faujasite, by for example, ion exchange or impregnation. Ion exchange is preferred. In any event, after the platinum group metal is added, the platinum group metal-containing faujasite can be activated, e.g., calcined at the temperatures, e.g., from about 500°F. to about 1500°F., described above.

One method for combining the platinum group metal by ion exchange comprises contacting the faujasite with an aqueous solution containing a water-soluble form of the metal to be deposited in the crystal structure of the faujasite. The metal ion-exchanges with the cations present in the faujasite. The exchanged material is then removed from the solution, dried and calcined or otherwise activated. The platinum group metal may also be added by impregnation. Thus, the faujasite, either with or without previous evacuation, can be soaked in either a dilute or concentrated aqueous solu-

tion of a water-soluble platinum group metal compound, often in an amount just sufficient to wet the material and be completely absorbed. Examples of such water-soluble platinum group metal compounds include chloroplatinic acid, chloropalladic acid, ammonium hexathiocyanoplatinate (IV), hexathiocyanoplatinic acid and the like. The solid material from this impregnation can be calcined or otherwise activated.

Although various refractory inorganic oxides known in the art may be utilized as a component in the catalyst employed in the second contacting step to improve the mechanical stability of the catalyst, the preferred oxide comprises a major amount of calcined or otherwise activated alumina. The oxide comprises a minor amount, preferably from about 5% to about 25%, more preferably from about 5% to about 20%, by weight of the total catalyst. Other suitable oxides, for example, include silica, silica-alumina, zirconia, magnesia and the like. It is preferred that the alumina have a surface area of from about 25 m²/gm. to about 600 m²/gm. The alumina may be derived from hydrous alumina predominating in alumina trihydrate, alumina monohydrate, amorphous hydrous alumina and mixtures thereof which alumina has a surface area from about 50 m²/gm. to about 500 m²/gm. The useful aluminas may contain, in addition, minor proportions of other well-known refractory inorganic oxides such as silica, zirconia, magnesia and the like. However, the preferred oxide for use in this catalyst is substantially pure alumina derived from hydrous alumina predominating in alumina monohydrates, amorphous hydrous alumina and mixtures thereof. More preferably, the alumina is derived from hydrous alumina predominating in alumina monohydrate.

The catalysts of either contacting step of the present invention can, if desired, be formed into macrosized particles by tableting, pelletizing, extruding and the like. The oxide component of the catalyst used in this second contacting step may, along with improving the mechanical stability of the catalyst, provide a catalyst which is more easily formed into such macrosized particles. The macrosized particles of the catalysts useful in the present invention can have any shape and be of any form, e.g., size, compatible with the environment in which such catalysts are to be used. Generally, these macrosized particles have a minimum linear dimension of at least about 0.01 inches. For example, these particles may have a cylindrical configuration, typically of from about 1/64 in. to about 1/4 in. or more, in diameter and from 1/16 in. to about 1 in. or more in length. Although formation of macrosized particles often occurs before calcination of the final compounded catalyst, it can be performed at any time found most convenient.

The process of the present invention is illustrated by the following examples which are not to be considered as limiting.

EXAMPLE I

A waxy, raw, mixed base deasphalted lubricating oil feedstock having the properties of the feedstock in Table I, below, was contacted in three runs with hydrogen in the presence of a calcined nickel-molybdena on alumina catalyst at a temperature of 750°F., a pressure of 1500 psig., a weight hourly space velocity of 0.5 and a hydrogen to feedstock ratio rate of 12,000 SCF/B. The catalyst, which contained 2.3 percent nickel (calculated as elemental nickel) and 15.6 percent molybdenum (calculated as molybdena) as oxides supported on activated alumina was pretreated with hydrogen sulfide at 650°F. for 2 hours using one SCF-H₂S/hr/100 grams of catalyst. The total product from this first reaction zone was second contacted in a second reaction zone at temperatures varying from 624°F. to 663°F., a pressure of 1500 psig., a weight hourly space velocity of 1.0 and hydrogen rate of about 12,000 SCF/B of hydrocarbon feed in the presence of an extruded calcined, reduced platinum-containing, faujasite-boehmite catalyst. The catalyst used in the second contacting step comprised about 80% by weight of a faujasite, about 90% of the cations of which were ammonium (derived from conventional ion exchange), the faujasite having pores of a diameter of about 12A and a silica-to-alumina mole ratio of about 4:1, about 0.5% by weight of platinum; and about 20% by weight of boehmite alumina. The catalyst was calcined so that the ammonium cations of the faujasite were converted to hydrogen ions. At least a portion of these hydrogen ions were removed from this faujasite leaving cation vacancies. The boehmite alumina was included prior to extrusion of the catalyst to improve the mechanical strength of the catalyst. The product from the second reaction zone was distilled to remove lighter hydrocarbon components.

The properties of the product obtained in each of these runs is set forth in Tables II and III. The products were dewaxed and found to have the properties set forth in Table IV.

TABLE I

	Feedstock
Gravity, ° API	23.6
Flash, °F.	560
Viscosity, KV at 120°F.	33.64
Pour, °F.	120+
Nitrogen, PPM	1300
Sulfur	0.5%
Specific Dispersion	140
5% Boiling Point	945°F.

TABLE II

RUN NO. PRODUCT ANALYSIS	¹		²		³	
	Wt. %	Vol. %	Wt. %	Vol. %	Wt. %	Vol. %
DRY GAS	0.65	0.95	1.18	2.23	0.07	0.09
TOT. C ₁	0.70	1.08	0.87	1.35	0.07	0.11
TOT. C ₃	0.33	0.48	0.0	0.0	0.03	0.04
C ₆ + H ₂ S	98.56		98.51		100.35	
NH ₃	0.51		0.51		0.54	
H ₂ O	0.16		0.16		0.17	
	0.02		0.02		0.02	
CONVERSION						
To 550°F. Minus	14.33		27.00		32.57	
110-400°F.	5.61	5.84	13.99	14.57	18.76	19.54
400-550°F.	7.28	7.58	11.53	12.00	14.15	14.73
to 550°F. Plus	85.67	89.20	73.00	76.01	67.43	70.22

TABLE II—Continued

RUN NO. PRODUCT ANALYSIS	1		2		3	
	Wt. %	Vol. %	Wt. %	Vol. %	Wt. %	Vol. %
H₂ CONSUMPTION	562/SCF/B		744/SCF/B		747/SCF/B	
WT. YIELDS ON FEED CONVERTED TO 550°F. MINUS						
DRY GAS	4.55		4.36		0.21	
TOT. C ₄	4.89		3.21		0.21	
TOT. C ₅	2.31		0.0		0.09	
110-400°F.	39.12		51.81		57.62	
400-550°F.	50.80		42.68		43.45	

TABLE III

Run Number	Analysis of Total Liquid Product		
	1	2	3
% Carbon	87.04	86.44	85.96
% Hydrogen	13.60	13.84	13.92
ppm Nitrogen	19	13	4
Run Number	Analysis of the 550°F + Fraction		
	1	2	3
% Carbon	86.57	86.16	—
% Hydrogen	13.67	13.80	—
Refractive Index at 80°F.	1.46150	1.45695	—
API Gravity	30.9	29.6	33.4

TABLE IV

Run Number	Lubricating Oil Inspections		
	3	1	2
Laboratory Analysis of Products			
Wax			
API Gravity	35.7	34.8	34.1
PMP, °F.	166.0	169.9	166.9
% Oil	1.842	3.628	5.433
Filtrate			
API Gravity	32.3	29.7	28.1
Flash Point, °F.	359	425	440
Fire Point, °F.	420	465	490
Pour Point, °F.	+10	+10	+10
ASTM Color	4.5	3.5	3.5
KV/100°F.	65.10	128.1	164.2
KV/210°F.	8.864	13.16	14.92
Carbon Res. (Con.)	.082	0.11	9.14
Specific Dispersion	102.6	101.8	107.1
ASTM Distillation			
IBP	580	437	536
5%	619	624	626
10	637	689	698
20	690	817	845
30	773	899	939
40	874	984	980
50	960	1026	1020
60	1016	1055 at 58%	1059
70	1053	—	—
80	—	—	—
Viscosity Index	118	106	98
Wt. % Yield of			
550°F. + Waxy Oil	67.4	73.00	85.67
Wt. % Yield of			
550°F. + Dewaxed Oil	52.9	55.3	64.5

These data illustrate that the product of the instant process has a high viscosity index and low aromatic content. The ASTM distillation of the dewaxed lube oil (Table IV) indicates a slightly heavier overall product than normally produced in prior art processes. This

means that a higher yield of higher viscosity oil is obtained. This is reflected in the measured KV of the total 550°F. + dewaxed fraction. It should also be noted that all of the above runs were made at 1500 psig. pressure which is significantly lower than the usual pressure of prior art processes, e.g., 2500 psig. It thus appears that the process herein disclosed permits the use of a lower pressure during the reaction while maintaining good product characteristics. These examples also illustrate that the outstanding benefits, e.g., lubricating oils having increased viscosity index and reduced hydrocarbon aromatic content, of the present invention are achieved without undue yield losses to lower boiling components. For example, in each of Runs 1, 2 and 3, the amount of feedstock converted to material boiling a 400°F. and lower, was less than 20 % by weight. This is an important advantage of the present process since high yields of high quality lubricating oils are obtained.

While this invention has been described with respect to various specific examples and embodiments, it is to be understood that the invention is not limited thereto and that it can be variously practiced within the scope of the following claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. In a process for producing a hydrocarbon lubricating oil of increased viscosity index and reduced aromatic hydrocarbon content from a raw, mineral lubricating oil feedstock containing at least about 0.3% by weight of sulfur and at least about 1000 ppm. by weight of nitrogen derived from a waxy mineral crude oil, the improvement which comprises first contacting said feedstock with hydrogen and with a sulfur-resistant hydrogenation catalyst at a temperature of about 600°F. to about 800°F. to form a first effluent oil and second contacting said first effluent oil with hydrogen and with a second catalyst at a temperature of about 500°F. to about 800°F., to produce a second effluent oil, recovering said hydrocarbon lubricating oil having an increased viscosity index and reduced aromatic hydrocarbon content relative to said feedstock from said second effluent oil, said second catalyst comprising a major amount of a faujasite in which at least 50 % of the cations are selected from the group consisting of hydrogen ion, rare earth ion and mixtures thereof, said faujasite having a silica-to-alumina mole ratio of greater than about 3:1, a minor catalytically-effective amount of at least one platinum group metal and a minor amount of at least one refractory inorganic oxide

effective to improve the mechanical strength of said second catalyst, said first and second contacting producing less than about 20% by weight of hydrocarbon material boiling below 400°F. based upon the weight of said feedstock.

2. The process of claim 1 wherein said first contacting is conducted at a pressure of from about 500 psig. to about 5000 psig., a weight hourly space velocity of about 0.1 to about 2 and a hydrogen to feedstock ratio of from about 5000 SCF/B to about 12,000 SCF/B.

3. The process of claim 2 wherein said second contacting is conducted at a pressure of about 500 psig. to about 5000 psig., a weight hourly space velocity of about 0.1 to about 2 and a hydrogen to effluent oil ratio of from about 5000 SCF/B to about 20000 SCF/B.

4. The process of claim 3 wherein at least 70% of the cations in said faujasite are selected from the group consisting of hydrogen ion, rare earth ion and mixtures thereof.

5. The process of claim 4 wherein the platinum group metal is platinum and is present in said second catalyst in an amount from about 0.1% to about 5.0% by weight of the total catalyst.

6. The process of claim 5 wherein the sulfur-resistant catalyst contains molybdenum and an ion group metal.

7. The process of claim 6 wherein the iron group

metal is nickel.

8. The process of claim 1 wherein said first contacting is conducted at a temperature of about 675°F. to about 775°F., a pressure of about 1000 psig. to about 3000 psig., a weight hourly space velocity of about 0.25 to about 1 and a hydrogen to feedstock ratio of from about 10,000 SCF/B to about 15,000 SCF/B, and said second contacting is conducted without intermediate separation of gas at a temperature of from about 600°F. to about 750°F., a pressure of from about 1000 psig. to about 3000 psig., a weight hourly space velocity of from about 0.25 to about 1 and a hydrogen to effluent oil ratio of from about 10,000 SCF/B to about 15,000 SCF/B.

9. The process of claim 8 wherein at least 70% of the cations in said faujasite are selected from the group consisting of hydrogen ion, rare earth ion and mixtures thereof.

10. The process of claim 9 wherein the platinum group metal is platinum and is present in said second catalyst in an amount from about 0.3% to about 2% by weight of the total catalyst.

11. The process of claim 10 wherein the sulfur-resistant catalyst contains molybdenum and nickel on alumina.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3,912,620
DATED : October 14, 1975
INVENTOR(S) : James P. Gallagher

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 9, line 25; delete the word "ion" and substitute
therefore --iron--.

Signed and Sealed this

tenth Day of February 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks