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PROCESS FOR THE CATALYTIC REFORMING
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This is a continuation-in-part of Serial Nos. 252,594; 302,018; and 353,378, which have issued as U. S. Patents No. 2,369,432; 2,325,033 and 2,325,034 respectively.

This invention relates to the treatment of impure hydrocarbon fractions, and especially to the conversion thereof and removal of impurities such as sulfur compounds therefrom, and also to catalysts for such processes.

Most petroleum fractions contain more or less sulfur which ordinarily is present principally in the form of organic sulfur compounds. In many instances the sulfur content in gases is so high as to render them objectionable for sale for fuel gas. In other instances crude oils and their various residua and distillates are so high in sulfur as to render them objectionable for uses to which they are adapted, for example as cracking stocks, fuel oils, lubricating oils, aromatic solvents, motor fuels, or the like. Some such and similar materials including shale oil and coal tar fractions also contain oxygen and nitrogen in the form of phenols, nitrogen bases and other compounds which are objectionable.

The principal object of the present invention is to provide a process whereby impure hydrocarbon fractions, especially those boiling above the gasoline range, may be treated, and a very high degree of conversion of the hydrocarbons to more desirable forms, and conversion of the non-hydrocarbons such as the organic sulfur compounds, phenols and high-boiling nitrogen bases, into readily removable forms such as hydrogen sulfide, water and lower boiling nitrogen bases, may be effected. A further object is to provide suitable catalysts for this process, as well as suitable processes for manufacture of such catalysts. A catalyst which will effect a high rate of sulfur conversion is of special value because of the fact that some fractions, such as petroleum fractions, will contain as much as about 20% of organic sulfur compounds although the actual sulfur content may be only about 3%, for example. Where sulfur conversion to hydrogen sulfide is effected, the organic compounds freed from the sulfur may be left in the fraction, these compounds frequently being especially valuable constituents of motor fuel, lubricating oil, etc. Therefore, sulfur conversion as distinguished from complete removal of the sulfur-bearing compounds is of great importance. Likewise, complete removal or conversion of phenols from aromatic fractions renders them more suitable as solvents, and the removal of nitrogen compounds improves various

hydrocarbon mixtures in which they may be present. Furthermore, the phenols may be converted to more valuable aromatics, and the heavy nitrogen bases may be converted to more desirable low boiling nitrogen bases. The hydrocarbons may also be converted, i. e. reformed or cracked, to obtain more desirable hydrocarbons.

I have discovered that these objects may be attained by passing such "impure" or sulfur-bearing and/or oxygen and/or nitrogen containing hydrocarbon fractions in the liquid or vapor phase over or through a catalyst comprising cobalt molybdate. When the fraction is a gasoline or gas oil, it is usually preferable to treat it in the vapor phase, heavier fractions generally being treated in the liquid phase. The operation is preferably conducted under pressure and in the presence of hydrogen.

The catalysts for the above process may be cobalt molybdate either as such or on a carrier. Where precipitated cobalt molybdate as such frequently effects a considerable degree of treatment and conversion, it is highly preferable to precipitate the cobalt molybdate in the presence of a hydrous gel, particularly an alumina gel which is a porous gel producible as herein described, and it appears to be preferable that the catalyst consisting of hydrous alumina gel and cobalt molybdate contain only about 10% to 30% by weight of cobalt molybdate. A given weight of cobalt molybdate included in such proportions in such a catalyst is much more effective than an equal weight of the cobalt molybdate employed by itself. I have further discovered that the catalyst is of outstanding value when the cobalt molybdate is precipitated in the presence of a washed wet aluminum hydroxide gel following its precipitation but before the hydrous alumina gel has been allowed to dry. Under these conditions the molybdate is distributed through the gel and may even react chemically with the gel. The dried catalyst is of such form that it is highly porous, active, and stable at high temperatures, and exhibits another characteristic distinct from the usual supported molybdate catalyst prepared by participating cobalt molybdate onto a dried support, in that when first introduced into use, its activity builds up gradually and continuously to a maximum activity as represented by high sulfur conversion which maximum activity is retained throughout the valuable life of the catalyst, as distinguished from the other catalysts whose activity builds up very rapidly to a maximum and then drops back in the early life of the cata-

lyst to an efficiency value as measured by conversion rate of very much less than the maximum sustained conversion rate of the preferred catalyst prepared by precipitation in the presence of the initially formed wet hydrous gel.

The present invention may, therefore, be said to be based broadly upon treatment of impure hydrocarbon fractions, especially those heavier than gasoline, employing cobalt molybdate catalysts. In a narrower aspect of the invention, the cobalt molybdate catalyst is carried upon a support preferably an alumina gel, although zirconia, titania, thorina, chromia and magnesia gels are also very effective, and preferably is precipitated in the presence of the original wet hydrous alumina or zirconia or other gel. The invention extends not only to the broad catalytic treatment above indicated, but also to specific methods of treating specific stocks, such as methods, especially liquid phase methods, for removing non-hydrocarbons such as sulfur, oxygen, and nitrogen compounds from hydrocarbon fractions such as residua, lubricating oils, and gas oils, and to concurrent conversion of hydrocarbons in such fractions by cracking, including reduction in molecular weight, dehydrogenation, polymerization and alkylation; and/or reforming, including hydroforming, aromatization, and isomerization in this category. The invention also extends to similar processes of conversion of pure hydrocarbons, as well as to the catalysts employed, and to the methods of preparing these catalysts.

The cobalt molybdate catalysts employed in the processes of this invention are prepared by processes which involve precipitation of cobalt from a water solution of a soluble cobalt salt such as the nitrate or sulfate, by the addition of an aqueous solution of normal ammonium molybdate preferably containing a slight excess of ammonia. Under these circumstances the precipitate is not a mixture of cobalt and molybdenum oxides, but a chemical compound, cobalt molybdate (CoMoO_4). The solutions are preferably dilute and warm, to facilitate washing of soluble salts such as ammonium nitrate from the precipitate. The ratio of cobalt to molybdenum is preferably equimolar, although a slight excess of cobalt may also be employed to advantage in some instances. Catalysts of unusual value are obtained by precipitating the cobalt molybdate on a carrier, especially when the carrier is a metal hydroxide such as hydroxide of aluminum, titanium, zirconium, thorium, or magnesium, or even chromium. It is preferred in these preparations that the metal hydroxide be not dried prior to the precipitation of the cobalt molybdate thereon. Under these circumstances the cobalt molybdate appears to be unusually active, and may actually enter into some chemical combination with the carrier. The catalyst need not be reduced to the free metal before use.

As specific examples of preferred catalysts, the preparation of two catalysts is described in the following paragraphs. In the descriptions "water" refers to distilled water; "cobalt nitrate" refers to $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (molecular weight 291); "ammonium molybdate" refers to ammonium paramolybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (molecular weight 1236); and "ammonium hydroxide" refers to concentrated ammonium hydroxide solution approximately 15 normal. The aqueous solution of "normal ammonium molybdate" referred to above is prepared by dissolving the ammonium paramolybdate and ammonia in water, in the

ratio of 1 mol of paramolybdate to 8 mols of ammonia.

A cobalt molybdate catalyst was prepared as follows:

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| 5 | Cobalt nitrate | 7.7 mols=2270 grams |
| | Ammonium molybdate | 1.1 mols=1365 grams |
| | Ammonium hydroxide | 12 mols=800 ml. |

The cobalt nitrate was dissolved in 10 liters of cold water. The ammonium molybdate and ammonia were dissolved in 6 liters of cold water. The molybdate solution was added to the cobalt solution with stirring and the grey pink precipitate which was formed was filtered off.

15 The precipitate was washed first on the filter, using a total of 6 liters of cold water. It was then resuspended in 6 liters of cold water and refiltered. It was dried in the oven for forty-eight hours at 220° F. The dried cake was light purple in color. It was ground and pelleted in one-fourth inch pellets. The product had an apparent bulk density of about 138 grams per 100 ml.

A cobalt molybdate on alumina catalyst was prepared as follows:

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| 25 | Aluminum nitrate $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (molecular weight 375) | 6 mols=2250 grams |
| | Ammonium hydroxide | 18 mols=1200 ml. |

The aluminum nitrate was dissolved in 10 liters of hot water. The ammonium hydroxide was diluted to 4 liters with cold water and added slowly with stirring to the aluminum nitrate solution. The resultant precipitate was washed by two successive suspensions in 10 liter portions of hot water. The filter cake, without further drying, was suspended in 10 liters of cold water and used with the following:

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| | Cobalt nitrate | 0.7 mols=200 grams |
| | Ammonium molybdate | 0.1 mols=120 grams |
| 40 | Ammonium hydroxide | 0.8 mols=50 ml. |

The cobalt nitrate was dissolved in the above alumina suspension. The ammonium molybdate and ammonium hydroxide were dissolved in 2 liters of water which was added slowly with stirring to the cobalt solution containing the suspended alumina. The solid material precipitated, which had a pinkish color, was filtered off and washed twice by resuspending in 10 liters of hot water and filtering. The color of the filtrate indicated considerable loss of cobalt molybdate. The final composition of the solid material was approximately 20% by weight of cobalt molybdate and 80% of alumina. The cake was dried in the oven for seventy-two hours at 200° F., during which time it assumed a characteristic dark greenish blue color and a vitreous appearance. When it was broken up into 10-20 mesh granules, these were found to be sufficiently hard to make pelleting unnecessary.

60 In the treating processes of this invention, the hydrocarbon feed stocks are contacted with the above catalysts by any suitable means. In a continuous system, for example, the catalysts may be placed in a fixed bed in a reaction chamber and the feed stock passed through this catalyst bed, or a moving catalyst bed or fluid catalyst system may be employed wherein the catalyst moves in a stream counter-current to or concurrent with the hydrocarbon stream through the reaction zone. A batch system may also be employed in which the catalyst and feed stock are mixed in a container and the mixture is subjected to reaction conditions. The liquid or vapor phase may predominate in any of these operations, or mixed phase operation may be employed. The presence

of hydrogen and/or carbon monoxide in the reaction mixture is greatly preferred. The reaction temperatures will depend largely on the treatment desired, but will generally be above 400° F. and below about 2000° F. When it is desired merely to convert non-hydrocarbons to easily removable forms without substantial concurrent conversion of hydrocarbons, the lower temperatures are preferred, such as below about 900° F. In the conversion of hydrocarbons by cracking and reforming, the higher temperatures, above about 800° F. and preferably above about 950° F. are generally employed. The lower temperature operations when used for non-hydrocarbon conversion, are generally carried out at pressures above about 150 lbs., and in the presence of at least about 1000 cu. ft. of hydrogen per barrel of feed. The higher temperature operations when used for hydrocarbon conversion, are generally accompanied by lower pressures and higher hydrogen ratios.

The following are examples of treating processes of this invention. In each instance in which sulfur-containing stocks were treated, the products were caustic washed to remove the hydrogen sulfide formed.

Residua from distillation of crude oils containing various S, N and O-compounds may be treated to remove such compounds, by contacting these stocks in the liquid phase with the above catalysts. For example, by heating a residuum obtained by distilling the gasoline and gas oil from a high sulfur crude with about 1% of its weight of cobalt molybdate on previously undried alumina gel, with hydrogen at a pressure of about 2000 lbs. and a temperature of about 500° to 600° F. for about an hour the bulk of the sulfur, oxygen, and nitrogen compounds contained in the stock may be converted to lower boiling compounds, largely hydrogen sulfide, water, and lower boiling nitrogen bases, which may be removed from the product by fractional distillation or washing with dilute caustic and with dilute mineral acid. The hydrocarbons are largely unaffected, but the product is greatly improved over the feed stock as regards suitability for use as fuel oil or as cracking stock.

Similar selective conversion of sulfur, oxygen, and nitrogen compounds may be obtained under the range of conditions outlined above for the lower temperature operations, i. e. at temperatures below about 900° F., and preferably below about 800° F., pressures above about 150 lbs. per square inch and up to about 10,000 pounds or more, hydrogen ratios above about 1000 cubic feet per barrel of liquid feed and up to 10,000 or more cubic feet per barrel, contact times of about 0.1 hour up to about 10 hours or more, and the same or other catalysts of this invention. For equivalent selectivity of conversion, operation at the higher temperatures in this range should be accompanied by lower contact times.

By operation at somewhat higher temperatures, in the liquid or mixed phase, residual oils and the like may be treated with conversion of hydrocarbons as well as sulfur, oxygen, and nitrogen compounds. For example, by carrying out residuum treating operations at temperatures about 900° F. to 1000° F. or more and lower pressures such as atmospheric to about 150 lbs., with contact times as low as about 0.1 second or less, with or without hydrogen, similar conversion of S, O, and N compounds takes place, with concurrent production of substantial yields of fixed hydrocarbon gases, gasolines, and gas oils, which when

freed of hydrogen sulfide, water, and low-boiling nitrogen bases, are improved motor fuels.

Lubricating oils stocks treated as in the lower temperature operation above have been greatly improved in viscosity index (Dean & Davis method) without appreciable loss in yield. As an example of a modification of this process, hydrogen was bubbled through a mixture of 150 ml. of lubricating oil stock and 15 g. of an unsupported cobalt molybdate catalyst at atmospheric pressure and a temperature of about 700° F., for a period of about 16 hours. After washing the product with dilute caustic and dilute sulfuric acid, it was found to have a sulfur content of 1.7%, against 3.0% for the stock; a viscosity, S. U. at 100° F. of 298 as against 595 for the stock, and a viscosity index of 49 as against 20 for the stock. Even better results may be obtained by operation under pressure and/or by employing more efficient means of contacting.

Gas oils and coking distillates may be treated either in the liquid phase or in the vapor phase. The following are examples of vapor phase operation:

A heavy gas oil from Los Angeles Basin crude was vaporized in the presence of 3,400 cubic feet of hydrogen per barrel of feed, and the mixture was passed at a temperature of 750° F., a pressure of 150 lb. and a rate of 1 volume (of liquid feed) per volume of catalyst per hour over a bed of cobalt molybdate on alumina catalyst prepared as described above. The sulfur content of the gas oil was reduced by this treatment from 0.9% to 0.2% with a recovery substantially of 100% by volume, and was an improved cracking stock or Diesel fuel. There was no substantial conversion of hydrocarbons such as production of gasoline. Over 23 volumes of liquid feed were treated without catalyst regeneration, and without apparent loss in catalyst activity.

The combined distillate obtained from a coking distillation of a high sulfur, heavy crude from Santa Maria Valley in California was employed as feed stock in another operation, which was carried out with the same catalyst and feed rate as in the previous example, but with twice as great a ratio of hydrogen to feed stock, a temperature of 900° F. and a pressure of 250 lb. The first 5 volumes (per volume of catalyst) of feed treated yielded a product in an 89% yield which had a sulfur content of only 0.2%, compared with 3.5% for the feed stock, a reduction of about 94%. There was substantial conversion of hydrocarbons as well as sulfur compounds in this operation, since the product contained 56% of gasoline, while the feed stock contained only 18% of gasoline. This indicates a conversion of over 46% of the higher boiling material in the feed to gasoline. The sulfur content of the gasoline in the feed stock was 2.65%, while that of the product gasoline was 0.04%.

In a similar run the feed stock employed was the same stock employed in the previous example except that the 18% of gasoline was removed prior to the treatment. The treating conditions were similar, except that the feed rate was doubled. The product obtained from the first 12 volumes of feed in a yield of 86% had a sulfur content of 0.76% and contained 38% of gasoline of 0.17% sulfur content.

A straight-run gasoline from Santa Maria Valley crude was passed in the vapor phase in admixture with about 3400 cubic feet of hydrogen per barrel of liquid feed over a cobalt molybdate catalyst prepared as above (without carrier) at

a temperature of 600° F. and a pressure of 250 lb., and a rate of 4 volumes of liquid feed per volume of catalyst per hour. The product (freed of H₂S) was essentially unchanged except for the reduction of the sulfur content, which was 0.72 for the feed, and 0.06 for the product. This raised the octane number of the gasoline containing 3 ml. of tetraethyl lead per gallon from 70 for the feed to 78 for the product, although the octane number without tetraethyl lead, 61, was substantially unchanged by the treatment.

In a hydroforming operation, a straight-run gasoline of low sulfur content having a boiling range of 220° to 273° F. and containing no olefins and 14% aromatic hydrocarbons was converted in a 71% yield to a product of slightly wider boiling range containing 3% olefins and 50% aromatics. The catalyst was a cobalt molybdate-alumina catalyst prepared as described above, the feed rate was 1 volume per volume of catalyst per hour, the hydrogen ratio was 3400 cubic feet per barrel of feed, the length of the run was 2 hours, the temperature was 950° F. and the pressure was 100 lb.

In another operation, employing a cobalt molybdate (no carrier) catalyst prepared as above, with a feed rate of 2.7 volumes per volume of catalyst per hour, a hydrogen ratio of 10,000 cubic feet per barrel of feed, a temperature of 950° F. and a pressure of 250 lb., the length of the run being nearly 20 hours, a 78% yield of product gasoline of 0.09% sulfur content was obtained from a cracked gasoline containing 0.6% sulfur. The octane numbers of the feed containing no tetraethyl lead and 3 ml. of tetraethyl lead per gallon were 72 and 78 respectively, while those of the product were 75 and 86, respectively.

Besides the above, extract fractions obtained by selective solvent treatment of lubricating oils, transformer oils, kerosene, stove oils, gasolines, and like fractions have been treated in the presence of the above catalysts, under conditions such as those described above, both in liquid and vapor phase, to obtain products much more suitable as aromatic solvents for use as thinners for lacquer, paint, varnish, and the like. Fractions from coal tar and shale oil are similarly improved by such treatment.

These catalysts, especially the cobalt molybdate-alumina catalyst, are particularly suitable for use at temperatures above about 950° F. up to 1500° F. and even 2000° F. Thus, they may be employed in fluid cracking processes with or without hydrogen, or precombustion type cracking processes, in which hot flue gases are admixed with the feed stock to obtain reaction temperatures up to 2000° F. or higher. The catalysts may be carried in the flue gas stream, the hydrocarbon stream, or pass through the mixture, for example.

Although the presence of hydrogen is preferred because it generally improves catalyst life, the treatment may be carried out in the absence of hydrogen. Carbon monoxide may be employed as a substitute for, or in addition to, hydrogen, and the presence of saturated low molecular weight hydrocarbons such as propane and butanes, is generally helpful. As indicated, the cobalt molybdate catalysts are effective even in the presence of hydrogen sulfide, water, ammonia, and the like.

Although desulfurization and hydrocarbon conversion were emphasized in most of the specific examples given above, the feed stocks boiling above the gasoline range usually contain oxygen and nitrogen compounds such as phenols

and nitrogen bases, especially those of high molecular weight. These are rather difficult to remove by ordinary extraction methods. By treatments such as those shown in the above examples however, the phenol contents of such fractions have been reduced by 90% or more, apparently by conversion to water and hydrocarbons. By the higher temperature treatments, especially of the higher-boiling fractions, the nitrogen bases in such fractions have been converted to ammonia and to lower boiling nitrogen bases such as pyrrole, pyridine, and quinoline homologs and the like, and by the lower temperature treatments, unsaturated nitrogen bases such as pyrrole and pyridine may be hydrogenated to saturated materials such as pyrrolidine and piperidine respectively, which are stronger bases. All of these relatively low-boiling converted nitrogen bases are useful chemicals. They are readily extractable from the products of the above treating processes by treatment with dilute mineral acids such as sulfuric or hydrochloric, and may be recovered from the acid extracts by making the extracts alkaline with a strong base such as caustic soda and skimming or distilling the liberated nitrogen bases therefrom.

The treating processes of this invention may be employed in stages, or may be followed by other treating processes if desired. The nitrogen base extraction step described above may be considered as one such instance. It is sometimes desirable to treat products with concentrated sulfuric acid or clay or the like to provide further refinement; or a low temperature desulfurization treatment may be followed by a high temperature hydrocarbon conversion treatment of the types described above. Two or more treating processes of the types included in this invention may be carried on successively if desired.

By the term "catalysts comprising cobalt molybdate" it is intended to include cobalt molybdate itself, as well as cobalt molybdate supported on carriers such as clay, bentonite, ceramics, and metal oxides, especially hydrous metal oxide (including hydroxide) gels, and especially those gels which have not previously been dried. It has also been found, however, that catalysts comprising chromites of cobalt as well as chromites and molybdates of the iron group elements related to cobalt, i. e., nickel and iron, when prepared by methods analogous to those described above for the catalysts comprising cobalt molybdate, are good catalysts for hydrocarbon treatment by the processes of this invention, the cobalt chromite and the catalysts supported on undried hydrous oxide gels especially those named above, being preferred. In the case of the chromites the method of preparation normally involves the precipitation of the metal (iron, cobalt, or nickel) chromate from a solution of a soluble metal salt and ammonium dichromate, preferably in the presence of the desired undried hydrous oxide gel, by the addition of a slight excess of ammonium hydroxide, washing the product substantially free of soluble salts, and heating it to decompose the chromate to a lower form such as the chromite.

By "catalytic reforming of hydrocarbon mixtures" in the following claims it is intended to include processes for conversion of compounds containing sulfur, oxygen or nitrogen to more readily removable compounds containing these elements, as well as processes involving reduction in molecular weight, dehydrogenation, poly-

merization or alkylation, hydroforming or aromatization, and isomerization, of hydrocarbons. These reactions are clearly distinguishable from reactions such as hydrogenation, oxidation, halogenation, nitration, etc., in which material not present in the hydrocarbon feed stock is added thereto. By "hydrogenation" it is meant to include only those processes in which there is a substantial net or overall consumption of hydrogen. Processes in which there may be incidental hydrogenation of molecular fragments, but the hydrogen may be supplied by concurrent dehydrogenation, aromatization, and the like, of the hydrocarbon mixtures, and which involve primarily conversion of sulfur, oxygen, and nitrogen compounds, without substantial overall consumption of hydrogen, are definitely within the scope of this invention. For example, we may desulfurize cracked gasolines under conditions such that some of the olefins therein are hydrogenated or cyclized. The "hydrocarbon mixtures" include fractions from petroleum, coal tar, or shale, which may result from distillation, pyrolysis and/or extraction, and like processes, and may or may not contain sulfur, oxygen and nitrogen compounds.

Although only certain sulfur, oxygen and nitrogen compounds have been disclosed specifically, the above processes are applicable to all other non-hydrocarbons found in impure hydrocarbon fractions, such as naphthenic acids, and other compounds containing sulfur and/or oxygen, and/or nitrogen.

Modifications of the invention which would occur to one skilled in the art are to be included in the scope of the invention as defined in the following claims:

I claim:

1. A process for the catalytic reforming of hydrocarbon mixtures which comprises contacting said mixtures at a temperature between about 500° F. and about 1000° F. with a catalyst comprising a compound selected from the class consisting of chromites and molybdates of iron, cobalt and nickel precipitated on a previously undried hydrous metal oxide gel.

2. A process for the catalytic reforming of hydrocarbon mixtures boiling above the gasoline range which comprises contacting said mixtures in the presence of a reducing gas at a temperature between about 500° F. and about 1000° F. with a catalyst comprising a compound selected from the class consisting of chromites and molybdates of iron, cobalt and nickel precipitated on a previously undried hydrous metal oxide gel.

3. A process for the catalytic reforming of hydrocarbon mixtures boiling above the gasoline range which comprises contacting said mixtures in the presence of hydrogen at a temperature between about 500° F. and about 1000° F. with a catalyst comprising a molybdate of a metal selected from the class consisting of iron, cobalt and nickel precipitated on a previously undried hydrous metal oxide gel.

4. A process for the catalytic reforming of hydrocarbon mixtures boiling above the gasoline

range which comprises contacting said mixtures in the presence of hydrogen at a temperature between about 500° F. and about 1000° F. with a catalyst comprising a chromite of a metal selected from the class consisting of iron, cobalt and nickel precipitated on a previously undried hydrous metal oxide gel.

5. A process for the catalytic reforming of gas oils which comprises contacting said gas oils in the presence of hydrogen at a temperature between about 500° F. and about 1000° F. with a catalyst comprising cobalt molybdate precipitated on a previously undried alumina gel.

6. A process for the removal of organic sulfur, oxygen and nitrogen compounds from lubricating oil stocks which comprises contacting said lubricating oil in the presence of hydrogen at a temperature between about 500° F. and about 1000° F. with a catalyst comprising cobalt molybdate precipitated on a previously undried alumina gel.

7. A process for the catalytic reforming of hydrocarbon mixtures boiling above the gasoline range which comprises contacting said mixtures in the presence of hydrogen at a temperature between about 500° F. and about 1000° F. with a catalyst comprising a molybdate of a metal selected from the class consisting of iron, cobalt and nickel precipitated on a previously undried hydrous metal oxide gel, said catalyst having been prepared by a method comprising precipitating said molybdate from a solution containing a salt of said metal and ammonium molybdate in the presence of an undried hydrous metal oxide gel, by the addition of ammonium hydroxide.

8. A process for the catalytic reforming of hydrocarbon mixtures boiling above the gasoline range which comprises contacting said mixtures in the presence of hydrogen at a temperature between about 500° F. and about 1000° F. with a catalyst comprising a chromite of a metal selected from the class consisting of iron, cobalt and nickel precipitated on a previously undried hydrous metal oxide gel, said catalyst being prepared by a method comprising precipitating the chromate of said metal from solutions of a salt of said metal and ammonium dichromate in the presence of an undried hydrous oxide gel by the addition of ammonium hydroxide, washing the precipitate and heating it to decompose the chromate to the chromite.

9. A process according to claim 2 in which the reducing gas is carbon monoxide.

10. A process according to claim 2 in which the hydrous metal oxide gel is alumina gel.

11. A process according to claim 2 in which the catalyst is cobalt molybdate precipitated on previously undried alumina gel.

12. A process according to claim 2 in which the reducing gas is hydrogen and the hydrocarbon mixture is a residual oil stock.

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