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3,788,970

COKE SUPPRESSING ADDITIVE

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No Drawing. Continuation-in-part of application Ser. No. 787,566, Dec. 27, 1968, now Patent No. 3,591,484. This application June 24, 1970, Ser. No. 49,513
Int. Cl. C10c 3/04
U.S. Cl. 208—22 5 Claims

ABSTRACT OF THE DISCLOSURE

A coke suppressing additive is prepared by contacting an oxidized heavy hydrocarbon fraction with an aromatic polycarboxylic acid and/or anhydride producing compound in the presence of an oxidant followed by treatment with hydrogen. The additive is particularly useful for suppressing coke formation in a hydrocracking process.

This application is a continuation-in-part of our copending application Ser. No. 787,566, filed Dec. 27, 1968, now U.S. Pat. 3,591,484.

This invention relates to a new coke suppressing additive and to the use of this additive in a hydrocracking process.

During the hydrocracking of high boiling hydrocarbons to lower boiling hydrocarbons, a carbonaceous deposit (coke) is formed and, in catalytic processes, is laid down on the catalyst. The deposition of coke tends to seriously impair the catalytic efficiency of the catalyst for the conversion reaction and this conversion can be retarded or suspended after coke, to the extent of only a few percent by weight, accumulates on the catalyst. The catalyst then has to be regenerated such as by removal of the coke in a stream of regenerating gas.

As is known, coke and other undesired products are formed at the expense of useful products such as gasoline. It also is obvious that in catalytic processes during the period of regeneration the catalyst is not being effectively employed for conversion purposes. It, accordingly, is highly desirable not only to afford a large overall conversion of the hydrocarbon charge, i.e. to provide a catalyst of high activity, but also to afford an enhanced yield of useful products such as gasoline, while maintaining undesired products such as coke at a minimum.

It is, therefore, an object of this invention to suppress coke formation in a hydrocracking process.

It has now been found that a coke suppressing additive can be obtained by the process which comprises (1) oxidizing a heavy hydrocarbon fraction with an oxidant optionally in the presence of an oxidation promoting catalyst, (2) contacting said oxidized heavy hydrocarbon fraction from step 1 with an aromatic polycarboxylic acid and/or anhydride producing compound in the presence of an oxidant and optionally in the presence of an oxidation promoting catalyst, (3) contacting the product from step 2 with hydrogen for a time sufficient to form a polymeric material and (4) recovering a polymeric material with coke suppressing activity.

The product of this invention is prepared by first contacting the heavy hydrocarbon fraction with an oxidizing amount of an oxidant optionally in the presence of an oxidation promotion catalyst for a time sufficient to effect oxidation of at least a part of the heavy hydrocarbon fraction. By the use of the term "at least a part" it is meant that oxidation step 1 preferably produces increases in oxygen content of the heavy hydrocarbon charge stock during the process of from about 0.25 wt. percent to about 5.0 wt. percent more preferably from about 0.5 wt. percent to about 3.0 wt. percent. The oxidized heavy hydrocarbon fraction is then contacted in the presence of an oxidant with an aromatic polycarboxylic acid and/or anhydride producing compound hereinafter referred to as aromatic polycarboxylic compound in an amount varying from about 0.1 wt. percent to about 20 wt. percent more preferably from about 0.5 wt. percent to about 10 wt. percent and still more preferably from about 0.5 wt. percent to about 5 wt. percent based upon the total charge of the oxidized heavy hydrocarbon fraction which term as used herein includes both oxidized and unoxidized hydrocarbon fraction. The product which is obtained from process step 2 is then contacted with hydrogen for a time sufficient to form the additive of this invention, which, in general, precipitates or separates from the unoxidized heavy hydrocarbon fraction in the form of a polymeric material. The unoxidized heavy hydrocarbon fraction merely acts as a diluent for the preparation of the product of this invention.

In carrying out process steps 1 and 2 an oxidant is utilized such as oxygen including air and activated oxygen, ozone, organic peroxides, organic hydroperoxides, organic peracids, optionally in the presence of a metal catalyst.

The concentration of oxidant in process step 1 is usually dependent upon the increase in oxygen content which is to be obtained during oxidation step 1 such as oxygen content increases as set forth above. In general, air rates of from about 500 to 20,000 preferably from about 2,000 to 12,000 standard cubic feet (s.c.f.) per barrel of hydrocarbon charge stock are utilized and liquid hourly space velocity (volume of feed per volume of catalyst per hour, L.H.S.V.) of from about 0.2 to about 10, more preferably from about 0.5 to about 6. In the case of ozone, organic peroxides, organic hydroperoxides and organic peracids a concentration of oxidant generally within the range of from about 1.0 to about 10 moles of oxidant per mole of oxygen incorporated into the hydrocarbon material is utilized more preferably from about 1.5 to about 4 moles of oxidant. It is preferred to use an excess of both air and other types of oxidants above that needed to incorporate the actual number of moles of oxygen (representing the oxygen increase) into the hydrocarbon charge stock, preferably from about 20 to about 500% excess oxidant. The quantity of oxidant which is utilized in process step 2 is in general within the above ranges of oxidant utilized in process step 1. The preferred oxidant in both steps 1 and 2 which is utilized in preparing the product of this invention is oxygen (preferably as air). When a catalyst is employed, it is preferred to use a catalyst concentration varying from about 0.0001 to about 10 wt. percent based upon the weight of the heavy hydrocarbon fraction and oxidized heavy hydrocarbon fraction of process steps 1 and 2 respectively still more preferably from about 0.10 to about 10 wt. percent, the catalyst being used at a concentration which is sufficient to promote the effectiveness of the oxidant. The temperature utilized in carrying out oxidation steps 1 and 2 can vary over a wide range and in general a temperature of from about 28° F. to about 450° F. is utilized, depending upon the oxidant, although higher and lower temperatures can be utilized. In general a time within the range of from about 15 minutes to about 24 hours preferably from about one half hour to about 20 hours is utilized in both process steps 1 and 2. In the case of a gas, the time can vary over a wide range depending upon the particular amount of gas such as oxygen or ozone which is passed into the reaction mixture. In general for the oxidation steps 1 and 2 utilizing oxygen, a temperature within the range of from about 100° F. to about 650° F. preferably within the range of from about 200° F. to about 400° F. is utilized. When ozone is utilized as the oxidant, a low temperature such as from 20° F. to about 125° F. is utilized. The number of moles of oxidant utilized can be obtained during the

time utilized for the oxidant contact steps. The oxidant contact steps in general are carried out from atmospheric pressure to about 20 atmospheres although pressures above 20 atmospheres for example up to about 100 atmospheres can be utilized.

The product from process step 2 is then contacted with hydrogen. In general a temperature of from 550° F. to about 900° F. preferably from about 650° F. to about 775° F.; pressures of from about 500 to about 3,000 p.s.i.g. preferably 1,000 to about 2,000 p.s.i.g.; and hydrogen rates of from about 2,000 to about 20,000 preferably from about 4,000 to about 12,000 standard cubic feet (s.c.f.) per barrel of feed are utilized in the hydrogen contact step.

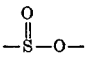
The organic oxidants include by way of example hydrocarbon peroxides, hydroperoxides and hydrocarbon peracids wherein the hydrocarbon radicals in general contains from about 1 to about 30 carbon atoms per linkage. With respect to the hydrocarbon peroxides and hydrocarbon hydroperoxides, it is particularly preferred that such hydrocarbon radical contain from 4 to 30 carbon atoms per peroxide linkage and more particularly from 4 to 16 carbon atoms per peroxide linkage. With respect to the hydrocarbon peracids the hydrocarbon radical which is attached to the carbonyl carbon in general contains from 1 to about 12 carbon atoms more preferably from about 1 to about 8 carbon atoms. It is intended that the term organic peracid includes by way of definition performic acid.

In addition, it is contemplated within the scope of this invention that the organic oxidants can be prepared in situ, that is the peroxides, hydroperoxides or peracids can be generated in the heavy hydrocarbon fraction and such organic oxidant is contemplated for use within the scope of this invention.

Typical examples of hydrocarbon radicals are alkyl such as methyl, ethyl, butyl, t-butyl, 3-methyl-1-pentyl, n-octyl and those aliphatic radicals which represent the hydrocarbon portion of a middle distillate or kerosene, cycloalkyl radicals such as cyclopentyl, alkylated cycloalkyl radicals such as mono and polymethylcyclopentyl radicals, aryl and cycloalkyl substituted alkyl radicals such as phenyl and alkylphenyl substituted alkyl radicals examples of which are benzyl, methylbenzyl, caprylbenzyl, phenylethyl, phenylpropyl, naphthylmethyl, naphthylethyl, aryl radicals such as phenyl, and naphthyl, alkaryl radicals such as xylyl, alkylphenyl, and ethylphenyl.

Typical examples of oxidants are hydroxyheptyl peroxide, cyclohexanone peroxide, t-butyl peracetate, di-t-butyl diperphthalate, t-butyl hydroperoxide, di-t-butyl peroxide, p-menthane hydroperoxide, pinane hydroperoxide, 2,5-dimethylhexane - 2,5 - dihydroperoxide and cumene hydroperoxide, organic peracids, such as performic acid, peracetic acid, trichloroperacetic acid, perbenzoic acid and perphthalic acid.

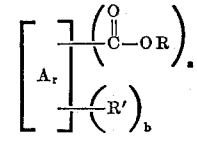
The catalyst which can be utilized in oxidant contact steps 1 and 2 vary with the particular oxidant, the particularly preferred catalysts for use with air being potassium sulfate promoted vanadium oxide on alumina, vanadium oxide plus molybdenum oxide on alumina promoted with magnesium oxide, aluminum vanadate, vanadium oxide such as when prepared by hydrolysis of butyl vanadate with water in the presence of a porous catalyst carrier, silver oxide, vanadium oxide and stannic oxide on pumice, and tin vanadate on asbestos. Examples of catalysts which can be utilized with ozone, organic peroxides, organic hydroperoxides and organic peracids are metals such as titanium, zirconium, vanadium, tantalum, chromium, molybdenum and tungsten, the most preferred catalyst metals being titanium, vanadium, and molybdenum. These catalysts can be incorporated into the oxidation system by any means known to those skilled in the art, and can be either a homogeneous or heterogeneous catalyst system. The catalyst can be incorporated by a variety of means and by the use of a variety of carriers. The particular catalyst carrier which is utilized is not critical with respect to the practice of this invention and can be for example, a support medium or an anion (including complex formation) which is attached to the metal (e.g. a ligand). Illustrative ligands include halides, organic acids, alcoholates, mercaptides, sulfonates and phenolates. These metals may be also bound by a variety of complexing agents including acetylacetones, amines, ammonia, carbon monoxide and olefins, amongst others. The metals may also be introduced in the form of organometallics including "ferrocene" type structures. The various ligands illustrated above which are utilized solely as carriers to incorporate the metal into the process system, in general have an organic radical attached to a functional group such as the oxygen atom of carbonyloxy group of the acid, the oxygen of the alcohol, the sulfur of the mercaptan, the



of the sulfonate, the oxygen of the phenolic compound and the nitrogen of the amines. The organic radical attached to the aforedescribed functional groups can be defined as a hydrocarbon radical and in general can contain from 1 to about 30 carbon atoms. Typical examples of hydrocarbon radicals are set forth above.

The metals contained on the heterogeneous catalyst can include individual or combinations of metals. These metals can be suspended on a suitable material, for example alumina, silica (or combinations of both) as well as activated clays or carbon, amongst others. The modes of contacting whereby the catalytic effect may be achieved may include slurry-bed reactions or continuous contacting over a stationary phase in a trickle-tube reactor.

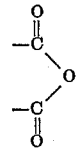
Typical examples of the preferred aromatic polycarboxylic acid and/or anhydride producing compounds are represented by the structural formula:



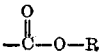
wherein A_r is an aromatic nucleus, each R is independently selected from the group consisting of hydrogen, a lower hydrocarbon radical having from about 1 to about 12 carbon atoms and any two groups represented by



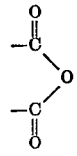
which are attached to adjacent carbon atoms on A_r can together form



each R′ is a hydrocarbon radical, *a* is an integer having a value of from 2 to 4 and *b* is an integer having a value of from 2 to 4 provided that the sum of $a+b$ is not greater than 6. The particularly preferred aromatic carboxylic acid and/or anhydride producing compounds are those compounds represented by the above formula wherein R is selected from alkyl having from 1 to about 6 carbon atoms, hydrogen and any two groups represented by



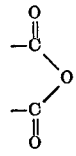
which together form



In a still more preferred embodiment of this invention, *b* is from 0 to 2 more preferably zero and R is selected from hydrogen and any two groups represented by



which together form



When *b* is greater than zero, it is preferred that R' have from about 1 to about 8 carbon atoms more preferably that R' is alkyl having from 1 to about 3 carbon atoms. Typical examples of hydrocarbon radicals representing R and R' are set forth above. In addition, R and R' are defined as hydrocarbon radicals which are non-interfering with respect to the coke suppressing activity of the product prepared using the aromatic polycarboxylic acid and/or anhydride producing compound. By non-interfering is meant that the substituents representing R and R' do not completely nullify the coke suppressing activity of the additive of this invention.

Typical examples of aromatic polycarboxylic acid anhydride producing compounds are phthalic anhyride, m-phthalic acid, terphthalic acid, pyromellitic anhydride, trimellitic anhydride, pyromellitic acid, trimellitic acid, dimethyl terphthalate, diisopropyl terphthalate, dibenzyl terphthalate and dimethyl-o-phthalate.

A wide variety of heavy hydrocarbon fractions and/or distillates can be used as starting reactants to prepare the products of this invention. Such heavy hydrocarbon fractions include full boiling range crude oils, topped or reduced crude oils, atmospheric distillates, vacuum tower bottoms, visbreaker bottoms product, heavy cycle stock from thermal or catalytically-cracked charge stocks, etc. A particularly preferred heavy hydrocarbon fraction which can be utilized to prepare products of this invention are the deasphalted atmospheric and vacuum tower residues which have been topped to temperatures of at least 550° F. at atmospheric pressure.

The coke suppressing additives of this invention are particularly useful for suppressing coke formation in a hydrocracking process, either thermal or catalytic. In general the charge stocks which can be utilized in the hydrocracking process are heavy hydrocarbon fractions which are set forth above as starting materials for producing the additives of this invention. In general the hydrocracking process is carried out in the presence of the coke suppressing additive or mixtures thereof at a total concentration of about from about 0.1 wt. percent to about 10 wt. percent more preferably from about 1 wt. percent to about 8 wt. percent based up on the weight of the hydrocarbon charge stock. The conditions that are utilized in the hydrocracking process are in general temperatures of from about 550° F. to about 850° F., preferably 675 to 775° F.; pressures of from about 500 to about 3,000 p.s.i.g. preferably 1,500 to 2,000 p.s.i.g., liquid hourly space velocities of from about 0.1 to about 10, preferably 0.5 to 2.5, volumes of feed per volume of catalyst per hour; and hydrogen rates of from about 2,000 to about 20,000 preferably 6,000 to 12,000, standard cubic feet (s.c.f.) per barrel of feed.

The hydrocracking catalyst utilized for the conversion of the aforementioned hydrocarbon charge stocks can be crystalline metallic alumino-silicate zeolite, having a platinum group metal (e.g. platinum or palladium) deposited thereon or composition therewith. These crystalline zeolites are characterized by their highly ordered crystalline structure and uniformly dimensioned pores, and have an alumino-silicate anionic cage structure wherein alumina and silica tetrahedra are intimately connected to each other so as to provide a large number of active sites, with the uniform pore openings facilitating entry of certain molecular structures. It has been found that crystalline alumino-silicate zeolites, having effective pore diameter of about 6 to 15, preferably 8 to 15 angstrom units, when composited with the platinum group metal, and particularly after base exchange to reduce the alkali metal oxide (e.g. NaO) content of the zeolite to less than about 10 wt. percent, are effective hydrocracking catalysts, particularly for the hydrocarbon oil feeds herein contemplated.

In addition, the catalyst can be a supported hydrogenation catalyst comprising a Group VIII metal in the Periodic Table, such as nickel, cobalt, iron or one of the platinum group metals such as palladium, platinum, iridium, or ruthenium on a suitable support. Generally, it is preferred that an oxide or sulfide of a Group VIII metal (particularly iron, cobalt or nickel) be present in mixture with an oxide or sulfide of a Group VI–B metal (preferably molybdenum or tungsten). Suitable carriers or supports include acidic supports such as: silica-alumina, silica-magnesia, and other well-known cracking catalyst bases; the acidic clays; fluorided alumina; and mixtures of inorganic oxides, such as alumina, silica, zirconia, and titania, having sufficient acidic properties providing high cracking activity.

The invention can be better appreciated by the following non-limiting examples.

In the following examples a San Ardo crude was utilized as the heavy hydrocarbon charge stock. The crude had the following properties:

Gravity, ° API	12.6
Carbon residue, wt. percent	9.4
Sulfur, wt. percent	2.0
Total nitrogen, wt. percent	0.82
DPI flask dist., wt. percent:	
IBP–400° F.	----
400–650° F.	16.6
650–850° F.	23.3
Residue	60.1

EXAMPLE 1

To a reactor equipped with a stirrer, heating means and gas inlet and exit tubes is charged a San Ardo crude and a potassium sulfate promoted vanadium oxide on alumina catalyst. During the continuous oxidation of the San Ardo crude, a temperature of 350° F., an air pressure of 50 p.s.i.g., a liquid hourly space velocity (L.H.S.V.) of 1.0 and an air rate of 6000 s.c.f.b. is maintained. The oxidized crude is reduced in temperature and charged to a pressure reactor together with one wt. percent phthalic anhydride. The temperature is increased to 300° F. and an air pressure of 600 p.s.i.g. is maintained for a period of 3 hours. The temperature is reduced to ambient temperature, and the product charged to a reactor. The temperature is increased to 750° F. and maintained under a hydrogen atmosphere of 1500 p.s.i.g. for a period of 2 hours. The temperature is reduced to ambient temperature and a carbon-like polymeric material is filtered from the liquid heavy hydrocarbon fraction. The polymeric material represents 6.4 wt. percent based upon the weight of San Ardo crude charge to the first oxidation step.

EXAMPLE 2

To a reactor equipped with a stirrer, heating means and gas inlet and exit tubes is charged a San Ardo crude and a potassium sulfate promoted vanadium oxide on alumina catalyst. During the continuous oxidation of the San Ardo crude a temperature of 350° F., an air pressure of 50 p.s.i.g., a liquid hourly space velocity (L.H.S.V.) of 1.0 and an air rate of 6000 s.c.f.b. is maintained. The oxidized crude is reduced in temperature and charged to a pressure reactor together with two wt. percent 4,5-dimethyl-o-phthalate. The temperature is increased to 300° F. and an air pressure of 600 p.s.i.g. is maintained for a period of 3 hours. The temperature is reduced to ambient temperature, and the product charged to a reactor. The temperature is increased to 750° F. and maintained under a hydrogen atmosphere of 1500 p.s.i.g. for a period of 2 hours. The temperature is reduced to ambient temperature and a carbon-like polymeric material is filtered from the liquid heavy hydrocarbon fraction.

EXAMPLE 3

To a reactor equipped with a stirrer, heating means and gas inlet and exit tubes is charged a San Ardo crude and a potassium sulfate promoted vanadium oxide on alumina catalyst. During the continuous oxidation of the San Ardo crude a temperature of 350° F., an air pressure of 50 p.s.i.g., a liquid hourly space velocity (L.H.S.V.) of 1.0 and an air rate of 6000 s.c.f.b. is maintained. The oxidized crude is reduced in temperature and charged to a pressure reactor together with one wt. percent trimellitic anhydride. The temperature is increased to 325° F. and an air pressure of 600 p.s.i.g. is maintained for a period of 3 hours. The temperature is reduced to ambient temperature and the product charged to a reactor. The temperature is increased to 750° F. and maintained under a hydrogen atmosphere of 1500 p.s.i.g. for a period of 2 hours. The temperature is reduced to ambient temperature and a carbon-like polymeric material is filtered from the liquid hydrocarbon fraction which remained.

EXAMPLE 4

To a reactor equipped with a stirrer, heating means and gas inlet and exit tubes is charged a San Ardo crude and a potassium sulfate promoted vanadium oxide on alumina catalyst. During the continuous oxidation of the San Ardo crude a temperature of 350° F., an air pressure of 50 p.s.i.g., a liquid hourly space velocity (L.H.S.V.) of 1.0 and an air rate of 6000 s.c.f.b. is maintained. The oxidized crude is reduced in temperature and charged to a pressure reactor together with 1.5 wt. percent pyromellitic anhydride. The temperature is increased to 300° F. and an air pressure of 600 p.s.i.g. is maintained for a period of 3 hours. The temperature is reduced to ambient temperature and the product charged to a reactor. The temperature is increased to 750° F. and maintained under a hydrogen atmosphere of 1500 p.s.i.g. for a period of 2 hours. The temperature is reduced to ambient temperature and a carbon-like polymeric material filtered from the liquid heavy hydrocarbon fraction.

EXAMPLE 5

To a reactor equipped with a stirrer, heating means and gas inlet and exit tubes is charged a San Ardo crude and a potassium sulfate promoted vanadium oxide on alumina catalyst. During the continuous oxidation of the San Ardo crude a temperature of 350° F., an air pressure of 50 p.s.i.g., a liquid hourly space velocity (L.H.S.V.) of 1.0 and an air rate of 6000 s.c.f.b. is maintained. The oxidized crude is reduced in temperature and charged to a pressure reactor together with 0.90 wt. percent di methyl terphthalate. The temperature is increased to 300° F. and an air pressure of 600 p.s.i.g. is maintained for a period of 3 hours. The temperature is reduced to ambient temperature and the product charged to a reactor. The temperature is increased to 750° F. and maintained under a hydrogen atmosphere of 1500 p.s.i.g. for a period of 2 hours. The temperature is reduced to ambient temperature and a carbon-like polymeric material filtered from the liquid heavy hydrocarbon fraction.

EXAMPLE 6

To a reactor equipped with a stirrer, heating means and gas inlet and exit tubes is charged a San Ardo crude and a potassium sulfate promoted vanadium oxide on alumina catalyst. During the continuous oxidation of the San Ardo crude a temperature of 350° F., an air pressure of 50 p.s.i.g., a liquid hourly space velocity (L.H.S.V.) of 1.0 and an air rate of 6000 s.c.f.b. is maintained. The oxidized crude is reduced in temperature and charged to a pressure reactor together with 2.2 wt. percent di cyclo hexyl o-phthalate. The temperature is increased to 290° F. and an air pressure of 700 p.s.i.g. is maintained for a period of 3 hours. The temperature is reduced to ambient temperature and the product charged to a reactor. The temperature is increased to 750° F. and maintained under a hydrogen atmosphere of 1500 p.s.i.g. for a period of 2 hours. The temperature is reduced to ambient temperature and a carbon-like polymeric material is filtered from the liquid heavy hydrocarbon fraction.

EXAMPLE 7

To a reactor equipped with a stirrer, heating means and gas inlet and exit tubes is charged a San Ardo crude and a potassium sulfate promoted vanadium oxide on alumina catalyst. During the continuous oxidation of the San Ardo crude a temperature of 350° F., an air pressure to 50 p.s.i.g., a liquid hourly space velocity (L.H.S.V.) of 1.0 and an air rate of 6000 s.c.f.b. is maintained. The oxidized crude is reduced in temperature and charged to a pressure reactor together with 1.3 wt. percent tere-phthalic acid. The temperature is increased to 300° F. and an air pressure of 600 p.s.i.g. is maintained for a period of 3 hours. The temperature is reduced to ambient temperature and the product charged to a reactor. The temperature is increased to 750° F. and maintained under a hydrogen atmosphere of 1400 p.s.i.g. for a period of 3 hours. The temperature is reduced to ambient temperature and a carbon-like polymeric material filtered from the liquid heavy hydrocarbon fraction.

EXAMPLE 8

Evaluation of the additive of this invention is carried out in an autoclave charged with San Ardo crude in comparative runs at 1500 p.s.i.g. hydrogen pressure and 725° F. for a period of 15 hours using as coke suppressant the product of Example 1. Data are as follows:

Run	A	B
Additive, wt. percent		6.4
Sulfur, wt. percent	1.00	1.02
Nitrogen, p.p.m.	6,872	8,168
Carbon residue	7.02	7.06
Coke, wt. percent	4.5	0.0
Yield, wt. percent:		
Light ends	4.7	2.5
IBP-400° F	13.9	12.6
400-650° F	33.7	32.2
650-850° F	22.4	24.1
850° F.+	25.1	28.6

The above results demonstrate the outstanding coke suppressing property of the additives of this invention. More particularly, a comparison between Runs A and B demonstrates that a hydrocracking process carried out in the absence of an additive produces 4.6 wt. percent coke whereas the same hydrocracking process utilizing the coke suppressing additive of this invention shows no coke formation.

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.

We claim:

1. A coke suppressing additive prepared by (1) oxidizing a crude petroleum oil to produce an increase in its oxygen content within the range of from about 0.25 wt. percent to about 5.0 wt. percent with an oxidant selected from the group consisting of air, oxygen, activated oxygen, ozone, organic peroxides, organic hydroperoxides and organic peracids, (2) interacting said oxidized crude petroleum oil from step 1 with from about 0.1–20% by weight based on said oxidized crude petroleum oil of a member of the group consisting of mononuclear aromatic polycarboxylic compounds containing from 2 to 4 carboxylic groups, their anhydrides and their lower hydrocarbon esters in which each lower hydrocarbon group contains from 1 to 12 carbon atoms in the presence of an oxidizing agent selected from the group consisting of air, oxygen, activated oxygen, ozone, organic peroxides, organic hydroperoxides and organic peracids, (3) contacting the product from step 2 with hydrogen at a temperature between about 550° F. and 900° F. and a pressure between about 500 and 3000 p.s.i.g. and (4) separating a carbon-like material from the liquid hydrogenation product.

2. The product of claim 1, wherein the aromatic polycarboxylic compound is phthalic anhydride.

3. The product of claim 1, wherein the oxidant in process steps 1 and 2 is air and step 1 is carried out in the presence of a vanadium oxide catalyst.

4. The product of claim 1 wherein the oxidant in process steps 1 and 2 is air, process step 1 is carried out in the presence of a vanadium oxide catalyst and the crude petroleum oil is a reduced crude.

5. The product of claim 1 in which the polycarboxylic compound contains 2 carboxylic groups.

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