

3,053,756
REFINING OF INDUSTRIAL HYDROCARBON MIXTURES

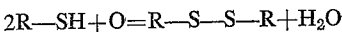
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This invention relates to the refining of hydrocarbons. It is already known to carry out the refining of industrial hydrocarbons or mixtures thereof with oxygen or oxygen-containing gases, as for example with air.

It has also already been proposed to treat diesel oils with air and then or simultaneously to lead them over active carbon.

The removal of sediment-forming constituents from fuel oils by treatment of the oils with air in the presence of oxidation catalysts has also already been recommended.

The action of the oxygen in these cases in the oxidation of the sulfur-containing compounds, as for example mercaptans, in gasolines is to form relatively harmless disulfides. Doctor-negative products are thus obtained according to the equation:



Nitrogenous compounds, as for example derivatives of pyrrole and its homologues (which are known to be frequently present in shale oil products, but also in many petroleum fractions) are polymerized, condensed or resinified with the aid of oxygen. The conversion products formed may then be removed from the hydrocarbon mixtures, for example by redistillation or by treatment with bleaching earths or active carbon.

Oxygen-containing compounds, such as coumarone and indene or their derivatives, behave similarly.

Diolfines and other readily reacting olefines are similarly brought to condensation and polymerization under the influence of the oxygen.

We have now found that industrial hydrocarbon mixtures, such as gasolines, diesel oils, fuel oils, lubricating oils and the like can be refined with oxygen-containing gases or with agents which yield oxygen and which are soluble in hydrocarbons, by using as catalyst an organo-metallic compound of the type $Me_a(R)_x(CO)_y$ in which Me represents a metal selected from the class consisting of metals of groups VIA, VIIA and VIII of the periodic system, *a* a whole number from 1 to 4, R an aromatic ligand (i.e. an attached atom or group), *x* one of the numbers 1 to 5, and *y* one of the numbers from zero to 9.

Examples of suitable metals are manganese, iron, cobalt, nickel, molybdenum and chromium.

Suitable aromatic ligands are for example benzene or its alkylated or arylated homologues, such as toluene, xylenes, mesitylene, hexamethylbenzene, ethylbenzene, diethylbenzenes, propylbenzene, diphenyl, diphenylmethane, triphenylmethane, tetraphenylmethane, diphenylethane, tetrahydronaphthalene, anthracene, phenanthrene, pyrene, benzpyrene and coronene. Cyclopentadiene or its alkylated or arylated homologues, such as methylcyclopentadiene, dimethylcyclopentadiene, ethylcyclopentadiene, diethylcyclopentadiene, phenylcyclopentadiene, fluorene and the like are also especially suitable.

In the treatment of industrial hydrocarbons with oxygen-containing gases or with agents which give off oxygen and are soluble in hydrocarbons, the reaction of the undesirable impurities is catalysed by the said organo-metallic compounds and insoluble slimy precipitates separate out after a short time. In most cases, the organo-

metallic compounds also decompose, especially when the hydrocarbons are exposed to the action of heat or light and when large amounts of oxygen are allowed to act at elevated temperature on the raw material to be refined. In such cases the precipitates obtained contain not only the reacted impurities but also the decomposed organo-metallic compounds.

The separation of the precipitates may be effected in a manner known per se by sedimentation, decantation, filtration, centrifuging, distillation or the like.

If it is undesirable for the organo-metallic compounds to remain in the raffinate, a decomposition of these compounds can be effected after the refining by heating or by irradiation with light, for example with mercury vapor lamps. When gasolines are being refined by the process according to this invention, and the organo-metallic compounds used exert an antiknock action, they need not be removed or completely removed from the refined gasoline.

The refined product may be after-treated in manner known per se with active carbon or bleaching earths.

The refining with oxygen-containing gases is in general effected in an industrially simple manner by blowing in air into the hydrocarbon mixture to be refined in stirring vessels, pressure vessels, columns, pipelines or the like, it being preferable always to add only such an amount of oxygen-containing gas as is dissolved by the hydrocarbons.

Instead of atmospheric oxygen, there may also be used compounds which readily give off oxygen, especially peroxides which are soluble in hydrocarbons, such as benzoyl peroxide, diacetyl peroxide, dilauroyl peroxide, dibenzoyl peroxide, di-para-toluoyl peroxide and di-tertiary-butyl peroxide.

Gasolines containing peroxides, as for example thermal reformates or cracking gasolines, which have stood for a long time in the air are also suitable in many cases as agents for supplying oxygen. These gasolines are thereby refined at the same time and can be recovered by distillation, if they are not to remain in the raffinate mixture. The reaction can be directed so that the peroxide oxygen completely disappears.

The following examples will further illustrate this invention but the invention is not restricted to these examples.

Example 1

0.030% by weight of ethylmercaptan is added to a straight-run gasoline of commerce so that the gasoline shows a clearly positive doctor test. To a series of samples of this gasoline containing mercaptan, each of 50 cc., there is added to each 0.1% by weight of the organo-metallic compounds specified in Table 1 which completely dissolves in the gasoline. Each of the samples is then enclosed in an ASTM-bomb (see C. Zerbe, Mineralole und Verwandte Produkte (Mineral Oils and Allied Products), 1952, page 519) and treated with oxygen under a pressure of 3 atmospheres. After standing for 10 minutes at 100° C., each bomb is rapidly cooled, opened and the ethyl mercaptan content of the sample determined.

TABLE 1

	Content of C_2H_5SH in grams per liter	Doctor test
blank sample	0.027	strongly positive.
$Ni(C_6H_5)_2$ 0.1% by weight	0	negative.
$Cr(mesitylene)_2$ 0.1% by weight	0	Do.
0.09% by weight of $Mn((C_6H_5)(CO))_3 + 0.01\%$ by weight of $Ni(C_6H_5)_2$	0	Do.

In the blank sample (without the addition of catalyst) it is always possible, after the end of the oxygen treat-

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ment, to detect 90% by weight of the ethyl mercaptan originally present. The doctor test is strongly positive.

In the samples which have been treated with organo-metallic compounds, the mercaptan has disappeared. The gasoline shows negative doctor tests and therefore contains no mercaptan sulfur.

Part of the catalyst is flocculated out by the development of heat. If the samples are exposed to sunlight or irradiated with ultraviolet light, the remainder of the organo-metallic compounds decompose within a few minutes and are precipitated quantitatively. The decomposed catalyst can easily be separated by decantation, centrifuging or filtration.

Example 2

A benzene mixture of commerce, which contains benzene, toluene and xylenes, has 0.05% by weight of ethyl mercaptan added thereto. If a solution of benzoyl peroxide in pure benzene is then added, oxidation of the ethyl mercaptan takes place only extremely slowly.

If the solution is equally divided into a sample A and a sample B and there is added to sample A such an amount of a concentrated solution of $\text{Ni}(\text{C}_5\text{H}_5)_2$ in benzene that this sample contains 0.01% by weight thereof, oxidation takes place instantaneously. The ethyl mercaptan is converted into the sulfide and sample A shows a negative doctor test. By short irradiation with an ultraviolet lamp (about 5 minutes), the decomposed catalyst is completely flocculated out and can readily be filtered off. A good benzene mixture free from mercaptan is obtained. Even after 3 hours, sample B shows a clearly more positive doctor test and thus contains, in contrast to sample A, mercaptan sulfur and is therefore corrosive.

Example 3

A clearly doctor-positive gasoline which originates from a catalytic cracking plant and shows a consumption of 2.8 ccs. of 0.005-normal AgNO_3 solution per 100 ccs. (mercaptan determination according to C. Zerbe—see Example 1) has added thereto a mixture of 8 parts of methylcyclopentadienyl manganese tricarbonyl and 2 parts of $\text{Cr}(\text{mesitylene})_2$. The total concentration of catalyst is 0.07%.

100 parts by weight of this gasoline to which the organo-metallic compounds have been added, then have added thereto 2 parts by weight of a thermally reformed gasoline which by reason of prolonged standing in contact with air has a peroxide number of 0.02, and the temperature is raised to 50° C.

This mixture (A) very soon shows a negative doctor test and has thus become free from mercaptan. The peroxide number of the mixture has fallen to zero.

In a blank sample (B) without added catalyst, mercaptan could still be clearly detected after half an hour.

By irradiation for a short time with an ultraviolet lamp, the catalyst mixture in sample A can be rapidly decomposed and the deposited flocks separated from the refined gasoline by filtration.

Example 4

A recycle oil from a catalytic cracking plant and which boils in the boiling range of a gas oil is mixed in the ratio 2:1 with a heavy gasoline from a thermal cracking plant. In general such mixtures are unstable. Upon standing, especially upon prolonged exposure to light, they deposit insoluble sediments which lead to cloudiness. 0.1% by weight of $\text{Ni}(\text{C}_5\text{H}_5)_2 + (\text{CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_3$ in the ratio 1:1 is added to 50 parts by weight of such a mixture (sample A).

Sample A, and also a second sample of the same size without additive (sample B), are treated in separate ASTM-bombs with oxygen at 7 atmospheres and 100° C. for 2 hours. After the test has been completed, sample A has become very pale and shows at the bottom of the vessel a resinous deposit consisting of organic insoluble

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substance and decomposed catalyst. It weighs 0.124 part by weight.

Sample B is considerably darker than sample A and does not show any deposit.

After filtration, sample A shows a color number of 1 in the Saybold colorimeter, and sample B a color number of 2.3. An untreated sample shows a color number of 2. Thus by catalytic refining with oxygen an improvement in color of the sample A treated according to this invention is achieved. Moreover sample A remains stable in light for 46 hours before traces of cloudiness occur, whereas sample B shows a strong cloudiness even after 14 hours upon standing in light under the same conditions. An untreated sample behaves similarly to sample B.

Example 5

A distillate fuel oil from Middle East crude oil with a typically unpleasant odor and strongly positive doctor test has 0.05% by weight of $\text{Ni}(\text{C}_5\text{H}_5)_2$ added thereto (sample A).

This sample, and also a second sample of the same fuel oil without added catalyst (sample B), are heated separately, each in an ASTM-bomb, at an oxygen pressure of 7 atmospheres for 15 minutes at 100° C. After cooling, releasing the pressure and opening the pressure vessels, sample A is practically odorless and shows a doctor negative reaction. Sample B smells almost as unpleasant as the untreated oil and is clearly doctor positive. In sample A the greater part of the catalyst has decomposed under the influence of heat and has flocculated out. By heating for a short time at 140° C., the last traces of dissolved catalyst in sample A can be decomposed and readily separated by simple filtration.

Example 6

A crude diesel oil fraction from a Texas crude oil shows a strongly positive doctor test and a consumption of 7.8 ccs. of 0.005-normal AgNO_3 solution per 100 ccs.

By adding 0.05% by weight of $(\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_2)_2$ to 50 parts by weight of this oil (sample A) and leaving the sample to stand under an oxygen pressure of 7 atmospheres for 5 minutes at 100° C., the sample is doctor negative after the end of the oxygen treatment. A part of the catalyst decomposes and is deposited. The product obtained shows no consumption of 0.005-normal AgNO_3 solution.

By short heating of the sample at 130° C., the remainder of the catalyst decomposes and can be filtered off as a brown precipitate with the deposited impurities. The filter residue, after washing with petroleum ether and drying, amounts to 0.1% by weight of the oil treated.

It contains the impurities which have been refined out from the oil and also the decomposed catalyst.

Another sample (sample B) treated with oxygen at the same time under the same conditions without added catalyst remains strongly doctor positive and has an unpleasant odor.

Example 7

0.09% by weight of pyrrole is dissolved in a shale oil gasoline. 0.05% by weight of $\text{Ni}(\text{C}_5\text{H}_5)_2$ are added to 50 parts by weight of the solution (sample A).

This sample A, and also a second sample of 50 parts by weight without added Ni-catalyst (sample B), are heated separately under an oxygen pressure of 7 atmospheres in ASTM-bombs at 100° C. for 10 minutes. After opening the pressure vessels it is found that a dark precipitate has settled from sample A. Sample B is clear and nothing has settled out from it.

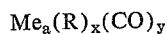
After exposure for a short time to a strong mercury vapor lamp for the purpose of decomposing the catalyst residue, sample A is filtered. Then the ASTM-glass dish values of sample A and of sample B are determined according to C. Zerbe, Mineralole und Verwandte Produkte, page 514.

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Sample A has only 9 mg./100 ccs. of gum residue, while on the contrary sample B shows a gum residue of 47 mg./100 ccs.

We claim:

1. A process for refining industrial hydrocarbons which are petroleum fractions selected from the group consisting of gasolines, diesel oils, fuel oils and lubricating oils which comprises treating said industrial hydrocarbons with oxygen in the presence of a catalyst of the formula



in which Me represents a metal selected from the class consisting of metals of groups VIA, VIIA and VIII of the periodic system, a represents one of the numbers from 1 to 4, inclusive, R represents a ligand selected from the group consisting of aromatic and cyclopentadiene hydrocarbons, x represents one of the numbers from 1 to 5, inclusive, and y represents one of the numbers from zero to 9, inclusive.

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2. A process as claimed in claim 1 wherein the catalyst is nickel dicyclopentadiene.

3. A process as claimed in claim 1 wherein the catalyst is chromium dimesitylene.

4. A process as claimed in claim 1 wherein the catalyst is manganese cyclopentadiene tricarbonyl.

5. A process as claimed in claim 1 wherein the catalyst is manganese di-monomethylcyclopentadiene tricarbonyl.

6. A process as claimed in claim 1 wherein the catalyst is $[\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_2]_2$.

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