

1

3,192,152

PROCESS FOR THE REMOVAL OF MERCAPTANS FROM HYDROCARBON OILS

Herve Maze, Jacques Mauborgne, and Rene Reinhold, Paris, France, assignors to Shell Oil Company, New York, N.Y., a corporation of Delaware

No Drawing. Filed July 18, 1962, Ser. No. 210,825

Claims priority, application France, July 21, 1961,

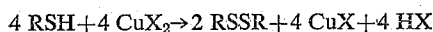
868,646

4 Claims. (Cl. 208—191)

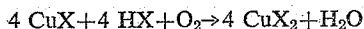
The invention relates to a process and a catalyst for the removal of mercaptans from hydrocarbon oils. More particularly, mercaptans are removed from hydrocarbon oils by a treatment with one or more copper compounds, preferably in the presence of oxygen.

The fundamental reactions taking place during this type of sweetening process are the same in principle for the various copper compounds. In the case of a copper compound CuX_2 the course of these reactions may be represented as follows:

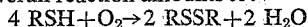
Reaction:



Regeneration:



Thus the overall reaction amounts to:



In principle the sweetening process is very attractive since, owing to their cupric-cuprous form, the copper compounds serve solely as oxidation medium. It follows from the above reactions that theoretically there is no consumption of chemicals other than oxygen.

However, when the process is carried out in practice, small quantities of copper compounds are dissolved in the hydrocarbon oil treated, which is a serious drawback, not only because this dissolution implies losses of copper compounds but also, what is more important, because even traces of copper compounds have a very unfavorable effect on the color and color stability of the refined hydrocarbon oil.

It has now been found in accordance with this invention that the complex copper compounds, supported on active carbon, are capable of acting as an oxidation catalyst for mercaptans, while these compositions have the very important advantage that the oils treated contain only a very slight amount of copper.

The invention relates to a process for the preparation of hydrocarbon oils entirely or substantially freed from mercaptans, by treating a hydrocarbon oil containing mercaptans with one or more copper compounds, preferably in the presence of oxygen, supported on active carbons.

Examples of hydrocarbons suitable for treatment according to the invention are both the fractions obtained by straight-run distillation of crude oil and the hydrocarbon oils obtained by thermal or catalytic cracking or by thermal reforming. The sweetening treatment is applied in particular to light hydrocarbon oils, such as gasoline and kerosine, and to fractions containing normally gaseous components, e.g. fractions containing propane/propene and butane/butene. The process is also suitable for use in the treatment of gas oils.

The hydrocarbon oils to be treated according to the

2

process of the invention are preferably free or substantially free from zinc, since it has been found that traces of zinc considerably reduce the life of the catalyst. The absence of zinc may be ensured, for example, by avoiding as far as possible contact between the hydrocarbon oils and materials containing zinc during the preparation and storage of the starting materials.

Should the hydrocarbon oil to be sweetened contain hydrogen sulfide and/or other fairly acid components, such as phenols and thiophenols, it is advisable to eliminate them entirely or in part, for instance, by means of a caustic wash before the sweetening treatment.

The elimination of mercaptans by means of a treatment with complex copper compounds supported on active carbon may be effected in various ways. For example, the complex copper compounds supported on active carbon may be used in the form of one or more fixed beds through which is passed the hydrocarbon oil to be treated, or as a slurry in the hydrocarbon oil to be treated. When the slurry technique is used the hydrocarbon oil is contacted for some time with the catalyst. The catalyst is then separated from the sweetened hydrocarbon oil in a separator, after which it may again be contacted with fresh quantities of hydrocarbon oil.

Oxygen, or a gas containing oxygen, such as air, may be used for the regeneration of the reduced copper compound, although use may also be made of such peroxides as ozone which form oxygen under the reaction conditions. The oxygen is preferably introduced into the hydrocarbon oil before the sweetening treatment, for example by injection of air under pressure, viz. the hydrocarbon oil is contacted with the cupric catalyst in the presence of oxygen and the reaction and the regeneration are effected in a single treatment. It is, however, also possible to carry out the reaction and the regeneration as separate treatments, for instance by following up a reaction phase with a regeneration phase, etc.

The temperatures at which the sweetening treatment is carried out is usually in the range of from 10° to 110° C. They may even be higher, provided they do not exceed the limit of stability of the complex copper compound employed. Temperatures between 20° and 65° C. are preferred.

During the sweetening treatment the space velocities generally vary from 10 to 25 pounds of hydrocarbon per hour per pound of catalyst, but they may be greater or less.

The sweetening treatment can be followed by any treatment known for eliminating the traces of copper compounds dissolved in the treated oil, but in many cases this aftertreatment may be omitted, since during the sweetening treatment according to the present invention the copper content of the product is usually lower than those found in the known processes.

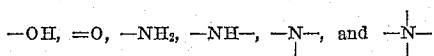
In certain cases it may be advantageous to subject the hydrocarbon oil before the sweetening treatment (and after any washing to eliminate the fairly acid components) to a light treatment with an acid such as hydrochloric acid. A very suitable method is to pass the hydrocarbon oil to be sweetened over active carbon impregnated with hydrochloric acid. This preliminary treatment eliminates the traces of metallic compounds, such as iron and zinc, as well as certain basic reaction compounds. The elimination of these compounds prolongs the activity of the catalyst.

In accordance with the process of the invention complex copper compounds supported on active carbon are used. Surprisingly, it has been found that the presence of active carbon as support material is essential for obtaining the best results. In particular, it has been found that when use is made of other support materials such as alumina, silica gel, the silica-alumina cracking catalyst etc., the activity of the catalysts obtained is considerably less than that of active carbon; as a result the admissible space velocities are much lower. Moreover, when use is made of complex copper compounds supported on active carbon the refined products have a much better color and their copper contents are much lower than when use is made of complex compounds supported on other materials.

Active carbons are well known and widely used in numerous industries and are available under various trade names from many manufacturers. Active carbon; its preparation and uses, is thoroughly discussed in the book *Active Carbon*, by John W. Hassler, Chemical Publishing Company, 1951.

Preferred complex copper compounds are the organo-cupric complexes, viz. the complex copper compounds containing one or more organic components.

Very suitable organo-cupric complexes are those based on one or more organic complexing agents containing at least one of the following configurations:



in the molecule since these complexing agents give very stable organo-cupric complexes.

The most attractive organic complexing agents are:

(a) Organic acids, preferably those containing at least one hydroxyl group in the molecule, e.g. tartaric acid, citric acid and glycolic acid;

(b) Alkyl amines such as dimethyl amine, diethyl amine and ethylene diamine;

(c) Alkanol amines such as mono-, di-, and triethanol amine, etc.;

(d) Urea and derivatives thereof, and

(e) Amino acids such as glycocoll, betaine, etc.

If it is desired to use compounds containing an amine configuration, their salts, e.g. their hydrochlorates, may be employed.

Furthermore, with the organic complexing agent or agents, one or more phosphates are preferably incorporated in the copper catalyst, for example mono- or di-ammonium phosphate, since this incorporation improves the color of the products.

The final catalyst should preferably contain 1% to 10% by weight of copper, based on active carbon. A preferred content is from 2% to 4% by weight of copper. The complexing agents may be present in amounts smaller than, equal to, or greater than the stoichiometric amounts corresponding to the specific copper complexes. If phosphates are used, a quantity of 2 to 5% by weight of P_2O_5 (based on active carbon) is preferably incorporated in the catalyst.

It should be noted that the catalyst may have a specific water content (for instance approximately 4%–20% based on active carbon), but activity may decline substantially when the support material absorbs excessive quantities of water. It is important therefore, that the starting hydrocarbon oil should contain little free water. The use of a hydrocarbon oil not saturated with water ensures prolonged activity of the catalyst, since the reaction water formed by the oxidation of the mercaptans into disulfides will be absorbed by the hydrocarbon oil to be treated, which is not saturated with water.

The complex copper compounds supported on active carbon and to be used in the process according to the invention may be prepared in any suitable way.

A preferred method of preparation is one in which an active carbon is impregnated with an aqueous solution

containing one or more cupric salts, is dried, and then impregnated with an aqueous solution containing the complexing agent or agents (and, if desired, with one or more phosphates) and again dried. Any suitable active carbon can be used. It is to be understood that the term active carbon is to apply to any form of carbon that possesses adsorptive power, a meaning well known and understood to those in the art.

EXAMPLES

I. Preparation of the catalysts

(A) *Preparation of a non-complex copper catalyst supported on active carbon.*—A quantity of active carbon (of which the granules had an average diameter of 0.7 mm.) is impregnated with an aqueous solution of cupric chloride containing $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in an amount corresponding to 3% by weight of copper based on the dry carbon.

After 16 hours of contact the impregnated carbon is dried by heating at 80°C . under partial vacuum. The procedure is as follows: When the temperature of the mass reaches 80°C . (thermometer dipping into the mass) a partial vacuum is applied and the mass is agitated, the temperature falls to 35°C ., the vacuum is then broken and air is allowed to enter. The carbon is again heated to 80°C ., air excluded, and the vacuum is applied, the procedure being repeated 15 to 20 times. The carbon is dried under partial vacuum from four to five hours. The resultant carbon, which still contains from 10% to 15% of water, is then dried at 110°C . to 120°C . until its water content is about 5% to 7%. The catalyst obtained will be referred to as catalyst A.

(B) *Preparation of catalysts containing complex copper compounds supported on active carbon.*—Samples of catalyst A are converted by the following process into active carbons containing one or more complex copper compounds.

The catalyst A is impregnated with a number of impregnation solutions in sufficient quantity to wet it without an appreciable excess of solution. In general, 1–2 liters of aqueous solution are needed to wet 1 kg. of dry catalyst A.

After 16 hours of contact the impregnated catalyst A is dried by a process similar to that already described for the preparation of the catalyst A itself, namely by heating to 80°C . under partial vacuum with frequent admission of air. Drying under partial vacuum lasts from four to five hours. The carbon is then dried at 100°C – 120°C . until the water content is from 5% to 7%.

Instead of being dried under partial vacuum the impregnated carbon may also be dried in a rotary furnace through which is passed hot air, etc.

The following impregnation solutions were used:

- (1) Monoethanol amine+di-ammonium phosphate (catalyst B1)
- (2) Diethanolamine+di-ammonium phosphate (catalyst B2)
- (3) Triethanolamine+di-ammonium phosphate (catalyst B3)
- (4) Urea+di-ammonium phosphate (catalyst B4)
- (5) Tartaric acid+di-ammonium phosphate (catalyst B5)
- (6) ammonium oxalate+ethylene diamine (catalyst B6)
- (7) ammonium oxalate+ethylene diamine+di-ammonium phosphate (catalyst B7)
- (8) diethylamine hydrochlorate (catalyst B8)
- (9) diethylamine hydrochlorate+di-ammonium phosphate (catalyst B9)

The concentrations of the different impregnation solutions are from 0.5% to 10% by weight.

When the catalyst A was impregnated with a solution of di-ammonium phosphate and ethanolamine (mono-, di-, or tri-), of urea or of tartaric acid, the amount of

each of the additives used was 5% by weight of dry catalyst A. For instance:

Weight of copper-containing active carbon (catalyst A) to be impregnated -----g-- 150

Impregnation solution prepared with:

Water -----cc-- 180

Di-ammonium phosphate -----g-- 7.5

Complexing agent -----g-- 7.5

The solutions thus prepared were invariably added in their entirety to the catalyst A.

For impregnation with ammonium oxalate+ethylene diamine (catalyst B6) the solution used consisted of 75 cc. of water, 3 g. of ammonium oxalate and 2.5 g. of ethylene diamine to impregnate 50 g. of the catalyst A. For the catalyst B7 a quantity of 2.5 g. of di-ammonium phosphate was also added to this solution.

For the preparation of catalyst B8, use was made of a solution of 2.5 g. of diethylamine hydrochlorate in 75 cc. of water to 50 g. of catalyst A. For the preparation of catalyst B9 a quantity of 2.5 g. of di-ammonium phosphate was also added to this solution.

(C) *Method of preparing complex copper compounds supported on alumina or silica gel.*—The support material to be treated (commercial activated alumina and silica gel) is impregnated with an aqueous solution of cupric chloride containing $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in a quantity corresponding to about 3% of copper applied to the dry support material.

The method of preparation is similar to that used for copper-containing active carbons (see above). The resultant masses are then impregnated with a solution of di-ammonium phosphate and monoethanolamine and dried exactly as in the above-described procedure for the preparation of the complex catalysts. Use was made of an impregnation solution prepared with 180 cc. of water, 7.5 g. of di-ammonium phosphate and 7.5 g. of monoethanolamine to 150 g. of alumina or silica gel.

The catalysts C1 (support material alumina) and C2 (support material silica gel) were obtained.

II. Sweetening tests

In all the experiments the starting material was a straight-run kerosine having the following characteristics:
Boiling range (A.S.T.M.), ° C. ----- Approx. 160–230
Total sulfur, percent----- 0.05–0.2
RSH sulfur, p.p.m. ----- 10–200
Copper, p.p.m. ----- Approx. 0.05
Saybolt color ----- >28

These kerosines were passed through a vertical column filled with 100 g. of a copper catalyst.

The kerosine, previously saturated at ambient temperature by injection of air, was slightly heated and introduced into the bottom of the column. The catalysts used were the various supported cupric compounds described above in section I. In each case, the kerosine leaving the column was practically free from mercaptans (mercaptan sulfur content <3 p.p.m.).

The following tables show the results obtained (Saybolt color determined immediately after sweetening).

PERCOLATION OVER 100 g. OF CATALYST B1

Volume percolated, liters	Temperature, ° C.	Space velocity, g./h.g.	Copper content, p.p.m.	Saybolt color
40-----	50	10.2	0.05	28
80-----	50	10.2	0.05	28
160-----	50	10.2	0.05	28
240-----	50	10.2	0.05	28
320-----	50/60	10.2/12	0.05	26
400-----	60	12	0.15	26
480-----	60	12	0.2	26

¹ The value 0.05 p.p.m. corresponds to the limit of accuracy of the method of analysis used. This value therefore indicates a copper content of 0.05 p.p.m. or even less.

² After 320 liters had been passed through, the temperature was increased from 50° to 60° C. and the space velocity from 10.2 to 12 g./h. g.

PERCOLATION OVER 100 g. OF CATALYST B2

Volume percolated, liters	Temperature, ° C.	Space velocity, g./h.g.	Copper content, p.p.m.	Saybolt color
40-----	50	13	0.05	27
80-----	50	13	0.05	26
160-----	50	13	0.05	25
240-----	50	13	0.05	23
320-----	50	13	0.05	23
400-----	50	13	0.05	23
480-----	50	13	0.05	23

PERCOLATION OVER 100 g. OF CATALYST B3

Volume percolated, liters	Temperature, ° C.	Space velocity, g./h.g.	Copper content, p.p.m.	Saybolt color
40-----	60	14.4	0.15	30
80-----	60	14.4	0.15	30
160-----	60	14.4	0.15	30
240-----	60	14.4	0.15	30
320-----	60	14.4	0.15	30
400-----	60	14.4	0.15	29

PERCOLATION OVER 100 g. OF CATALYST B4

Volume percolated, liters	Temperature, ° C.	Space velocity, g./h.g.	Copper content, p.p.m.	Saybolt color
40-----	60	16	0.05	28
60-----	60	16	0.05	28
80-----	60	16	0.05	28
100-----	60	16	0.05	28

PERCOLATION OVER 100 g. OF CATALYST B5

Volume percolated, liters	Temperature, ° C.	Space velocity, g./h.g.	Copper content, p.p.m.	Saybolt color
160-----	60	10.4	0.05	30
340-----	60	10.4	0.05	29
500-----	60	10.4	0.05	27

PERCOLATION OVER 100 g. OF CATALYST B6

Volume percolated, liters	Temperature, ° C.	Space velocity, g./h.g.	Copper content, p.p.m.	Saybolt color
40-----	60	16	0.18	24
80-----	60	16	0.37	21

PERCOLATION OVER 100 g. OF CATALYST B7

Volume percolated, liters	Temperature, ° C.	Space velocity, g./h.g.	Copper content, p.p.m.	Saybolt color
40-----	60	16	0.05	27
80-----	60	16	0.05	27
100-----	60	16	0.05	27

PERCOLATION OVER 100 g. OF CATALYST B8

Volume percolated, liters	Temperature, ° C.	Space velocity, g./h.g.	Copper content, p.p.m.	Saybolt color
40-----	60	16	1.2	27
80-----	60	16	1.5	25

PERCOLATION OVER 100 g. OF CATALYST B9

Volume percolated, liters	Temperature, ° C.	Space velocity, g./h.g.	Copper content, p.p.m.	Saybolt color
40-----	60	16	0.05	28
80-----	60	16	0.05	28
100-----	60	16	0.05	28

7

The comparative experiments with catalysts B6 and B7 and with B8 and B9 show the favorable effect of the phosphate on the color and in particular on the copper content of the products.

PERCOLATION OVER 100 g. OF CATALYST A
(Comparative experiment only)

Volume percolated, liters	Tempera- ture, ° C.	Space velocity, g./h.g.	Copper content, p.p.m.	Saybolt color
40-----	60	13	0.2	12
80-----	60	13	1.35	14

This experiment may be directly compared with the experiment with catalyst B2 (same starting material, etc.); the comparison shows the very favorable effect of the complexing agent on the color and copper content of the products.

PERCOLATION OVER 100 g. OF CATALYST C1

Volume percolated, liters	Tempera- ture, ° C.	Space velocity, g./h.g.	Copper content, p.p.m.	Saybolt color
10-----	60	2.4	0.05	19
20-----	60	2.4	0.05	22
30-----	60	2.4	1.5	18
40-----	60	2.4	>5	<-6

PERCOLATION OVER 100 g. OF CATALYST C2

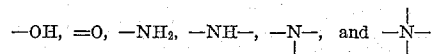
Volume percolated, liters	Tempera- ture, ° C.	Space velocity, g./h.g.	Copper content, p.p.m.	Saybolt color
10-----	60	1.4	0.05	15
20-----	60	1.4	0.45	12
24-----	60	1.4	1.2	8

These two experiments may be readily compared with the test with catalyst B1 and it is quite evident that only catalyst B, which contains active carbon as support material, gives satisfactory results.

8

We claim as our invention:

1. A process for sweetening mercaptan-containing hydrocarbon oils which comprises contacting the oil with an active-carbon-supported organo cupric complex which contains at least one of the radicals selected from the group consisting of



- 10 and recovering a hydrocarbon oil substantially free from copper.

2. A process for sweetening mercaptan-containing hydrocarbon oils which comprises contacting the oil in the presence of oxygen with an active-carbon-supported cupric complex of a member of the group consisting of alkyl amines, alkanol amines, alkanolic acids, and amino acids, and recovering a hydrocarbon oil substantially free from mercaptans and copper.

3. The process of claim 2 wherein copper is present on the active carbon in the amount of 1% to 10% by weight basis carbon.

4. The process of claim 2 wherein the active carbon also contains 2 to 5% by weight, basis active carbon, of P_2O_5 .

References Cited by the Examiner

UNITED STATES PATENTS

2,338,371	1/44	Workman	208—191
2,539,808	1/51	Brooner	208—192
2,744,854	5/56	Urban	208—191
2,792,334	5/57	Maguerian	208—191
2,920,050	1/60	Blacet et al.	252—444
2,920,051	1/60	Wiig et al.	252—444

FOREIGN PATENTS

1,117,807 11/61 Germany.

ALPHONSO D. SULLIVAN, *Primary Examiner*.

MAURICE A. BRINDISI, *Examiner*.