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2,918,426

SWEETENING OF HYDROCARBONS CONTAINING MERCAPTANS AND/OR MERCAPTIDES WITH A CHELATE AND OXYGEN

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6 Claims. (Cl. 208—206)

The present invention relates to the treatment of hydrocarbons and mixtures of hydrocarbons containing mercaptans and/or mercaptides, in which these compounds are converted into disulfides.

It is known that it is possible to effect sweetening of petroleum-type hydrocarbons, or of their distillation fractions, by oxidation with oxygen or any gaseous mixture containing oxygen, of the mercaptans and/or mercaptides contained therein to disulfides, in the presence of chelate organo-metallic compounds, obtained by condensation of an iminophenol and a metal of group VIII of the periodic system, or of suitable compounds to form the chelate compound in situ.

In United States patent specification No. 2,659,691 and in the applications Serial No. 340,918 of March 6, 1953, now U.S. Patent No. 2,823,173, Serial No. 385,274 of October 9, 1953, now abandoned, and Serial No. 411,256 of February 18, 1954, there are described processes for sweetening petroleum fractions, and various preferred embodiments of these processes.

It has, however, been found by the applicants that the direct application of such a process under general conditions may lead to the occurrence of secondary reactions, which are inconvenient and limit the economic advantage of the process. In fact, on oxidation of the mercaptans and/or mercaptides, it is possible that the degree of oxidation corresponding to the formation of the disulfides may be exceeded and other oxidation products may be formed; these products, although present in small quantities, nevertheless have the disadvantage of being sufficiently unstable to decompose, in turn, under normal storage conditions, for example, into various products having an acid reaction and causing, inter alia, the formation of gums, reduction of the induction period of the petroleum fractions, regeneration of small quantities of mercaptans and so on.

This invention relates to a method of oxidizing mercaptans and/or mercaptides to disulfides, by the action of oxygen or any gaseous mixture consisting essentially of oxygen, in the presence of chelate organo-metallic compounds, obtained by condensation of an iminophenol and a metal of group VIII—or of suitable compounds to form the chelate compound in situ—under determined conditions of temperature and pressure.

Various manners of performance and improvements characteristic of the present invention will be explained in the following description.

It has been found that it is possible to avoid the development of secondary reactions during the oxidation of mercaptans and/or mercaptides to disulfides, and to limit, in fact prevent, in this way the formation of oxidation products other than disulfides, by working at a temperature greater than the ambient temperature and of about 30° C. or more, and at atmospheric pressure.

Moreover, the present invention permits a very considerable increase of the speed of oxidation of the mer-

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captans and/or mercaptides to disulfides, that is, a reduction in the time required for attaining sweetening of the "sour" petroleum fractions by the action of atmospheric oxygen in the presence of chelate organo-metallic compounds or of compounds suitable for forming them in situ.

Another considerable advantage of the method according to the invention is to effect substantial economies in the amounts used of the chelate organo-metallic compounds, or of compounds suitable for forming them in situ, while enabling sweetening of the treated products to be effected at speeds of reaction that are satisfactory from the industrial viewpoint.

Specific embodiments of the invention will now be described by way of example.

EXAMPLE 1

In this example, specially intended to show that the method according to the invention limits, or rather prevents, the formation of compounds more oxidized than the disulfides, a known mercaptan—tert.-butyl mercaptan—is oxidized in solution in a defined hydrocarbon, namely benzene.

Four 1-litre samples of benzene, containing 0.410 g. of sulfur in the form of tert.-butyl mercaptan, are treated at atmospheric pressure with pure oxygen in the presence of 0.49 ml. of a cresol solution containing 41 mg. of bis (disalicylal-ethylenediimine)- μ -aquodicobalt and 41 mg. of lead, in the form of cresolate, at temperatures of 15° C., 25° C., 35° C. and 45° C.

The results, shown in Table I, indicate that, when the method is performed at a temperature greater than ambient temperature, the amount of oxygen consumed is hardly different from the theoretical, corresponding to the oxidation of mercaptans into disulfides: namely, two atoms of sulfur for one atom of oxygen (i.e. S:O=2).

On the other hand, at low temperature, this consumption becomes much more considerable and very considerably exceeds the theoretical value.

Table I

Temperatures (° C.)	15	25	35
S _{RSR} (mg. per 100 ml.) at 0 minutes	41	41	41
S _{RSR} (mg. per 100 ml.) at 30 minutes	14	6	3
Volume of O ₂ —theoretical (ml.)	4.5	6.1	6.65
Volume of O ₂ —consumed (ml.)	0.3	6.6	7.2
V(O ₂)			
S(mg.)—theoretical	0.177	0.177	0.177
V(O ₂)			
S(mg.)—consumed	0.345	0.188	0.190

EXAMPLE 2

As stated hereinabove, one advantage of the method forming the subject of the invention is the avoidance of the formation of secondary reactions and, in particular, of those liable to lead to substantial reductions of the induction periods (stability to oxidation) of the fractions treated.

Thus, for example, two samples (1) and (2) of petrols having the following characteristics:

Petrol (1):	
Density at 15° C.	0.720.
Boiling range	30° to 180° C.
S _{RSR}	0.010 g. per 100 ml.
Induction period	419.
Petrol (2):	
Density at 15° C.	0.715.
Boiling range	34° to 148° C.
S _{RSR}	0.004 g. per 100 ml.
Induction period	320.

made sweet by treatment with a cresol solution containing 7 percent by weight of the chelate compound—bis (disalicylal-ethylenediimine)- μ -aquodicobalt—and 7 per-

cent by weight of lead, in the form of cresolate, at temperatures of -10°C ., $+15^{\circ}\text{C}$. and $+35^{\circ}\text{C}$., gave the induction periods indicated in Table 2.

Table 2

Temperature ($^{\circ}\text{C}$.)	Induction period for petrol (1)	Induction period for petrol (2)
-10	306	190
$+15$	396	210
$+35$	644	250

Examples 3 and 4 hereinbelow, which are likewise non-limitative, have the object of illustrating first the increase in the speed of oxidation of the mercaptans and/or mercaptides to disulfides; namely for given ratios of chelate organo-metallic compounds—or suitable compounds for forming the chelate compound in situ—to the quantity of sulfur, in the form of mercaptans, contained in the fractions treated. They further illustrate that, by means of the process forming the subject of the invention, it is possible to obtain a determined result—for example, the sweetness of the fractions treated—in a definite time,

This table gives the sulfur contents, in the form of mercaptans and in g. per 100 ml., depending on the reaction time, the reaction temperature and the ratio:

$$\frac{\text{chelate}}{S_{\text{RSH}}} \text{ (1/5, 1/7 and 1/10)}$$

used.

EXAMPLE 4

To twelve samples of a paraffin originating from Kuwait and having the following characteristics:

Density at 15°C 0.8025.
Boiling range 200° to 247°C .
 S_{RSH} 0.008 g. per 100 ml.

there is first added a benzene solution containing 1 g. of disalicylal-ethylenediimine per 100 ml., and then a second benzene solution containing 0.1 g. of cobalt and 0.55 g. of lead per 100 ml., in the form of naphthenates; the quantities of these solutions added are in the stoichiometric ratio corresponding to bis(disalicylal-ethylenediimine)- μ -aquodibicobalt, and the samples are then treated under the working conditions given in Table 4, in which the results are grouped.

Table 4

Time (hours).....	1				2			
	15	35	45	60	15	35	45	60
Temperature ($^{\circ}\text{C}$.).....								
Ratio of chelate/ S_{RSH}	0.036	0.0048	0.0016	0.0011	0.0012	0.0032	0.0008	0.0008
	0.026	0.0056	0.0025	0.0016	0.0016	0.0047	0.0008	0.0010
	0.018	0.0072	0.0040	0.0032	0.0032	0.0053	0.0016	0.002

Time (hours).....	6				22			
	15	35	45	60	15	35	45	60
Temperature ($^{\circ}\text{C}$.).....								
Ratio of chelate/ S_{RSH}	0.036	0.0024	0.0004	0.0004	0.0006	0.0018	¹ D.S.	D.S.
	0.026	0.0039	0.0004	0.0008	0.0010	0.001	D.S.	D.S.
	0.018	0.0043	0.0012	0.0016	0.0020	0.0016	0.0004	0.0010

¹ D.S. = "Doctor Sweet."

and with a considerable saving in the amounts of catalyst required.

EXAMPLE 3

Twelve identical samples of a light petrol originating from Iraq and having the following characteristics:

Density at 15°C 0.697.
Boiling range 34° to 147°C .
 S_{RSH} 0.014 g. per 100 ml.

are treated with a cresol solution containing 7 percent by weight of the chelate compound—bis(disalicylaethylenediimine)- μ -aquodibicobalt—and 7 percent by weight of lead, in the form of cresolate, as will be apparent from Table 3, in which the results obtained are grouped.

Table 3

Time (hours).....	1				2			
	15	35	45	60	15	35	45	60
Temperature ($^{\circ}\text{C}$.).....								
Ratio of chelate/ S_{RSH}	1/5	0.005	0.002	0.002	0.0015	0.003	0.0005	0.0005
	1/7	0.007	0.0025	0.0025	0.003	0.0065	0.0015	0.0015
	1/10	0.009	0.0035	0.003	0.007	0.008	0.003	0.0025

Time (hours).....	6				24			
	15	35	45	60	15	35	45	60
Temperature ($^{\circ}\text{C}$.).....								
Ratio of chelate/ S_{RSH}	1/5	0.002	¹ D.S.	D.S.	D.S.	0.0015	D.S.	D.S.
	1/7	0.006	0.001	0.00065	0.0005	0.0055	0.0005	0.0005
	1/10	0.007	0.002	0.001	0.004	0.006	0.001	D.S.

¹ D.S. = "Doctor Sweet."

This table gives the sulfur contents, in the form of mercaptans, and in g. per 100 ml., depending on the reaction time, the reaction temperature and the ratio:

$$\frac{\text{cobalt}}{S_{\text{RSH}}} \text{ (0.036, 0.026 and 0.018)}$$

used.

The results in Tables 3 and 4 clearly show the favourable influence of an increase of temperature on the speed of oxidation of the mercaptans and/or mercaptides to disulfides.

Moreover, taking into account the time within which it is desired to effect the operation and the rate of conversion of mercaptans and/or mercaptides to disulfides

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that it is desired to obtain, it is easy to choose the temperature at which it is necessary to perform the process to use the minimum quantity of chelate; it will be seen that an increase in the temperature permits considerably smaller quantities of chelate to be used.

While this invention has been described and exemplified in terms of its preferred embodiments, those skilled in the art will appreciate that modifications can be made without departing from the scope of the invention as defined in the appended claims.

We claim:

1. A process for oxidizing a member of the group consisting of mercaptans and mercaptides to disulfides in which the oxidation is effected by the action of oxygen, at a temperature of about 30° C. at least and at atmospheric pressure, in the presence of chelate organo-metallic compounds.

2. A process for oxidizing a member of the group consisting of mercaptans and mercaptides to disulfides, in which the oxidation is effected by the action of a gas containing oxygen, at a temperature of about 30° C. at least and at atmospheric pressure, in the presence of chelate organo-metallic compounds.

3. A process for oxidizing a member of the group consisting of mercaptans and mercaptides to disulfides, in which the oxidation is effected by the action of oxygen, at a temperature of about 30° C. at least and at atmospheric pressure, in the absence of chelate organo-metallic

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compounds, obtained by condensation of iminophenol and a metal of group VIII.

4. A process for oxidizing a member of the group consisting of mercaptans and mercaptides to disulfides, in which the oxidation is effected by the action of a gas containing oxygen, at a temperature of about 30° C. at least and at atmospheric pressure, in the presence of chelate organo-metallic compounds, obtained by condensation of iminophenol and a metal of group VIII.

5. A process for sweetening petroleum distillate hydrocarbons, in which they are treated with a gas consisting essentially of oxygen, at a temperature of about 30° C. at least and at atmospheric pressure, in the presence of chelate organo-metallic compounds.

6. A process for sweetening petroleum distillate hydrocarbons, in which they are treated with a gas consisting essentially of oxygen, at a temperature of about 30° C. at least and at atmospheric pressure, in the presence of chelate organo-metallic compounds, obtained by condensation of an iminophenol and a metal of group VIII.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,918,426

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Joseph Quiquerez et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 5, line 28, for "in the absence" read --- in the presence ---.

Signed and sealed this 24th day of May 1960.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents