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METHODS OF REFINING PETROLEUM PRODUCTS

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This invention relates to improved methods of refining petroleum products and is particularly suited for the sweetening of gasoline, kerosene, solvents and other cracked or distilled petroleum products.

As we have disclosed in our co-pending application, Serial No. 133,058, filed December 15, 1949, now United States Patent 2,659,691, of which this application is a continuation-in-part, we discovered that certain chelate compounds, when added to petroleum products containing appreciable quantities of sulfur in the mercaptan form, catalyze the oxidation of the mercaptans and yield "sweet" products.

Without guessing at the mechanism of the action of said chelate compounds, we have now discovered that the sweetening of mercaptan-bearing petroleum products may be effectively and economically achieved by forming chelate compounds in the product undergoing treatment by bringing together certain Schiff bases and compounds of group VIII metals of the periodic table. Otherwise stated, we found that it is advantageous to form such chelate compounds in situ in the product being refined. In practicing our invention, we presently prefer chelate compounds containing cobalt, such as are made by introducing certain iminophenols into the petroleum product to be treated and then adding a solution of a cobalt compound. Thereafter, the sweetening operation is carried out in the presence of oxygen or an oxygen-containing gas, although in certain instances the oxygen-dissolved in the petroleum product will be sufficient.

The features of the invention can perhaps best be appreciated by reference to specific examples as follows:

EXAMPLE 1

To one liter of a petroleum spirit which had an end boiling point of 200° C., obtained from an Iraq crude oil and containing 0.033% by weight of sulfur as mercaptans, we added 33 mg. of the Schiff base resulting from the action of salicyl aldehyde on ethylene diamine. To this oil was added 100 cm.³ of a 10% solution of cobalt acetate in methanol; the mixture was agitated with air for one hour and then left to stand. The analytic results of this treatment are set forth below in Table 1 in terms of the diminishing mercaptan content as a function of time.

Table 1

Time	Weight percent mercaptans
3 minutes	0.028
60 minutes	0.015
4 hours	0.011
24 hours	0.003

EXAMPLE 2

One liter of a straight run Iraq petroleum spirit having an end boiling point of 200° C. and containing 0.033% by weight of sulfur as mercaptan was treated with 40 mg. of disalicylal diimine propylene and 10.2 mg. of cobalt in the form of cobalt oleate.

The Schiff base is introduced into the petroleum spirit either dissolved in toluene or in an alcohol, though the latter is preferable as is shown in the accompanying Table 2 which illustrates the disappearance of the mercaptans in the oil with time as the treated oil is allowed to stand.

Table 2

Charge of Petroleum Spirit	1 liter	1 liter
Initial percent of sulfur as mercaptans (by vol.)	0.0237	0.0237
Grams of disalicylal propylene diimine added	0.040	0.040
Solvent for the disalicylal	Toluene	Methanol
Grams cobalt added (in form of oleate)	0.0102	0.0102
Weight percent sulfur (as mercaptans)	0.033	0.008
After 1 hour		0.033
After 6 hours	0.025	
After 24 hours	0.014	0.000

We also found that the sweetening treatment is greatly accelerated by the presence of alkali as is brought out in the following example.

EXAMPLE 3

As will be seen in the Table 3*a*, the use of alkali makes one liter batches of the Iraq petroleum spirit of Example 2, equal quantities of cobalt oleate and disalicylal propylene diimine but varying the solvent for the Schiff base and in some instances, adding alkali. The test batches were agitated with air, allowed to rest, and the mercaptan content measured. The results of these tests are set forth in Table 3.

Table 3

Number of test	1	2	3	4	5
Charge of Petroleum Spirits	1,000 cm.³	1,000 cm.³	1,000 cm.³	1,000 cm.³	1,000 cm.³
Percent S as mercaptans (by vol.)	0.0237	0.0237	0.0237	0.0237	0.0237.
Grams disalicylal propylene diimine added	0.040	0.040	0.040	0.040	0.040.
Solvent for the Schiff base	Toluene	Methanol	Methanol	Methanol	Toluene.
Grams cobalt added (as oleate)	0.0102	0.0102	0.0102	0.0102	0.0102.
Other reagents	None	None	50 cm.³ of 10% NaOH aq. sol'n.	20 cm.³ of 10% NaOH meth. sol'n.	20 cm.³ of 10% NaOH Meth. sol'n.
PERCENT BY WEIGHT OF S, AS MERCAPTAN					
0 hour	0.033	0.033	0.033	0.033	0.033.
1 hour		0.008	0.004	0.000	0.000.
6 hours	0.025		0.000		
24 hours	0.014	0.000			

As will be seen in the Table 3a, the use of alkali makes it possible to very appreciably reduce the amounts of reagents used to obtain the desired sweetening in a given time.

Table 3a

Number of test	1	2	3	4	5	6
Charge of Petroleum spirits	1,000 cm.³	1,000 cm.³	1,000 cm.³	1,000 cm.³	1,000 cm.³	1,000 cm.³
Gram S in charge as mercaptans	0.252	0.252	0.252	0.252	0.252	0.252.
Grams disalicylal propylene diimine added (in solution in 1% methanol).	0.032	0.024	0.016	0.008	.016	0.008.
Milligms. Co added (as oleate)	8.16	6.12	4.08	2.04	4.08	2.04.
Other reagents	None	None	None	None	50 cm.³ of 10% aq. sol'n of NaOH.	25 cm.³ of 10% aq. sol'n of NaOH.
WEIGHT PERCENT SULFUR (AS MERCAPTAN)						
0 hours	0.035	0.035	0.035	0.035	0.035	0.035.
3 hours	0.005	0.009	0.015	0.023		
5 hours	0.003	0.006	0.014	0.020	0.004	0.004.
20 hours	0.001	0.004	0.012	0.020	0.002	0.004.

As pointed out above, the present invention is not limited to the use of fatty acid salts of the Group VIII metals. For instance, one may use other compounds of cobalt such as naphthenates, alkylphtalates, alcoholates, enolates, phenolates, alkylphenolates, aminophenolates, and so on, and more generally any cobalt compound which is soluble in the hydrocarbons. Moreover, the cobalt compound (or other group VIII metal) may be added to the oil being treated in an excess of alcohol, phenol or of an alkyl phenol. Particular instances of the applications of these discoveries are hereinafter pointed out.

EXAMPLE 4

We took one liter of a straight-run gasoline derived from a Middle East crude oil. This gasoline had a final boiling point of 205° C. and contained 0.029% by weight of sulfur as mercaptans; to this sample we added 0.040 gram of disalicylal propylene diimine and then we added 0.15 gram of a mixture of cresol and cobalt cresolate, the total cobalt being added thus amounting to 0.0102 gram. We agitated the resulting solution in the presence of air and allowed it to stand. After some three hours, the gasoline sample contained no more than 0.006% sulfur in the form of mercaptans.

EXAMPLE 5

To one liter of gasoline containing 0.035% by weight of sulfur as mercaptans we added 1.6 cm.³ of a solution of 1% of disalicylal ethylene diimine in methanol. We next added 0.0177 gram of acetyl acetonate of cobalt, this being equivalent to, or corresponding to 0.0021 gram of cobalt. Six hours after the addition of these reagents the mercaptan content of the gasoline had dropped to 0.004% as sulfur.

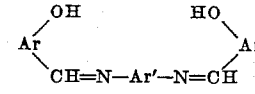
While we presently prefer to use Schiff bases resulting from the condensation of orthohydroxybenzaldehyde with an aliphatic diamine, it is within the scope of this invention to use Schiff bases resulting from more or less complex diamines reacted with orthohydroxybenzaldehydes having other substituents on the aromatic ring. Suitable amines include ethylene or propylene diamine, diaminodimethylamine, diaminodipropylamine, and so on. A specific example is the use of diaminodipropylamine, $NH_2—(CH_2)_3—NH—(CH_2)_3—NH_2$.

EXAMPLE 6

We added to 1 liter of gasoline, initially containing 0.033% sulfur in the form of mercaptans, 0.020 gram of disalicylal dipropylaminodiimine and 0.00485 gram of cobalt as the oleate thereof. To these we added 50 cm.³ of a 10% aqueous solution of NaOH; after three hours the concentration of the mercaptans in the gasoline had fallen to 0.004%, as sulfur.

We have also found that the condensation products of aromatic compounds having an orthohydroxyaldehyde structure—the prototype of which is orthohydroxybenzaldehyde—on aromatics or hydroaromatics cyclic diamines also produces in conjunction with cobalt salts, chelate compounds which are likewise capable of being formed in situ in the petroleum products, and thus make possible the sweetening of these products by oxidation of the mercaptans, in accordance with the characteristics as above defined.

The compounds have the general formula:



in which:

Ar represents aromatic, benzenic, naphtenic or similar radicals, simple or substituted, and

Ar' represents a cyclic, aromatic or hydroaromatic radical, simple or substituted.

The following examples illustrate these specific embodiments of the refining process according to our invention.

EXAMPLE 7

In 10 l. of straight run gasoline from Iraq petroleum with an end point of 205° C. containing 0.030% by weight of sulfur in the form of mercaptans, there is dissolved 0.19 g. of disalicylal phenylenediimine obtained by the condensation of salicylaldehyde on orthophenylenediamine, then 0.04 g. of cobalt in the form of cobalt oleate. This is agitated with 50 cm.³ of a 10% solution of soda in a mixture of water and methanol: After three hours, the petrol contains less than 0.002% sulfur in the form of mercaptans.

EXAMPLE 8

As in the preceding example, 10 liters of Middle East gasoline having an end point of 200° C.—containing 0.030% sulfur in the form of mercaptans—is treated with cobalt oleate and 0.22 g. of disalicylal-naphtylenediimine, obtained by condensation of the salicylaldehyde on the 1-8-diamino-naphtalene: After five hours the petrol contains 0.003% sulfur in the form of mercaptans.

EXAMPLE 9

1,000 cm.³ of Middle East gasoline having an end point of 200° C., containing 0.033% sulfur in the form of mercaptans, are treated as in the preceding examples with cobalt oleate and 0.185 g. of disalicylal-cyclohexylenediimine obtained by condensation of the salicylaldehyde on the 1-2 diamino cyclohexane.

After three hours it will be found that the petrol contains less than 0.002% sulfur in the form of mercaptans.

While the foregoing specific examples are concerned with the treatment of gasoline, the invention also encompasses the treatment of other cracked or distilled petro-

leum products such as heavy gasolines, white spirits, kerosenes and so forth, as is described in the following illustrative examples.

EXAMPLE 10

To one cubic meter of a solvent having a boiling range of 120°–200° C. and containing 0.038% sulfur as mercaptans, we added 600 cm.^{3} of a kerosene solution of cobaltoleate and 16 grams of disalicylal propylene diimine, the coblat solution titrating 6.8 grams of cobalt per liter. To this we added two liters of a 5% solution of caustic soda in water and alcohol, agitated the resulting mixture and stored it. After five hours, the treated solvent mixture did not titrate over 0.002% sulfur as mercaptans.

EXAMPLE 11

Similarly, we added 0.010 gram of cobalt stearate and 0.040 gram of disalicylal propylene diimine to one cubic meter of a kerosene having a boiling range of 200°–250° C. and containing 0.031% sulfur in the form of mercaptans. This was then air agitated with a 10% aqueous solution of caustic soda and allowed to rest. After 20 hours the mercaptan sulfur content had dropped to 0.009%.

It is also within the scope of our invention to practice the process in a continuous manner. For example, one may continuously introduce into a mechanical or baffle mixer the petroleum product to be sweetened, the charge product containing therein a small quantity of an appropriate Schiff base, a dilute water or alcohol-water solution of alkali, and a small stream of charge which contains a small percentage of a group VIII metal compound. Air may also be supplied if the charge of oil is deficient in dissolved oxygen. The emulsion formed in the mixer is then conducted to a decanter wherein it separates to an alkali-alcohol-water or alkali dilute water phase which is recycled to the mixer and the sweetened product which is continuously withdrawn from the decanter.

EXAMPLE 12

In a specific embodiment of this aspect of our invention we continuously passed through a stationary mixer 100 liters per hour of a 10% caustic potash solution in equal volumes of water and methanol. We also supplied to the mixer 1000 liters per hour of a gasoline containing 0.030% sulfur in the form of mercaptans, the gasoline being derived from an Iraq crude and being pretreated with 0.008 gram per liter of disalicylal propylene diimine. We also supplied to the mixer a small stream (e. g. about 10 liters per hour), of the same gasoline but containing 0.2 gram per liter of cobalt in the form of cobalt oleate or cobalt ricinoleate. The emulsion formed in the presence of oxygen was continuously decanted, the sweetened gasoline separated and the recovered alkali-alcohol-water phase recycled in at the indicated rate.

EXAMPLE 13

A static or mechanical mixer is continuously fed by 100 l./h. with a 10% solution of caustic soda in a mixture of equal volumes of water and methanol. This mixture received on the one hand, 1000 litres per hour of Iraq petrol—containing 0.030% sulfur in the form of mercaptans, to which has been added 0.010 g./l. of the Schiff base resulting from the condensation of the salicylaldehyde on orthophenylenediamine—and on the other hand, 10 litres per hour of the same petrol containing 0.2 g./l. of cobalt in the form of an oleate. The emulsion formed in the mixer is poured off, giving a hydroalcoholic alkaline phase which is re-cycled to the mixer, and a petrol containing less than 0.001% sulfur in the form of mercaptans.

EXAMPLE 14

In still another embodiment of this aspect of our invention, we sweetened a straight run petroleum spirit which had an end point of 200° C. and contained 0.033% sulfur as mercaptans to a final sulfur content of 0.003%. We added 0.040 gram per liter of disalicylal ethylene diimine and 1% of methanol to the unsweetened spirit and then circulated it through a bed composed of an activated carbon charged with cobalt nitrate. The effluent, treated gasoline was then either washed with water or with a dilute soda solution and the methanol thus removed from the spirit was recovered by known means.

While in certain instances, the sweetening treatments described leave the sweetened product somewhat colored, such color may advantageously be eliminated by decanting, water washing, dilute alkali washing, or filtration through decolorizing clay, depending upon the particular conditions of a given use.

While in the foregoing specification we have particularly pointed out and described specific examples of our invention, and certain modifications and alternatives, it is to be noted that these are not intended to be exhaustive of the invention but on the contrary are presented with a view to illustrating and explaining the invention, the principles thereof and the best manners of applying it in practical use in order that others skilled in the art may be enabled to practice the invention and apply it under various circumstances and in various ways each as may be best suited to the conditions of a particular use.

We claim:

1. The process of sweetening a liquid petroleum product which comprises adding to said product in the presence of oxygen a minor quantity of an iminophenol and a minor quantity of a group VIII metal compound in a form miscible with said petroleum product to thereby form in situ in said product an organic compound of said group VIII metal having at least one chelate bond.

2. The process of sweetening a liquid petroleum product which comprises oxidizing mercaptans therein in the presence of oxygen while there is present in the petroleum product itself a small quantity of an iminophenol and a minor quantity of a group VIII metal compound in a form miscible with said petroleum product.

3. The process of sweetening a liquid petroleum product which comprises oxidizing mercaptans therein in the presence of oxygen while there is present in the petroleum product itself small quantities of an iminophenol and a cobalt compound in a form miscible with said petroleum product.

4. The process of sweetening a liquid petroleum product which comprises oxidizing mercaptans therein in the presence of oxygen while there is present in the petroleum product itself a small quantity of a cobalt compound in a form miscible with said petroleum product and a small quantity of a Schiff base.

5. The process according to claim 4 wherein said Schiff base is formed by the condensation of an aliphatic diamine with an aromatic orthohydroxyaldehyde.

6. The process according to claim 4 wherein said Schiff base is formed by the condensation of an aromatic orthohydroxyaldehyde on an aromatic cyclic diamine.

7. The process according to claim 4 wherein said Schiff base is formed by the condensation of an aromatic orthohydroxyaldehyde on an hydroaromatic cyclic diamine.

8. The process according to claim 4 wherein said Schiff base is formed by the condensation of an aromatic orthohydroxyaldehyde on an aromatic cyclic diamine with simple rings.

9. The process according to claim 4 wherein said Schiff base is formed by the condensation of an aromatic orthohydroxyaldehyde on an aromatic cyclic diamine with condensed rings.

10. The process according to claim 4 wherein said Schiff base is formed by the condensation of an aromatic orthohydroxyaldehyde on an aromatic cyclic diamine with branched rings.

11. The process according to claim 4 wherein said Schiff base is formed by the condensation of an aromatic

orthohydroxyaldehyde on an hydroaromatic cyclic diamine with simple rings.

12. The process according to claim 4 wherein said Schiff base is formed by the condensation of an aromatic orthohydroxyaldehyde on an hydroaromatic cyclic diamine with condensed rings.

13. The process according to claim 4 wherein said Schiff base is formed by the condensation of an aromatic orthohydroxyaldehyde on an hydroaromatic cyclic diamine with branched rings.

14. The continuous process of sweetening a liquid petroleum product which comprises supplying said petroleum product to a mixing zone, maintaining a concentration of free oxygen in said reaction zone sufficient to oxidize mercaptans therein, supplying a dilute caustic water-alcohol solution to said zone, supplying an iminophenol to the zone while also introducing to said zone a small stream of said petroleum product containing a minor quantity of a group VIII metal organic compound in a form miscible with said petroleum product, conducting the effluent stream from the mixing zone to a separation zone, removing the aqueous phase from the separation zone and recycling it to the mixing zone.

15. The continuous process of sweetening a liquid petroleum product which comprises supplying said petroleum product to a mixing zone, maintaining a concentration of free oxygen in said reaction zone sufficient to oxidize mercaptans therein, supplying a dilute caustic aqueous solution to said zone, supplying an iminophenol to the zone while also introducing to said zone a small stream of said petroleum product containing a minor quantity of a group VIII metal organic compound in a form miscible with said petroleum product, conducting the effluent stream from the mixing zone to a separation zone, removing the aqueous phase from the separation zone and recycling it to the mixing zone.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,823,173

February 11, 1958

Andre Gislon 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 2, line 33, Table 2, second column thereof, opposite "Weight percent sulfur (as mercaptans)", for "0.008" read -- 0.033 --; same column 2, line 34, Table 2, second column thereof, opposite "After 1 hour", for "0.033" read -- 0.008 --.

Signed and sealed this 10th day of February 1959.

(SEAL)

Attest:

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Attesting Officer

ROBERT C. WATSON

Commissioner of Patents