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3,691,066

## HYDROGENATION OF UNSATURATED GASOLINES

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9 Claims

### ABSTRACT OF THE DISCLOSURE

The selective hydrogenation of unsaturated gasolines e.g. steam cracker gasoline can be carried out over a supported nickel catalyst at 50–250° C., 200–3000 p.s.i.g., 0.2–10 v./v./hr. and 200–5000 s.c.f. of H<sub>2</sub>/B even when the feedstock contains 10–3000 p.p.m. wt. of mercaptan sulphur. Poisoning of the catalyst by the mercaptan sulphur is prevented because the mercaptans are converted to thiophenes during processing to a level of below 30 p.p.m. wt. of mercaptans in the product, particularly below 10 p.p.m. wt. The diene content is reduced from 4–55% wt. to below 0.5% wt. Total sulphur content of the feedstock is 0.1–1.5% wt., of which 0.003–1.0% wt. may be thiophenic sulphur and such feedstocks may be produced by the thermal cracking of high sulphur content, high boiling petroleum fractions. They may be inhibited with a phenolic inhibitor.

The preferred catalyst is 1–50% wt. nickel on sepiolite and presulphiding of the catalyst is optional.

Runs of over 500 hours, particularly over 1000 hours are possible.

This invention relates to the selective hydrogenation of unsaturated gasolines.

U.K. patent specification No. 848,232 describes and claims a process for improving a gasoline by the destruction of gum-forming constituents thereof, said gasoline containing acyclic mono-olefins together with at least one diolefin which comprises passing said gasoline with hydrogen over a supported catalyst which under the operating conditions, contains nickel, present in major proportion as elemental nickel, said conditions comprising a combination of temperature, pressure, feedstock flow rate and hydrogen flow rate which constitute a hydrogenation severity such that diolefins are converted substantially completely to mono-olefins without appreciable conversion of said acyclic mono-olefins to saturated hydrocarbons. The preferred gasoline feedstocks have a sulphur content of 0.005 to 0.04% wt. and are hydrogenated at 0–200° C. In view of the well known susceptibility of nickel catalysts to poisoning by sulphur compounds, this finding that a nickel catalyst could hydrogenate a sulphur-containing gasoline at low temperatures was surprising. This unexpected success was subsequently attributed to the fact that in the gasoline feedstocks used, which were produced by high temperature thermal cracking, the sulphur was present largely as thiophene sulphur with less than 10 p.p.m. of mercaptan sulphur. This thiophene sulphur gave only a limited sulphiding of the nickel and did not progressively sulphide and poison it.

Further experiments confirmed this significant difference in behaviour as between on the one hand thiophenes and related compounds and on the other hand mercaptans, hydrogen sulphide and other sulphur compounds. Typical findings are shown, for example, in U.K. patent specification No. 1,002,823. When a feedstock containing 10% vol. isoprene, 10% vol. isohexenes, 80% vol. n-heptane and 0.2 g./100 ml. of n-butyl mercaptan was passed

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over a nickel-sepiolite catalyst the catalyst was not selective for diolefin hydrogenation and its activity steadily declined. When 0.5 g./100 ml. of thiophene were also added selectivity improved but activity continued to decline. The conclusion drawn was that with a feedstock containing both mercaptans and thiophene the catalyst might become selective but would steadily lose activity.

As indicated above, the hydrogenation feedstocks used up to now have been low in mercaptan sulphur due to the use of naphthas of moderate sulphur content as feedstocks to the high temperature thermal crackers. At the sulphur levels of most naphthas the mercaptans are destroyed in the cracking leaving only thiophenes in the gasoline product. However attention is now being given to the use of higher boiling materials such as gas oils or waxy distillates as cracking feedstocks. These feedstocks, which often contain much higher amounts of sulphur, do not necessarily give gasolines with wholly thiophenic sulphur when cracked and the gasolines produced from them may contain from 0.01 to 1.5% wt. sulphur of which 10 to 300 p.p.m. may be mercaptan sulphur. Surprisingly it has now been found that gasolines with these high total and mercaptan sulphur contents can also be hydrogenated over a nickel catalyst without significant sulphur poisoning.

This unexpected finding is believed to be due to the fact that mercaptans react with olefins under the hydrogenation conditions to give thiophenes. Analysis of the feedstock to and the product from a selective hydrogenation unit has shown that the mercaptan content declines and the thiophene content increases as between feed and product. Analysis of the nickel catalyst at the end of an extended run has also confirmed that the catalyst is not excessively sulphided and that the mercaptans have not progressively sulphided the catalyst, as would have been expected.

According to the present invention, therefore, a process for the selective hydrogenation of a hydrocarbon fraction boiling in the range 15–225° C. containing diolefins, mono-olefins, aromatics and sulphur compounds, the diolefin content being from 4 to 35% weight and the sulphur content being 0.01–1.5% wt. of which 10 to 300 p.p.m. by weight is mercaptan sulphur comprises passing the feedstock together with hydrogen over a supported nickel catalyst which under the operating conditions is present in major proportions as elemental nickel at a temperature of 50 to 250° C., a pressure of 200 to 3000 p.s.i.g. (1379 to 20,685 kN/m.<sup>2</sup> g.), space velocity of 0.2 to 10 v./v./hr. and a hydrogen treating rate of 200–5000 s.c.f./b. (1504 to 37,600 mol/m.<sup>3</sup>) and recovering a product having a reduced diolefin content of below 0.5% weight and a reduced mercaptan sulphur content of below 30 p.p.m. by weight, preferably below 10 p.p.m. by weight.

Comparative experiments have shown that the mercaptan containing feedstocks are more difficult to treat and that there is some reduction in catalyst activity. However this reduction in activity is, as indicated above, considerably less than that which would have been predicted and is quite tolerable. The preferred conditions are:

Temperature—100–200° C.  
Pressure—250–1500 p.s.i.g. (1725 to 10,343 kN/m.<sup>2</sup> g.)  
Space velocity—0.5–5 v./v./hr.  
Hydrogen treating rate—500–2000 s.c.f./b. (3760 to 15,040 mol/m.<sup>3</sup>)

The preferred lower limits for temperature and pressure and the preferred upper limit for space velocity are governed by the fact that catalyst activity is enhanced by increased temperature, pressure and contact time. The preferred upper limits for temperature and pressure and the preferred lower limit for space velocity are governed by practical and economic considerations.

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The object of the invention is to reduce the diolefin content of the feedstock to a level below 0.5% wt. (corresponding to a diene value of below 2) to render the product stable. The diolefin content of below 0.5% wt. excludes dicyclopentadiene. It can then be used either as a motor gasoline component or as feedstock to a further hydrogenation stage for the complete saturation of the mono-olefins and the production of a material from which the aromatics can be extracted. Some hydrogenation of mono-olefins may be inevitable in reducing the diolefin content to the value specified but particularly when the material is to be given a further hydrogenation this will be an advantage. The reduction in the mercaptan content besides preventing the poisoning of the catalyst, is also useful in improving the quality of the product. Other characteristics of the product, e.g. existent and accelerated gum contents, have also been found satisfactory.

The hydrogen consumption will depend on the composition of the feedstock and the extent of saturation required. For most normal feedstocks it will be in the range 150 to 500 s.c.f./b. (1128 to 3760 mol/m.<sup>3</sup>).

The temperature may be raised progressively during the process to maintain the hydrogen consumption at the desired level. The rate of increase will, however, be low and operations of several hundred hours duration are possible. Thus the process of the present invention has been found, surprisingly, to operate for at least 500 hours before catalyst regeneration or replacement is required, more particularly at least 1000 hours. As shown by the specific examples a run of over 3000 hours has, in fact, been achieved..

Any gasoline feedstock containing diolefins, mono-olefins, aromatics and sulphur as specified above may be used, including gasolines produced by catalytic or thermal cracking at temperatures below 593° C. However the process is particularly suitable for gasolines produced by thermal cracking above 593° C., for example those produced by cracking at 593–900° C., in the presence of diluent steam and/or an inert heat transfer agent such as sand. As indicated above when the feedstock to the thermal cracker is naphtha there will usually be very little mercaptan sulphur in the gasoline product but such sulphur can occur in gasolines produced by thermal cracking of unusually high sulphur content naphthas and will also occur when higher boiling feedstocks are cracked (e.g. feedstocks with a sulphur content of about 0.15% wt. or higher). The most likely gasolines to be treated by the present invention are thus those produced by the thermal cracking of feedstocks boiling above 200° C. and containing at least 0.15% wt. of sulphur. The gasolines produced will normally contain appreciable amounts of thiophenic as well as mercaptan sulphur (e.g. from 0.03 to 1.0% wt. of thiophene sulphur) and the total sulphur content will be, as indicated above, in the range 0.01 to 1.5% wt.

Fresh wholly elemental nickel catalyst is not selective in its hydrogenation activity and will hydrogenate mono- and diolefins and aromatics and the fact that mono-olefins and aromatics remain unhydrogenated in the present process is due to the partial sulphiding of the nickel catalyst by the thiophenic sulphur normally present in the feedstock. No positive action to make the catalyst selective is therefore required except to allow an adequate amount of thiophene sulphur-containing feedstock to pass over the catalyst.

It has been found that it is even possible to start up the process directly with the mercaptan containing feedstock. Presumably the conversion of mercaptan to thiophene is sufficiently rapid to prevent the mercaptan sulphiding the catalyst, and there is preferential sulphiding with the thiophene initially present or produced from the mercaptan. However with high nickel catalysts, low feedstock space velocities and low thiophene content feedstocks the time taken for the catalyst to become selective may be appreciable. It may sometimes, therefore, be desirable to presulphide the catalyst or speed-up the sulphiding, either

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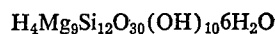
by sulphiding the catalyst before the feedstock is passed over the catalyst or by adding a suitable compound to the feedstock during start up. The sulphur compound used should be thiophenes or compounds which behave similarly to thiophene, viz thiacycloalkanes having at least 4 carbon atoms in the ring and dialkyl monosulphides. The temperature of sulphiding is desirably below 200° C. and preferably hydrogen is present.

Suitable techniques for pre-sulphiding or assisting the sulphiding of the nickel are described in U.K. patent specification Nos. 972,245 and 979,307.

It should be emphasised, however, that the catalyst is predominantly elemental nickel during processing. The actual sulphur nickel atomic ratio in the catalyst is likely to be in the range 0.01 to 0.4, more particularly 0.01 to 0.2, based on the elemental nickel content of the unreacted catalyst.

Preferably the catalyst contains from 1 to 50% wt. of nickel, more particularly 10 to 30% wt.

Suitable supports may be refractory oxides or other refractory compounds of metals of Groups II, III and IV of the Periodic Table, particularly those having a low activity for cracking and polymerising reactions. Thus the support may be chalk, alumina, silica gel or kieselguhr. The preferred catalyst support is, however, sepiolite, which is a commercially available clay mineral, which occurs naturally and which can also be prepared synthetically. It has the ideal formula:



and is also known as Meerschaum. Sepiolite is particularly characterised by a low activity for cracking and polymerising reactions, but such activity may be further reduced by the addition of from 0.1 to 5% wt. of alkali metal or alkaline earth metal.

The catalyst may be prepared by any suitable technique. Examples of suitable techniques are disclosed in the previously mentioned patent specifications.

The feedstocks to the selective hydrogenation unit will, in commercial practice, normally be fed directly from the thermal cracker with a minimum of intermediate storage time. If the product from the thermal cracker has to be stored for any length of time it is preferably inhibited with a phenolic inhibitor (e.g. 2,4-dimethyl-6-tert-butylphenol sold under the trademark "Topanol A"). The presence of such an inhibitor in an amount of up to 0.04% wt. does not adversely affect the hydrogenation and may, possibly, have some beneficial effect. Experiments have shown that a phenolic inhibitor, unlike a phenylene diamine type inhibitor, does not have any effect on the mercaptan content of gasolines during storage at ambient temperature and there is no question of the reduced content of mercaptan in the product found in the present invention being due to inhibitor sweetening of the feedstock during storage and before the hydrogenation.

The invention is illustrated by the following examples.

#### EXAMPLE 1

A catalyst of 12% nickel on alumina was prepared as follows: Pseudo-boehmite was formed by adding 1 kg. of aluminium isopropoxide to 3 litres of 20 vol. hydrogen peroxide at room temperature and stirring for 24 hours. It was left to age for 4 days without stirring, then stirred for 24 hours before filtering and washing the filter cake with 20 litres of deionised water. (All these steps were also at room temperature.) The gel was dried at 120° C., calcined at 400° C. for 2 hours and pelleted to 1/8 x 1/8 in. pellets. The pellets were impregnated with a solution of nickel formate in 0.88 SG ammonia solution to give a 12% wt. nickel content, dried at 110° C. and reduced at 350° C. for 4 hours in a stream of hydrogen.

The catalyst was then used for selective hydrogenation of a mercaptan-free, thiophene-containing steam cracker gasoline for 750 hours during which time it became partially sulphided to a S:Ni atomic ratio of 0.06:1.

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The effect of mercaptan sulphur content on catalyst activity and selectivity was then studied under the following conditions:

Pressure—3450 kN/m.<sup>2</sup> g. (500 p.s.i.g.)

Space velocity—2 v./v./hr.

Hydrogen treating rate—10,500 mol/m.<sup>3</sup> (1400 s.c.f./b.)

The feedstock was re-run steam cracker gasoline having the following inspection data:

Boiling range—ASTM 50 to 185° C.

Diolefin content—7–9% wt. (including 1.8% wt. of di-cyclopentadiene)

Diene value—16.5

Bromine No.—50

Total sulphur content—60 p.p.m. wt.

Thiophene sulphur content—50 p.p.m. wt.

Topanol A—0.036% wt.

At a predetermined point in the experiment (201 hours on stream) 100 p.p.m. by weight of mercaptan was added. Temperature was adjusted during the run to maintain a diene value below 2. The results are shown in Table 1 below.

TABLE 1

Hours on stream	Mercaptan in feed, p.p.m. wt.	Temp., ° C.	H <sub>2</sub> consumption, mole/m. <sup>3</sup>	Diene value	Mercaptan in product, p.p.m. wt.
23–47.....	0	90	2,295	1.3	0
177–201.....	0	90	1,740	1.6	0
n-Butyl mercaptan					
220–244.....	100	90	1,540	3.2	3
277–301.....	100	120	2,070	1.2	3
301–517.....	100	130	2,180–1,935	1.4	3–5
613–637.....	100	130	2,020	1.8	5
638–710.....	100	130	1,875	2.2	4
710–734.....	100	130	1,920	2.4	4
782–806.....	100	140	1,970	1.9	-----
806–830.....	100	140	2,000	1.8	-----
830–854.....	100	140	1,933	1.4	-----
994–1,018.....	100	150	2,113	1.0	6
Iso-butyl mercaptan					
1,018–1,261....	100	150	2,015	1.2	12
1,261–1,453....	100	150	1,888	1.5	11

<sup>1</sup> +2,000 p.p.m. thiophene.

The table shows that a satisfactory product was obtained with a mercaptan-free feedstock. The effect of adding 100 p.p.m. by weight of mercaptan was to reduce catalyst activity but this was compensated for by an increase of temperature to 120° C. Steady and satisfactory operation at 130° C. was maintained for over 200 hours when a rise in diene value occurred over the period 613–734 hours on stream. This rise was again counteracted by an increase in temperature to 140° C. Operation at this temperature continued for over 150 hours with an improvement in diene value rather than a further decline, and operation at 150° C. gave a further improvement. Changing from n-butyl to iso-butyl mercaptan at 1018 hours on stream had little effect apart from a small increase in the mercaptan content of the product. Adding thiophene at 1261 hours on stream also had little effect. The run was terminated voluntarily at 1453 hours on stream.

Table 2 below gives a GLC analysis of a portion of the product at 613–637 hours on stream confirming that the catalyst was selectively hydrogenating diolefins without significant hydrogenation of mono-olefins.

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TABLE 2

	Feed	Product
C <sub>4</sub> paraffins.....	Tr.	0.1
C <sub>4</sub> mono-olefins.....	0.1	0.3
C <sub>4</sub> diolefins.....	Tr.	0.0
Total.....	0.1	0.4
C <sub>5</sub> paraffins.....	7.5	8.1
C <sub>5</sub> mono-olefins.....	3.5	8.4
C <sub>5</sub> diolefins.....	4.4	0.14
Total.....	15.4	16.64
Cyclo C <sub>3</sub> paraffins.....	0.4	0.8
Cyclo C <sub>3</sub> mono-olefins.....	0.7	1.1
Cyclo C <sub>3</sub> diolefins.....	1.7	0.04
Total.....	2.8	1.94
Ethyl benzene.....	1.7	4.5
Styrene.....	4.0	0.9
Total.....	5.7	5.4
Dicyclopentadiene.....	1.8	0.4
9,10 dihydro DCPD.....	-----	2.3
Tetrahydro DCPD.....	-----	0.2
Total.....	1.8	2.9

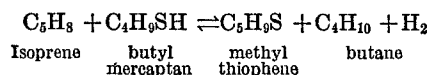
Table 3 below gives a full analysis of the sulphur compounds in the feed and product at 325–349 hours on stream confirming that the mercaptans had been converted during the hydrogenation to thiophenes.

TABLE 3

P.p.m. by weight		
	Feed	Product
Total sulphur.....	160	130
Mercaptan.....	107	5
Disulphide.....	6	2
Mono sulphide.....	20	5
Thiophenic.....	50	135

An analysis of the catalyst at the end of the run showed that it had a S:Ni atomic ratio of 0.06:1 further confirming that the mercaptan sulphur had not been deposited on the catalyst.

The explanation as to why mercaptans are converted to thiophenes is not clear but a suggested overall reaction mechanism is as follows:



## EXAMPLE 2

A catalyst of nickel formate on sepiolite was reduced to elemental nickel on sepiolite at 350° C. and atmospheric pressure in a stream of hydrogen flowing at 1000 vol./vol./hr. for 4 hours. The nickel content of the catalyst was 10% wt.

Presulphiding of the catalyst was carried out using heptane containing 0.1% wt. thiophene to give a catalyst with a sulphur:nickel atomic ratio of 0.06:1. The presulphiding conditions used were:

Temperature, ° C.—100

Pressure—atmospheric

Heptane space velocity, v./v./hr.—4.0

Once through H<sub>2</sub> flow, v./v./hr.—1200

Duration, hours—12

The run was started up under the following conditions:

Temperature, ° C.—90

Pressure, kN/m.<sup>2</sup> g.—3450 (500 p.s.i.g.)

Space velocity, v./v./hr.—2.0

Hydrogen treating rate, mol/m.<sup>3</sup>—10,500 (1400 s.c.f./b.)

The feedstock was a re-run steam cracker gasoline having the following inspection data:

Boiling range ASTM—50 to 180° C.

Bromine No.—47

Diolefin content—6.5% wt. (including 3.5% wt. of di-cyclopentadiene)

Diene value—18.3

Total sulphur—45 p.p.m. wt.

Thiophene sulphur—35 p.p.m. wt.

Sulphide sulphur—10 p.p.m. wt.

Mercaptan sulphur—<2 p.p.m. wt.

Topanol A—0.036% wt.

This mercaptan-free feedstock was processed up to 365 hours on stream to ensure that the process was functioning normally. 100 p.p.m. wt. of mercaptan sulphur (as n-butyl mercaptan) were then added to the feedstock. The results are set out in Table 4 below.

TABLE 4

Hours on stream	Mercaptan in feed, p.p.m. wt.	Temp., ° C.	H <sub>2</sub> consumption, mole/m. <sup>3</sup>	Diene value	Mercaptan in product, p.p.m. wt.
125-365-----	0	90	2,180	1.2	0
	n-butyl mercaptan				
380-404-----	100	90	2,083	1.9	10
413-773-----	100	110	2,053	1.5	7
785-929-----	100	110	1,835	1.9	8
949-1,093-----	100	120	1,865	1.6	15
1,093-1,237-----	100	125	1,745	2.0	-----
1,237-1,533-----	100	130	1,993	1.6	10

<sup>1</sup> +2,000 p.p.m. thiophene.

These results confirm the results given in Example 1 showing, in fact that the nickel-sepiolite catalyst is more tolerant of mercaptan sulphur, requiring a lesser rate of temperature increase to maintain catalyst activity.

Table 5 below gives a full analysis of the feed and product at 1509-1532 hours on stream.

TABLE 5

	P.p.m. by weight	
	Feed <sup>1</sup>	Product
Hydrogen sulphide-----	<2	<2
Elemental sulphur-----	<2	<2
Mercaptan sulphur-----	100	10
Disulphide sulphur-----	<2	<2
Organic sulphides-----	10	( <sup>2</sup> )
Unreactive (or thiophenic) sulphur-----	2,035	<sup>3</sup> 1,900-2,100
Total sulphur-----	2,145	<sup>3</sup> 2,100

<sup>1</sup> The feedstock actually processed was the original feed to which 2,000 p.p.m. of thiophene and 100 p.p.m. mercaptan sulphur (as n-butyl mercaptan) had been added.

<sup>2</sup> Very low content.

<sup>3</sup> Repeatability of total sulphur determination at this level is ±10%.

### EXAMPLE 3

This was a continuation of the pilot-plant run of Example 2 in which the effect of varying pressure and hydrogen gas rate were examined. At 1533 hours on stream, the reactor pressure was reduced to 1725 kN/m.<sup>2</sup> g. (250 p.s.i.g.) and the run continued under the following conditions for the next 410 hours:

Catalyst bed temperature, ° C.—130

Reactors pressure, kN/m.<sup>2</sup> g.—1725 (250 p.s.i.g.)

Space velocity, v./v./hr.—2.0

Hydrogen treating rate, mol/m.<sup>3</sup>—10,500 (1400 s.c.f./b.)

Mercaptan sulphur added to feed (as n-butyl mercaptan), p.p.m. wt.—100

Thiophenic sulphur added to feed (as thiophene), p.p.m. wt.—2000

The results are set out in Table 6 below:

TABLE 6

Hours on stream	Mercaptan in feed, p.p.m. wt.	Temp., ° C.	H <sub>2</sub> consumption, mole/m. <sup>3</sup>	Product diene value	Mercaptan in product, p.p.m. wt.
1,613-1,636-----	100	130	1,707	1.9	30
1,733-1,756-----	100	130	1,512	1.6	-----
1,901-1,924-----	100	130	1,361	1.5	20

This shows that the reaction hydrogen pressure can be reduced to a value as low as 1725 kN/m.<sup>3</sup> g. (250 p.s.i.g.) without any detrimental effect on product diene value. The product mercaptan content is still significantly lower than that of the feedstock, although somewhat higher than for the previous period of operation at double the pressure.

In order to investigate the effect of hydrogen gas rate, the hydrogen treating rate was then reduced from 10,500 mol/m.<sup>3</sup> to 3760 mol/m.<sup>3</sup> (500 s.c.f./b.) at 1949 hours on stream and the run continued under the following conditions for the next 960 hours:

Catalyst bed temperature, ° C.—130

Reactor pressure, kN/m.<sup>2</sup> g.—1725 (250 p.s.i.g.)

Space velocity, v./v./hr.—2.0

Hydrogen treating rate, mol/m.<sup>3</sup>—3760 (500 s.c.f./b.)

Added mercaptan and thiophenic sulphur contents, p.p.m. wt.—100 and 2000 resp.

The run results are set out in Table 7 below:

TABLE 7

Hours on stream	Mercaptan in feed, p.p.m. wt.	Temp., ° C.	H <sub>2</sub> consumption, mole/m. <sup>3</sup>	Product diene value	Mercaptan in product, p.p.m. wt.
1,979-2,002-----	100	130	1,316	1.5	18
2,051-2,074-----	100	130	1,293	1.8	12
2,171-2,194-----	100	130	1,534	1.5	8
2,507-2,530-----	100	130	1,549	2.1	<2
2,795-2,818-----	100	130	1,376	2.0	<2
2,923-2,946-----	100	135	1,233	1.5	-----
2,967-3,090-----	100	135	1,331	1.3	-----

The results of Table 7 show a very slow increase in product diene value with time at the low hydrogen rate used. This increase was however, rectified by increasing the temperature by 5° C. to 135° C. at 2915 hours on stream. The mercaptan content of the product in Table 7 is lower than that of Table 6 suggesting that a low hydrogen rate assists the conversion of mercaptan to thiophene.

Examples 2 and 3 together show a run of over 3000 hours duration, much of it at low pressure and low hydrogen rate. The catalyst was still active and selective at the end of this run, the operating temperature being still only 135° C.

### EXAMPLE 4

This example examines the effect of omitting the pre-sulphiding of the nickel-sepiolite catalyst.

A nickel formate on sepiolite catalyst (10 percent wt. Ni) was reduced to elemental nickel on sepiolite in the manner described in Example 2. This catalyst was then used directly to process re-run steam-cracker gasoline containing 100 p.p.m. weight mercaptan sulphur (added as n-butyl mercaptan) without any presulphiding with thiophene. The feedstock containing the 100 p.p.m. of mercaptan sulphur was fed over the reduced catalyst at ambient temperature and low hydrogen pressure (690 kN/m.<sup>2</sup> g.) and the severity of the operating conditions gradually increased over 80 hours on stream until the following conditions were attained:

Catalyst bed temperature, ° C.—110

Reactor pressure, kN/m.<sup>2</sup> g.—3450 (500 p.s.i.g.)

Space velocity, v./v./hr.—2.0

Hydrogen treating rate, mol/m.<sup>3</sup>—10,500 (1400 s.c.f./b.)

Feedstock inhibitor used—Topanol A

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Satisfactory product diene values (in the range 0.6 to 1.6) were obtained under the above conditions over a period of 560 hours on stream. Product mercaptan contents varied from <2 p.p.m. weight early in the run to 4 p.p.m. weight at the end.

We claim:

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1. A process for the selective hydrogenation of a hydrocarbon fraction boiling in the range 15–225° C. containing diolefins, mono-olefins, aromatics and sulphur compounds, the diolefin content being from 4 to 35% wt. and the sulphur content being 0.01–1.5% wt. of which 10 to 300 p.p.m. by weight is mercaptan sulphur comprising passing the fraction as feedstock together with hydrogen over a supported nickel catalyst which under the operating conditions is present in major proportion as elemental nickel at a temperature of 50 to 250° C., a pressure of 200 to 3000 p.s.i.g. (1379 to 20,685 kN/m.<sup>2</sup> g.), a space velocity of 0.2 to 10 v./v./hr. and a hydrogen treating rate of 200–5000 s.c.f./b. (1504 to 37,600 mol/m.<sup>3</sup>) and recovering a product having a reduced diolefin content of below 0.5% wt. and a reduced mercaptan sulphur content of below 30 p.p.m. by weight.

2. A process as claimed in claim 1 wherein the temperature is 100 to 200° C., the pressure 250–1500 p.s.i.g. (1725 to 10,343 kN/m.<sup>2</sup>g.), the space velocity 0.5 to 5 v./v./hr., and the hydrogen treating rate 500 to 2000 s.c.f./b. (3760 to 15,040 mole/m.<sup>3</sup>).

3. A process as claimed in claim 1 wherein the feedstock contains from 0.003 to 1.0% wt. of sulphur as thiophene sulphur.

4. A process as claimed in claim 1 wherein the catalyst is presulphided at a temperature below 200° C. with a

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thiophene, a thiacycloalkane having at least 4 carbon atoms or a dialkyl mono sulphide prior to contacting the mercaptan-containing feedstock.

5. A process as claimed in claim 1 wherein the catalyst is contacted directly with the mercaptan-containing feedstock without any presulphiding.

6. A process as claimed in claim 1 wherein the process is operated for at least 500 hours on stream.

7. A process as claimed in claim 1 wherein the catalyst comprises from 1 to 50% wt. of nickel on a support.

8. A process as claimed in claim 1 wherein the support is a refractory oxide or other refractory compound of metals of Groups II, III and IV of the Periodic Table.

9. A process as claimed in claim 1 wherein the feedstock contains a phenolic inhibitor.

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U.S. Cl. X.R.

208—217

UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,691,066 Dated September 12, 1972

Inventor(s) Carruthers et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 2, Line 68, for "ocntact"	read	-- contact --
Col. 3, Line 61, for "excvept"	read	-- except --
Col. 5, TABLE 1 under heading "Diene value", second line, for "1.6"	read	-- 0.6 --
Col. 6, Line 50 in the formula, for "C <sub>5</sub> H <sub>9</sub> S"	read	-- C <sub>5</sub> H <sub>6</sub> S --
Col. 7, TABLE 5, left- hand column, fourth line, for "sElphur"	read	-- sulphur --
Col. 8, TABLE 7, left- hand column, last line, for "2067-3090"	read	-- 2967-3090 --

Signed and sealed this 1st day of May 1973.

(SEAL)  
Attest:

EDWARD M. FLETCHER, JR.  
Attesting Officer

ROBERT GOTTSCHALK  
Commissioner of Patents