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PROCESS FOR REMOVING NITROGEN

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This invention relates to the removal of nitrogen-containing compounds from petroleum fractions.

It has been found that nitrogen-containing compounds are deleterious in certain refining processes because of their poisonous effect on catalysts. It is also speculated that nitrogen-containing compounds contribute to discoloration, formation of sludges and gum and general instability of petroleum products. It is, therefore, highly desirable to develop effective means for the removal of these nitrogen-containing compounds. In general, nitrogen-containing compounds are classified as basic and non-basic types. The basic type can usually be removed by a simple acid washing, but the removal of the non-basic types presents a more difficult problem. Both the basic and non-basic nitrogen-containing compounds can be removed by the method of the present invention.

In accordance with the invention, the nitrogen content of a nitrogen-containing petroleum fraction is reduced by a process comprising contacting said nitrogen-containing petroleum fraction with a mixture of heavy metal salts selected from the group consisting of iron salts and zinc salts. The unreacted salts and metal salt complexes, formed by the reaction of the metal salts and the nitrogen-containing compounds, are thereafter separated from the petroleum fraction. In one preferred embodiment of the invention, the basic nitrogen-containing compounds are selectively removed before treatment of the petroleum fraction with a mixture of heavy metal salts. In another preferred embodiment of this invention, the olefin and sulfur contents of the nitrogen-containing petroleum fraction are reduced before treatment with the heavy metal salts. In yet another preferred embodiment of this invention, the heavy metal salts and metal salt complexes, which are separated from the treated oil, are regenerated for reuse.

The charge stocks for this process comprise any nitrogen-containing petroleum fraction. By "nitrogen-containing petroleum fraction" is meant any petroleum fraction comprising nitrogen-containing compounds in admixture with other compounds and hydrocarbons. In particular, the charge stock may comprise any nitrogen-containing petroleum fraction boiling between about 40° C. and 550° C. or higher at atmospheric pressure. For example, naphthas, furnace oils, gas oils, full range crudes, lubricating oils, or residuums, may be employed. Nitrogen-containing petroleum fractions boiling between 200° C. to 400° C., i.e., furnace oils and gas oils are preferred charge stocks for the process of this invention since the method of this invention is particularly applicable to stabilizing such charge stocks against, for example, gum formation, and also for preparing such charge stocks for further catalytic treatment as noted above. The charge stocks for this process may also comprise some sulfur-containing compounds. The preferred charge stock for the process of this invention is one of low sulfur content. The sulfur

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content of the charge stock may be lowered by any suitable means. One preferred means, for example, is by a mild hydrogenation.

The nitrogen content of a nitrogen-containing petroleum fraction may be reduced by contacting the nitrogen-containing petroleum fraction with selected heavy metal salts. It has now been found that a mixture of heavy metal salts selected from the group consisting of iron salts and zinc salts has a synergistic effect in removing nitrogen-containing compounds from a nitrogen-containing petroleum fraction. By "iron salts" is meant any compound of iron with a negative organic or inorganic radical. By "zinc salts" is meant any compound of zinc with a negative organic or inorganic radical. Suitable organic salts of iron and zinc include, for example, the formates, acetates, and propionates. Suitable inorganic salts of iron and zinc include, for example, the sulfates, nitrates, phosphates and halides, such as, the chlorides. The inorganic salts of iron and zinc are preferred and, in particular, the metal halides are preferred. The most preferred metal salts are the iron and zinc chlorides.

The heavy metal salts of this invention may be prepared by any suitable method. For example, ferric chloride may be prepared by heating ferric oxide in a stream of chlorine to a temperature between 600° and 1000° C. The ferric chloride, which is formed during the reaction, sublimates and may be removed and thereafter condensed. Zinc chloride may suitably be formed by direct reaction of zinc or zinc oxide with aqueous hydrochloric acid.

Any suitable means may be employed for contacting the heavy metal salts and the nitrogen-containing charge stock. For example, the charge stock may be passed through a column packed with the salts, or the salts may be slurried with the charge stock and thereafter separated. The treated charge stock and salts may be separated by any suitable means, for example, by filtration, centrifugation or decanting. It is preferred that the charge stock be in the liquid phase for improved contacting with the heavy metal salts. In addition, if desired, the more viscous type charge stocks may be diluted with an inert solvent, such as, a low boiling saturated aliphatic hydrocarbon, for example, isohexane, to improve contacting between the salts and the charge stock.

The temperature of contacting may be between -50° C. to 200° C. or higher. In general, room temperature is preferred, although increased temperatures may aid in promoting complex formation and thus reduce the required contact time. The lower temperature which may be employed is limited by the solidification point of the charge stock. The upper temperature which may be employed is limited by the thermal decomposition of the metal salt complexes, and the promotion of undesirable side reactions between the metal salts and other components of the charge stock, such as, the halogenation of aromatic compounds if a halogen salt is employed.

Atmospheric pressure is the preferred pressure, but pressures below atmospheric or pressures up to 100 p.s.i.g. or higher may be employed, if desired, to maintain the charge stock in the liquid phase.

The contact time should be sufficient for complex formation to occur between the nitrogen-containing compounds and the metal salts. Contact times may be de-

creased by improved contacting between the metal salts and the nitrogen-containing compounds, such as, by increased agitation or mixing, and by increasing the temperature of contacting as noted above. Contact times of at least about two minutes may be employed with preferred contact times between 10 minutes and four hours.

The molar ratio of zinc to iron may be from 1:10 to 10:1 with preferred molar ratios from 1:1 to 2:1. The amount of heavy metal salt mixture to be employed is a function of the amount of nitrogen in the charge stock. In general, the molar ratio of salt mixture to nitrogen, calculated as the monoatom, in the charge should be at least 1:1, with preferred molar ratios between 60:1 and 200:1. Additional amounts of salt mixture will be required if other components, such as certain sulfur and oxygen compounds, are present in the charge stock which tend to react with the heavy metal salts.

The separated metal salt complexes may then be regenerated in any suitable manner. By regeneration is meant the recovery of the heavy metal salts from the metal salt complexes. Regeneration usually involves decomposition of the complexes into a metal-containing portion and a nitrogen-containing compound portion followed, if required, by a conversion of the metal-containing portion to the desired metal salt. Before regeneration it may be desirable to wash the salts with a suitable solvent, such as a low molecular weight aliphatic hydrocarbon, such as isohexane, to remove any residual amounts of treated charge stock physically adhering to the salts.

One preferred method of regeneration involves thermally decomposing the metal salt complexes at temperatures between 250° C. and 600° C. in the presence of an inert gas, such as nitrogen. The nitrogen-containing compounds may be removed from the decomposition zone by any suitable means, such as by an inert sweep gas, such as nitrogen, and thereafter condensed. The metal-containing portion may, in some cases, be immediately ready for reuse while in other cases further processing may be required.

Another preferred method of regeneration is the oxidative regeneration of the metal salt complexes to form metal oxides and combustion products of the organic material. The metal oxides may then be converted to the desired metal salts by reaction of the metal oxides with the appropriate reactant in any manner well known in the art.

The invention will be further described with reference to the following specific examples. The charge stock for the following specific examples, unless indicated otherwise, is a hydrogenated fluid catalytically-cracked furnace oil whose inspections are given on Table I below.

TABLE I

Gravity, ° API	25.7
Boiling range, ° C.:	
10% point	246
50% point	280
90% point	316
End point	339
FIA (ASTM D1319):	
Aromatics, volume percent	60.4
Olefins, volume percent	1.9
Saturates, volume percent	37.7
Total nitrogen, p.p.m.	160
Basic nitrogen, p.p.m.	25
Sulfur, weight percent	0.09

Three sets of experiments were performed to evaluate the effectiveness of various metal salts for removing the nitrogen-containing compounds from the hydrogenated furnace oil. In the first set of experiments, 25 grams of each of the salts listed in Table II below were separately contacted with 250 milliliter portions of the hydrogenated

furnace oil by slurring and shaking for three hours at room temperature and atmospheric pressure.

In the second set of experiments, the procedure of the first set was repeated except in the second set 10 milliliters of water were added to each oil plus salt mixture.

In the third set of experiments, 250 milliliters of the hydrogenated furnace oil were passed by gravity at atmospheric pressure through an adsorption column (100 centimeters×2.5 centimeters diameter) packed with a dry mixture of sand and salt in a 4:1 weight ratio of sand to salt.

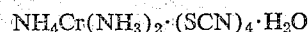
All of the treated portions of the oil, including those from the adsorption column, were analyzed for nitrogen content. The results of all of these experiments are shown in Table II below.

TABLE II

Example Number	Salt Employed	Nitrogen Analysis, p.p.m.		
		First Set	Second Set	Third Set
1.	FeCl ₃ ·6H ₂ O	80	120	110
2.	ZnCl ₂	110	150	120
3.	CuCl ₂ ·2H ₂ O	160	150	170
4.	CoCl ₂ ·6H ₂ O	170	160	160
5.	HgCl ₂	150	160	170
6.	NH ₄ Cr(NH ₃) ₂ ·(SCN) ₄ ·H ₂ O	160	180	160

¹ These values are within the limit of experimental error for the nitrogen analysis method.

A comparison of the results from all three sets of experiments shows that only the zinc and iron salts were even partially effective for lowering the nitrogen content of the charge stock. The addition of water or sand to the salts appeared to lessen the effect of the salts and are, therefore, not preferred diluents. The



salt used in Example 6 in Table II is the so-called Reineke salt which is used in analytical work for the complexing and identification of nitrogen-containing compounds, as described, for example, in an article entitled "Colorimetric Determination of Nitrogenous Substances in Complex Mixtures as Reineckates," by M. Masse in *Pharmaceutica Acta Helvetica*, vol. 33, p. 880 (1958). The fact that this Reineke salt was not effective for nitrogen removal makes the results with the iron and zinc salts of this invention even more unexpected.

A series of experiments was then run to determine the effectiveness of a combination of salts for the removal of nitrogen-containing compounds. The results of these experiments are shown in Table III below. Again, 25 grams of each salt were contacted with 250 milliliter portions of the hydrogenated furnace oil by slurring and shaking for three hours at room temperature and atmospheric pressure.

TABLE III

Example Number		Nitrogen, p.p.m.
7.	FeCl ₃	80
8.	FeCl ₃ +ZnCl ₂	6.4
9.	FeCl ₃ +ZnCl ₂ +CuCl ₂	2.9
10.	FeCl ₃ +ZnCl ₂ +CuCl ₂ +CoCl ₂	6.4
11.	FeCl ₃ +ZnCl ₂ +CuCl ₂ +CoCl ₂ +HgCl ₂	6.4

¹ The hydrated forms of the iron, copper, and cobalt salts were used as in Table II above.

The experiments in Table III show that mixtures of iron and zinc salts are unexpectedly superior in nitrogen-removing ability to either salt alone and the presence of other heavy metal salts does not appear to enhance the ability of the iron and zinc salts to remove nitrogen-containing compounds.

In yet another series of experiments, the effect of salt concentration on nitrogen removal was investigated. In

these experiments 250 milliliters of the charge oil were admixed with varying amounts of a mixture of iron and zinc chlorides wherein the molar ratio of iron to zinc was 1.98:1. The results of these are shown in Table IV below.

TABLE IV

Example Number	Weight of Salts		Nitrogen in Product, p.p.m.
	FeCl ₃ ·6H ₂ O, grams	ZnCl ₂ , grams	
12.....	5	5	11.1
13.....	10	10	11.0
14.....	15	15	6.3
15.....	20	20	8.5
16.....	25	25	6.4
17.....	30	30	5.4
18.....	50	50	0.6

A comparison of Examples 12 through 18 on Table IV shows that, in general, an increasing salt concentration results in the formation of products with a lower nitrogen content.

Comparing Example 12 with Examples 1 and 2 shows the synergistic effect of a mixture of iron and zinc salts; for the use of 10 grams of the mixture of salts in Example 12 resulted in a far greater reduction in nitrogen content than 25 grams of either salt alone as in Examples 1 and 2.

In the following four examples the charge stock was a hydrogenated furnace oil from which the basic nitrogen-containing compounds were removed by washing with hydrochloric acid (1 N). The properties of this charge stock are the same as those in Table I above, except the total nitrogen is 120 parts per million and the basic nitrogen is essentially zero parts per million.

Example 19

Five hundred milliliters of the charge oil were slurried with 50 grams of ferric chloride at room temperature and atmospheric pressure for three hours in a closed system. The precipitates were removed from the oil by filtration, and the oil was washed with water repeatedly to remove entrained salts, and finally dried. A portion (450 grams) of the resultant oil was then treated with 50 grams of zinc chloride; the precipitates were separated as above; and the oil washed with water and dried. The resultant oil contained 28 parts per million of nitrogen.

Example 20

Example 19 was repeated except the oil was treated first with the zinc chloride, and then with the ferric chloride. After the initial zinc chloride treatment the oil contained 110 parts per million of nitrogen, while after treatment with both salts individually the oil contained 28 parts per million of nitrogen.

The results of Examples 19 and 20 indicate the sequence of treatment with the iron and zinc salts individually is not critical with respect to the final nitrogen content.

Example 21

Example 19 was repeated except 100 grams of each salt were employed. The nitrogen content of the resultant oil was 25 parts per million showing that increased amounts of the salts used individually had very little additional benefit. Two hundred milliliters of this resultant oil containing 25 parts per million of nitrogen were then slurried with a mixture of 20 grams of ferric chloride and 20 grams of zinc chloride for three hours at room temperature and the product from this treatment unexpectedly contained only 2.5 parts per million of nitrogen.

Example 22

Example 21 was repeated except the sequence of the individual salt addition was as in Example 20. The nitrogen content of the products from successive treatments with 100 gram portions of zinc chloride and ferric chlo-

ride, and then a mixture of 20 grams of zinc chloride and 20 grams of ferric chloride was 110 parts per million, 19.3 parts per million, and 2.4 parts per million respectively.

A comparison of Examples 21 and 22 shows again that the sequence of salt addition is not critical with respect to the final nitrogen content.

A comparison of Examples 19 and 21 shows the synergistic effect in using a mixture of iron and zinc chlorides. In Example 19, 100 total grams of separate 50 gram portions of the two salts lowered the nitrogen content of the oil to 28 parts per million. In Example 21, 200 total grams of the separate salts lowered the nitrogen content of the oil to only 25 parts per million. An additional treatment with only 40 grams of a 1:1 weight mixture of the salts unexpectedly reduced the nitrogen level to 2.5 parts per million. These same conclusions can be drawn by a comparison of Examples 20 and 22.

Example 23

In this example, 250 milliliters of a crude gas oil, whose analysis is given in Table VI below, were slurried with a mixture of 25 grams of ferric chloride and 25 grams of zinc chloride at room temperature with constant agitation for three hours.

TABLE VI

Gravity, ° API	32.5
Boiling range, ° C.:	
10% point	277
50% point	338
90% point	386
End point	404
Total nitrogen, p.p.m.	380
Basic nitrogen, p.p.m.	126
Sulfur, weight percent	0.86

After treatment, the crude gas oil was filtered and water washed to remove final traces of the salt. Analysis of the treated gas oil showed the nitrogen content had been decreased from the original 380 parts per million to 7.3 parts per million.

The metal salt complexes were considered freed of entrained oil after repeatedly pulverizing the metal salt complexes to reduce the particle size of the complexes followed by repeated washings of the complexes with isohexane.

It was also found that regeneration of the metal salt complexes could be effected by thermal decomposition.

As an example of this, a three gram portion of the pulverized and washed metal salt complexes was heated in a tube at the rate 7° to 8° C. per minute until a temperature of 450° C. was reached. A stream of nitrogen was continuously passed through the tube to remove any volatilized material. The volatilized material was thereafter condensed and found to have a nitrogen content of 1.09 percent.

A mixture of metal salt complexes, wherein the weight ratio of iron chloride to zinc chloride was 1:1, was also regenerated by heating the complexes in an open crucible to combust the organic material and form metallic oxides. Due to the volatility of the zinc chloride, a portion of the zinc was probably lost to the atmosphere. Suitable apparatus could easily be installed, of course, to limit any loss of metallic compounds during regeneration. The remaining metallic oxides were dissolved in boiling 4 N hydrochloric acid; the water thereafter removed on a steam bath, and the corresponding chlorides dried in an oven maintained at 90° C. until dry enough to be pulverized.

A portion of a 1:1 weight mixture of iron and zinc chlorides, which had been used to remove nitrogen-containing compounds from a hydrogenated furnace oil, was regenerated by oxidation and reformation of the chlorides as described above, and the mixture of regenerated salts was tested for activity in the following manner.

Example 24

Sixteen grams of the regenerated salt mixture were slurried with 80 milliliters of the hydrogenated furnace oil whose analysis is given in Table I above. The mixture was stirred for three hours at room temperature. The nitrogen content of the product was 26 parts per million showing that the regenerated salts can be reused.

Example 25

Example 24 was repeated except eight grams of zinc chloride were added to the 16 grams of regenerated salt mixture and 120 grams of oil were used to maintain the same salt to oil ratio. The nitrogen content of the product was 2.7 parts per million.

As noted above, both the basic and non-basic nitrogen-containing compounds can be removed by the method of the present invention. By "basic nitrogen-containing compounds" is meant those nitrogen-containing compounds which form hydrochloric acid soluble hydrochlorides.

As also noted above, the sulfur content of the charge stock may be lowered by any suitable means, such as, by a mild hydrogenation. By a mild hydrogenation is meant hydrogenation conditions whereby the olefin and sulfur contents of the charge stock are reduced while effecting little or no hydrogenation of the aromatic constituents.

Resort may be had to such variations and modifications as fall within the spirit of the invention and the scope of the appended claims.

I claim:

1. A process for reducing the nitrogen content of a nitrogen-containing petroleum fraction which comprises contacting said nitrogen-containing petroleum fraction with a mixture of at least one iron halide and at least one zinc halide.

2. A process for reducing the nitrogen content of a nitrogen-containing petroleum fraction boiling between 40° C. and 550° C. which comprises contacting said nitrogen-containing petroleum fraction in the liquid phase at a temperature between -50° C. and 200° C. with a mixture of at least one iron halide and at least one zinc halide.

3. A process according to claim 2 wherein the molar ratio of iron to zinc in the mixture of halides is between 1:10 and 10:1.

4. A process according to claim 3 wherein the molar ratio of metals in the mixture of halides to nitrogen in the nitrogen-containing petroleum fraction is at least 1:1.

5. A process for reducing the nitrogen content of a nitrogen-containing petroleum fraction boiling between 200° C. and 400° C. which comprises contacting said nitrogen-containing petroleum fraction in the liquid phase at a temperature between -50° C. and 200° C. with a mixture of at least one iron halide and at least one zinc halide.

6. A process for reducing the nitrogen content of a nitrogen-containing petroleum fraction boiling between

40° C. and 550° C. which comprises contacting said nitrogen-containing petroleum fraction in the liquid phase at a temperature between -50° C. and 200° C. with a mixture of iron chloride and zinc chloride.

7. A process according to claim 6 wherein the nitrogen-containing petroleum fraction boils between 200° C. and 400° C.

8. A process according to claim 6 wherein the molar ratio of iron to zinc in the mixture of metal chlorides is between 1:10 and 10:1.

9. A process according to claim 8 wherein the molar ratio of metals in the mixture of metal halide to nitrogen and nitrogen-containing petroleum fraction is at least 1:1.

10. A process for reducing the nitrogen content of a nitrogen-containing petroleum fraction comprising basic and non-basic nitrogen-containing compounds which comprises treating said nitrogen-containing petroleum fraction to selectively remove the basic nitrogen-containing compounds, and thereafter contacting the treated nitrogen-containing petroleum fraction with a mixture of at least one iron halide and at least one zinc halide.

11. A process according to claim 10 wherein the iron halide is ferric chloride and the zinc halide is zinc chloride.

12. A process for treating a nitrogen-containing petroleum fraction comprising sulfur, olefins and nitrogen-containing compounds which comprises subjecting said nitrogen-containing petroleum fraction to hydrogenation to reduce the sulfur and olefin content thereof and thereafter contacting the hydrogenated petroleum fraction with a mixture of at least one iron halide and at least one zinc halide to reduce the nitrogen content of the hydrogenated petroleum fraction.

13. A process according to claim 12 wherein the iron halide is ferric chloride and the zinc halide is zinc chloride.

14. A process for reducing the nitrogen content of a nitrogen-containing petroleum fraction which comprises contacting said nitrogen-containing petroleum fraction with a mixture of at least one iron halide and at least one zinc halide, separating the iron and zinc halides and metal salt complexes formed by the reaction of the iron and zinc halides and the nitrogen compounds present in the nitrogen-containing petroleum fraction; thereafter regenerating said metal salt complexes; and thereafter recycling said regenerated metal salts.

15. A process according to claim 14 wherein the iron halide is ferric chloride and the zinc halide is zinc chloride.

16. A process for reducing the nitrogen content of a nitrogen-containing petroleum fraction which comprises contacting said nitrogen-containing petroleum fraction with a mixture of ferric chloride and zinc chloride.

References Cited by the Examiner

UNITED STATES PATENTS

2,138,566	11/38	Benedict	208—254
2,925,375	2/60	Fleck et al.	208—212

ALPHONSO D. SULLIVAN, *Primary Examiner.*