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METHOD OF STABILIZING PETROLEUM PRODUCTS

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The present invention is concerned with the elimination of the traces of metallic compounds contained in hydrocarbons of the petroleum type.

It is well known, on the one hand, that petroleum products or their fractions of distillation often contain traces of metals, present in the form of various compounds, which were introduced either by pollution or by being brought in during the course of handling, either consecutively during the various processes of refining, such as for example sweetening processes by the action of metallic salts, such as cupric chloride or ferric sulfate, or by the action of organo-metallic compounds with chelated links, etc. These metallic compounds which are contained in a state of solution or of fine suspension in the hydrocarbon compounds, are apt to produce either a certain instability in course of time, with development of cloudiness and a coloration and the slow formation of a precipitate, or a noxious effect during the combustion of the said products in explosion engines or internal combustion engines.

It is known, on the other hand, that it is possible to reduce these noxious effects of metallic compounds contained in petroleum products by compounding them in the form of organo-metallic compounds with chelated links by intimate association with imino-phenols, such as amongst others, Schiff bases, for example disalicylal propylene diimine, etc. It is also possible to limit the effects of the said instability of petroleum products by simple filtration, for example; methods of this kind, however, remove more or less completely only the consequences of this instability and not the instability iself.

The invention has for its object a method of elimination of metallic compounds contained in hydrocarbons of the petroleum type, or in their distillation fractions, the said method consisting in the formation in situ of an organo-metallic compound with chelated links by the action of an alkyl imino-phenol, followed by the decomposition of the said chelated compound by an acid reaction agent in the solid state.

A special application of the invention is constituted by a process of stabilization of petroleum products which have been subjected to a sweetening treatment by oxidation in air of the mercaptans which they contain, in the presence of organo-metallic compounds with chelated links, the said method consisting in removing the traces of metallic compounds which remain in the sweetened products by decomposition of the said chelated compounds by means of an acid reaction agent in the solid state.

The other developments and improvements represented by the present invention will be brought out during the course of the description which follows.

The applicants have found, on the one hand that the treatment for removing traces of metals present in products of the petroleum type in the form of organo-metallic compounds with chelated links, may be effected by simple filtration through a solid mass having an acid reaction, and in particular a crystalline acid salt, such as for example (and without any limitation being implied by this

enumeration) an acid sulfate of an alkali metal or an alkaline earth metal, an acid phosphate of an alkali metal or of an alkaline earth metal, a bifluoride of an alkali metal, etc.

There is also a certain advantage to be derived from using such a crystalline salt mixed with an inactive material serving as a simple inert filling medium, such as coke or a neutral salt, such as sodium chloride, so as to avoid the formation of deposits by the acid salt setting into a mass during the course of the operation.

On the other hand, the applicants have found that if the metals to be eliminated are present in the petroleum products in a chemical form which is such that the above treatment is not adequate to eliminate them, on the contrary, this same treatment will ensure the removal of the said metals if there is added first of all to the same petroleum products an alkyl imino-phenol, or certain Schiff bases capable of producing by formation in situ, a chelated organic compound of the metal to be eliminated. The Schiff bases to be used are, for example, those which result from the condensation of an ortho-hydroxy-benzaldehyde with a diamine.

In addition, the applicants have proved that the formation in situ of the said chelated metallic compounds can only be obtained rapidly and easily when the metals to be eliminated from the hydrocarbons are present in an ionizable form, for example in the form of a chloride, an oleate, a stearate, a naphthenate, an enolate or a cresolate, etc., this enumeration being furthermore not given in any limiting sense.

Thus, for example, to a petrol having an initial and final boiling point of 100°–160° C. and a density of 0.738, and containing spectrographically less than 0.03 mg. per litre of copper, there is added:

To a sample (1): 1.0 mg. per litre of copper in the form of naphthenate of copper.

To a sample (2): 1.0 mg. per litre of copper in the form of naphthenate of copper. From this sample (2) four fractions 2*a*, 2*b*, 2*c*, 2*d* are made, to which there is added respectively:

Fraction (2*a*): 1 mg. per litre of Schiff base (disalycylal-propylene-diimine), in the form of a commercial product at 80%.

Fraction (2*b*): 3 mg. per litre of the same Schiff base; fraction (2*c*): 10 mg. per litre of the same Schiff base; fraction (2*d*): 30 mg. per litre of the same Schiff base. It should be observed that with this commercial Schiff base, the stoichiometric quantity necessary for the formation of chelate of copper is 6 mg. per litre.

To a sample (3): containing copper in the metallic form, by pollution. After filtration, the concentration of copper is 0.6 mg. per litre. From this sample (3), the same fractions are taken and the same additions made as in the case of sample (2).

This series of fractions is subjected to a filtration over a bed of sodium bisulfate at a speed of 20 litres of hydrocarbon per litre of the mass of the filter and per hour. The results obtained are given in the following table:

Sample No.	Amount of Schiff base added, mg./l.	Copper in petrol	
		Before filtration, mg./l.	After filtration, mg./l.
1	0	1	0.5
2*a*	1	1	0.04
2*b*	3	1	0.04
2*c*	10	1	0.03
2*d*	30	1	0.03
3*a*	1	0.6	0.5
3*b*	3	0.6	0.3
3*c*	10	0.6	0.4
3*d*	30	0.6	0.5

The results obtained in the case of the samples 2*a*, 2*b*, 2*c* and 2*d* clearly show the effectivness of the method of elimination in accordance with the invention. In addition, a comparison of the results relating to the samples of the series (2) illustrates very clearly the catalytic role played by the alkyl imino-phenol, or by the Schiff base, in the elimination of the traces of metals by the method in accordance with the invention. It will be seen in fact, that it is not necessary that the alkyl imino-phenol should be present in a stoichiometric quantity with respect to the said metals in the process of purification. In addition, the trifling results obtained in the case of the samples of the series (3) support the indication given above to the effect that the metal to be eliminated should be in an ionisable form.

The applicants have furthermore observed that the treatments known as sweetening of petroleum products by oxidation in air of the mercaptans in the presence of organo-metallic compounds with chelated links, are accompanied by a precipitate which is easy to remove by simple filtration; but in addition, if there remains an excess of chelated compound in the sweetened petroleum product, this product may remain colored and may have a certain instability which is indicated by the development of cloudiness, this being the result of a slow precipitation of traces of metallic compounds. The presence of this undesirable excess of chelated compound may especially occur in the case in which the sweetening of the petroleum product is carried out during storage by an addition of small quantities of chelated compound, but in excess however, with respect to the mercaptans, and in particular if the hydrocarbon includes large proportions of aromatic compounds.

In these various circumstances, it is preferable, in order to improve the color of the product and to make it perfectly stable, to destroy the chelated compound which remains in it in excess, either in an active form as a catalyst or in an inactive form. To this end, the method of operation consists, in conformity with the present invention, in subjecting the petroleum products to the treatment described above, after the said sweetening operation has been effected.

The examples given below, which are not given in any sense by way of limitation, illustrate the various methods of operation and developments of the invention.

Example 1.—A thermal cracking petrol (with initial and final boiling points: 35°–200° C.; d_{15}=0.750) containing 0.005% by weight of sulphur in the form of mercaptan had added to it 7 grams per cu.m. of disalicylal propylene diimino cobalt and 7 grams per cu.m. of litharge in solution in 70 cu.m. of cresol.

The petrol is sweet after storage for 20 hours, but it is colored and slowly becomes cloudy.

In accordance with the invention, this pertol is filtered through a bed loaded with a mixture of equal weights of technical bisulfate of sodium and chloride of sodium. This filter is supplied at a rate of 200 litres per hour per 2 kg. of bisulfate which constitutes the charge of the filter. Finally, the petrol thus treated is colorless, stable and freed from every identifiable trace of metals.

Example 2.—A fraction of paraffin (initial and final boiling points 170°–280° C.; d_{15}=0.800) having a color of Saybolt+22, containing 0.003% by weight of sulfur in the form of mercaptan is made sweet by the addition of 2 grams per cu.m. of disalicylal propylene diimino cobalt and 2 grams per cu.m. of lead in the form of cresolate, in solution in 20 cu.cm. of cresol. After storage for 24 hours, the Saybolt color fell to +14. An alkaline wash is then carried out in order to deodorise the product from the natural cresols which are already present, and from the added cresol, this alkaline wash being immediately followed by washing with water so as to remove all traces of alkaline cresolate; the color is then Saybolt+22. The product is then filtered through a mixture of bisulfate of sodium and marine salt. The paraffin thus treated has a color of +24 Saybolt, no longer contains any metals in quantities which can be treated, and is stable during storage.

Example 3.—To a fraction of paraffin (with initial and final boiling points: 190°–250° C.; d_{15}=0.770), containing 0.016% of sulfur by weight in the form of mercaptans, there is added 7 grams per cu.m. of disalicylal propylene diimino cobalt in the form of a solution of a petroleum solvent with 60% by volume of aromatic hydrocarbons and initial and final boiling points of 140°–200° C., this solution contains 16.6 grams per litre of disalicylal propylene diimine, 348 grams per litre of cobalt in the form of naphthenate and 20 grams per litre of lead in the form of naphthenate. After 24 hours storage, the paraffin thus treated only contained 0.003% by weight of sulfur in the form of mercaptan, and its Saybolt color was +11.

In applying the invention, this product is then filtered on a bed of acid sodium phosphate in crystalline form; the paraffin thus treated does not contain any metals and its Saybolt color is +22.

Example 4.—The same paraffin which was treated as indicated at the beginning of Example 3 so as to remove the mercaptans, was filtered through a bed charged with ammonium bifluoride (HF, NH_4F). The paraffin thus treated then contains only traces of metals and its Saybolt color is +20.

Example 5.—A total Iraq petrol obtained by distillation (initial and final boiling points 40°–120° C.; d_{15}=0.725), containing 0.025% by weight of sulfur in the form of mercaptans is made sweet by stirring in the presence of a fifth of the volume of an aqueous solution containing 40 grams per litre of cupric chloride, 40 grams per litre of sodium chloride and 1 cu.cm. per litre of concentrated hydrochloric acid; the petrol thus treated contains 0.40 mg. per litre of copper.

From this petrol, two fractions are made; one fraction is directly filtered through a bed of bisulfate of sodium and the other is filtered through a similar bed after the addition of 1 mg. per litre of disalicylal propylene diimine. After these treatments, the first fraction still contains 0.20 mg. per litre of copper, whilst the second only contains 0.06 mg. per litre of copper.

What we claim is:

1. In a method for decolorizing and stabilizing petroleum distillate hydrocarbons and for the elimination therefrom of metallic compounds, the steps which comprise forming in situ in said petroleum hydrocarbons an organo-metallic compound with a chelated bond by the action of an alkyl imino-phenol and then decomposing said chelated compound by reaction with a solid acid salt of a metal selected from the group consisting of alkali and alkaline earth metals.

2. In a method for the decolorizing and stabilizing of petroleum distillate hydrocarbons which have previously been subjected to a sweetening treatment including the oxidation of mercaptans in said hydrocarbons by an oxidizing gas in the presence of an organo-metallic chelate compound, the steps which comprise reacting the resultant of said chelate compound with a solid acid salt of a metal selected from the group consisting of alkali and alkaline earth metals for the decomposition thereof, and separating the products of said reaction.

3. In a method for decolorizing and stabilizing petroleum distillate hydrocarbons and for the elimination therefrom of metallic compounds, the steps which comprise forming in situ in said petroleum hydrocarbons an organo-metallic compound with a chelated bond by the action of an alkyl imino-phenol and then decomposing said chelated compound by reaction with a solid acid salt of a metal selected from the group consisting of alkali and alkaline earth metals.

4. In a method for decolorizing and stabilizing petroleum distillate hydrocarbons and for the elimination therefrom of metallic compounds, the steps which com-

prise forming in situ in said petroleum hydrocarbons an organo-metallic compound with a chelated bond by the action of an alkyl imino-phenol and then decomposing said chelated compound by reaction with a solid acid salt selected from the group consisting of sulfates, phosphates, and fluorides of alkali and alkaline earth metals.

5. In a method for the decolorizing and stabilizing of petroleum distillate products which have been subjected to a sweetening treatment by the oxidation of mercaptans therein by an oxidizing gas in the presence of a condensation product of a chelate with a metal of group VIII of the periodic table, the steps which comprise filtering said petroleum hydrocarbons and the resultant of said oxidation reaction through a filter bed comprising a solid crystalline acid salt of a metal selected from the group consisting of alkali and alkaline earth metals, effecting reaction between said resultants of said oxidation reaction and said filter bed, and separating from said thus-treated hydrocarbons the resultants of said reaction with said solid crystalline acid salt filter.

6. In a method for the decolorizing and stabilizing of

petroleum distillate products which have been subjected to a sweetening treatment by the oxidation of mercaptans therein by an oxidizing gas in the presence of a condensation product of a chelate with a metal of group VIII of the periodic table, the steps which comprise decomposing the resultant products of said sweetening and oxidation treatment with said chelate compounds by filtering said hydrocarbons and said resultants through a filter bed composed of solid crystalline acid salts of a metal selected from the group consisting of alkali and alkaline earth metals, effecting reaction and decomposition of said resultants during said filtration thereof substantially in the absence of reaction between said acid salts and said petroleum hydrocarbons, and separating the resultants of said reaction with said acidic filter bed from said sweetened petroleum hydrocarbons.

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