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RETARDATION OF COKE FORMATION

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ABSTRACT OF THE DISCLOSURE

The formation of coke in high-temperature petroleum treatments is retarded by adding to the oil a coke-retarding amount of a coke retarder selected from the group consisting of elemental phosphorus and compounds thereof. Very small amounts of these coke retarders are effective, while they generally become ineffective above about 0.5%, based on the weight of the oil.

The present invention relates to a method for retarding the formation of coke in the high-temperature treatment of oils.

The formation of coke in various high-temperature treatments of oils, particularly crude oils, has been a persistent problem. In processes such as visbreaking, catalytic cracking, and distillation, the coke that is formed has a tendency to inactivate catalysts and to clog the equipment, decreasing its efficiency of operation, and requiring periodic cleaning. The temperature at which coking becomes a problem depends upon a number of factors, particularly the characteristics of the oil being treated. As a general matter, such coke formation tends to become a problem at temperatures above about 700° F.

It has now been found that the formation of coke may be significantly retarded in the high-temperature treatment of oils by incorporating into the oils a coke-retarding amount of a coke retarder selected from the group consisting of phosphorus, phosphorus compounds, and mixtures thereof.

More particularly, it has been found that elemental phosphorus and a number of phosphorus compounds exhibit a coke retardation effect if employed within the proper percentage range. These coke retarders have been found to be effective even at very low levels. Excellent coke retardation has been achieved, for example, with as little as 0.001% coke retarder incorporated into the oil. It is important, however, that excessive coke retarder not be employed, as excessive amounts have been found to actually accelerate rather than retard coke formation. The maximum amount of retarder that may be employed while still achieving coke retardation depends upon the nature of the oil being treated and upon the type of inhibitor being employed. As a general matter, more than about 0.5% inhibitor, based on the weight of the oil, will accelerate the production of coke, and is therefore undesirable. However, with many inhibitor-oil combinations, this coke acceleration will begin at a lower level. Therefore, the optimum proportion of inhibitor should be individually determined for each oil-inhibitor combination. It has also been found that, in coking operations, the addition of such coking retarders improves the quality of coke formed. An additional advantage of the method of the present invention is that it reduces the amount of dehydrogenation occurring during thermal processing. The coke retarders in accordance with the present invention have been found to be effective in the reduction of coke formation with oils which contain coke promoting metals such as vanadium, nickel, and the like.

The most preferred coke retarder in accordance with the present invention is elemental phosphorus, which may be used in the yellow, white, or red forms. However, certain organic and inorganic phosphorus compounds have also been found to be effective. Phosphorus pentoxide and phosphorus pentasulfide have been found to be particularly effective inorganic compounds, while tributyl phosphine and triethyl thiophosphite are effective organic compounds.

In carrying out the method of the present invention, the phosphorus or phosphorus compound is introduced into the oil either during or prior to heating. It may be introduced directly in the form of a solid, liquid, vapor, or dispersion, or may be placed on a support such as alumina before introduction into the oil.

The following examples are intended to illustrate the present invention, and should not be construed as limitative, the scope of the invention being determined by the appended claims.

EXAMPLE 1

0.05 gram of yellow phosphorus was added to 50.2 grams of a domestic sour crude oil, giving a phosphorus concentration of 0.1% by weight, and the mixture was heated to distill out 50 ml. of oil over a one-hour period. The remaining material was refluxed for 34 minutes, and was then cooled down by the rapid addition of toluene, to obtain 1.97 grams of toluene-insoluble coke. This procedure was repeated without the phosphorus addition, and yielded 2.70 grams of coke. Thus, the addition of 0.1% yellow phosphorus gave a 27% reduction in coke formation.

EXAMPLE 2

Example 1 was repeated, except that 0.0044 gram (0.0088%) yellow phosphorus was employed. 2.27 grams of coke were obtained, demonstrating a 16% reduction in coke formation as compared with a similar run in the absence of phosphorus. As this example demonstrates, the use of elemental phosphorus is effective in the retardation of coke formation even at extremely low levels.

EXAMPLE 3

The procedure of Example 1 was repeated, except that 0.04 gram (0.08% red phosphorus was substituted for the yellow phosphorus. 2.18 grams of coke were obtained, showing a 19% reduction in coke formation as compared to a sample with no coke inhibitor.

EXAMPLE 4

The following example was conducted in order to illustrate the deleterious effect of excess phosphorus. The procedure of Example 1 was repeated, except that 0.19 gram (0.4%) yellow phosphorus was incorporated into the crude oil. The experiment yielded 3.02 grams of coke as compared with 2.70 grams without any phosphorus additive. An identical run, in which red phosphorus was substituted for the yellow phosphorus, produced 3.59 grams of coke.

EXAMPLE 5

A sample of sour crude oil was spiked with 0.05 $VO(C_5H_7O_2)_2$, to represent a vanadium impurity often found in crude oils. Various inhibitors were added, and the amount of coke formed was measured. The results were shown in the following table.

Additive, wt. percent:	Coke formed, wt. percent
None	8.8
0.27% yellow phosphorus	5.8
0.13% tributyl phosphine	4.9
0.17% triethyl thiophosphite	5.3

As the above table demonstrates, significant reductions in coke formation are achieved by the addition of elemental phosphorus and phosphorus compounds.

EXAMPLE 6

0.0023 gram (0.0046%) phosphorus pentasulfide was added to 50.4 grams of a domestic sour crude oil containing about 10 p.p.m. nickel, 30 p.p.m. vanadium, and less than 1 p.p.m. iron. The mixture was distilled and the coke formation measured in accordance with the procedure set forth in Example 1. 2.19 grams coke were yielded. This represents a 19% reduction in coke formation as compared to a similar test run on the same crude oil without any coke inhibitor.

EXAMPLE 7

The procedure of Example 6 was repeated, except that only 0.0005 gram (0.001%) phosphorus pentasulfide was used. 2.28 grams of coke were obtained, showing a 15% reduction in coke formation when the additive was used.

EXAMPLE 8

To illustrate the deleterious effect of excess phosphorus sulfides, 0.034 gram phosphorus pentasulfide was added to 50.4 grams of domestic sour crude, representing about 0.067%. In this case, 3.87 grams of cake were formed. An identical run, but with 0.0044 grams of phosphorus pentasulfide, representing only 0.0088%, 2.59 grams of coke were yielded, again illustrating that extremely small amounts of phosphorus compounds are effective.

Obviously, many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and it is

intended to cover in the appended claims all such modifications and variations as fall within the true spirit and scope of the invention.

We claim:

1. In the high-temperature treatment of oils, a method for retarding the formation of coke comprising: incorporating into said oil a coke-retarding amount of a coke retarder selected from the group consisting of elemental phosphorus, phosphorus pentoxide, phosphorus pentasulfide, tributyl phosphine, triethyl thiophosphite, and mixtures thereof.

2. The method as defined in claim 1 wherein said coke retarder is elemental phosphorus.

3. The method as defined in claim 1 wherein said coke retarder is phosphorus pentoxide.

4. The method as defined in claim 1 wherein said coke retarder is phosphorus pentasulfide.

5. The method as defined in claim 1 wherein said coke retarder is tributyl phosphine.

6. The method as defined in claim 1 wherein said coke retarder is triethyl thiophosphite.

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