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DIESEL FUEL

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1 Claim. (Cl. 44—57)

This invention is concerned with improving combustion characteristics of high boiling fuel oils, more particularly with improving the ignition quality of Diesel fuel oils by a reaction of an inorganic hypochlorite.

It has the object of providing a method for effectively increasing the ignition quality of Diesel fuels with some elimination of objectionable mercaptans from the fuel oils.

Other objects and advantages of the invention will be made apparent by the following description.

It is known that elementary sulfur and certain polysulfide compounds were found to be fairly effective ignition accelerators in Diesel fuels and that it has been proposed to use a doctor sweetening treatment on sour Diesel fuels having a high mercaptan content with an excess of added sulfur to convert the mercaptans into ignition accelerating organic polysulfides. However, the practical use of these treatments is hampered by (1) common fuel specifications limiting the total sulfur content of the fuels, and (2) the corrosive action of the sulfur incorporated into the fuel.

It has also been known to subject certain mineral oil fractions, primarily straight run gasoline and similar light non-cracked products, to the treating action of an aqueous alkaline hypochlorite solution. In sweetening such petroleum oil fractions with hypochlorite solutions, particularly solutions of sodium and calcium hypochlorite, for best results it was considered necessary to treat the oil with the solution at substantially atmospheric temperatures in order to avoid reaction of the hydrocarbon components.

Though the use of hypochlorites for refining light petroleum distillates is not new, it has not assumed commercial importance on account of its limited applicability. It was found impractical for sweetening cracked gasolines and kerosenes. Thus, any use of hypochlorites on heavier oils, such as gas oils, heating oils, or Diesel fuels, became regarded as entirely unjustifiable.

Now I have found that if a Diesel fuel oil is treated with an aqueous alkaline hypochlorite solution at elevated temperatures, a product having a remarkably improved cetane rating is obtained. Furthermore, I have determined by chemical analysis of the product treated in accordance with my invention that very little, if any, chlorination of the fuel takes place but that a certain change in chemical properties is effected.

The reason for this unexpected result is not clearly understood, but it is believed that the active ingredients of the solution (oxygen and chlorine) react with mercaptans and possibly other components of the fuel to form a product in situ which contributes to the superior ignition qualities observed. However, it is to be clearly understood that my invention is not to be limited to any theory advanced in explanation thereof.

In the present invention, an inorganic hypochlorite ostensibly reacts with mercaptans and forms ignition accelerating compounds which are more potent than organic di- and polysulfides. The reaction of the hypochlorite agent gave results far superior to those obtained by treating mercaptan-enriched Diesel fuels with a doctor solution (sodium plumbite) or its modifications. It does not require addition of free sulfur. It has given satisfactory results when applied to fuels containing very low concentrations of mercaptans. It has been found to work well on fuels of low sulfur content. If desired, the hypochlorite may be reacted with a mercaptan to form an ignition accelerator compound soluble in Diesel fuel and the reaction product incorporated in a Diesel fuel.

As a specific embodiment, the process of the present invention is suitably applied to petroleum gas oil which meets requirements of Diesel fuel specifications and with very little mercaptan sulfur present before the treatment with the hypochlorite solution. The hypochlorite treating solution may be prepared by chlorination of a caustic alkali solution, but other convenient methods may be used. In a satisfactory treatment, the treating solution is maintained alkaline, the hypochlorite solution is intimately mixed in a minor proportion with the fuel at a suitably elevated temperature until the desired improvement of ignition quality is obtained, and thereafter, the treated fuel is water-washed.

The process is illustrated by the following specific examples:

Example I

The hypochlorite solution was prepared by bubbling chlorine gas thru approximately 20° Bé. aqueous NaOH solution which was cooled in an ice bath to prevent an excessive rise in temperature. The anlysis of the prepared solution showed about 4.66 weight per cent available chlorine, 7.40 weight per cent NaOH, and 8.88 weight per cent total sodium content. Ten liters of gas oil hydrocarbons containing about 3 mg. of mercaptan sulfur per 100 ml. of oil and having a total sulphur content of 0.22% by weight by bomb analysis were agitated with two liters of the hypochlorite

solution for 30 min. at about 200° F. to 210° F. in a closed iron agitator (turbo-mixer). After separating the oil from the partially spent hypochlorite solution by settling, the oil product was washed with two 10 liter batches of hot water and was then filtered thru paper.

Inspections of the oil before and after the treatment are summarized in the following table:

Table 1

	Initial gas oil	Hypochlorite treated gas oil
Cetane number	56.4 (57)[1]	62.6 (64).[1]
Gravity, °A. P. I.	37.5	37.3.
I. B. P., °F.	441	446.
50% B. P., °F.	542	542.
F. B. P., °F.	639	636.
Vis. @ 100° F. (S. U. S.)	37.8	38.0.
Cloud, A. S. T. M., °F.	10	14.
Pour, °F.	10	10.
Flash, PM, °F.	225	218.
Bomb sulfur, per cent	0.22	0.20.
Aniline point, °F.	167	167.
Cu strip corrosion, 3 hrs. @ 212 °F.	Barely pass.	Pass.
Chlorine content, per cent	0	0.
Odor	Mercaptans.	Sweet.
Doctor test	N. G.	Pass.
Mercaptan sulfur, mg./100 ml.	3.0	0.5.

[1] Figures in parentheses are results obtained at a different laboratory.

The fuel oil was chemically analyzed before and after the treatment to determine the action of the hypochlorite agent on the composition. The results are summarized as follows:

Table 2

	Initial gas oil	Hypochlorite treated gas oil
Per cent carbon	86.18	86.24
Per cent hydrogen	13.60	13.60
Per cent sulfur	0.22	0.20
Total	100.0	100.04
Peroxide No.	0.04	10
Mercury No.	1	21
Demulsability @ 100 °F.	1,620	1,620

These analytical results indicate that the treatment can be carried out without appreciable chlorination of the fuel components and without making any substantial change of the sulphur content in giving the fuel the remarkably good increase of about 7 cetane number units. The high order of ignition quality improvement thus obtained can be appreciated by comparison with the effectiveness of various ignition accelerator additions, even the outstanding alkyl nitrates. Moreover, this extraordinary cetane number increase does not entail any material reduction in heating value, since the hydrogen and carbon content is not lowered as in the use of previously known additives.

The active ignition promoting compound formed gave a much higher cetane number increase than could be accounted for on a basis that the less than 0.01% of mercaptan sulfur was converted to polysulfide sulfur. It is possible for the mercaptans to have been converted to other types of oxidized sulfur derivatives, such as sulfines, sulfoniums, sulfoxides, sulfonic compounds, etc., but the exact nature of the converted mercaptans has not been determined. It is also possible that other reactive components of the fuel, such as hydrocarbons, participate in the reaction to form the ignition promoting substance.

It is of interest to note that the treatment made a significant increase in the peroxide number, which is indicative of the formation of substances similar to peroxides in potent oxidizing properties. The peroxide number is a well known test devised to measure the gram equivalents of active oxygen per 1000 liters of a material. It is determined quantitatively by the oxidation of ferrous sulfate to ferric sulfate and titration of ferric salt formed with a standardized titanous chloride solution. More details on this analytic operation are described in the Ind. and Eng. Chem. Journal, vol. 23, 1254, (1931). This highly sensitive test makes possible the determination of extremely small amounts of peroxidic oxygen, such as of the order of 0.01%, which does not show up in ordinary chemical analyses. Thus, it is possible that active oxygen or some other active oxidizing function is introduced into the fuel in extremely small amounts. In gasoline motor fuels, low peroxide numbers of 1–3 are obtained when such fuels are very unstable and undergo rapid deterioration with gum formation, but high peroxide number Diesel fuel products prepared in accordance with the present invention, i. e., with peroxide numbers above 3, were found to be satisfactorily stable. The mercury number increase may also be regarded as indicating the same change as shown by the peroxide number increase. Taking these changes into consideration, it is evident that the amount of the active ignition acelerating ingredient formed in the fuel to make a cetane number increase of 6 to 7 is less than about 0.1%.

EXAMPLE II

The hypochlorite solution described in Example I was employed to treat three separate portions of gas oil whose physical and chemical characteristics have also been described therein. Ten liter portions of gas oil were agitated with two liter portions of hypochlorite solution while maintaining all conditions, except temperature, exactly as has been outlined in the preceding example. In this case, one 10 liter portion of oil was treated with hypochlorite at 80° F. The second 10 liters were treated at temperatures between about 150° F. and 155° F. and the third 10 liter portion at temperatures of about 200° F. to 210° F. After separating the oil from the partially spent hypochlorite solution by settling, each treated 10 liter portion was washed separately with 10 liter batches of hot water and then filtered through paper.

Cetane numbers of the several portions of oil after treatment at the varying temperatures mentioned are compared with the cetane number of the initial gas oil in the following table:

Table 3

Temperature of treat, °F.	Cetane number	Doctor
Original oil	56.4	N. G.
80	57.4	Pass.
150-155	62.0	Do.
200-210	62.6	Do.

Thus, it may be seen from these data that by treating the gas oil at relatively high temperatures, as compared with usual practice for sweetening naphtha, the cetane rating was raised approximately 7 units over that of the original oil. When treating oils at relatively low temperatures, e. g., 80° F., an increase of only 1 unit was effected. Therefore, it is concluded that treating Diesel fuel oils in accordance with my invention results in a markedly superior product if the tem-

perature is suitably elevated to above 80° F., and preferably to within the range of about 125° F. to about 210° F.

It is also noteworthy that while treating the oil with hypochlorite solution at ordinary temperatures (80° F.), a product passing the doctor test but with only a negligible rise in cetane number was obtained. When employing my invention, i. e., treatment at high temperatures with hypochlorite and in the presence of mercaptan sulfur, a sweet product of high cetane rating results.

Diesel fuels treated in the manner described with an alkaline hypochlorite solution may be used as such or may be blended with an untreated Diesel fuel stock to form a blend having improved ignition quality.

It is within the contemplation of this invention to treat gas oils which are practically sweet, or which have been partly desulfurized or sweetened, by any suitable refining method even though the hypochlorite is capable of effecting some elimination of mercaptan sulfur when accomplishing the desired improvement in ignition quality. The present process was found to effect a substantial improvement in the ignition quality of gas oils which contained practically no reactive sulfur (free sulfur or polysulfide sulfur), and also, it was found effective for increasing the cetane numbers of sour and cracked gas oils having high sulfur contents without making any decided desulfurization.

Since with the present procedure the improvement of ignition quality is not essentially accompanied by substantial desulfurization, it is preferred to apply the described treatment to Diesel fuel oils which do not have extremely high sulfur contents. A preferred starting oil for the ignition quality improving treatment is a gas oil or similar high boiling petroleum fraction boiling mainly above 450° F. with an end point below 750° F. with a sulfur content within specification limits, such as below 1%, and with a mercaptan sulfur content less than 0.05%, e. g., about 0.001% to 0.01%.

Although caustic soda is preferred for use in the hypochlorite solution, being the most practical, other metals may be used in the reagent, e. g., aluminum, zinc, magnesium, iron, copper, potassium, or calcium. One of the additional modifications which may be carried out is to use with the hypochlorite treating agent a small amount of an oxidizing agent or a chlorinating agent, such as chlorine gas, hypochlorous acid, hydrogen chloride, or other halogens. Also, the treating conditions may be influenced by exposure of the reaction mixture to light, varying the intensity of agitation and varying the time of contact. The reaction may be followed by various purification treatments, such as filtering, contact with adsorbents, or the like.

While the invention has been described in terms of preferred embodiments thereof, the examples given are not intended to be taken as a limitation on the scope of the invention but only illustrative, and all modifications or variations coming within the scope of the invention are to be included therein.

I claim:

The method of improving a Diesel fuel which comprises reacting a mercaptan with an inorganic hypochlorite to form an oil-soluble ignition accelerator possessing oxidizing potency of active oxygen and incorporating said accelerator into a petroleum fuel oil adapted for operation of a Diesel engine.

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