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DIESEL FUEL

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10 Claims. (Cl. 44—9)

This invention is concerned with improving the operation of Diesel engines through the use of a fuel containing a novel ignition accelerator.

In compression ignition engines of the Diesel type, where the fuel is injected into the compressed air within the engine cylinder, it is important for maximum efficiency in the engine operation that the delay period between injection and ignition be short, thereby insuring ease of starting and smooth engine operation. Improperly delayed ignition gives rise to the phenomenon known as "knocking," similar to that which occurs in an Otto cycle engine when the ignition is improperly accelerated.

For the purpose of decreasing the ignition delay period of a Diesel fuel it has been proposed to admix with the fuel prior to its injection into the engine various compounds which will react under the engine conditions to reduce the ignition delay period. In addition to improving the operating characteristics of the engine the use of the ignition accelerators in Diesel fuels permits efficient operation at lower compression pressures and thereby allows engine designs of less mass or weight, thus reducing the manufacturing and operating costs per unit of power output. Also, the use of ignition accelerators widens the range of available Diesel fuels, since they may be employed to form normal grades of Diesel type fuels from inferior base stocks, as well as to improve the usual grades of fuels.

The present invention is based upon the discovery that the oil-soluble reaction products of primary aliphatic amines with sulfur dichloride are effective ignition accelerators for Diesel fuels.

We do not wish to be bound by any theory as to the chemical composition of the reaction products contemplated by this invention, and for reasons which will hereinafter appear, we prefer to define our improved accelerator as a reaction product. However, for purposes of clarity in the description the reaction products contemplated herein may be described as aliphatic thiamines. As stated above, these products are formed by the reaction of about three molecular proportions of a primary aliphatic amine with one molecular proportion of sulfur dichloride and are characterized by the general formula RNS, in which R represents an aliphatic hydrocarbon radical and N and S are the conventional symbols for nitrogen and sulfur respectively. The reaction whereby these compounds are produced may be represented by the following equation:

$$3(RNH_2)+SCl_2 \rightarrow RNS+2(RNH_2 \cdot HCl)$$

Lengfeld and Stieglitz's analyses on "ethyl thiamine" (Berichte 28 2743 (1895)) indicated the empirical formula C_2H_5NS; their molecular weight determinations indicated the actual formula as $(C_2H_5NS)_4$. This being the case, the reaction can more properly be represented as

$$12(RNH_2)+4(SCl_2) \rightarrow (RNS)_4+8(RNH_2 \cdot HCl)$$

A method for preparing and isolating compounds of the general type described above is illustrated by the following example:

One hundred and twenty grams of mono-n-butyl amine is dissolved in 400 cc. of a low boiling hydrocarbon such as is obtained by carefully fractionating commercial petroleum ether and retaining the fraction boiling between 33° C. and 40° C. This solution was formed in a one-liter, three-neck balloon flask fitted with a mechanical stirrer, a dropping funnel, and a two-way adapter carrying a reflux condenser and a thermometer. To this solution 56.5 grams of sulfur dichloride was added from the dropping funnel over a period of about one hour, the reaction mixture being stirred during such addition. The temperature was maintained between 7° and 20° C. during the addition of the sulfur dichloride and for about forty-five minutes thereafter; this was allowed to complete the reaction. After completion of the reaction, which was attended by precipitation of amine hydrochloride, such precipitate was removed by filtration. The filtrate was allowed to stand over night, during which time additional amine hydrochloride precipitated out. This was subsequently removed by filtration. The filtrate was then vacuum-distilled at room temperature to remove the solvent; the residue, a medium red-brown oil, was highly unstable as evidenced by the fact that it ignited spontaneously and burned when dropped on a hot metal plate.

The unstable character of the butyl thiamine, prepared and isolated according to the above procedure, verifies the observations made by Lengfeld and Stieglitz (Berichte 28, 2743, (1895)), who described the preparation and properties of ethyl thiamine.

Because of the unstable character of these thiamines and the hazard which would be involved in their preparation and use in the isolated state, we consider it preferable to synthesize these products in situ, preferably using a portion of the fuel from which the final blend is to be made as the solvent and eliminating, of course, the distillation step described in the foregoing procedure.

Our invention, therefore, contemplates, as an additional object, the provision of an improved method for preparing a Diesel fuel, which involves admixing about three molecular proportions of a primary aliphatic amine and about one molecular proportion of sulfur dichloride with a convenient amount of a hydrocarbon fuel oil and controlling the temperature conditions so that the added ingredients react to form an aliphatic thiamine and to precipitate amine hydrochloride. The amine hydrochloride is removed by filtration and the filtrate is diluted with the same or another hydrocarbon fuel to give a final product having the desired combustion characteristics.

Procedures for obtaining fuel compositions according to the method last described above and the combustion characteristics of fuel compositions so obtained will now be given in the following illustrative examples:

Example I

Twenty grams of sulfur dichloride were added slowly to a cooled solution of 44 grams of mono-n-butyl amine and 340 grams of a 40.1 A. P. I. gravity fuel oil having the following characteristics: Pour point: —20° F.; Flash point: 158° F.; Color: 0.8 Lovibond; Aniline point: 154.5° F.; and Per cent sulfur: 0.10. After the reaction had gone to completion, the precipitated butyl amine hydrochloride was filtered off to give a blending base containing about 1.69 per cent sulfur. This base was blended with the original base fuel stock to give a final fuel oil having a sulfur content of 0.5 per cent. The ignition quality of the fuel was determined in a converted C. F. R. engine, using the ignition delay method, the results being expressed in cetane numbers, which represent the percentage of cetane in a cetane-alpha methyl naphthalene blend having the same ignition delay period as the sample being tested. The original base fuel stock had a cetane number of 56, and the blend prepared according to this procedure had a cetane number of 66, thus showing an improvement in the ignition quality of ten cetane members.

Example II

Eighty grams of sulphur dichloride were reacted with a solution of 170 grams of mono-n-butyl amine in 828 grams of the same base fuel stock described in Example I to give a final blending stock which contained 2.70 per cent sulfur, 0.9 per cent nitrogen, and 0.24 per cent chlorine. This blending stock was blended with original base fuel stock to give final compositions containing, respectively, one-fourth of one per cent and one per cent of sulfur. The cetane numbers of these blends were 62 and 63, representing improvements, respectively, of 6 and 12.

Example III

A solution of 26.4 grams of sulfur dichloride in 75 cc. of the same base fuel stock described in Example I was reacted with a solution of 70 grams of mono-n-amyl amine in 450 grams of the base fuel stock. The resultant blending stock containing the amyl thiamine had a sulfur content of 1.33 per cent, 0.55 per cent nitrogen and 0.16 per cent chlorine. A fuel oil blend of this stock having a sulfur content of 0.27 per cent gave a cetane number of 59.5 or an improvement of 3.5, and the same improvement was obtained from a blend having a sulfur content of 0.5 per cent.

It will be understood that the amount of thiamine contained in a Diesel fuel, or more specifically the amount of the oil-soluble reaction product of the primary aliphatic amine and sulfur dichloride, may be varied over relatively wide limits, depending upon the character of the original base stock and the improvement which it is desired to effect. It is also to be understood that the specific examples given above are merely illustrative and are not to be construed as limiting the scope of the invention as defined by the appended claims.

We claim

1. An improved Diesel fuel oil having in admixture therewith a minor proportion of the aliphatic thiamine obtained by reacting about three molecular proportions of a primary aliphatic amine with one molecular proportion of sulfur dichloride, said aliphatic thiamine being present in an amount sufficient to decrease the ignition delay period of the fuel.

2. An improved Diesel fuel oil having in admixture therewith a minor proportion of the butyl thiamine obtained by reacting about three molecular proportions of n-butyl amine with one molecular proportion of sulfur dichloride, said butyl thiamine being present in an amount sufficient to decrease the ignition delay period of the fuel.

3. An improved Diesel fuel oil having in admixture therewith a minor proportion of the amyl thiamine obtained by reacting about three molecular proportions of n-amyl amine with one molecular proportion of sulfur dichloride, said amyl thiamine being present in an amount sufficient to decrease the ignition delay period of the fuel.

4. An improved Diesel fuel oil having in admixture therewith a minor proportion of an alkyl thiamine in an amount sufficient to decrease the ignition delay period of the fuel.

5. An improved Diesel fuel oil having in admixture therewith a minor proportion of butyl thiamine in an amount sufficient to decrease the ignition delay period of the fuel.

6. An improved Diesel fuel oil having in admixture therewith a minor proportion of amyl thiamine in an amount sufficient to decrease the ignition delay period of the fuel.

7. An improved Diesel fuel oil having in admixture therewith a minor proportion of a compound characterized by the general formula RNS in which R represents an aliphatic hydrocarbon radical.

8. The method of preparing an improved Diesel fuel containing an aliphatic thiamine which includes the operation of: admixing with a hydrocarbon fuel oil about three molecular proportions of a primary aliphatic amine and about one molecular proportion of sulfur dichloride; cooling the mixture to maintain a reaction temperature between about 0° C. and 20° C.; and separating the reaction precipitate from the reaction mixture containing the aliphatic thiamine formed therein.

9. The method of preparing an improved Diesel fuel containing an aliphatic thiamine which includes the operation of: admixing with a hydrocarbon fuel oil about three molecular proportions of a primary aliphatic amine and about one molecular proportion of sulfur dichloride; cooling the mixture to maintain a reaction temperature between about 0° C. and 20° C.; separating the reaction precipitate from the reaction mixture, and then diluting the liquid product containing

the aliphatic thiamine formed by said reactants with a liquid hydrocarbon fuel.

10. The method of accelerating the ignition of a hydrocarbon fuel in an internal combustion engine wherein liquid fuel is injected into compressed air in the cylinder and is spontaneously ignited therein, which comprises forming an admixture of a minor proportion of an aliphatic thiamine with the fuel prior to its ignition.

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Patent No. 2,218,447. CERTIFICATE OF CORRECTION. October 15, 1940.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, first column, line 45, for the word "members" read --numbers--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 18th day of March, A. D. 1941.

Henry Van Arsdale,
Acting Commissioner of Patents

(Seal)