

March 2, 1948.

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2,437,041

HYDROCARBON FUEL OILS

Filed Feb. 29, 1944

2 Sheets-Sheet 1

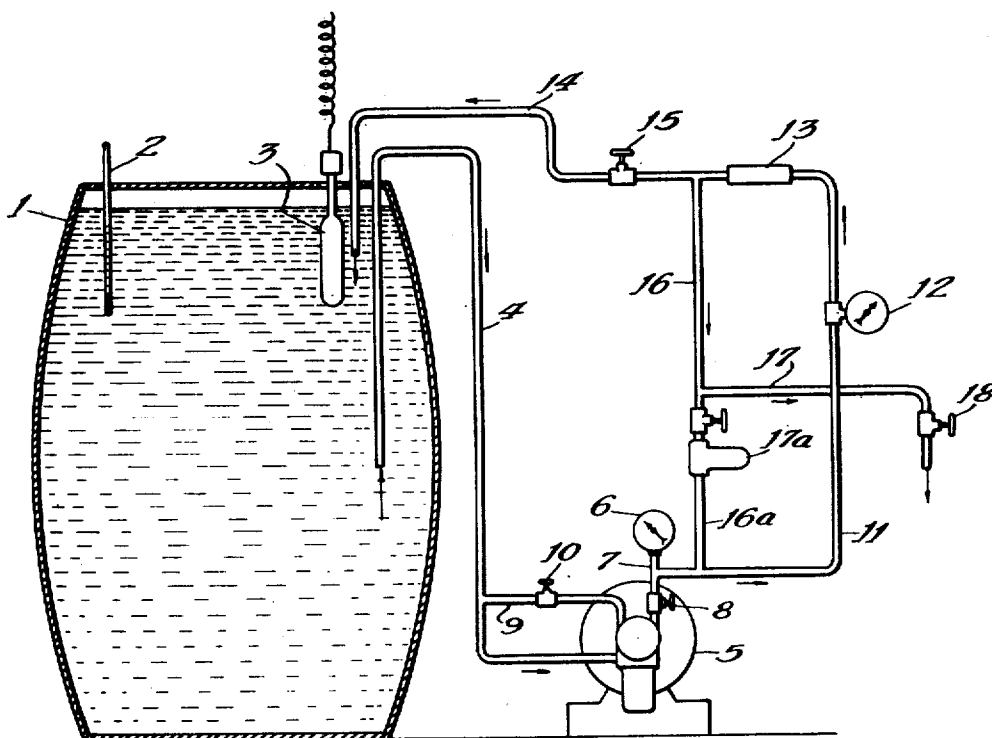


Fig. 1.

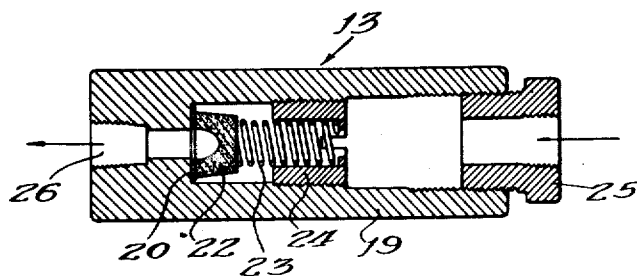


Fig. 2.

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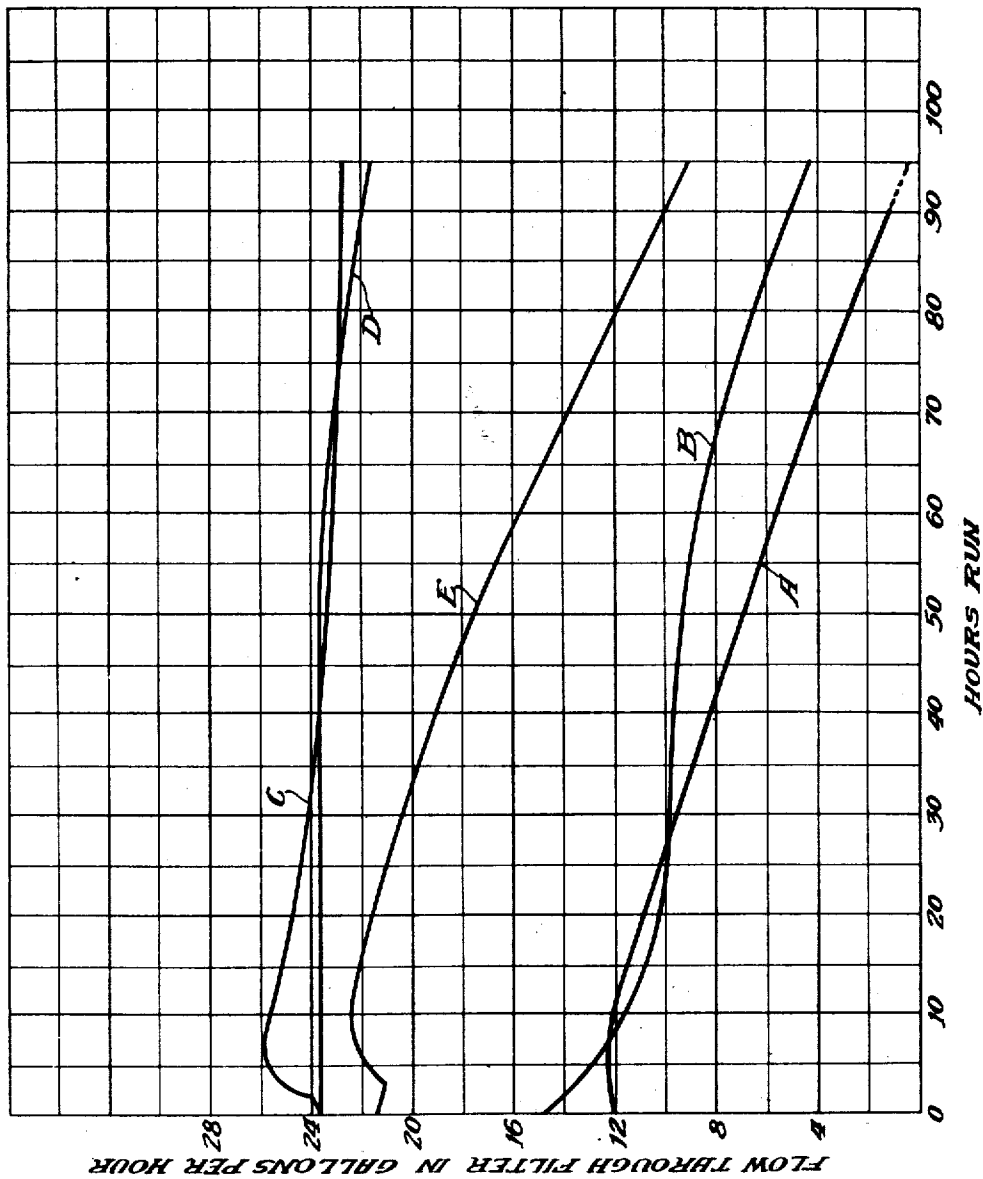


Fig. 3.

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UNITED STATES PATENT OFFICE

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HYDROCARBON FUEL OIL

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10 Claims. (Cl. 44—66)

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This invention relates to improvements in hydrocarbon fuels, particularly hydrocarbon fuels such as furnace or burner oils and fuels for compression-ignition internal combustion engines such as Diesel engines. More specifically the invention relates to hydrocarbon fuel oil compositions which are substantially unsuceptible to filter clogging and to the method of inhibiting the filter clogging tendency of such hydrocarbon fuels.

The requirements for acceptable fuels for oil burners and for Diesel engines include freedom from the tendency to clog filter screens and the numerous fine passages and openings present in fuel oil burners and in Diesel engines. The fuel oil used in such equipment can interfere with the performance of various parts in such equipment in several ways, among which are clogging, gumming, corrosion, etc. Particularly detrimental to good performance are sediments, which may be of the so-called casual type or so-called non-casual type. Casual sediments include sand, dirt, iron rust, dust, water emulsions and miscellaneous debris. The nature of casual sediments is such that its avoidance is entirely a problem of keeping the original oil clean and free of added dust, etc. The non-casual sediment is that sediment which may form in an oil during use. Such sediment is a hydrocarbon sediment originating mainly in the oxidation and polymerization of all, or a portion of the oil. It is very finely divided as it forms and either clogs small openings and fine pores of the filters or it can coagulate into coarser sediment to form massive deposits which also clog openings in the filter. It is responsible for the major part of so-called sediment difficulties.

The tendency of fuels to clog filters varies with different fuels. For example, it has been observed that virgin fuels or fuels containing a substantial amount of virgin stocks clog filters to a lesser degree than do fuels of cracked stocks. It has also been noted that certain fuels do not begin to clog filters until such fuels have been passed through the filter for a period of time. The period during which there is no substantial clogging of the filter is referred to as the "induction period." Obviously it is highly desirable for a fuel to have a long induction period since this increases the life of the filter and eliminates frequent shut-downs.

It is an object of the present invention to provide a hydrocarbon fuel having substantially non-clogging tendencies.

It is another object of the invention to provide

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a hydrocarbon fuel inhibited against the tendency to cause clogging.

Still another object of the invention is to provide a method of inhibiting the clogging tendency of hydrocarbon fuels.

Still another object of the invention is to provide a hydrocarbon fuel having a relatively long induction period.

Another object of the invention is to provide a method of increasing the induction period of a hydrocarbon fuel.

Other objects and advantages of the invention will become apparent from the following description thereof read in conjunction with the accompanying drawings which form a part of the specification and in which:

Figure 1 is a diagrammatic illustration of an apparatus for determining the clogging time of hydrocarbon fuels;

Figure 2 is an enlarged sectional view of the filter element of Figure 1; and

Figure 3 is a chart showing the clogging times of a hydrocarbon fuel as such, and the fuel modified in accordance with the present invention.

I have discovered that the foregoing objects can be attained by adding to hydrocarbon fuels, particularly those hydrocarbon fuels which normally have a tendency to cause clogging of filters, small openings and the like, small amounts of a complex glyceride phosphoric acid ester, such as a phosphatide, for example lecithin, cephalin and the like, treated in the manner hereinafter described, alone or in combination with small amounts of a metal deactivator, such as, for example, the condensation product of an aldehyde or a ketone with a primary amine, particularly polyalkylene amine having at least three amino nitrogen atoms, two or more of which are primary nitrogen atoms. The complex glyceride phosphoric acid ester, such as a phosphatide, is used in small but sufficient amounts; namely, from about 0.001% to about 0.1% and preferably from about 0.01% to about 0.05%, to inhibit clogging. The condensation products of the aforementioned type are used in small amounts, for example from about 0.0005% to about 0.05% and preferably from about 0.001% to about 0.005%.

The phosphatidic material such as lecithin used in the herein-described invention must be treated in order to obtain the desired effect of the invention. I have discovered that while the so-called technical phosphatides are effective to a small extent, the full advantages of the invention are not attained with the same. In order to obtain the desired results, I have found it

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desirable to dissolve from about 10% to about 50% of the phosphatide, such as lecithin, in a solvent such as a petroleum oil, for example kerosene, distillate fuel oil, naphtha, or lubricating oil, adding thereto from about 1% to about 20% of a filter-aid such as Filter-Cel and filtering the mixture through a fine medium such as filter paper or the like. The filtrate containing the filtered phosphatide can be used as such for adding to the hydrocarbon fuel, or the solvent, when a volatile solvent is used, can be removed and the solvent-free filtered lecithin employed. Phosphatides treated in the manner just described will be referred to hereinafter and in the appended claims as "filtered phosphatide" or as "filtered lecithin."

A method of treating the phosphatide is illustrated by the following example: Fifteen grams of a technical grade soya bean lecithin was dissolved in 100 cc. of furnace oil and 5 grams of Filter-Cel added to the solution. The mixture was then filtered through filter paper with the aid of a vacuum pump. The filtrate which was deep red and sparkling clear was then used as such for the herein-described purpose.

The clogging effect of fuel oils was determined in the apparatus illustrated in Figure 1 of the accompanying drawings in the following manner. Referring to Figure 1, the oil in a container 1, for example a barrel of about 50 gallon capacity, is maintained at a temperature of about 140° F., as indicated by thermometer 2, by heating means, for example an electric heater 3. The oil is then pumped through a pipe 4 extending into the container 1 substantially to the half-way mark, by means of a suitable pump 5, for example a standard oil burner pump having a sediment bulb and a fine mesh screen (not shown), for separating out any coarse casual sediment. A pressure gauge 6 is connected to the pump 5 by means of pipe 7 provided with a valve 8. The outlet pressure on the pump 5 is regulated by means of a by-pass line 9 and by-pass regulator valve 10. Oil leaving the pump 5 passes through line 11 provided with a suitable pressure gauge such as a Bourdon gauge 12, and passes through a filter element 13. The oil passes through the filter element 13 and is returned to the container 1 through line 14 provided with a valve 15. The outlet pressure of pump 5 is regulated by passing the oil from the container 1 through the by-pass line 9 and regulating the flow therethrough by means of valve 10. A sensitive Bourdon gauge measures the oil pressure immediately before the oil enters the filter and since the outlet line 14 is opened to the atmosphere and is unthrottled, the pressure indication on the Bourdon gauge is equal to the pressure drop across the filter element 13. The pressure drop across the filter element 13 is kept constant and the flow therethrough measured by closing valve 15 in line 14 and by-passing the fuel oil through lines 16 and 17 and valve 18. By withdrawing a portion of the fuel oil in this manner into a graduated container the rate of flow through the filter element 13 can be measured and regulated to a constant flow. The oil withdrawn through lines 16 and 17 for measuring the rate of flow is returned to container 1. In the event the filter becomes completely clogged, pressure on the system is released by means of safety valve 17a in valved line 16a.

Referring to Figure 2, the filter element 13 comprises a holder 19 provided with a shoulder 20 on which rest gasket 21 and sintered copper

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filter 22. Filter 22 is held against the shoulder 20 by means of compression spring 23 and threaded runner 24. Line 11 of the system is coupled to the filter element 13 by means of the threaded bushing 25 and line 14 of the system is connected to the outlet of the filter element 13 through threaded portion 26 of the holder 19.

In making a test a minimum oil sample of about 50 gallons is used to secure the high oil to surface ratio generally met with in practice. Before a test is made, the oil in the container is allowed to stand overnight to permit any coarse casual sediment to settle out. The oil used in the test maintained at a temperature of about 140° F. is circulated through the filter element 13, and the rate of flow and clogging time noted. The effectiveness of filtered phosphatide, for example filtered lecithin, is demonstrated by the data graphically shown in Figure 3. The liquid hydrocarbon fuel oil used in the tests from which the data were obtained was a furnace oil made of a blend of virgin gas oil and mildly cracked gas oil. This oil had the following specification:

Gravity-----	34 to 39° A. P. I.
Flash-----	150-175° F. (tag open flash cup).
10% recovery---	Less than 440° F.
90% recovery---	Less than 570° F.
End point-----	610-650° F.

The rate of filter clogging using the above furnace oil is graphically illustrated by line A (corrected to an initial flow rate of 12 gallons per hour from an actual initial flow rate of 14.9 gallons per hour and a flow rate of 3.8 gallons per hour after 94 hours) of Figure 3. This shows a rapid decline in the flow through the filter indicating rapid clogging of the sintered copper filter. The effect of an ordinary technical phosphatide such as technical lecithin on the clogging rate of the furnace oil is graphically illustrated by line B of Figure 3. In this test 0.01% technical lecithin was added to the furnace oil. The data obtained show only a slight improvement over the furnace oil containing no lecithin. As indicated by lines A and B of Figure 3, both the inhibited furnace oil and the furnace oil containing technical lecithin cause rapid clogging of the filter without any induction period.

However, when 0.01% of filtered lecithin was added to the furnace oil very superior results were obtained as strikingly shown by the data graphically illustrated by line C of Figure 3. It will be noted that the peculiar accelerated drop of flow rate occasioned by the use of technical lecithin is completely absent in line C.

Although the ultimate clogging time of the furnace oil treated with the filtered lecithin is greatly improved, no induction period is indicated. Still further improvement can be obtained by adding to the liquid hydrocarbon fuel oil containing the filtered complex glyceride phosphoric acid ester small amounts of a metal deactivator, such as a condensation product obtained by the reacting of aromatic ortho hydroxy aldehyde or ketone such as 2-hydroxybenzaldehyde, 2,4-dihydroxybenzaldehyde, 2-hydroxy-3-methoxy benzaldehyde, 2,2'-dihydroxybenzophenone, etc., with a primary amine, particularly a polyalkylene amine, containing at least three nitrogen atoms of which at least two are primary amino nitrogen atoms such as, for example, methyl diamine, ethylene diamine, diethylene triamine, 1:10-decylene diamine, triethylene tetramine, propylene diamine, tetraethylene pentamine, N,N'dibeta amino ethylene piper-

azine, or the condensation product obtained by reacting an aromatic, aliphatic, alicyclic, or heterocyclic aldehyde or ketone such as crotonaldehyde, butyraldehyde, heptaldehyde, isobutyraldehyde, methyl hexyl ketone, furfural, acetaldehyde, acetophenone, benzaldehyde, acetone, vanillin, valeraldehyde, octyl aldehyde, cinnamaldehyde, hexone, diisobutyl ketone and the like, with a primary amine, particularly a polyalkylene amine having at least 3 nitrogen atoms of which at least two are primary amino nitrogen atoms of the type above described.

Examples of reaction products of the foregoing type are disalicylal ethylene diamine, di(2-hydroxy-3-methoxybenzyl)-propylene diamine, furfural triethylene tetramine, benzaldehyde tetraethylene pentamine, disalicylal N,N'-dibeta amino ethyl piperazine, dihydroxy benzophenone diethylene triamine, tributylaldehyde triethylene tetramine, tetra di-isobutyl ketone, tri-propylene tetramine and the like.

The effectiveness of small amounts of a filtered phosphatide and the condensation products of the foregoing type when used in combination in small amounts in liquid hydrocarbon fuels in increasing the induction period and the clogging time of such fuels, is demonstrated by the data graphically presented in line D of Figure 3. These data were obtained by determining the rate of flow in gallons per hour through the filter using a furnace oil containing 0.01% filtered lecithin and 0.002% furfural triethylene tetramine. As shown by line D of Figure 3, this fuel oil had an unusually long induction period of 60 hours and a very good rate of flow through the filter even after this induction period. That this improvement over the use of filtered lecithin alone is not due entirely to the furfural triethylene tetramine is demonstrated by the data graphically shown by line E of Figure 3. These data show that furfural triethylene tetramine when used alone has no effect on the induction period and has a much less effect in maintaining the rate of flow through the filter than does filtered lecithin alone. However, the combination of filtered lecithin and furfural triethylene tetramine produces the unusual and unexpected results represented by the data graphically shown in line D of Figure 3. The apparent increase in flow at the start of some of the tests is due to a decrease in the viscosity of the oil as it is being heated up.

The induction period and clogging time of the hydrocarbon fuel oil and the hydrocarbon fuel oil containing the adjuncts of the present invention employed in the foregoing tests are summarized in the following table:

Fuel Oil Sample	Induction Period, Hours	Clogging Time, Hours ¹
A. Control Fuel Oil.....	0	150
B. Control +0.01% Filtered Lecithin.....	0	800+
C. Control +0.002% furfural triethylene tetramine.....	0	158
D. Control +0.01% Filtered Lecithin +0.002% furfural triethylene tetramine.....	60	800+

¹ Corrected to same initial flow rate.

As shown by the above data the addition of small amounts of a complex glyceride phosphoric acid ester, such as filtered lecithin, greatly extends the clogging time of the fuel oil, that is the fuel oil containing the filtered lecithin is substantially free of any tendency to clog small openings such as are present in a sintered copper filter,

such as is used in various Diesel engines. However, there is no evidence of any induction period during which time there is no falling off in the flow rate of the fuel through the filter. However, when a small amount of a metal deactivator such as furfural triethylene tetramine is added to the fuel oil containing small amounts of filtered lecithin, an induction period of sixty hours is attained without any substantial change in the clogging time of the fuel oil. This is surprising and unpredictable in view of the fact that a fuel oil containing .002% furfural triethylene tetramine has a clogging time of only about 158 hours and no induction period.

It has heretofore been observed that the tendency of organic substances to oxidize in the presence of certain metals can be substantially reduced by adding to such organic substances certain compounds which have the property of rendering the metal inactive. Such compounds exhibiting this property are commonly referred to as metal deactivators. The term "metal deactivators" as used herein and in the appended claims means those compounds which exhibit metal deactivating properties.

While the present invention has been described by reference to various representative compounds and has been illustrated by reference to specific examples thereof, the invention is not to be limited to the various named compounds or to the specific examples but includes within its scope such modifications as come within the spirit of the appended claims.

I claim:

1. A normally liquid hydrocarbon fuel oil, normally susceptible to the formation of non-casual sediment and which normally causes clogging of small apertures, containing a filtered technical grade phosphatide substantially free of liquid hydrocarbon precipitable constituents, obtained by dissolving said phosphatide in a hydrocarbon solvent, and filtering the mixture, said filtered phosphatide being used in small but sufficient amounts to inhibit the clogging tendency of said hydrocarbon fuel oil.

2. A fuel oil composition as described in claim 1 in which the phosphatide is lecithin.

3. A normally liquid hydrocarbon fuel oil, normally susceptible to the formation of non-casual sediment and which normally causes clogging of small apertures, containing a filtered technical grade phosphatide substantially free of liquid hydrocarbon precipitable constituents, obtained by dissolving said phosphatide in a hydrocarbon solvent, mixing the solution with a filter-aid and filtering the mixture, and a metal deactivator, said filtered phosphatide and said metal deactivator being employed in small but sufficient quantities to substantially inhibit the clogging tendency of said hydrocarbon fuel oil.

4. A fuel oil composition as described in claim 3 in which the metal deactivator is obtained by reacting an amine selected from the class consisting of primary amines and polyalkylene compounds having at least three amino nitrogen atoms, of which at least two are primary nitrogen atoms, with a carbonyl compound selected from the group consisting of aromatic aldehydes, aromatic ketones, aliphatic aldehydes, aliphatic ketones, alicyclic aldehydes, alicyclic ketones, heterocyclic aldehydes, heterocyclic ketones, aromatic ortho hydroxy aldehydes and aromatic ortho hydroxy ketones.

5. A fuel oil composition as described in claim 3 in which the metal deactivator is a condensation

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product obtained by reacting an aliphatic aldehyde with a polyalkylene amine having at least three amino nitrogen atoms, of which at least two are primary nitrogen atoms.

6. A fuel oil composition as described in claim 3 in which the metal deactivator is a condensation product obtained by reacting a heterocyclic aldehyde with a polyalkene amine having at least three amino nitrogen atoms, of which at least two are primary nitrogen atoms.

7. A fuel oil composition as described in claim 3 in which the phosphatide is lecithin and the metal deactivator is furfural triethylene tetramine.

8. A fuel oil composition as described in claim 3 in which the metal deactivator is a condensation product obtained by reacting an aromatic ortho hydroxy aldehyde with a polyalkene compound having at least three amino nitrogen atoms of which at least two are primary nitrogen atoms.

9. In a system having small passages subject to clogging, employing a normally liquid hydrocarbon fuel oil normally having the tendency to cause clogging of said passages, the method of substantially inhibiting such clogging, comprising employing in said system a normally liquid hydrocarbon, normally susceptible to cause clogging, containing from about 0.001 to about 0.1% of a filtered technical grade phosphatide substantially free of liquid hydrocarbon precipitable constituents, obtained by dissolving said phosphatide in a hydrocarbon solvent, mixing the solvent with a filter-aid and filtering the mixture, and from about 0.005% to about 0.05% of a metal deactivator obtained by condensing an amine selected from the group consisting of primary amines and

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polyalkylene compounds having at least three amino nitrogen atoms of which at least two are primary nitrogen atoms, with a carbonyl compound selected from the group consisting of aromatic aldehydes, aromatic ketones, aliphatic aldehydes, aliphatic ketones, alicyclic aldehydes, alicyclic ketones, heterocyclic aldehydes, heterocyclic ketones, aromatic ortho hydroxy aldehydes and aromatic ortho hydroxy ketones.

10. A normally liquid hydrocarbon fuel oil which is susceptible to the formation of non-casual sediment and which normally causes clogging of small apertures, containing from about 0.001% to about 0.1% of a filtered technical grade lecithin substantially free of liquid hydrocarbon precipitable constituents, obtained by dissolving about 10% to about 50% of the lecithin in a hydrocarbon solvent, mixing therewith from about 1% to about 20% to a filter-aid and filtering said mixture, and from about 0.005% to about 0.05% of furfural triethylene tetramine.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,155,678	Oosterhout	Apr. 25, 1939
2,165,651	Rees et al.	July 11, 1939
2,181,122	Downing et al.	Nov. 28, 1939
2,208,105	Rathbun	July 16, 1940
2,322,007	Fischer	June 15, 1943

Certificate of Correction

Patent No. 2,437,041.

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It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows: Column 5, in the table, left-hand portion thereof, strike out the letters "A" to "D", inclusive, and insert instead the numerals 1 to 4; column 7, line 8, claim 6, and line 17, claim 8, for "polyalkene" read *polyalkylene*; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 4th day of May, A. D. 1948.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.

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product obtained by reacting an aliphatic aldehyde with a polyalkylene amine having at least three amino nitrogen atoms, of which at least two are primary nitrogen atoms.

6. A fuel oil composition as described in claim 3 in which the metal deactivator is a condensation product obtained by reacting a heterocyclic aldehyde with a polyalkene amine having at least three amino nitrogen atoms, of which at least two are primary nitrogen atoms.

7. A fuel oil composition as described in claim 3 in which the phosphatide is lecithin and the metal deactivator is furfural triethylene tetramine.

8. A fuel oil composition as described in claim 3 in which the metal deactivator is a condensation product obtained by reacting an aromatic ortho hydroxy aldehyde with a polyalkene compound having at least three amino nitrogen atoms of which at least two are primary nitrogen atoms.

9. In a system having small passages subject to clogging, employing a normally liquid hydrocarbon fuel oil normally having the tendency to cause clogging of said passages, the method of substantially inhibiting such clogging, comprising employing in said system a normally liquid hydrocarbon, normally susceptible to cause clogging, containing from about 0.001 to about 0.1% of a filtered technical grade phosphatide substantially free of liquid hydrocarbon precipitable constituents, obtained by dissolving said phosphatide in a hydrocarbon solvent, mixing the solvent with a filter-aid and filtering the mixture, and from about 0.005% to about 0.05% of a metal deactivator obtained by condensing an amine selected from the group consisting of primary amines and

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polyalkylene compounds having at least three amino nitrogen atoms of which at least two are primary nitrogen atoms, with a carbonyl compound selected from the group consisting of aromatic aldehydes, aromatic ketones, aliphatic aldehydes, aliphatic ketones, alicyclic aldehydes, alicyclic ketones, heterocyclic aldehydes, heterocyclic ketones, aromatic ortho hydroxy aldehydes and aromatic ortho hydroxy ketones.

10. A normally liquid hydrocarbon fuel oil which is susceptible to the formation of non-casual sediment and which normally causes clogging of small apertures, containing from about 0.001% to about 0.1% of a filtered technical grade lecithin substantially free of liquid hydrocarbon precipitable constituents, obtained by dissolving about 10% to about 50% of the lecithin in a hydrocarbon solvent, mixing therewith from about 1% to about 20% to a filter-aid and filtering said mixture, and from about 0.005% to about 0.05% of furfural triethylene tetramine.

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[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.