United States Patent [19]

Schiff

[11] **3,767,574**

[45] **Oct. 23, 1973**

[54] **GASOLINE ADDITIVE**

[75] Inventor: **Sidney Schiff,** Bartlesville, Okla.

[73] Assignee: **Phillips Petroleum Company,** Bartlesville, Okla.

[22] Filed: **Dec. 6, 1971**

[21] Appl. No.: **205,361**

[52] **U.S. Cl.** **252/51,** 44/58, 44/72, 208/18

[51] **Int. Cl.** **C10m 1/32**

[58] **Field of Search** 252/51; 44/58, 72; 208/18

[56] **References Cited**

UNITED STATES PATENTS

2,696,473	12/1954	Sokol	252/51
3,227,761	1/1966	Brunn et al.	252/51
3,275,554	9/1966	Wagenaar	252/51
3,280,032	10/1966	Sandri et al.	252/51
3,438,757	4/1969	Honnen et al.	44/58
3,573,010	3/1971	Mehmedbasich	44/72

Primary Examiner—Werten F. W. Bellamy
Attorney—Quigg & Oberlin

[57] **ABSTRACT**

An oil composition, useful as a gasoline additive, is prepared by halogenating and aminating in succession a paraffinic lubricating oil to thus produce a composition having in the range of 2.0 to 26.0 weight percent halogen and 0.20 to 4.0 weight percent nitrogen.

10 Claims, No Drawings

GASOLINE ADDITIVE

Deposits resulting from materials in fuels remain a continuing problem in the smooth operation of internal combustion engines. The narrow tolerances and constricted openings, particularly in the carburetor, ports and valves of the engine, permit numerous opportunities for deposits to seriously reduce operating efficiency. Therefore, detergents are included in fuels not only to maintain the carburetor clean, but extended detergent action is also desirable. That is, the detergent should also operate to clean the ports and valves through which the fuel-air mixture moves, so as to permit unrestricted flow into the piston chambers. It is extremely difficult to obtain a satisfactory detergent which is effective in the various areas and under the different conditions at which deposits occur in the engine. The problems are made more severe by the low concentrations which must be used in the fuel.

It is thus an object of this invention to provide a gasoline additive which inhibits the buildup of deposits on internal portions of internal combustion engines.

Other objects, aspects and the many advantages of this invention will be apparent to those skilled in the art from a study of the following specification and appended claims.

In accordance with this invention there is provided an oil composition, useful as a gasoline additive, which is prepared by subjecting a light paraffinic lubricating oil to a two-step process consisting of a halogenation step and an amination step. In the halogenation step the light paraffinic oil is reacted with a sufficient quantity of a halogen to thereby produce a halogenated oil product which contains in the range of 5–30, and preferably 7–26, percent by weight halogen by total weight of the halogenated oil product. Subsequent to the halogenation step the halogenated oil product is reacted with a sufficient quantity of a primary amine to thereby produce the oil composition of this invention which contains in the range of 2–26, preferably 3–22, and still more preferably 4–16 percent by weight halogen by total weight of oil composition and in the range of 0.20–4.0, preferably 0.3–2.0, percent by weight nitrogen by total weight of oil composition.

The preferred paraffinic oil to be treated according to the process of this invention has the properties as set out in Table I below.

TABLE I

PARAFFINIC LUBRICATING OIL PROPERTIES

Saybolt Universal Viscosity at 100°F, seconds	300–375
Saybolt Universal Viscosity at 210°F, seconds	52–58
Viscosity Index	95–105
Cloud Point, °F (approximate)	+15
Pour Point, °F maximum	+10
Carbon Residue, maximum, weight %	0.05
ASTM Color, maximum	2.5
API Gravity 60°/60°F (approximate)	29
Cleveland Open Cup Flash Point, °F, minimum	450
Cleveland Open Cup Fire Point, °F (approximate)	515
Pensky-Martens Flash Point, °F, minimum	425
Molecular Weight, Average	400

The oil composition of this invention can be prepared from selected paraffinic hydrocarbon fractions having a viscosity at 100° F measured in Saybolt Universal Seconds within the range of 300–375. The presently preferred paraffinic oil for the gasoline additive of the invention is a refined lubricating oil stock prepared by solvent extraction and dewaxing. It is noted that the pour point value provided in Table I, above, is indicative of the extent of dewaxing.

Petroleum fractions which contain substantially no asphalt, either in the natural state or when deasphalted, and which have been treated to reduce the content of aromatic type hydrocarbons therein are suitable materials for the preparation of the additive of the invention. These include lubricating oils produced from Oklahoma City, Okmulgee, West Edmond, Burbank, Pennsylvania, Mid-Continent, California, East Texas, West Texas, Gulf Coast, Venezuela, Borneo, and Arabian crudes. The source of the crude oil from which the petroleum fraction is derived does not significantly influence the preparation or properties of the oil composition of this invention provided the petroleum fraction has been prepared by subjecting the crude to certain necessary treatments to exclude undesired materials therefrom.

In the preparation of the preferred petroleum fraction from which the oil composition of this invention is produced a crude oil is topped, that is distilled, to remove therefrom more volatile lower molecular weight hydrocarbons such as gasoline and light gas oil and then vacuum-reduced to remove heavy gas oil and light lubricating oil of the SAE 10 and 20 viscosity grade.

The SAE 20 viscosity grade oil is solvent extracted with a selective solvent which will separate the paraffinic hydrocarbons from the more aromatic type hydrocarbons. Suitable selective solvents for aromatic hydrocarbons include, among others, the various phenols, liquid sulfur dioxide, furfural and β,β'-dichlorodiethyl ether. This solvent extraction step for removal of the more highly aromatic compounds can be carried out in accordance with the well-known concurrent or countercurrent solvent extraction techniques.

The paraffinic material from the above-described solvent extraction step, which is the raffinate phase, is subjected to a dewaxing technique wherein high freezing point materials are removed by conventional techniques such as, for example, propane dewaxing. The resulting dewaxed oil has a pour point maximum of +10° F. It is this oil which is thereafter halogenated and aminated to produce the oil composition of this invention.

The most preferred oil for use in the preparation of the oil composition of this invention has a viscosity of 352 SUS at 100°F. Such an oil has an average molecular weight of about 400. It is noted that the molecular weight of the paraffinic oil can be determined by various known methods including the freezing point depression method.

The halogens preferred for use herein in the halogenation of the paraffinic oil for the production of the oil composition of this invention are bromine and chlorine. It was previously mentioned that the paraffinic oil is treated with a sufficient quantity of halogen to produce a halogenated oil product containing in the range of 5–30 and preferably 7–26 percent halogen by weight of halogenated product. A sufficient quantity of halogen, that is that quantity required to produce a halogenated oil product containing halogen within the above percentage range, is in the range of 0.5 to 2 mols halogen per one mole of paraffinic oil.

The primary amines useful in the amination step of this invention are broadly defined as being selected from aliphatic, cycloaliphatic, and aromatic amino compounds having 2 to 10 carbon atoms per molecule

and at least one primary amine group. Examples of such primary amines useful herein are those represented by any one of the following general formulas:

$$R\text{-}(NH_2)_m, \text{ and}$$

$$NH_2CH_2CH_2NH[CH_2CH_2NH]_nCH_2CH_2NH_2$$

wherein R is an aliphatic, cycloaliphatic, or aromatic hydrocarbon radical having 2–10 carbon atoms and a valence equal to m, m is an integer having the value 1, 2 or 3, and n is an integer having the value 0, 1, 2, or 3.

Some specific examples of primary amines useful herein are ethylamine, propylamine, hexylamine, ethylenediamine, propylenediamine, 1,6-hexanediamine, aniline, diethylenetriamine, triethylenetetramine, pentaethylenehexamine, 2-ethylhexylamine, 2,2-dimethyloctylamine, 2,2-dimethyl-1,7-octanediamine, cyclohexylamine, and 1,4-cyclohexanediamine.

It was mentioned above that the quantity of primary amine required was that amount sufficient to produce an aminated oil composition having in the range of 2–26 percent by weight halogen and in the range of 0.20–4.0 percent by weight nitrogen. This quantity of amine can be more specifically stated as being in the range of 0.5–5.0, preferably 1.0–2.0, equivalents of amine per equivalent of halogen contained in the halogenated oil product. Thus, upon completion of the halogenation step, the quantity of halogen contained in the halogenated product is determined by analysis from which is calculated the equivalents of halogen contained in the halogenated product. Thereafter, the quantity of amine utilized in the amination step is determined by application of the above-mentioned ratio of equivalents of amine per equivalent of contained halogen. In this connection it is noted that one equivalent of halogen is equal to one atomic weight of halogen and, further, the number of equivalents of amine is equal to the molecular weight of the amine utilized in the amination divided by the number of primary amine groups (NH_2 groups) contained in the amine.

As previously stated, the oil composition prepared according to the process of this invention is especially useful as a gasoline additive. The preferred additives are those compounds wherein the halogen is chlorine and the primary amine is ethylenediamine; the halogen is chlorine and the primary amine is diethylenetriamine; the halogen is chlorine and the primary amine is triethylenetetramine; and the halogen is chlorine and the primary amine is 2-ethylhexylamine.

The oil composition of this invention, when used as a gasoline additive, is added directly to gasoline. The quantity of additive utilized is in the range of 0.02 to 0.1 parts by weight additive per 100 parts by weight gasoline. When gasoline containing the additive of this invention is utilized in conventional internal combustion engines, the buildup of hard refractory deposits on intake valves is substantially diminished. In addition, the additive, in gasoline, is effective as an upper cylinder lubricant, a carburetor cleaner, a solvent for valve deposits and a fuel line cleaner.

The halogenation of the paraffinic oil can be conducted according to any means known in the art for halogenation. According to one halogenation process the paraffinic oil is first dissolved in a solvent which does not halogenate. One such solvent is carbon tetrachloride. The solution of paraffinic oil in solvent is thereafter treated with halogen, preferably with the halogen being in the vapor phase, such treatment being conducted in the presence of ultraviolet light for a time sufficient to effect the production of the halogenated oil product having the halogen content in the ranges previously specified. When the halogenation reaction is complete, the solvent is removed from the halogenated oil product by conventional means such as by distillation.

It has been found that satisfactory halogenation occurs by bubbling halogen through the solution at the rate of 10–50 cc of gas per minute per 0.25 mole oil for a time in the range of ½-10 hours.

Subsequent to the halogenation step and the removal of the halogenated oil product from the solvent, the halogenated material is dissolved in a suitable solvent and thereafter the desired amine is added with heating and stirring to effect the desired amination. At the conclusion of the reaction the volatiles are removed by convenient means such as, for example, distillation, and the resulting oil composition is washed several times with an alcohol-water solution.

As previously mentioned, the halogenated oil product is dissolved in a suitable solvent. Such solvents include aromatic hydrocarbons, ethers, alcohols and mixtures thereof. Some specific examples are xylene, dioxane, tetrahydrofuran (THF), isobutyl alcohol and normal butyl alcohol. Examples of solvent mixtures are: (volume ratios) xylene/n-butyl alcohol, 3/1 to 6/1; xylene/isobutyl alcohol, 2/1; THF/n-butyl alcohol, 2/1; dioxane/n-butyl alcohol, 4/1. The quantity of solvent utilized is in the range of 0.33 to 2.0 volumes solvent per one volume of halogenated oil product.

The halogenated oil, solvent, and amine are stirred at a temperature less than the boiling point of the solvent in the range of 70°C to 150°C for a time in the range of 0.5 to 2 hours.

The following example will further illustrate the process of this invention to persons skilled in the art. However, it is to be understood that this example is for purposes of illustration and should not be construed as to limit the scope of the invention.

EXAMPLE I

In a series of runs a paraffinic oil having an average molecular weight of about 400 and a viscosity of 352 SUS at 100° F was treated as follows. The oil (115 grams) was dissolved in 175 ml of carbon tetrachloride. Chlorine gas was bubbled through the oil-carbon tetrachloride solution in the presence of ultraviolet light for 2 hours at the rate of 30 cc of gas per minute. The temperature was approximately 75° F. At the end of the 2-hour period the carbon tetrachloride solvent was removed from the chlorinated oil product by distillation at 210° F under a vacuum of approximately 15–20 mm of mercury.

The chlorinated oil (40 g.) was dissolved in a solution consisting of 30 ml xylene and 5 ml n-butyl alcohol. Thereafter the dissolved chlorinated oil was reacted with a primary amine at 100° C for 1 hour. The reaction mixture was thereafter vacuum distilled at 160° C to remove solvent. The resulting aminated product was then washed several times with an isopropyl alcohol-water (10/90) solution.

The results of the various runs along with the specific primary amines, solvents, and quantities utilized are set out in Table I below.

TABLE I

Run	Amine	Solvent	Wt. percent chlorine in chlorinated oil	Ratio of equivalents amine/equivalent chlorine	Wt. percent chlorine in additive	Wt. percent nitrogen in additive
1	Ethylenediamine	Xylene n-butyl alcohol	7.4	2.4	3.8	0.31
2	do	do	9.7	1.0	7.7	.32
3	Diethylenetriamine	do	9.7	1.5	6.5	.60
4	Triethylenetetramine	do	9.7	2.0	8.0	.86
5	2-Ethylhexylamine	do	12.4	1.1	7.8	.63
6	do	Xylene	12.4	0.57	8.8	.53
7	do	Dioxane	12.4	1.1	7.1	2.03
8	do	do	8.9	1.6	6.8	0.63
9	do	Dioxane n-butyl alcohol	12.4	1.1	8.2	.58
10	do	THF*/n-butyl alcohol	12.4	1.1	10.3	.39
11	do	Xylene i-butyl alcohol	12.4	1.1	8.8	.46

*Tetrahydrofuran.

EXAMPLE II

The chlorinated-aminated oil products of runs 1 and 4 from Example I (and Table I) above were evaluated as gasoline additives in a test used to measure the buildup of hard refractory deposits on automotive intake valves.

Three runs were involved. In the first run a commercial automotive type premium gasoline sample (100 ml) was tested as control for purposes of comparison. In the second and third runs two gasoline samples (100 ml per sample) taken from the same source as the gasoline sample utilized in the first run were each combined with 0.04 parts by weight additive per 100 parts by weight of gasoline sample. In the second run the additive was the product of run 1, Example I. In the third run the additive was the product of run 4, Example I.

The raw gasoline stock utilized, which contained tetraethyl lead and oxidation inhibitor but no other additives, had the characteristics set out in Table Ii below.

TABLE II

API Gravity, 60/60°F	67.5
Distillation Characteristics:	
Initial boiling point	91°F
10 percent point	110°F
50 percent point	203°F
90 percent point	337°F
End point	420°F
Percent recovered	97.0
Percent loss	1.2
Motor Octane Number	92.4
Research Octane Number	99.0
Reid Vapor Pressure	11.98 psi
Tetraethyl lead content	2.10 ml per gallon
Percent Sulfur	0.03
ASTM Gum Content (unwashed)	5.6 milligrams/100 ml.
ASTM Gum Content (heptane washed)	2.7 milligrams/100 ml.
Pona Analysis (paraffins, olefins, naphthenes and aromatics)	
Paraffins	69.1%
Olefins	8.3%
Naphthenes	6.9%
Aromatics	15.7%

Prior to testing, the raw gasoline stock was filtered by passing it one time through a 0.3 micron filter. To the gasoline filtrate there was then added 0.04 parts by weight of sulfurized terpene per 100 parts by weight filtrate. This procedure thus produced the gasoline source from which was taken the three samples utilized in the runs of this Example.

The experimental test procedure utilized was a modification of the method described in "A Bench Technique for Evaluating the Induction System Deposit Tendencies of Motor Gasolines," A. A. Johnston and E. Dimitroff, (Society of Automotive Engineers, Fuels and Lubricants Meeting, Houston, Texas, November 1–3, 1966, paper No. 660783).

Briefly, in accordance with the above modified procedure, the test gasoline (2 ml/minute) is mixed with a flow of air (28 Ft^3/HR) to form a gasoline-air mixture. The mixture is thereafter discharged from a nozzle as a spray against an aluminum deposit pan of known weight. The deposit pan, which is preheated to a stabilized temperature, is maintained at that temperature while the mixture is sprayed against the pan. After 100 ml of test gasoline is sprayed, the gasoline flow is terminated, but the airflow and temperature are maintained constant for another 15 minutes. Thereafter, the air flow is terminated and the deposit pan is permitted to cool to room temperature. The cool pan is then washed with heptane, dried, and placed in a desiccator until cooled to room temperature. The pan is then weighed. The difference between the final and original weights is considered to be indicative of the deposit tendencies of the gasoline which is reported as mg/100 ml of test gasoline. The test results are shown in Table III.

TABLE III

Run No.	Fuel Tested	Mg. Deposit/100 ml Gasoline Deposit Pan Temp. °F 350	Deposit Pan Temp. °F 375
1A	Gasoline with no additive	4.0	
1B	Gasoline with no additive		5.6
2A	Gasoline with additive 2	0.1	
2B	Gasoline with additive 2		3.8
3A	Gasoline with additive 8	0.2	
3B	Gasoline with additive 8		4.3

From the above results it is clearly shown that the additive of this invention significantly reduces the tendency of automotive gasoline to form deposits on engine surfaces.

Reasonable variations and modifications of this invention can be made or followed in light of the foregoing disclosure and examples without departing from the spirit and scope thereof.

That which is claimed is:

1. An oil composition prepared according to the process comprising reacting a paraffinic oil having a viscosity in the range of 300 to 375 SUS at 100° F and a viscosity index of 95 to 105 with a sufficient quantity of a halogen to thereby produce a halogenated oil product containing in the range of 5 to 30 percent by weight of said halogen and thereafter reacting said halogenated oil product with a sufficient quantity of a primary amine to thereby produce said oil composition having in the range of 2.0 to 26.0 percent by weight of said halogen and 0.20–4.0 percent by weight of nitrogen.

2. The oil composition of claim 1 wherein said paraffinic oil has a maximum pour point of +10° F and an average molecular weight of 400.

3. The oil composition of claim 1 wherein said halogen is one of bromine and chlorine.

4. The oil composition of claim 1 wherein said primary amine is an aliphatic, cycloaliphatic, or aromatic compound having 2 to 10 carbon atoms per molecule, and at least one primary amine group.

5. The oil composition of claim 1 wherein the quantity of said halogen utilized to produce said halogenated oil product is in the range of 0.5 to 2 mols halogen per one mol of said paraffinic oil.

6. The oil composition of claim 1 wherein the quantity of said primary amine utilized to produce said oil composition is in the range of 0.5 to 5.0 equivalents of amine per equivalent of halogen contained in said halogenated oil product.

7. The oil composition of claim 1 wherein said halogen is chlorine and said primary amine is ethylenediamine.

8. The oil composition of claim 1 wherein said halogen is chlorine and said primary amine is diethylenetriamine.

9. The oil composition of claim 1 wherein said halogen is chlorine and said primary amine is triethylenetetramine.

10. The oil composition of claim 1 wherein said halogen is chlorine and said primary amine is 2-ethylhexylamine.

* * * * *