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3,458,443

## LUBRICATING OIL COMPOSITION

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5 Claims

### ABSTRACT OF THE DISCLOSURE

A lubricant for a refrigerating system containing a halo-alkane refrigerant comprises a mineral lubricating oil having certain specified properties and {tetra(diphenylphosphito)pentaerythritol}.

This invention relates to an improved lubricating oil composition for use in refrigerating systems. The lubricating oil composition of the invention is characterized by having greatly improved stability and compatibility in the unique environment of a mechanical refrigeration system wherein the lubricant is in intimate contact with a halo-alkane refrigerant.

Refrigeration systems, such as mechanical compressor refrigerators and air conditioning units, operate by effecting the compression and expansion of a refrigerant. A gaseous refrigerant is compressed and cooled in one stage of the system where the contained heat is removed and is then passed through an expansion valve where the pressure is reduced and the liquid evaporates to absorb heat in the expansion stage of the system. Alternate cycles of compression and expansion are continuously carried out while the refrigeration system is in operation. Refrigeration systems of the type described are enclosed or hermetically sealed and must contain a lubricant within the sealed system which is effective to lubricate the moving parts thereof.

The base oils used in lubricants for refrigeration systems must have certain essential characteristics. These oils must have a low pour point so that they will flow freely at extremely low temperatures. The base oil must also have a low "floc" point, that is a low temperature at which floc forms in a mixture of the lubricant and refrigerant, in order to avoid clogging of the fine orifices in the system. Refined mineral oils and certain sulfonic oils are useful for formulating lubricants for refrigeration systems because of their excellent oiliness characteristics, low pour points and low floc points.

Conventionally refined base oil stocks per se are generally not used in refrigeration systems. This is because of the unusual conditions existing in such systems whereby the lubricant and refrigerant are in intimate contact or are admixed with one another. Under the conditions of elevated temperature and pressure which occur in a refrigeration system, the base oil and halo-alkane refrigerant react with one another. This reaction is believed to bring about the formation of halogen-acid reaction products which are corrosive and lead to degradation of and sludging in the lubricant in the system.

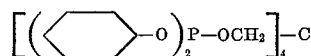
A major essential requirement for lubricants for refrigeration systems is that they be stable and compatible with halo-alkane refrigerants over long periods of time. This is normally accomplished by severe refining of the base oil and/or by incorporating a multitude of additives in a conventionally refined refrigeration oil. It has now been discovered, however, that a single unique additive permits the formulation of a refrigeration lubricating oil composition having an outstanding level of stability and compatibility in refrigeration service.

In accordance with this invention, it has been dis-

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covered that the compound [tetra(diphenylphosphito)pentaerythritol] when incorporated in a suitable base oil provides a compounded lubricant for refrigeration systems that is characterized by being remarkably stable against deterioration and sludge formation. This discovery was most surprising and unexpected since no other single additive is known which imparts the forgoing essential properties together with an effective level of load-carrying and other properties to a lubricating composition for use in refrigeration systems.

The lubricating oil composition of the invention therefore comprises a major proportion of a mineral lubricating oil having a viscosity at 100° F. in the range from 75 to 600 SUS, a pour point below about -20° F., a haze point below -30° F. and a floc point below about -50° F., containing from about 0.005 to 1.0 percent by weight of the additive compound [tetra(diphenylphosphito)pentaerythritol] having the formula:



The preferred concentration of the additive in the oil is in the range from 0.01 to 0.5 weight percent.

The base oil used for formulating the lubricant of the invention is a wax-free, low aniline point mineral oil, preferably naphthene oil although paraffin oils are suitable. The properties of a typical base oil are as follows:

|                      |             |
|----------------------|-------------|
| Gravity              | 23.0—27.0   |
| Flash, COC ° F.      | min. 330    |
| Visc. SUS at 100° F. | 150—160     |
| Color, ASTM          | max. 1.5    |
| Pour, ° F.           | max. -40    |
| Freon haze, ° F.     | max. -60    |
| Freon floc, ° F.     | max. -80    |
| Dielectric strength  | min. 25,000 |

In systems using refrigerants which are miscible with the oil, floc point and haze point tests are valuable indicators of the low temperature performance of the oil. Both of these tests are conducted on a mixture of ten percent oil in Refrigerant 12 (Freon 12) sealed in a glass tube and cooled at a rate of 1-2° F. per minute with observations after each 5° F. drop in temperature. The temperature at which the first evidence of haziness is discernible in the oil is the Freon 12 haze point. On further cooling, the wax particles coalesce and individual agglomerates may be observed. The temperature at which the initial agglomerates or flocs are observed is the Freon 12 floc point. The floc point test is briefly referred to on p. 126 of vol. 53, No. 10, 1967 issue of Texaco Inc.'s publication, "Lubrication."

The examples in the tables below illustrate the practice of this invention. In the examples, the concentration of the additive employed is given in weight percent. The base oil employed in these examples was a highly refined, wax-free oil particularly intended for use in refrigeration systems. This base oil had the following properties:

|                            |        |
|----------------------------|--------|
| Gravity                    | 25.2   |
| Flash, COC ° F.            | 355    |
| SUS at 100° F.             | 153    |
| Color, ASTM                | <1.0   |
| Pour ° F.                  | -55    |
| Neut. No. (ASTM D-974)     | 0.01   |
| Haze, ° F.                 | -60    |
| Floc                       | -80    |
| Dielectric strength, volts | 40,000 |
| Water, p.p.m.              | 15     |

The lubricating oils of the invention were tested for stability in a copper plating proclivity test and in sealed tube tests. In the copper plating test, equal volumes of the oil undergoing test and carbon tetrachloride are added

to a bottle together with a steel and copper couple. The bottle is sealed and stored at a temperature of 160° F. The test cells are visually observed daily for signs of galvanic action or transfer of copper to the steel strip. This is evidenced by a bright copper plating on the steel strip.

In this test, non-inhibited base oils will fail in a period from 48 to 72 hours as evidenced by copper plating of the steel strip. A minimum of 400 hours' aging under the test conditions without any signs of copper plating on the steel strip is an acceptable criterion for the lubricating oil to pass this test and is the actual requirement of a major air-conditioner manufacturer. The results of the copper plating tests are given in Table I below:

TABLE I.—COPPER PLATING TEST

| Lubricant composition                                              | Additive conc. wt. percent | Hours to copper plating |
|--------------------------------------------------------------------|----------------------------|-------------------------|
| Example 1..... Base oil.....                                       | 0.03                       | 48, 72                  |
| Example 2..... Base oil [tetra(diphenylphosphito)pentaerythritol]. | 0.03                       | 1 456, 456              |
| Example 3..... do.....                                             | 0.09                       | 1 456, 456              |

<sup>1</sup> Tests terminated before failure.

Other base oils ranging in viscosity up to 600 SUS at 100° F. show the same improvement from the use of the additive as was obtained in the examples of Table I.

The effectiveness of the lubricants of the invention was also tested in sealed tube tests which are modifications of the test described in "A Method of Evaluating Refrigerator Oils" by Elsey, Flowers and Kelley which appeared in "Refrigerating Engineering" for July 1952, pp. 737-742. Briefly, the procedure employed involves putting equal amounts of the lubricant being tested and of Refrigerant 12 into a Pyrex glass test tube together with copper wire and a steel strip to form a couple in the oil-refrigerant mixture. The test tube is hermetically sealed and then aged at 347° F. for specific periods of time.

Instability in the refrigeration lubricant will bring about or permit a reaction between the lubricant and Refrigerant 12 (CCl<sub>2</sub>F<sub>2</sub>) to take place with the result that some Refrigerant 22 (CHClF<sub>2</sub>) is produced in the sealed tube. The amount of Refrigerant 22 produced is determined by analysing the mixture in the test tube after an accelerated aging period usually 14 days, but longer periods were also used to demonstrate this invention. An oil passes this stability test if there has been substantially no production of Refrigerant 22 during the accelerated aging period. The results of this test with the lubricants of the invention are given in Table II below.

TABLE II.—SEALED TUBE TEST AT 347° F.

| Lubricant Composition                                            | Additive conc. wt. percent | Refrigerant 22, wt. percent at— |         |          |          |
|------------------------------------------------------------------|----------------------------|---------------------------------|---------|----------|----------|
|                                                                  |                            | 14 days                         | 64 days | 120 days | 200 days |
| Example 4... Base oil.....                                       | 0.03                       | 0.77                            | 5.95    | 0.00     | 0.02     |
| Example 5... Base oil [tetra(diphenylphosphito)pentaerythritol]. | 0.03                       | 0.00                            | 0.00    | 0.00     | 0.00     |

In still another procedure of the sealed tube test, the test oils were heated in the presence of R-12 and catalysts at 400° F. for 14 days. The free chloride content of the test mixture is determined at the end of the test period. Results are given in Table III below:

TABLE III.—SEALED TUBE TEST AT 400° F.

| Lubricant composition                                              | Additive conc. wt. percent | Free chloride, mg. 14 days |
|--------------------------------------------------------------------|----------------------------|----------------------------|
| Example 6..... Base oil.....                                       | 0.03                       | 82                         |
| Example 7..... Base oil [tetra(diphenylphosphito)pentaerythritol]. | 0.03                       | 0.7                        |

The foregoing test results demonstrate that [tetra(diphenylphosphito)pentaerythritol] is a remarkably new and effective additive for formulating a refrigerator oil composition. This is particularly borne out by the fact that heretofore a multiple of two or more additives were required to provide an acceptable refrigerator oil formulation. The lubricants of this invention are also equally or more stable in the presence of other refrigerants, such as trichloromonofluoromethane, tetrafluoromethane, monochlorotrifluoromethane and dichlorotetrafluoroethane.

Obviously, many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. A lubricating oil composition effective for use in a refrigerating system containing a halo-alkane refrigerant which comprises a major proportion of a mineral lubricating oil having an SUS viscosity at 100° F. in the range from about 75 to 600, a pour point below about -20° F., a haze below -30° F., and a floc below -50° F., containing from about 0.001 to 1.0 weight percent of {tetra(diphenylphosphito)pentaerythritol}.

2. A composition according to claim 1 containing from about 0.01 to 0.25 weight percent of said {tetra(diphenylphosphito)pentaerythritol}.

3. A composition according to claim 1 in which said mineral lubricating oil is a naphthenic oil.

4. A composition according to claim 1 in which said mineral lubricating oil is a paraffinic oil.

5. A composition according to claim 1 in which said mineral oil has a viscosity at 100° F. in the range of 150 to 160, a pour point below -40° F., a haze below -60° F. and a floc below -80° F.

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W. CANNON, Assistant Examiner

U.S. Cl. X.R.

UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,458,443 Dated July 29, 1969

Inventor(s) WILLIAM T. SHEPHERD

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 4, delete "Texaco Development Corporation" and insert --Texaco Inc.--

SIGNED AND  
SEALED  
JUN 23 1970

(SEAL)

Attest:

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