United States Patent Office

3,132,102

Patented May 5, 1964

3,132,102

HYDROCARBON COMPOSITIONS

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No Drawing. Filed July 1, 1960, Ser. No. 40,171

6 Claims. (Cl. 252—42.4)

This invention relates to the stabilization of non-fluid petroleum hydrocarbon-containing compositions normally susceptible to deterioration in the presence of oxygen at ambient temperatures. More particularly, this invention relates to the protection of grease and petroleum wax against catalyzed oxidation.

The non-fluid petroleum hydrocarbon compositions which are stabilized according to this invention involve unique problems which are very different from the problems confronted in the art of stabilized fluid hydrocarbon media, such as gasoline, lubricating oils and turbine oils. In these fluid media the focal point of the oxidation is the unsaturated hydrocarbons contained therein.

The compositions stabilized according to this invention normally undergo catalyzed oxidation reactions at ambient temperatures, that is, temperatures in the order of about 60 to about 200° F.

The problem of increasing the resistance of petroleum wax—paraffin wax and microcrystalline wax—to oxidation is considerably different from the problem involved in the protection of greases against oxidation. A priori the problems involved in stabilizing petroleum waxes are vastly different from the problems involved in stabilizing fluid petroleum hydrocarbon compositions such as gasoline, lubricating oils and turbine oils. It is well known that petroleum waxes are composed chiefly of paraffinic hydrocarbons which are insensitive toward oxidation. However, even if extreme care is exercised in the manufacture of petroleum waxes to remove the natural content of resinous or asphaltic oil, petroleum waxes tend to form disagreeable odors and undergo darkening in color. These transformations result from oxidation and polymerization reactions involving traces of impurities in the wax, these reactions being catalyzed by the action of light, particularly ultra-violet light and by traces of metallic impurities. Not only do these reactions result in disruption of product specifications, but the rancidity of the wax is particularly undesirable. Petroleum waxes find wide-spread use in the preparation of paper coatings, food containers and food wrappings. Many foodstuffs packaged in paper or containers coated with petroleum waxes acquire a disagreeable taste when the petroleum wax becomes rancid.

In the art of grease technology, it is known that the acid salts or soaps used as thickening agents in greases are major factors in contributing to the oxidative deterioration of the greases. The prevention of grease deterioration involves inhibiting the oxidation of the oil component as catalyzed by the presence of a metal compound as well as the oxidation of the metallic thickening agent itself. The net result is that the stabilization of grease involves inhibiting both of these types of oxidation simultaneously.

Greases are normally susceptible to oxidative deterioration during manufacture, and storage in containers; and when in contact with working parts such as friction bearings, etc., and under dynamic service conditions.

An object of this invention is to provide stabilized non-fluid petroleum hydrocarbon-containing compositions which would otherwise be susceptible to deterioration in the presence of oxygen at ambient temperatures. Another object is to provide additives which when incorporated in such compositions impart thereto unusual resistance to deterioration in the presence of oxygen at ambient temperatures. Still another object is to provide stabilized grease compositions. A further object is to provide stabilized petroleum waxes. Other important objects of this invention will become apparent from the ensuing description.

According to this invention the above and other objects are accomplished by providing non-fluid petroleum hydrocarbon-containing compositions normally susceptible to deterioration in the presence of oxygen at ambient temperatures containing, in amount sufficient to inhibit such deterioration, a small antioxidant quantity, up to 5 percent of 4,4′-thiobis(2-methyl-6-tert-butylphenol).

According to one embodiment of this invention, there is provided a petroleum wax normally susceptible to undesirable catalyst-promoted oxidation and polymerization reactions containing, in amount sufficient to inhibit such reactions, a small quantity of 4,4′-thiobis(2-methyl-6-tert-butylphenol).

According to another embodiment of this invention there is provided a grease composition consisting essentially of a mineral lubricating oil and a metallic soap thickening agent, said grease composition being normally susceptible to oxidative deterioration containing, in amount sufficient to inhibit such deterioration, a small antioxidant quantity of 4,4′-thiobis(2-methyl-6-tert-butylphenol).

Example 1

To illustrate the benefits derived from this invention, a typical paraffin wax composition of this invention is subjected to comparative tests with other paraffin wax compositions. The method employed involves compounding an improved paraffin wax by admixing 0.005 weight percent of 4,4′-thiobis(2-methyl-6-tert-butylphenol) with the wax. The wax employed had a melting point of about 138° F. and was produced by dewaxing a waxy raffinate from a furfural solvent refining process, and involved recrystallization of the wax from solvent to produce a pure wax having no odor, 0.09 percent oil and a peroxide number of 0. A weighed portion of this improved wax is placed in a glass container, covered and placed in an oven at 250° F. The test sample is removed periodically and smelted by at least two people to attempt to detect the characteristic odor of oxidized wax. If oxidized wax odor is present, a portion of the test sample is analyzed for peroxide number while the remainder is replaced in the oven for further testing. This procedure is repeated until the test sample reaches a peroxide number of 5. An equal portion of the uninhibited wax, when subjected to this test, reached a peroxide number of 5 in about 10 hours while the sample which contained 4,4′-thiobis(2-methyl-6-tert-butylphenol) did not oxidize to a peroxide number of 5 until after 599 hours at the test conditions. Thus, even in the small concentration employed, 4,4′-thiobis(2-methyl-6-tert-butylphenol) is an outstandingly effective inhibitor of oxidation in paraffin wax.

Stable paraffin wax compositions of this invention are further illustrated by the following specific examples wherein all parts are by weight.

Example 2

To 100 parts of melting paraffin wax having a viscosity of 40 SUS at 210° F. is added 1 part of 4,4′-thiobis(2-methyl-6-tert-butylphenol).

Example 3

One part of 4,4′-thiobis(2-methyl-6-tert-butylphenol) is added to and mixed with 1000 parts of molten microcrystalline wax having a melting point of 160° F. and a viscosity of 70 SUS at 210° F.

Example 4

To 100 parts of melted microcrystalline wax having an average molecular weight of about 500 and a melting point of 156° F. is added 2 parts of 4,4'-thiobis(2-methyl-6-tert-butylphenol) and the mixture is stirred.

Example 5

To illustrate the grease embodiment of this invention, recourse is had to a modified standard ASTM method for determining the oxidation stability of lubricating greases by the oxygen bomb method, ASTM designation D–942–50, described in the ASTM standards for 1952, part 5, pages 405 and 406. According to this method, a sample of grease is oxidized in a bomb heated to 250° F. and filled with oxygen at an initial pressure of 110 pounds per square inch. Pressure is observed and recorded at stated intervals. The degree of oxidation after a given period of time is determined by the corresponding decrease in oxygen pressure.

A series of tests is conducted according to this procedure. A typical antioxidant-free grease is used. This grease is of NLGI No. 2 grade and contains approximately 8 percent by weight of lithium soap. The grease titrates 0.01 percent alkaline as sodium hydroxide. In one test, the uninhibited grease is subjected to the above oxygen bomb test. In another test 0.50 percent by weight of 4,4'-thiobis(2-methyl-6-tert-butylphenol) is blended with the grease and the resulting composition subjected to the bomb test. The results of these experiments show that a typical grease composition of this invention exhibits a greatly increased resistance against oxidation as compared to the uninhibited grease.

Other oxygen stable grease compositions of this invention are illustrated by the following specific examples wherein all parts and percentages are by weight.

Example 6

To a complex calcium base lubricating grease consisting of 81.2 percent of SAE 20 mineral base oil having a viscosity index of 40 and a viscosity at 100° F. of 300 Saybolt Universal seconds (SUS), 12 percent of 12-hydroxy stearic acid, 2.5 percent of boric acid, and 4.3 percent of lime is added and mixed 1 percent of 4,4'-thiobis(2-methyl-6-tert-butylphenol) based on the weight of the grease.

Example 7

Two percent of 4,4'-thiobis(2-methyl-6-tert-butylphenol) is added to and mixed with a complex calcium base lubricating grease initially composed of 3.7 percent of stearic acid, 3.7 percent of partially dehydrated castor oil, 4.0 percent of hydracrylic acid, 3.2 percent of lime and 85.4 percent of mineral lubricating oil having a viscosity of 150 SUS at 100° F.

Example 8

A lithium containing grease is prepared by admixing 150 parts of hydrogenated fish oil fatty acids having a liter of 54, 25 parts of palm oil, 25 parts of naphthenic acid, 40 parts of acetic acid, 700 parts of Coastal pale oil having a viscosity of 100 SUS at 100° F., 80 parts of lithium hydroxide and 800 parts and Coastal red oil having a viscosity of 2000 SUS at 100° F. This mixture is heated to 425° F., cooled by panning and milled. To this grease is blended 9 parts of 4,4'-thiobis(2-methyl-6-tert-butylphenol).

Example 9

A mixture of 13.8 parts of lithium stearate, 1.7 parts of calcium stearate, 33.8 parts of a California solvent-refined paraffinic base oil having a viscosity of 356 SUS at 100° F., and 50.7 parts of a California solvent-refined paraffinic base oil having a viscosity of 98 SUS at 100° F. is heated to 425° F. for a period of 15 minutes. The mixture is cooled to room temperature and milled. To this mixture is added and mixed 0.2 part by weight of 4,4'-thiobis(2-methyl-6-tert-butylphenol).

Example 10

To an aluminum base lubricating grease consisting of 11 percent of aluminum stearate, 1 percent of lithium stearate and 88 percent of a mineral oil of a viscosity of 100 SUS at 100° F. is added and mixed 5 percent based on the grease of 4,4'-thiobis(2-methyl-6-tert-butylphenol).

Example 11

A total of 0.1 percent by weight of 4,4'-thiobis(2-methyl-6-tert-butylphenol) is added to and mixed with a barium base lubricating grease made from 16 percent of barium sulfonates, 4.2 percent of ethane sulfonic acid, 6.4 percent of barium octahydrate, and 73.4 percent of mineral oil of a viscosity of 320 SUS at 100° F. and having a viscosity index of 40.

Example 12

To grease consisting of 15 percent of a soda soap prepared from equal amounts of stearic acid and of rosin, 10 percent of candelilla wax and 75 percent of mineral lubricating oil of a viscosity of 100 at 210° F. and a viscosity index of 72 is added and mixed 1 percent of 4,4'-thiobis-(2-methyl-6-tert-butylphenol).

Example 13

To a lead soap-containing grease consisting of 1.17 parts of litharge, 2.94 parts of hydrogenated fish oil fatty acids, 40 parts of blown asphalt, 25 parts of mineral oil of 180 SUS at 210° F. and 31 parts of oil of 125 SUS at 100° F. is added 1.5 percent by weight of 4,4'-thiobis-(2-methyl-6-tert-butylphenol).

In the grease embodiments of this invention the stabilizer is used in amounts sufficient to increase the oxidation stability of the grease compositions. In general, these amounts range from about 0.1 to about 5 percent by weight of the grease, 0.5 to about 2.0 percent by weight being especially preferred because these amounts greatly increase the resistance of grease toward oxidative decomposition under normal service conditions. In the petroleum wax embodiments of this invention, the amount of the above-described inhibitors used ranges from about 0.005 to about 2 percent by weight of the wax.

The petroleum waxes stabilized according to this invention comprise paraffin wax and microcrystalline wax. These materials are solid, ductile, wax-like mixtures of high molecular weight hydrocarbons, normally derived from that part of crude petroleum commonly designated as paraffin distillate. Paraffin wax is composed mostly of straight chain paraffin hydrocarbons and usually has a melting point between about 120 and 150° F. Microcrystalline wax is composed chiefly of branched chain paraffinic hydrocarbons and has a melting point of about 150 to about 185° F.

Suitable lubricating oils for the improved grease compositions of this invention include a variety of mineral oils, such as naphthenic base, paraffin base and mixed base mineral oils. Such oils may be mixed with synthetic oils, e.g., alkylene oxide polymers such as polypropylene oxide polymers, and other hydrocarbon lubricants, e.g. lubricating oils derived from coal products. Other synthetic oils which may be used with mineral oils include esters of alkylene oxide-type polymers, e.g., acetylated propene oxide polymers containing hydroxyl groups, dicarboxylic acid esters, polyesters, esters of polyhydric alcohols and liquid esters of acids of phosphorus and silicon.

The thickening agents which are suitable for use in the grease compositions of this invention are metallic soaps of the type normally used in grease for this purpose. The organic portion of the molecule of these soaps can be derived from animal or vegetable fats or fatty acids, wool grease, rosin or petroleum acids and the like. Ordinarily, metallic soaps of fatty acids containing from 10 to about

30 carbon atoms are very satisfactory thickening agents, with those soaps containing from about 16 to about 22 carbon atoms usually being most desirable. The metal portion of such soaps can be one or more metals such as aluminum, barium, calcium, cadmium, cobalt, lead, lithium, magnesium, mercury, nickel, sodium, strontium, zinc and the like. Ordinarily, soaps of metals of groups I and II of the periodic table are most satisfactory as thickening agents. If desired, the above described metal soap thickening agents such as silica gel; clay-base agents such as bentonite treated with quaternary ammonium compounds, attapulgus clay treated with surface active agents, etc.; and carbon black.

The thickening agents are incorporated in the grease compositions of this invention in amounts sufficient to form the grease. Amounts of thickening agents from about 3 percent to about 50 percent by weight of the finished composition can be used. Amounts from about 5 percent to about 25 percent are ordinarily sufficient.

The greases of this invention may contain other ingredients such as unsaponified monohydric and polyhydric alcohols, particularly glycerol; alkaline substances such as excess alkali; moisture; and fillers which contribute to the body of the grease because of their bulk.

The antioxidant of this invention may be prepared by the reaction of 2-methyl-6-tert-butylphenol with sulfur dichloride as illustrated by the following example.

Example 14

A solution of 32.8 parts of 2-methyl-6-tert-butylphenol in 18 parts petroleum ether (B. 36–38°) was stirred while a solution of 10.3 parts of freshly distilled SCl_2 in 5 parts petroleum ether was added slowly at 15–20°. The exothermic reaction was controlled with external cooling. After half the SCl_2 solution had been added, the reaction mixture was stirred at 20–28° C. for ½ hour. The rest of the SCl_2 was then added slowly at 20° and then the mixture was stirred at 24–28° for 2 hours. The reaction mixture was filtered, and the addition of a small amount of fresh solvent caused precipitation of a crystalline product. After washing with solvent, 22.3 parts of the crude product were recovered. This represents 62.3 percent yield of 4,4'-thiobis(2-methyl-6-tert-butylphenol) having a melting point of 114–117.5°. Treatment with activated charcoal and recrystallization from cyclohexane gave white crystals having a melting point of 124–125° C. Analysis of the compound showed it to contain about 9.05 percent sulfur (calculated sulfur content for 4,4'-thiobis(2-methyl-6-tert-butylphenol) is 8.94 percent).

This application is a continuation-in-part of my prior copending applications, Serial No. 779,068, now Patent

No. 3,069,384, filed December 9, 1958, and Serial No. 829,202, filed July 24, 1959.

I claim:

1. A non-fluid petroleum hydrocarbon-containing composition normally susceptible to deterioration in the presence of oxygen at ambient temperatures, said composition being selected from the group consisting of metallic soap-thickened mineral oil and petroleum wax, containing, in amount sufficient to inhibit such deterioration, up to about 5 percent of an antioxidant consisting essentially of 4,4'-thiobis(2-methyl-6-tert-butylphenol).

2. A grease composition consisting essentially of mineral lubricating oil and a metallic soap thickening agent, said grease composition being normally susceptible to oxidative deterioration containing, in amount sufficient to inhibit such deterioration, up to about 5 percent of an antioxidant consisting essentially of 4,4'-thiobis(2-methyl-6-tert-butylphenol).

3. The product of claim 1 wherein said composition is petroleum wax.

4. A stabilized non-fluid petroleum hydrocarbon-containing composition containing a chemical capable of catalyzing oxidation thereof and containing, in amount sufficient to inhibit such oxidation, up to about 5 weight percent of an antioxidant consisting essentially of 4,4'-thiobis(2-methyl-6-tert-butylphenol), said composition being selected from the group consisting of metallic soap-thickened mineral oil and petroleum wax.

5. The product of claim 4 wherein said composition is petroleum wax.

6. The product of claim 2 wherein said metallic soap is present in from about 3 to 50 weight percent concentration.

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