Patented May 4, 1954

2,677,659

UNITED STATES PATENT OFFICE

2,677,659

MINERAL OIL COMPOSITIONS HAVING STABILIZED LOW POUR POINTS

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No Drawing. Application March 21, 1952, Serial No. 277,909

17 Claims. (Cl. 252—33.4)

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This invention relates to lubricating oil compositions. More particularly, it is concerned with oil compositions having stabilized low pour points.

As is well known, the A. S. T. M. pour point of a waxy mineral lubricating oil may be substantially lowered by adding to the oil a small amount of a certain type of chemical agent having wax-modifying properties. Such agents are known as pour point depressants. Oils of low pour point are, of course, highly desirable for use where low temperatures are encountered. Thus, automobile engine oils designed for winter use are generally fortified with pour depressants in order to provide easier starting and better lubrication of the engine parts in cold engines.

A major problem has been encountered, however, in the use of pour depressants, viz., pour point reversion. This is the tendency of an oil, which has had its pour point lowered by the addition of a pour depressant, to revert to a higher pour point when subjected to temperature cycling, as, for example, during winter storage. Thus, an oil containing a pour depressant may have an initial A. S. T. M. pour point of —20° F., but during storage may be found to be solid at temperatures much higher than the original pour point. This tendency for pour point reversion has been found to be particularly pronounced where the pour depressant is of the metal detergent type. This type of pour depressant comprises certain metal salts of organic acids which are available commercially for use in lubricating oils, and which function as detergents as well as pour depressants. The two-fold action of these salts is, of course, highly advantageous. Unfortunately, however, the problem of pour point reversion which is associated with their use, greatly discounts their value.

It is the object of this invention to provide a practical means of counteracting the pour reversion tendency in oil compositions containing these detergent salts as pour depressants, so that the pour points of such compositions are rendered substantially stable.

In accordance with the present invention, we have now found that the pour point of a lubricating oil which has been lowered by the addition thereto of a detergent salt type pour point depressant may be stabilized by addition to the oil

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of a small amount of an acidic organic compound, particularly an organic acid. The invention, therefore, comprises the use, in combination, in oil to provide a stable low pour point therein of (1) a minor amount of a metal organic detergent type pour point depressant and (2) a minor amount of an organic acid.

The metal organic pour depressant

The invention contemplates and is applicable to any metal organic detergent salt having pour depressant properties. Salts of this character are described in detail in previously issued patents of the present inventor, viz., Nos. 2,197,835 and 2,263,445. These salts may be broadly defined as oil-miscible metal organic compounds having a wax-substituted aryl nucleus therein. These include: Wax-aryl metal oxides, such as metal phenates, metal salts of wax-aryl acids, such as carboxylates and thio-carboxylates, metal salts of wax-hydroxy-aromatic acids, such as wax-phenol carboxylates and metal salts of wax-aryl sulfonic acids, such as wax benzene sulfonates. Other metallo-wax-aryl compounds, such as those shown in previously issued Patent No. 2,197,835 and sulfurized metal salts of the aforesaid types, such as those disclosed in detail in previously issued Patent No. 2,263,445 are also included.

In general, it appears that the metal constituent of the wax-aryl-metallo compound may be any metal. Metals which provide particularly useful detergent pour depressants in oil, however, belong to the silver, copper, tin, aluminum, iron, alkali and alkaline earth analytical groups, especially the alkaline earth group. The salts of barium are particularly preferred. As non-limiting examples of such compounds, the following may be mentioned:

Barium wax-phenol carboxylate
Calcium wax-phenol carboxylate
Aluminum wax-phenol carboxylate
Sulfurized barium wax-phenol carboxylate
Barium wax-benzene sulfonate
Zinc wax-benzene sulfonate
Barium wax-naphthalene sulfonate
Calcium wax-phenate
Barium wax-phenate
Lead wax-phenate
Sodium phenate of wax-phenol disulfide

The acidic compound

The acidic organic compounds capable of stabilizing the low pour point of an oil containing a pour depressant salt of the above-described type include the following: Mono- and poly-carboxylic acids of the aliphatic, aromatic and heterocyclic series. The aliphatic acid may be saturated or unsaturated and may have a molecular weight as low as formic acid or as high as montanic acid. Suitable saturated monobasic acids are, for example, formic, acetic, butyric, capric, palmitic, stearic and montanic acids. Unsaturated monobasic acids are acrylic acid, oleic acid and the like. Suitable saturated aliphatic polybasic acids include succinic, adipic, and sebacic acids, while unsaturated polybasic acids include acids such as fumaric and maleic acids.

The aromatic monocarboxylic acid may be, for example, benzoic or naphthoic acid while the polybasic acid may be an acid such as phthalic or terephthalic acid. Proper oil solubility of the aromatic acid can be assured by having one or more alkyl substituents, such as a butyl group, in the aromatic ring.

The heterocyclic carboxylic acids include, for example, furoic, alkylated furoic and nicotinic acids.

Other types of acids which are suitable for use in the invention include non-benzenoid cyclic mono- and polycarboxylic acids, such as abietic and camphoric acids; alkane sulfonic acids, such as methane and ethane sulfonic acids; alkaryl sulfonic acids, such as amyl phenyl sulfonic acid and wax phenyl sulfonic acid; organic acids of sulfur, such as thiolacetic acid; mercaptans, such as dodecyl mercaptan; alkyl hydrogen phosphites and phosphates, such as didecyl hydrogen phosphite; alkaryl acid phosphites and phosphates, such as diamylphenyl acid phosphite and phosphate; alkane phosphinic and phosphonic acids, such as dimethyl phosphinic, methyl phosphonic and dodecane phosphonic acids. The acids of the invention may or may not contain other substituent groups, such as halogen, hydroxyl, amino, thio, keto, cyano, azo, nitro, etc.

Although as aforestated, the principle of the invention is applicable to metal organic detergent salt pour depressants in general, it will be illustrated herein by means of the sulfurized barium salt of wax-phenol carboxylate which is typical of the detergent-type pour depressant salts contemplated herein.

Preparation of sulfurized barium wax-phenol carboxylate

(*a*) PREPARATION OF WAX-ALKYLATED PHENOL

A paraffin wax melting at approximately 120° F. and predominantly comprised of hydrocarbons having at least 20 and an average of about 24 carbon atoms in their molecules, is melted and heated to about 200° F., after which chlorine is added until the desired weight (about 14 per cent) is incorporated in the wax. A sufficient quantity of this chlorinated wax to provide 3 atomic proportions of chlorine is then heated to a temperature varying from just above its melting point to not over 150° F. One mol of phenol (C_6H_5OH) is then mixed with the chlorowax. The mixture is then heated to about 150° F. and a quantity of anhydrous aluminum chloride, corresponding to about 3 per cent of the weight of the chlorowax in the mixture, is slowly added with active stirring. The rate of addition of the aluminum chloride should be sufficiently slow to avoid violent foaming and during the addition the temperature should be held at about 150° F. After the aluminum chloride has been added the temperature of the mixture may be increased slowly over a period of from 15 to 25 minutes to a temperature of about 250° F. and then should be more slowly increased to about 350° F. To control the evolution of HCl gas, the temperature of the mixture is preferably raised from 250° F. to 350° F. at a rate of approximately one degree per minute, the whole heating operation occupying approximately two hours from the time of adding the aluminum chloride. If the emission of HCl gas has not ceased when the final temperature is reached, the mixture may be held at 350° F. for a short time to allow completion of the reaction. However, to avoid possible cracking of the wax, the mixture should not be heated appreciably above 350° F., nor should it be held at that temperature for any extended length of time.

It is important that all unreacted, or non-alkylated, phenol remaining in the reaction mixture, as well as aluminum chloride, be removed. This can be conveniently effected by washing the product several times with a mixture of water and an alcohol, such as butanol, preferably at elevated temperature, say 175° F. The product may then be treated with steam. This latter step will insure complete removal of the unreacted material and also dry the product.

It will be understood that a wax-substituted phenol prepared according to the above procedure, in which a quantity of chlorowax containing three atomic proportions of chlorine and having a chlorine content of 14 per cent is reacted with one mol of phenol, is designated as "wax-phenol (3–14)". Similarly, "wax-phenol (3–10)" and "wax-phenol (1–10)" may also be prepared by the reaction of sufficient amounts of chlorinated wax, containing 10 per cent by weight of chlorine, to provide 3 atomic proportions and 1 atomic proportion of chlorine per mol of phenol, respectively, in the reaction and are useful in the invention. In general, an amount of chlorowax, containing from about 10 to 18 per cent by weight of chlorine may be used in the reaction to supply between 1 and 4 atomic proportions of chlorine per mol of phenol used.

(*b*) PREPARATION OF THE SULFURIZED BARIUM SALT OF WAX-PHENOL CARBOXYLIC ACID (3–14)

Barium oxide is reacted with methanol at room temperature to form a solution of barium methylate. The reaction mixture is then filtered to obtain the pure solution which may contain an amount of barium methylate equivalent to 10 per cent barium by weight.

One hundred grams of wax phenol, prepared as indicated in (*a*), is dissolved in 150 grams of mineral oil (S. U. V. 100 sec. at 100° F.) and heated with stirring to 167° F. An amount of the barium methylate solution equivalent to 8.78 grams barium is then added while allowing the methanol to distil. After stirring for 15 minutes at 167° F., the temperature is gradually increased to 383° F. and CO_2 is introduced over a 4-hour reaction period at 383° to 395° F. The batch is then cooled to 266° F. preparatory to the introduction of elementary sulfur (3.88 grams) which is sprinkled in and the batch stirred for 15 minutes at 266° to 285° F. to insure complete solution of the sulfur. The whole is then cooled to 167° F.

Additional barium methylate, equivalent to 29.2 grams barium, is then added with the simulta-

neous distillation of methanol. After reacting the mixture 15 minutes, the temperature is gradually raised to 266° F., followed by filtration of the product through filtering clay. The filtrate is then analyzed for barium and diluted with additional mineral oil to give the finished product of 6 per cent barium content.

Pour point stability

The ability of the acidic organic compounds herein contemplated in stabilizing the pour points of oils containing a pour depressant of the metal detergent type is demonstrated by the test results shown in Table I. In these tests oil blends of the sulfurized barium salt of wax-phenol carboxylic acid (3–14) both with and without an added acidic compound were prepared and subjected to laboratory temperature cycling tests. The base oil used in all these tests was a mid-continent, solvent-refined oil having a kinematic viscosity of 8.39 centistokes at 210° F. and an A. S. T. M. pour point of +25° F. This oil was blended with 1 per cent by weight of a commercial additive consisting of 1 part of the sulfurized barium salt of wax-phenol carboxylic acid (3–14), prepared as described hereinabove, and 1 part of a reaction product of alpha-pinene with phosphorus pentasulfide (antioxidant). This blend had an A. S. T. M. pour point of −25° F. In the table, this oil blend is designated as Blend A. The other blends tested (containing the acidic organic compounds) were prepared by simply adding a small amount of the particular acidic organic compound to Blend A.

The test procedure involved the following steps:

1. Fifty-gram samples of the oil blends in standard, tall-form, four-ounce bottles were preheated to 115° F. and then allowed to cool to room temperature.

2. The samples were then cooled to −20° F. over a 22-hour period and maintained at this temperature for 24 hours.

3. The samples were allowed to warm to +50° F. over a 44-hour period and kept at this temperature for about 4 hours.

4. The samples were finally cooled to −20° F. over a 54-hour period. They were observed for fluidity at five-degree intervals beginning with +20° F. during the final cooling stage. In examining the sample for fluidity, it was first tilted slightly. If no flow was observed, the bottle was tilted to a horizontal position and held for five seconds. The sample was reported as being solid if no flow was observed after this time. The stable pour point is reported as five degrees above the observed solid point.

Certain of the stable pour points shown in the table are reported as −15° F. which means that these blends were fluid at −15° F. which was the lowest temperature obtained in the final cooling stage of that particular test. Where a final temperature of −20° F. was attained, those blends which still flowed are reported as having stable pour points of −20° F.

It will be seen from the table that the stable pour point obtained for Blend A was +15° F., which amounts to a reversion of 40 degrees (from −25° F.), whereas in each of the other blends tested the acidic compound inhibited the reversion of the pour point, the greatest reversion being only 10 degrees where 0.1 per cent by weight of the acidic compound was used; and, in certain instances where even smaller amounts of the acidic compound was used, reversion was substantially completely inhibited.

TABLE

Compound Added To Blend A	Concn., Wt. Per-cent	Stable Pour Point, ° F.
None		+15
Acetic Acid	.05	+15
	.10	−15
Stearic Acid	.05	−15
	.10	−10
Abietic Acid	.05	−15
	.10	−15
Furoic Acid	.02	<−20
	.05	<−20
Sebacic Acid	.02	−15
	.05	−10
Diglycolic Acid	.02	<−20
	.05	<−20
Maleic Anhydride	.02	<−20
	.05	<−20
Phthalic Anhydride	.05	−10
	.10	−15
Didodecyl Malonic Acid	.05	+5
	.10	−15
Mixed Methane- and Ethanesulfonic Acids	.05	−15
	.10	−15
Salicylic Acid	.02	<−20
	.05	<−20
Anthranilic Acid	.01	−10
	.02	−15
Didecyl Hydrogen Phosphite	.05	−5
	.10	−15
Dodecane Phosphonic Acid	.05	<−15
	.10	<−15
Diamyl Phenyl Acid Phosphate	.05	−10
	.10	<−15
Magnesium Stearate	.05	<−15
	.10	<−15

The amount of the detergent-type pour depressant salt used in the oil is that sufficient to substantially lower the pour point of the oil, i. e., from about 0.05% to about 5%, usually about 1.0% by weight. On the other hand, the amount of the acidic organic compound required to stabilize the pour point of the oil will be a minor amount, i. e., from about 0.01% up to about 1%, by weight, although usually from 0.01% to 0.10% is sufficient. In blending certain of the less oil-soluble compounds, it is desirable to first prepare a concentrated solution in an alcohol, such as n-butanol, and then blend the desired concentration in the oil.

The pour stabilizing acidic compounds of the invention may be added to oils containing other improving agents along with the detergent-type pour depressant, such as antioxidants, extreme pressure agents, rust inhibitors, etc.

Concentrated oil blends of the stabilized additives of the invention may be prepared and marketed, such "concentrates" of the additives providing a readily soluble form of the additive combination for addition to further quantities of oil to improve the pour point characteristics thereof.

Although the invention has been illustrated herein by certain specific examples, it is not intended that the scope thereof be limited thereby in any way, but only as indicated by the appended claims in which it is intended to claim all novelty inherent therein as well as all modifications coming within the scope and spirit of the invention.

What is claimed is:

1. A lubricating oil composition having a stabilized low pour point comprising a major proportion of a waxy mineral lubricating oil, a minor proportion, sufficient to lower the pour point of said oil, of a metal salt of an organic acid having a wax-substituted aryl nucleus therein and a minor amount, sufficient to stabilize the lowered pour point of said oil, of an organic acid.

2. A lubricating oil composition having a sta-

bilized low pour point comprising a major proportion of a waxy mineral lubricating oil, a minor proportion, sufficient to lower the pour point of said oil, of a metal salt of an organic acid having a wax-substituted aryl nucleus therein and a minor amount, sufficient to stabilize the lowered pour point of said oil, of a carboxylic acid.

3. A lubricating oil composition having a stabilized low pour point comprising a major proportion of a waxy mineral lubricating oil, a minor proportion, sufficient to lower the pour point of said oil, of a metal salt of an organic acid having a wax-substituted aryl nucleus therein and a minor amount, sufficient to stabilize the lowered pour point of said oil, of a sulfonic acid.

4. A lubricating oil composition having a stabilized low pour point comprising a major proportion of a waxy mineral lubricating oil, a minor proportion, sufficient to lower the pour point of said oil, of a metal salt of an organic acid having a wax-substituted aryl nucleus therein and a minor amount, sufficient to stabilize the lowered pour point of said oil, of an organic phosphorus-containing acid.

5. A lubricating oil composition having a stabilized low pour point comprising a major proportion of a waxy mineral lubricating oil, a minor proportion, sufficient to lower the pour point of said oil, of a metal salt of a wax-substituted phenol carboxylic acid and a minor amount, sufficient to stabilize the lowered pour point of said oil, of a carboxylic acid.

6. A lubricating oil composition having a stabilized low pour point comprising a major proportion of a waxy mineral lubricating oil, a minor proportion, sufficient to lower the pour point of said oil, of a metal salt of a wax-substituted phenol and a minor amount, sufficient to stabilize the lowered pour point of said oil, of a carboxylic acid.

7. A lubricating oil composition having a stabilized low pour point comprising a major proportion of a waxy mineral lubricating oil, a minor proportion, sufficient to lower the pour point of said oil, of a metal salt of a wax-substituted aryl sulfonic acid and a minor amount, sufficient to stabilize the lowered pour point of said oil, of a carboxylic acid.

8. A lubricating oil composition having a stabilized low pour point comprising a major proportion of a waxy mineral lubricating oil, a minor proportion, sufficient to lower the pour point of said oil, of a metal salt of a wax-substituted phenol carboxylic acid and a minor amount, sufficient to stabilize the lowered pour point of said oil, of a sulfonic acid.

9. A lubricating oil composition having a stabilized low pour point comprising a major proportion of a waxy mineral lubricating oil, a minor proportion, sufficient to lower the pour point of said oil, of a metal salt of a wax-substituted phenol and a minor amount, sufficient to stabilize the lowered pour point of said oil, of a sulfonic acid.

10. A lubricating oil composition having a stabilized low pour point comprising a major proportion of a waxy mineral lubricating oil, a minor proportion, sufficient to lower the pour point of said oil, of a metal salt of a wax-substituted aryl sulfonic acid and a minor amount, sufficient to stabilize the lowered pour point of said oil, of a sulfonic acid.

11. A lubricating oil composition having a stabilized low pour point comprising a major proportion of a waxy mineral lubricating oil, a minor proportion, sufficient to lower the pour point of said oil, of a metal salt of a wax-substituted phenol carboxylic acid and a minor amount, sufficient to stabilize the lowered pour point of said oil, of an organic phosphorus-containing acid.

12. A lubricating oil composition having a stabilized low pour point comprising a major proportion of a waxy mineral lubricating oil, a minor proportion, sufficient to lower the pour point of said oil, of a metal salt of a wax-substituted phenol and a minor amount, sufficient to stabilize the lowered pour point of said oil, of an organic phosphorus-containing acid.

13. A lubricating oil composition having a stabilized low pour point comprising a major proportion of a waxy mineral lubricating oil, a minor proportion, sufficient to lower the pour point of said oil, of a sulfurized barium salt of a wax-substituted phenol carboxylic acid and a minor amount, sufficient to stabilize the lowered pour point of said oil, of maleic acid.

14. A lubricating oil composition having a stabilized low pour point comprising a major proportion of a waxy mineral lubricating oil, a minor proportion, sufficient to lower the pour point of said oil, of a sulfurized barium salt of a wax-substituted phenol carboxylic acid and a minor amount, sufficient to stabilize the lowered pour point of said oil, of stearic acid.

15. A lubricating oil composition having a stabilized low pour point comprising a major proportion of a waxy mineral lubricating oil, a minor proportion, sufficient to lower the pour point of said oil, of a sulfurized barium salt of a wax-substituted phenol carboxylic acid and a minor amount, sufficient to stabilize the lowered pour point of said oil, of salicyclic acid.

16. A lubricating oil composition having a stabilized low pour point comprising a major proportion of a waxy mineral lubricating oil, a minor proportion, sufficient to lower the pour point of said oil, of a sulfurized barium salt of a wax-substituted phenol carboxylic acid and a minor amount, sufficient to stabilize the lowered pour point of said oil, of dodecane phosphonic acid.

17. A lubricating oil composition having a stabilized low pour point comprising a major proportion of a waxy mineral lubricating oil, a minor proportion, sufficient to lower the pour point of said oil, of barium wax phenate and a minor amount, sufficient to stabilize the lowered pour point of said oil, of maleic acid.

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2,197,835	Reiff	Apr. 23, 1940