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Howland et al.

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[54] **GASOLINE ANTI-ICING ADDITIVES**

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[73] Assignee: **Union Oil Company,** Los Angeles, Calif.

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[52] **U.S. Cl.** **44/58,** 44/63, 44/DIG. 1, 44/DIG. 4, 44/72

[51] **Int. Cl.** **C10l 1/26**

[58] **Field of Search** ..... 44/58, 63, 56 D, 69 P

[56] **References Cited**

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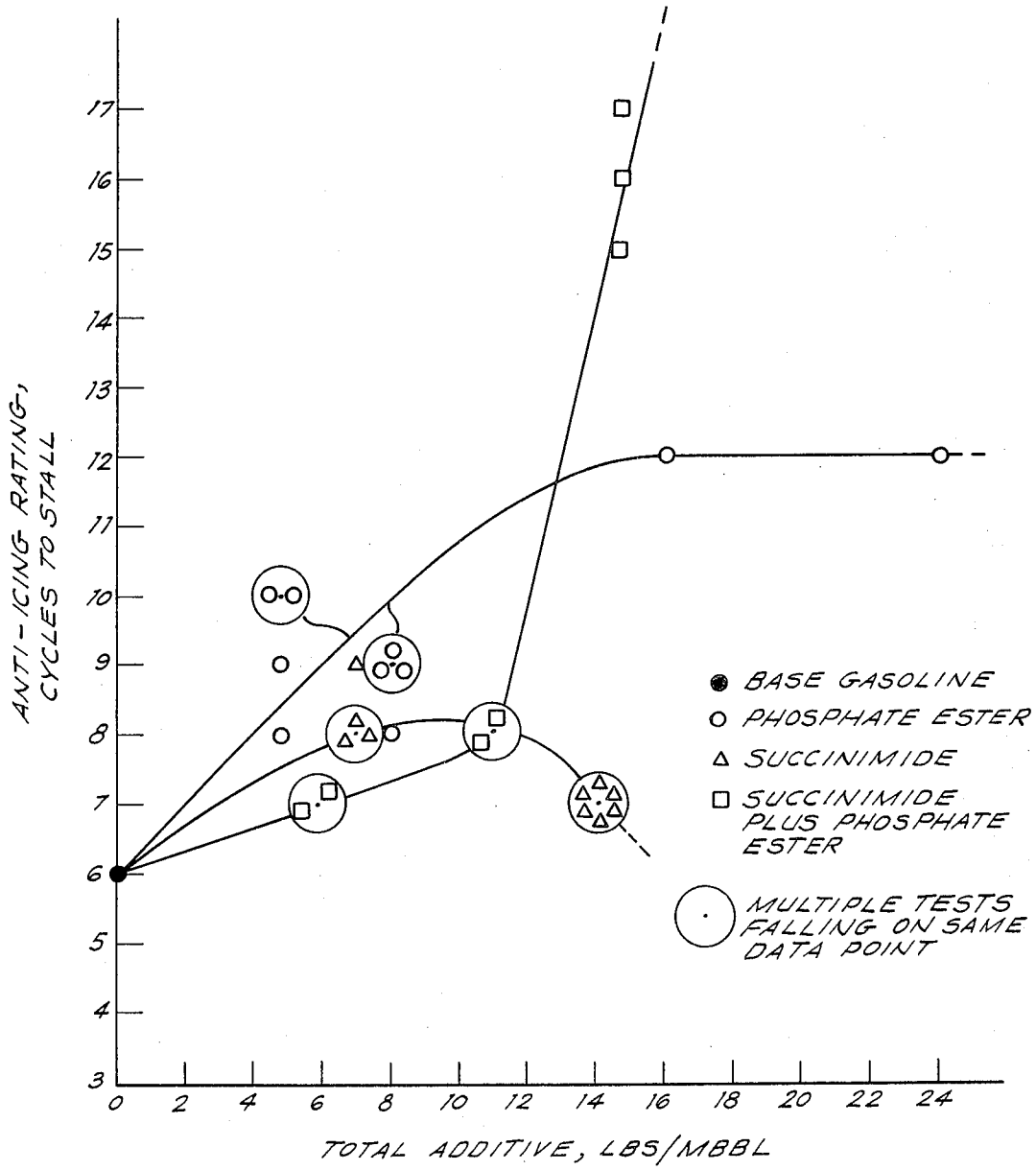
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[57] **ABSTRACT**

A combination of two specific types of known gasoline additives is found to provide, in addition to good overall carburetor detergency, a synergistic degree of anti-icing activity. One additive is an alkyl aminoalkyl phosphate, while the other is a succinimide condensation product of an alkylene polyamine wit an alkenyl succinic anhydride.

9 Claims, 1 Drawing Figure



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GASOLINE ANTI-ICING ADDITIVES

BACKGROUND AND SUMMARY OF THE INVENTION

A great variety of chemical additives have previously been proposed for use as detergents and/or dispersants in gasolines, for the primary purpose of removing and/or preventing the formation of deposits of dirt, gum, lacquer and the like in the induction system of internal combustion engines, primarily on the internal surfaces of the carburetor throat and associated parts. Some of these detergent additives are known to be effective in varying degrees as anti-icing agents, while others are of little or no value for that purpose. This is not particularly surprising, since the formation and removal of ice from carburetor surfaces bears little apparent analogy to the formation and removal of dirt, gum and lacquer deposits from such surfaces.

As is well known, the operation of carburetor-fed internal combustion engines under cool, humid weather conditions is apt to result in frequent stalling of the engine, especially during the warm-up period. Such stalling is a definite safety hazard as well as a decided inconvenience. It is now recognized that stalling of this nature is attributable to the formation of ice on the throttle plate and the nearby surfaces of the carburetor barrel. The water which forms the ice does not come from the gasoline, but from the air entering the carburetor. As noted above, stalling generally occurs in cool, humid weather when the temperature is between about 35° and 65°F., and the relative humidity is above about 65 percent. The most critical conditions are temperatures of about 40–60°F., and 90–100 percent relative humidity.

As the gasoline evaporates in the carburetor, it reduces the temperature of the surrounding metal surfaces by as much as 40–50°F. Moisture in the incoming air comes in contact with these parts and begins to build up ice on the throttle plate and in the carburetor barrel. The higher the humidity, the faster is the buildup of ice. Then, when the engine is idling, the throttle plate closes and the ice chokes off the normal flow of air through the small clearance between the throttle plate and the carburetor wall. This causes the engine to stall. The engine can usually be restarted when the heat from the exhaust manifold melts the ice sufficiently. However, stalling will continue until the engine is completely warmed up.

Carburetor icing occurs in some vehicles when cruising at speeds of 30–60 mph. Such icing is a considerable problem in the case of certain trucks and cars equipped with carburetors having venturi type fuel-air mixing tubes (emulsion tubes). The ice builds up on the tube and restricts the flow of air, thereby enriching the fuel mixture and reducing efficiency.

We have now discovered that these icing problems can be materially reduced by adding to the gasoline fuel certain minor proportions of two different additives which have previously been suggested for use individually as detergent additives. Neither of the additives alone is exceptionally effective for anti-icing, but surprisingly, the combination is synergistic in that it is much more effective than the same proportion of either additive alone. The first additive, referred to herein as the "succinimide" additive, is a complex condensation product of approximately equal mole-ratios of a relatively low molecular weight alkenyl succinic anhydride with an alkylene polyamine such as diethylene triamine. It is almost completely ineffective for anti-icing when used alone. The second additive is a mono alkyl, mono(amino alkyl)phosphate, referred to herein as the "phosphate ester" additive. Used alone it is fairly effective for anti-icing, but considerably less effective than the combination.

DETAILED DESCRIPTION

Additive Proportions

As will be apparent from the data presented hereinafter in the Examples and plotted graphically in the accompanying drawing, the synergistic anti-icing effect is critical to the use of certain minimum proportions of the additives. It is found that the desired synergistic results are obtained when the additives are employed in the following proportions:

TABLE 1

	Pounds per Thousand Barrels of Gasoline[1]	
	Broad Range	Preferred Range
Phosphate Ester	3–20	4–10
Succinimide	5–30	6–15

(1) One pound per thousand barrels = 4 parts per million.

In addition, the overall proportion of the combined additives should fall within the range of about 13–40, preferably 13.5–20 pounds per thousand barrels. It should be observed that these additives are often supplied commercially as concentrates in an inert solvent; the proportions cited above are on a solvent-free basis.

Preferred synergistic weight ratios of the two additives to each other range between about 20/80 to 60/40 of phosphate ester to succinimide. A premixed "package" comprising the two additives in these relative proportions may be conveniently utilized, with or without an added solvent such as toluene or other petroleum distillate. Other additives may also be included in the package, such as a mineral lubricating oil to reduce intake valve deposits. In some cases, the presence of a lubricating oil may actually enhance the anti-icing effect of the two-component additive. Suitable lubricating oils may have a viscosity at 100°F. of 200 to 700 SSU, a viscosity index above 70 and an A.P.I. gravity of 25 to 32. A particularly suitable oil, referred to herein as "300 neutral oil", has a viscosity of about 320 SSU at 100°F. and at 210°F. of about 52.2, a V.I. of about 85, a flash point of 445°F. and an A.P.I. gravity of about 28.6.

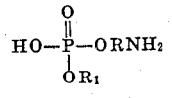
A preferred additive package for use herein is composed as follows:

	Volume - %
Succinimide B[1]	39
Phosphate Ester DMA-4[1]	28
Xylene-Kerosene Solvent	33

(1) Described hereinafter

The Alkyl Aminoalkyl Phosphate Additive

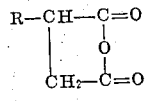
Suitable alkyl aminoalkyl phosphates for use herein correspond to the formula:



wherein R is an alkylene group containing from 4 to about 25, preferably six to 20 carbon atoms, and R_1 is an alkyl group having from five to about 25, preferably 10–20 carbon atoms. The sum of the carbon atoms R and R_1 should be in the range of 18–36, preferably 20–30. Suitable exemplary compounds include dodecyl 8-aminooctyl phosphate, octadecyl 6-aminohexyl phosphate, dodecyl 12-aminododecyl phosphate, decyl 6-aminododecyl phosphate, and the like. A particularly suitable phosphate additive is marketed by the E.I. du-Pont de Nemours Co. under the trade name DMA-4, and contains 27 total carbon atoms, analyzing 64.7% C, 12.9% O, 6.4% P, and 3.0% N.

The Succinimide Additive

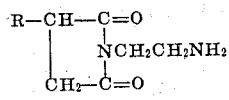
This additive can best be described as a condensation product of approximately one mole of an alkenyl succinic anhydride of the formula:



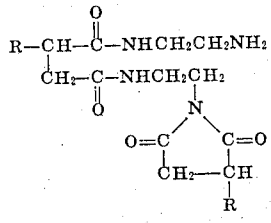
with about 0.60 to 1.5 moles of an alkylene polyamine of the formula:

$$H_2N(R_1NH)_xH,$$

wherein R is an alkenyl group having from 8 to about 50, preferably 15–40, carbon atoms, R_1 is a lower alkylene radical of about two to eight carbon atoms, and x is a number from 1 to about 10, preferably 2 to 6. The resulting product is a complex mixture of monomeric and polymeric amides and imides with an average molecular weight normally in the range of about 400 to 800. Where ethylene diamine is employed as the amine, representative reaction products are believed to include compounds such as:



and



but the presence of other specific amides, imides and amide-imides is not to be excluded.

The condensation reaction is carried out at temperatures of about 120–250°F., preferably 150–200°C., until about 1 mole of water per mole of alkenyl succinic anhydride employed has been split off. Preferably an inert solvent such as toluene or xylene is employed. The reaction is normally complete in about 1–5 hours, depending upon the temperature employed. Suitable condensation procedures are described in more detail in U.S. Pat. No. 2,182,178.

Suitable alkenyl succinic anhydride starting materials include compounds wherein R in the above formula is n-octenyl, iso-dococenyl, di-isobutenyl, tri-isobutenyl, tetra-isobutenyl, hexa-isobutenyl, deca-isobutenyl, and the like. Such compounds are well known in the art, and are normally prepared by reacting the appropriate olefin with maleic anhydride, as described in more detail in e.g., U.S. Pat. Nos. 3,172,892 and 3,443,918.

Suitable exemplary alkylene polyamine reactants include ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, propylene diamine, dipropylene triamine, di(tetramethylene)triamine, and the like.

The succinimide reaction products prepared as described above are fairly effective as carburetor detergent gasoline additives. However, we have found that at concentration levels effective for carburetor detergency, they are almost completely ineffective for de-icing. Strangely enough, at lower concentration levels which are relatively ineffective for carburetor detergency, they appear to function somewhat more effectively for de-icing. But even at these low concentrations they are not as effective as the combination of additives when used at the herein prescribed concentrations.

A preferred succinimide additive for use herein is marketed by the American Oil Co. under the trade name, "Amoco 575".

Base Fuels

The gasoline stocks to which the succinimide and aliphatic amine may be added with synergistic anti-icing effect include any petroleum fraction boiling in the conventional gasoline range of about 100° to 400°F., and preferably having an ASTM 50 percent boiling point between about 180 and 220°F. The 50 percent boiling point of a gasoline is a critical indicia of its icing propensity. As a rule of thumb, gasolines with 50 percent boiling points below 180°F. are considered severe, such that the surfactant-type additives utilized herein are relatively ineffective; for these highly volatile gasolines freeze point depressants such as alcohols or glycols may be required. Gasolines having a 50 percent point above about 220°F. are unlikely to cause icing. Hence, for practical purposes the principal utility of the combined additives of this invention resides in their use in gasolines having a 50 percent boiling point between about 180° and 220°F.

Typical commercial gasolines which may be utilized herein may comprise straight run gasolines, catalytically cracked gasolines, catalytic reformates and alkylates, and blends thereof. The fuel may also contain other conventional additives such as lead alkyls, organic halide lead scavengers, phenolic anti-oxidants, metal deactivators such as disalicylal-ethylene diamine, etc.

EXAMPLES

To demonstrate the above described synergistic results, a series of anti-icing test runs was carried out using various combinations and proportions of the respective additives. The base gasoline employed in all runs was a leaded blend of a light hydrocracked gasoline, a reformate, and a heavy catalytically cracked

gasoline, the blend having an ASTM boiling range substantially as follows:

Percent Overhead	°F.
I.B.P.	92
10	126
20	140
50	196
90	355
95	413
E.P.	432

Test Equipment

A single cylinder CFR engine coupled to a constant speed dynamometer was used for the tests. The test gasoline was fed to the engine through a special carburetor operating in an atmosphere of controlled temperature and humidity. When carburetor ice formed during a test, the constant speed dynamometer maintained engine speed, so the engine would not stall. The presence and amount of carburetor ice formed as indicated by an increase in manifold vacuum. A vacuum transducer and strip chart recorder were used to provide a record of the variation in manifold vacuum as a test progressed.

A spill-type carburetor was used to assure a constant air-fuel ratio. The conventional float and needle valve assembly was removed and a circular weir (overflow drain) installed inside the float chamber. The gasoline flow to the carburetor was adjusted so that a small amount of gasoline would overflow, thereby always providing a fixed level of gasoline in the float chamber.

An atmosphere of controlled temperature and humidity was supplied to the carburetor by means of an air conditioning unit. A gasoline injection system, injecting gasoline into the cylinder was used to fire the cylinder during stabilization periods when the carburetor was without fuel.

Test Procedure

The actual test procedure consisted in running the engine at constant speed while the throttle was cycled on a fixed time schedule between a cruise and an idle setting. The number of cycles required to develop enough ice to cause a 1 inch Hg increase in manifold vacuum at the idle setting was taken as an arbitrary stalling condition.

Each test was preceded by a careful purge and restabilization procedure. During the purge period an auxiliary air heater mounted in the carburetor inlet tube was energized. This added heat dried out moisture condensed during the preceding test and brought the carburetor throttle body back to test conditions more quickly. The temperature of the throttle body dropped to about 25°F. during each test. After the throttle body was heated to 50°F., the auxiliary heater was turned off and the engine was stabilized for an additional 3 minutes with fuel supplied directly to the cylinder by the injection system. Fuel flowed through the carburetor only during the actual test period.

Additives

The succinimide additive (Succinimide "B") was identified as a condensation product of one mole of a polyisobutenyl succinic anhydride having an average of approximately 29 carbon atoms in the polyisobutenyl radical, with about 0.75 mole of diethylene triamine.

The resulting product was a mixture of amides and imides having a number average molecular weight of about 700, and analyzing 4.9 weight-percent nitrogen.

The phosphate ester was the above described duPont DMA-4.

The results of the various runs were as follows:

TABLE 2

Run No.	Additive	Concentration, Lbs/M Bbl[1]	Anti-Icing Rating, Cycles to Stall
1	None	—	6
2	None	—	6
3	Succinimide B	7	8
4	Succinimide B	7	8
5	Succinimide B	7	8
6	Succinimide B	7	9
7	Succinimide B	14	7
8	Succinimide B	14	7
9	Succinimide B	14	7
10	Succinimide B	14	7
11	Succinimide B	14	7
12	Succinimide B	14	7
13	Phosphate Ester	4.8	8
14	Phosphate Ester	4.8	9
15	Phosphate Ester	4.8	10
16	Phosphate Ester	4.8	10
17	Phosphate Ester	8.0	8
18	Phosphate Ester	8.0	9
19	Phosphate Ester	8.0	9
20	Phosphate Ester	8.0	9
21	Phosphate Ester	16	12
22	Phosphate Ester	24	12
23	(Succinimide B (Phosphate Ester	3.5) 2.4)	7
24	Repeat of run 23		7
25	(Succinimide B (Phosphate Ester	7) 4.0)	8
26	Repeat of run 25		8
27	(Succinimide B (Phosphate Ester	9.1) 5.6)	15

TABLE 2 – Continued

Run No.	Additive	Concentration, Lbs/M Bbl[1]	Anti-Icing Rating, Cycles to Stall
28	Repeat of run 27		16
29	Repeat of run 27		17

(1) Solvent-free basis.

The foregoing data is plotted graphically in the accompanying drawing, and it is evident from the graph that the combined additives of runs 28–30 represent a synergistic improvement over the single additives of runs 3–23. It is further evident from runs 24–27 that these synergistic results are critical to the use of certain minimum proportions of the two additives.

Other exemplary synergistic additive combinations include but are not limited to the following:

Additive	Concentration in Gasoline Lbs/M Barrels
Succinimide C[1]	8.0
Octyl, 12-amino dodecyl phosphate	6.0
Succinimide D[2]	10.0
Lauryl, 12-amino lauryl phosphate	5.0
Succinimide E[3]	12.0
Hexyl, 12-amino octadecyl phosphate	8.0

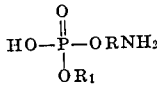
(1) A condensation product of 0.8 moles of propylene diamine with one mole of a 625 Av. molecular weight polyisobutenyl succinic anhydride.
(2) A condensation product of 0.9 mole of tetraethylene pentamine with one mole of a 350 Av. molecular weight polyisobutenyl succinic anhydride.
(3) A condensation product of 1.2 moles of dipropylene triamine with one mole of a 550 Av. molecular weight polyethylene succinic anhydride.

The following claims are believed to define the true scope of the invention.

We claim:

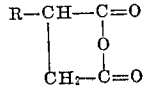
1. An anti-icing gasoline composition comprising a base gasoline boiling substantially in the range of about 100°–400°F., and dissolved therein:

1. between about 3 and 20 pounds per thousand barrels of an alkyl aminoalkyl phosphate having the formula:



wherein R is an alkylene group having from four to about 25 carbon atoms, and R_1 is an alkyl group having from five to about 25 carbon atoms, the sum of the carbon atoms in R and R_1 being in the range of 18–36; and

2. between about 5 and 30 pounds per thousand barrels of a succinimide condensation product of one mole of an alkenyl succinic anhydride of the formula:



with about 0.6 to 1.5 moles of an alkylene polyamine of the formula:

$$H_2N(R_1NH)_xH,$$

wherein R is an alkenyl group having from eight to about 50 carbon atoms, R_1 is a lower alkylene radical of about two to eight carbon atoms, and x is a number from 1 to about 10;

and wherein the combined proportion of components 1 and 2 in the gasoline is between about 13 and 40 pounds per thousand barrels.

2. A composition as defined in claim **1** wherein the weight-ratio of component 1 to component 2 is between about 20/80 and 60/40.

3. A composition as defined in claim **1** wherein said alkylene polyamine is diethylene triamine.

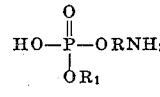
4. A composition as defined in claim **1** wherein the combined proportion of said components 1 and 2 in the gasoline is between about 13.5 and 20 pounds per thousand barrels.

5. A composition as defined in claim **1** wherein said base gasoline has a 50 percent boiling point between about 180° and 220°F.

6. A composition as defined in claim **1** wherein the weight-ratio of component 1 to component 2 is between about 20/80 and 60/40; said alkylene polyamine is ethylene diamine or diethylene triamine; the combined proportion of said components 1 and 2 in the gasoline is between about 13.5 and 20 pounds per thousand barrels; and wherein said base gasoline has a 50 percent boiling point between about 180° and 220°F.

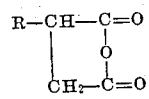
7. A synergistic anti-icing additive for gasoline comprising:

1. an alkyl aminoalkyl phosphate having the formula:



wherein R is an alkylene group having from four to about 25 carbon atoms, and R_1 is an alkyl group having from 50 to about 25 carbon atoms, the sum of the carbon atoms in R and R_1 being in the range of 18 to 36; and

2. a succinimide condensation product of one mole of an alkenyl succinic anhydride of the formula:



with about 0.6 to 1.5 moles of an alkylene polyamine of the formula:

$H_2N(R_1NH)_xH$,

wherein R is an alkenyl group having from eight to about 50 carbon atoms, R_1 is a lower alkylene radical of about two to eight carbon atoms, and x is a number from 1 to about 10;

the weight ratio of component 1 to component 2 being between about 20/80 and 60/40.

8. An additive as defined in claim **7** including in addition a paraffinic lubricating oil.

9. An additive as defined in claim **7** wherein said component 2 has an average molecular weight between about 400 and 800.

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