

[54] **GASOLINE ANTI-ICING ADDITIVES (A)**

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[58] Field of Search.....**44/58, 63, 71, 72, DIG. 1**

[56] **References Cited**

UNITED STATES PATENTS

2,706,677 4/1955 Duncan et al.**44/72 X**

3,438,757 4/1969 Honnen et al.**44/72 X**
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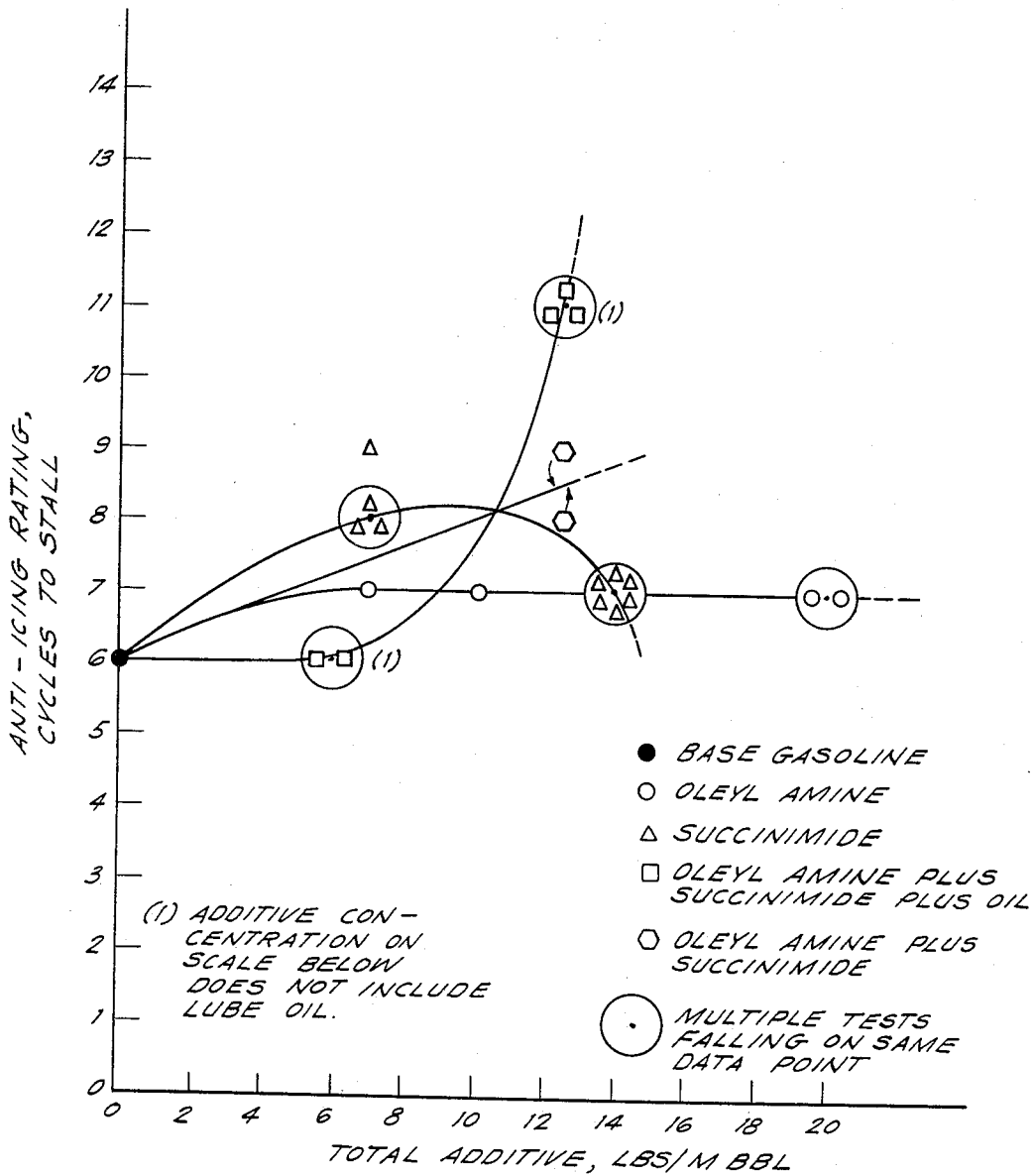
[57] **ABSTRACT**

A combination of two known types of surfactant gasoline additives with a non-surfactant lubricating oil additive is found to provide, in addition to good overall carburetor detergency, a synergistic anti-icing effect, as compared to any one or two of the additives alone. One of the surfactant additives is a succinimide condensation product of an alkylene polyamine with an alkenyl succinic anhydride, while the other is a long-chain primary alkyl- or alkenyl amine.

10 Claims, 1 Drawing Figure

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GASOLINE ANTI-ICING ADDITIVES (A)

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% 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 build-up 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 surfactant type additives which have previously been suggested for use individually as carburetor detergents, and a non-surfactant lubricating oil additive which is conventionally used in gasolines to reduce intake valve deposits. Neither of the surfactant additives alone, nor the combination thereof, is particularly effective for anti-icing but surprisingly, when the lubricating oil is added (which in itself is totally inactive as a de-icer), the com-

bination of surfactant additives becomes much more effective for anti-icing. In a sense therefore, the three-component additive combination is synergistic over any one component alone, or the two-component surfactant combination.

The first surfactant 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. The second surfactant additive is a long-chain alkyl or alkenyl amine such as oleyl amine.

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 I

Pounds per Thousand Barrels of Gasoline⁽¹⁾

	Broad Range	Preferred Range
Aliphatic Amine	2.5–20	3–10
Succinimide	6–30	7–15
Lubricating Oil	50–350	100–300

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

In addition, the combined proportion of the amine and succinimide additives should fall within the range of about 11–40, preferably 11.5–20 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 aliphatic amine to succinimide. The relative proportion of lubricating oil to the other two additives is not critical within the concentration ranges cited in the Table, for the minimum concentration of 50 pounds per thousand barrels is higher than is needed to induce the desired anti-icing synergism with any of the recited proportions of the other two additives. The lubricating oil is used in these high proportions in order to obtain other desired effects thereof, mainly to effectively reduce intake valve deposits.

A premixed "package" comprising the three additives in the relative proportions discussed above may be conveniently utilized, with or without an added solvent such as toluene, xylenes or other petroleum distillate. A preferred additive package for use herein is composed as follows:

Volume — %

Oleyl Amine

1.3

Succinimide B ⁽¹⁾	2.7
300 Neutral Oil ⁽¹⁾	54.0
Light Petroleum Solvent	42.0

⁽¹⁾ Described hereinafter

Preferably the package should contain about 10 to 50 volumes of lubricating oil per volume of the combined surfactant additives.

The Aliphatic Amine Additive

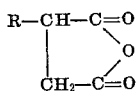
The aliphatic amines contemplated for use herein comprise those having the formula, RNH_2 , wherein R is a straight or branched-chain alkyl or alkenyl radical having from 12 to about 50, preferably 14 to 25 carbon atoms. Suitable exemplary amines include dodecylamine, isododecyl amine, tetradecyl amine, hexadecyl amine, octadecyl amine, octadecenyl amine, oleylamine, tetra-isobutenyl amine, hexa-isobutenyl amine, deca-isobutenyl amine, and the like. Mixtures of any two or more of such amines may also be utilized. These amine additives are well known in the art as carburetor detergents (see e.g., U.S. Pat. No. 3,011,879), but are in themselves almost completely ineffective for de-icing, either alone or in combination with a lubricating oil. It hence came as a distinct surprise to find that the amine-lubricating oil combination could enhance the effectiveness of the succinimide type additives.

The Lubricating Oil Additive

The hydrocarbon oil which is added to the gasoline, and which cooperates with the amine and succinimide additives to reduce icing, may be any light, medium or heavy paraffinic lubricating oil of low wax content. Preferably it is a solvent dewaxed, distillate oil having a viscosity at 100°F. of 200 to 1000 SSU, a viscosity index above 70, and an A.P.I. gravity of about 25 to 32. A typical such 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.

The Succinimide Additive

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

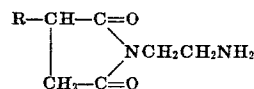


with about 0.60 to 1.5 moles of an alkylene polyamine of the formula:

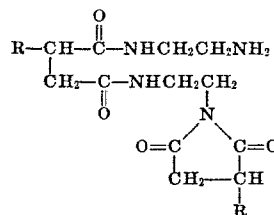


wherein R is an alkenyl group having from eight to about 50, preferably 15-40 carbon atoms, R_1 is a lower alkylene radical of about two to eight carbon atoms, and x is a number from 1 to about 10, preferably 2 to 6. The resulting product is a complex mixture of monomeric and polymeric amides and imides 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:

4



and



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

The condensation reaction is carried out at temperatures of about 120°-250°C., preferably 150°-200°C., until about one 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-dodecenyl, 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 Company under the trade name "Amoco 575".

Base Fuels

The gasoline stocks to which the lubricating oil, 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 e.g., 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 reformat, 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 was 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" 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 three 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 aliphatic amine was oleylamine sold under the trade name "Armeen OD" by Armour and Company.

The lubricating oil was the above described 300 neutral oil.

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	7.0	8
4	Succinimide B	7.0	8
5	Succinimide B	7.0	8
6	Succinimide B	7.0	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	Oleylamine	7	7
14	Oleylamine	10	7
15	Oleylamine	20	7
16	Oleylamine	20	7
17	(Oleylamine	3.5)	
18	(Succinimide B	9.05)	8
19	Repeat of Run 17		9
20	(Oleylamine	2.5)	6
21	(Succinimide B	3.5)	
22	(Neutral Oil	155)	
23	Repeat of Run 19		6
24	(Oleylamine	3.5)	11
25	(Succinimide B	9.05)	
26	(Neutral Oil	155)	
27	Repeat of Run 21		11
28	Repeat of Run 21		11

(1) Solvent-free basis.

The foregoing data is plotted graphically in the accompanying drawing, and it is evident from the graph that the three-component additive of runs 21-23 represents a synergistic improvement over the additives of runs 3-18. It is further evident from runs 19 and 20 that these synergistic results are critical to the use of certain minimum proportions of the surfactant additives.

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

Additive	Concentration in Gasoline, Lbs/M Barrels
Succinimide C(1)	12.0
n-Dodecylamine	4.0
Neutral Oil (300 SSU/100°F)	200
Succinimide D(2)	6.0
Hexaisobutenylamine	10.0
Neutral Oil (500 SSU/100°F)	400.0
Succinimide E(3)	10.0
Tetraisobutenylamine	8.0
Neutral Oil (300 SSU/100°F)	80.0

(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.

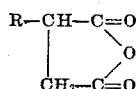
(3) A condensation product of 1.2 moles of dipropylene triamine with one mole of a 550 Av. molecular weight polyethylene succinic anhydride.

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 2.5 and 20 pounds per thousand barrels of an aliphatic amine of the formula RNH_2 , wherein R is an alkyl or alkenyl radical having from 12 to about 50 carbon atoms;
2. between about 6 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:



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

3. between about 50 and 350 pounds per thousand barrels of a paraffinic lubricating oil;

and wherein the combined proportion of components (1) and (2) in the gasoline is between about 11 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 said aliphatic amine is oleylamine.

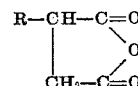
5. A composition as defined in claim 1 wherein the combined proportion of said components (1) and (2) in the gasoline is between about 11.5 and 20 pounds per thousand barrels.

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

7. 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 diethylene triamine; said aliphatic amine is oleylamine; the combined proportion of said components (1) and (2) in the gasoline is between about 11.5 and 20 pounds per thousand barrels; and wherein said base gasoline has a 50 percent boiling point between about 180° and 220°F.

8. A synergistic anti-icing additive for gasoline comprising a paraffinic lubricating oil, and dissolved therein:

1. an aliphatic amine of the formula RNH_2 , wherein R is an alkyl or alkenyl radical having from 12 to about 50 carbon atoms; 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:



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.

9. An additive as defined in claim 8 wherein said aliphatic amine is oleylamine and said alkylene polyamine is diethylene triamine.

10. An additive as defined in claim 8 containing about 10-50 volumes of said paraffinic lubricating oil per volume of the combined components (1) and (2).

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