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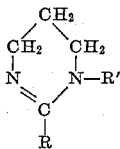
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SALTS OF TETRAHYDROPYRIMIDINES AND N-ALKYL SUCCINAMIC ACIDS

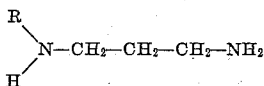
Harry J. Adress, Jr., Pitman, and Paul Y. C. Gee, Woodbury, N.J., assignors to Socony Mobil Oil Company, Inc., a corporation of New York
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2 Claims. (Cl. 260-256.4)

The present invention relates to improved non-lubricating petroleum distillate fractions, and novel chemical compounds useful as addition agents for providing same. More particularly, the invention relates to distillate fuels containing such an additive that inhibits said fuels against rusting of ferrous metals, to gasolines in which the additive imparts anti-stall properties and functions as a carburetor detergent, and to fuel oils in which the additive imparts anti-screen clogging properties and serves as a sediment stabilizer.

In U.S. Patent No. 2,961,308, there is disclosed a motor fuel containing a tetrahydropyrimidine of the following structure in an amount sufficient to inhibit the formation of deposits in carburetors of gasoline engines:

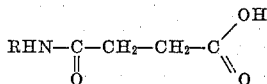


wherein R is naphthenyl and R' is an aliphatic hydrocarbon radical having 8 to 18 carbon atoms. As is also disclosed in said patent, such tetrahydropyrimidines can be prepared from the condensation of naphthenic acid with an aliphatic hydrocarbon-substituted propylene diamine having the formula:



wherein R is an aliphatic hydrocarbon group containing between about 8 and about 18 carbon atoms.

In U.S. Patent No. 2,982,629, there is disclosed a motor fuel containing certain succinamic acids in an amount sufficient to inhibit stalling of internal combustion engines, said succinamic acids having the formula:



wherein R is an alkyl group containing between about 10 and about 30 carbon atoms and having a tertiary carbon atom directly attached to the nitrogen atom. As is also disclosed in Patent No. 2,982,629, such amic acids can be made, for example, by heating a mixture of equimolar amounts of succinic acid anhydride with an appropriate tertiary alkyl primary monoamine at 65-150° C. for a period varying between one and three hours, the addition occurring readily without the formation of water.

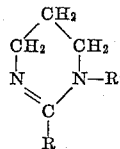
The present invention is based on the discovery that by use of a salt formed by the aforedefined substituted tetrahydropyrimidine with the succinamic acid, marked and unexpected improvements are provided in petroleum distillate fractions, and among such improvements are synergistic effects with respect to anti-screen clogging characteristics in fuel oils. Over and above such an improvement, use of the aforedefined salt also imparts to the appropriate petroleum distillate fractions, inhibition against rusting, carburetor detergency, and stabilization against sedimentation.

The salts embodied for use herein can be prepared by

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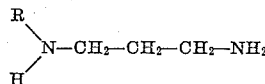
heating a mixture of substantially equimolar amounts of the defined substituted tetrahydropyrimidine and the succinamic acid as for example, at about 100° C. for several hours and, more specifically, for about three hours.

In further reference to the substituted tetrahydropyrimidine component of the salt embodied herein, particularly useful in such a component of the formula.



derived by condensation of certain aliphatic hydrocarbon substituted propylene diamines as aforedefined with naphthenic acids which, as is well known to those familiar in the art, are monocarboxylic acids found in crude petroleum and petroleum distillates and are obtained as mixtures rather than pure compounds. Particularly utilizable for providing the naphthenyl radical R in the substituted tetrahydropyrimidine are naphthenic acids containing between about 10 and about 30 carbon atoms and which can have an acid number (mg. KOH per gram) varying between about 120 and about 220, corresponding to an average molecular weight of between about 275 and 420. A particularly useful naphthenic acid has an average molecular formula C₁₉H₃₄O₂; an average molecular weight of 297; an acid number of 178; about 5% unsaponifiables and distills, at a pressure of 2 mm. Hg, over the range of 315-485° F.

The diamine reactant used to prepare the tetrahydropyrimidine, and which governs the R' aliphatic hydrocarbon radical in the aforedefined structure of the substituted tetrahydropyrimidine is a N-aliphatic hydrocarbon substituted propylene diamine of the formula:



wherein R is an aliphatic hydrocarbon group containing from about 8 carbon atoms to about 18 carbon atoms. The diamine reactant can be a pure compound, but, in practice, it will often be a mixture of pure diamines. Several mixtures of diamine reactants are available on a commercial scale. One is a mixture of N-substituted propylene diamines of the formula set forth hereinbefore, wherein about 20 percent of the R groups are hexadecyl, about 17 percent are octadecyl, about 26 percent are octadecenyl, and about 37 percent are octadecadienyl. In a similar mixture, 8 percent of the R groups are octyl, about 9 percent are decyl, about 47 percent are dodecyl and about 18 percent are tetradecyl, about 8 percent are hexadecyl, about 5 percent are octadecyl, and about 5 percent are octadecenyl. In still another mixture, about 2 percent of the R groups are tetradecyl, about 24 percent are hexadecyl, about 28 percent are octadecyl, and about 46 percent are octadecenyl.

The amines utilizable in forming the succinamic acid component of the salt embodied for use herein are tertiary alkyl primary monoamines in which a primary amino group (-NH₂) is directly attached to a tertiary carbon atom and which contains between about 10 and about 30 carbon atoms per tertiary alkyl group. The amines all contain the group,



Non-limiting examples of the amines are t-dodecyl primary amine, t-tetradecyl primary amine, t-pentadecyl

primary amine, t-hexadecyl primary amine, t-octadecyl primary amine, t-eicosyl primary amine, t-tetracosyl primary amine, and t-triacontyl primary amine. Further specific examples include a mixture of primary amines having a tertiary carbon atom of a tertiary alkyl group attached to the amino ($-\text{NH}_2$) group and containing 12 to 15 carbon atoms per molecule and averaging 12 carbon atoms per molecule, and containing, by weight, about 85 percent t-dodecyl primary amine, about 10 percent t-pentadecyl primary amine, and relatively small amounts, i.e., less than 5 percent amines having less than 12 or more than 15 carbon atoms; a mixture of tertiary alkyl primary amines containing 18 to 24 carbon atoms per molecule, having a tertiary carbon attached to the $-\text{NH}_2$ group, and containing, by weight, about 40 percent t-octadecyl primary amine, about 30 percent t-eicosyl primary amine, about 15 percent t-docosyl primary amine, about 10 percent t-tetracosyl amine and a small amount, less than 5 percent, other amines.

The petroleum distillates which can be improved by practice of this invention include gasolines which, in general, are mixtures of hydrocarbons having an initial boiling point falling between about 75° F. and about 135° F. and an end-boiling point falling between about 250° F. and about 450° F.; fuel oils that are hydrocarbon fractions having an initial boiling point of at least 100° F., an end-boiling point no higher than about 75° F., and boiling substantially continuously throughout their distillation range and generally known as distillate fuel oils, inclusive of straight run distillate fractions, catalytically or thermally cracked (including hydrocracked) distillate fuel oils, or mixtures of straight-run distillate fuel oils, naphthas and the like, with cracked distillate stocks, etc. Particularly contemplated are the Nos. 1, 2 and 3 fuel oils used in heating and as diesel fuel oils, and the jet combustion fuels. The domestic fuel oils generally conform to the specifications set forth in ASTM Specifications D396-48T. Specifications for diesel fuels are defined in ASTM Specifications D975-48T, and typical jet fuels are defined in Military Specification MIL-F-5624B.

The amount of the salt, embodied for use herein, that is added to the petroleum distillate will depend upon the intended purpose and the particular salt. Generally speaking, and in order to achieve beneficial results, the additive may be used in amounts as low as about 5 p.p.m., i.e., about one pound of additive per thousand barrels of the distillate up to about 200 pounds/thousand barrels of oil but, preferably, in amounts of from about 10 to about 200 pounds/thousand barrels of the petroleum distillate.

If desired, the petroleum distillate fractions embodied herein, such as fuel oils, can contain other additives for the purpose of achieving other results. Thus, for example, there can be present foam inhibitors and ignition and burning quality improvers, examples of such additives being silicones, dinitropropane, amyl nitrate, metal sulfonates, and the like. Petroleum distillates of the motor gasoline type can contain small amounts of other addition agents such as anti-knock agents, scavengers, preignition additives, gum inhibitors, and the like.

In order to further describe the invention, the following examples are set forth for purposes of illustration and not limitation, and without intent that the invention be limited to the specific compositions set forth in the examples.

PREPARATION OF ADDITIVE

A. A mixture of 100 grams (0.36 mole) of a naphthenic acid having an acid number of 200 and 143 grams (0.36 mole) of Duomeen T were refluxed in xylene solution for four hours, Duomeen T being a product of the structure $\text{RNHCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$, wherein R is 30% hexadecyl, 25% octadecyl and 45% octadecenyl, supplied by Armour & Co. The reaction mixture was then slowly heated to 275° C. over a period of 8 hours. Thirteen grams (0.72 mole) of water was collected resulting in production of

a mixture consisting of 30% 2-naphthenyl-3-hexadecyl-tetrahydropyrimidine, 25% 2-naphthenyl-3-octadecyl-tetrahydropyrimidine, 45% 2-naphthenyl-3-octadecenyl-tetrahydropyrimidine.

B. A mixture of 200 grams (1 mole) Primene 81R and 100 grams (1 mole) succinic anhydride was stirred for 3 hours at 95° C., thereby forming a succinamic acid of the formula:



wherein R is derived from a mixture of highly branched primary amines of C_{12} - C_{15} carbon atoms, the primary amine group of which is directly attached to a tertiary carbon atom, derived from Primene 81R, a product supplied by Rohm & Haas Co.

C. A mixture of 700 grams of the product of A and 300 grams of the product of B was stirred for 3 hours at 100° C. to form the salt, i.e., the salt formed by the 2,3-disubstituted tetrahydropyrimidine with the succinamic acid of B. Such a salt-forming reaction is characterized by a substantial rise in temperature.

The ability of the aforesaid additive to improve petroleum distillate fractions is demonstrated by its use in compositions, as defined hereinafter, in the described tests.

Screen clogging

The anti-screen clogging characteristics of a fuel oil were determined as follows: The test is conducted using a Sundstrand V3 or S1 home fuel oil burner pump with a self-contained 100-mesh monel metal screen. About 0.05 percent, by weight, of naturally formed fuel oil sediment, composed of fuel oil, water, dirt, rust, and organic sludge is mixed with 10 liters of the fuel oil. This mixture is circulated by the pump through the screen for 6 hours. Then, the sludge deposit on the screen is washed off with normal pentane and filtered through a tared Gooch crucible. After drying, the material in the Gooch crucible is washed with a 50-50 (volume) acetone-methanol mixture. The total organic sediment is obtained by evaporating the pentane and the acetone-methanol filtrates. Drying and weighing the Gooch crucible yields the amount of inorganic sediment. The sum of the organic and inorganic deposits on the screen can be reported in milligrams recovered or converted into percent screen clogging. Using the salt prepared in Example 1C, blended in a hydrofined fuel oil, the blend was subjected to the aforesaid screen clogging test along with the fuel oil per se and blends of the fuel oil plus the tetrahydropyrimidine component (Example 1A) of the salt, and the fuel oil plus the succinamic component (Example 1B) of the salt. The results from the screen clogging test were as follows:

Additive	Concentration, lbs./1,000 barrels of fuel oil	Screen Clogging, percent
Blank.....	0	100
Example 1C (salt) ¹	25	9
Example 1B (pyrimidine) component.....	17.5	34
Do.....	25.0	21
Example 1A (succinamic) acid component.....	7.5	53
Do.....	25.0	26

¹ The salt-forming ratio of the components, by weight=17.5 of the pyrimidine component and 7.5 of the succinamic acid component.

As is apparent from the foregoing, the salt embodied for use in practice of this invention not only markedly reduced the screen clogging characteristics of the fuel oil but, as is further apparent, the salt functioned synergistically in that, at the same concentration, the salt reduced screen clogging substantially more than resulted from use of the same concentration of each component used individually in the fuel oil; and, furthermore, the salt at the shown concentration of 5 lbs./1000 barrels of oil gave markedly higher protection against screen clog-

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ging than would be expected from a summation of the protection provided by use, individually in the oil, of each component in the amount that it would be present if it were in the form of the salt embodied for use herein.

The ability of a salt, embodied for use herein, to inhibit sedimentation is demonstrated by the results, set forth in the following tabulation, obtained in a 12 weeks' storage test.

FUEL OIL STORAGE TEST.—TWELVE WEEKS' STORAGE AT 110° F. (HYDROREFINED FUEL OIL)

Inhibitor	Conc., lbs. per 1,000 bbls.	Sediment, mg./liter
Blank fuel.....	0	17
Ex. 1C.....	25	4

The ability of a salt, as embodied for use herein, to inhibit a gasoline against rusting of ferrous metal is demonstrated by the results in the following tabulation:

ASTM RUST TEST D665 IN GASOLINE BLEND

Inhibitor	Conc., p.p.m.	Rust Test Result
Blank gasoline.....	0	Fail.
Example 1C.....	10	Pass.

In a gasoline, the salts utilized for practice of this invention are highly effective anti-stalling agents as is demonstrated by the performance thereof in the following test (Chevrolet Engine Test).

A standard Chevrolet engine, equipped with a Holley single downdraft carburetor, was mounted in a "cold" chamber refrigerated to about 40° F. A thermocouple was attached to the throttle plate shaft to record the plate temperature. A ½-inch insulating gasket was placed between the carburetor and manifold to prevent heat conduction. An asbestos sheet covered the entire manifold system to shield the carburetor from convection and radiation. A spray chamber was used to saturate the incoming air with moisture before entering an ice tower which cooled the air to about 35° F.

In conducting a test, the engine was first run for about 10 minutes at 2000 r.p.m. to bring the engine temperature to equilibrium. The engine was then shut off. When the throttle shaft temperature rose to 40° F., the engine was restarted with the idle speed set at 450 r.p.m. so that the base fuel stalled at idle in 10 seconds or less after a run-time of 20 to 50 seconds. Run-time means the time that the engine was run at 2000 r.p.m. before returning to idle.

All the runs were started when the throttle shaft reached 40° F. At the instant of starting, the throttle arm was moved to the 2000 r.p.m. position and a stop watch started. At the end of the selected run-time, the throttle arm was moved to the idle position. The time required to stall was recorded. Several tests were made at each run-time and averaged.

In evaluating an additive, the base fuel was first tested followed by several concentrations of the additive. The system was flushed between tests with the fuel to be run next. Any improvement caused by the additive was reflected in a longer run-time (as compared to the base fuel) to cause stalling in 10 seconds or less when the engine was idled. The more effective the additive, the longer the run-time.

ANTI-STALL TEST IN GASOLINE

Inhibitor	Conc., lbs./1,000 bbls.	Run Time to 10 sec. Stall Time (sec.)
Blank fuel.....	0	70
Ex. 1C.....	25	152

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Still other desirable properties imparted to a gasoline by addition thereto of a salt as defined hereinbefore include inhibition against bacterial growth and carburetor detergency. When used in a gasoline in a concentration of 25 lbs./1000 barrels, and stored at room temperature for ten weeks, the salt of Example 1C hereof reduced the bacteria count of the gasoline from 1122 million to 88 million.

As a carburetor detergent, the salt embodied herein is exceptionally effective as is evidenced by the data set forth hereinafter, obtained in the following carburetor detergency test:

The deposit-forming tendencies of a fuel are determined in an 8-hour engine test. This accelerated test, when run on fuels that contain no detergents, produces an amount of deposit equivalent to the amount observed in 4,000 miles of operation in field tests on taxicab fleets. A six-cylinder Chevrolet engine is equipped with notched rings to increase the amount of blowby. The engine is operated for eight hours, using the fuel under test, at alternate idle and running cycles. In the idle cycle, the engine is run at idling speed of 400 r.p.m. with no load, for five minutes. Then, for one minute, the engine is run at a speed of 2500 r.p.m., under a load of 30 B.H.P. and at 9.4 in. mercury manifold pressure. During the running cycle, the blowby and exhaust are released into the carburetor air intake during the idling cycle. After 8 hours' operation at alternate run and idle, the carburetor is examined and rated as to the amount of deposit in the throttle throat. In the rating scale, a rating of 0 (zero) indicates a clean carburetor; 1=trace deposits; 2=light deposits; 3=medium deposits; and 4=heavy deposits.

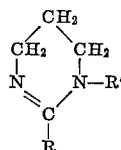
Gasoline	Concentration of Additive, lbs./M bbls.	Engine Rating	Percent Reduction in Deposits
Base.....	0	3.8	-----
Base+Ex. A (pyrimidine) component.....	17.5	1.6	83
Base+Ex. B (succinamic) acid component.....	7.5	3.2	32
Base+Ex. C (salt).....	25	1.2	90

As is apparent from the foregoing, use of the salt of Example C resulted in an exceptionally high percentage of reduction in engine deposits. Since the salt contained the components of Examples A and B in a ratio of 17.5 to 7.5, respectively, it is obvious that the 90% reduction provided by the salt is particularly an unexpected improvement and, especially so, when it is considered that the combination of the components would be expected to be less effective than the pyrimidine component per se in view of the rather unsubstantial reduction provided by the succinamic acid component per se.

Although the present invention has been described with preferred embodiments, it is to be understood that modifications and variations may be restored to, without departing from the spirit and scope of this invention, as those skilled in the art will readily understand. Such variations and modifications are considered to be within the purview and scope of the appended claims.

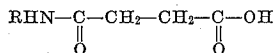
What is claimed is:

1. A tetrahydropyrimidine salt of a succinamic acid, said pyrimidine having the formula,



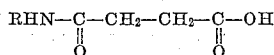
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wherein R is naphthenyl and R' is an aliphatic hydrocarbon radical of about 8 to about 18 carbon atoms, and said succinamic acid having the formula,



wherein R is an alkyl group containing between about ten and about thirty carbon atoms and having a tertiary carbon atom attached to the nitrogen atom.

2. A mixture consisting of a salt of tetrahydropyrimidine and succinamic acid having the formula,



wherein R is an alkyl group containing between about ten and about thirty carbon atoms and having a tertiary carbon atom attached to the nitrogen atom and wherein said tetrahydropyrimidine is a mixture consisting of 30%

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2-naphthenyl - 3 - hexadecyltetrahydropyrimidine, 25% 2-naphthenyl-3-octadecyltetrahydropyrimidine and 45% 2-naphthenyl-3-octadecenyltetrahydropyrimidine.

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