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NAPHTHENYL-ACYLATED POLYAMINES AND USES

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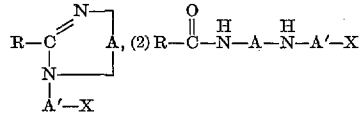
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Int. Cl. C10l 1/22, 1/18

U.S. Cl. 44—63 1 Claim

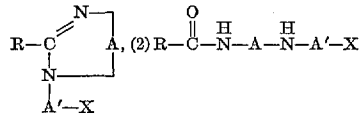
ABSTRACT OF THE DISCLOSURE

Acylated polyamines such as compounds of the formulae:

(I) 

(3) salts of (1) and (2), and (4) mixtures of (1) and (2) and/or (3); where R is a naphthenyl moiety, A and A′ are alkylene moieties (straight chain or branched), and X is a polar moiety such as, for example, hydroxy, amino, carboxyl-containing, etc.; and to hydrocarbon fuels in the gasoline range containing said compounds. These fuels possess anti-icing, anti-fouling and corrosion inhibiting properties.

This invention relates to acylated polyamines such as compounds of the formulae:

(I) 

(3) salts of (1) and (2), and (4) mixtures of (1) and (2) and/or (3); where R is a naphthenyl moiety, A and A′ are alkylene moieties (straight chain or branched), and X is a polar moiety such as, for example, hydroxy, amino, carboxyl-containing, etc.; and to hydrocarbon fuels in the gasoline range containing said compounds. These fuels possess anti-icing, anti-fouling and corrosion inhibiting properties.

THE ICING PROBLEM

Engine stalling due to carburetor icing occurs most frequently under engine idling conditions and particularly under weather conditions of relatively high humidity and at a temperature below about 60° F. While this problem has been in existence for many years, it has of late become of increased importance because of recent engine design. Most post-war cars are provided with automatic chokes and provide no means for manual operation of the throttle so that operators of such cars are no longer able to regulate idle speeds during warm-up periods to prevent stalling. Furthermore, the idle speed of automobiles equipped with automatic transmissions is rather critical during the warm-up period and the fastest idle rate which may be used is limited to avoid creeping. Another factor in carburetor icing is the high volatility of motor fuels now provided for present-day engines.

It has been established that the cause of engine stalling in cool humid weather is the formation of ice in the engine carburetor. On such cool moist days, the gasoline evaporated in the carburetor produces a sufficient refrigerating effect to condense and freeze the moisture present in the air entering the carburetor. Fuel vaporization in the fuel carburetor under such conditions can cause a temperature drop in the carburetor of up to 50° F.

below that of the entering air; as a result, up to the time of complete engine and radiator warm-up, this drop in temperature causes formation of ice crystals in the carburetor. The maximum refrigeration of the type referred to takes place under conditions of light load operation. As cooling of the carburetor parts takes place, ice begins to form as soon as these parts are refrigerated to a temperature below about 30° F., so that, when the throttle is closed to the idle position, the ice formed in the carburetor, particularly that formed on the throttle plate and the adjacent walls, closes the narrow air ports, thereby restricting the normal flow of the air to the engine, causing repeated engine stalling. While an engine stalled, because of carburetor icing, can be readily started because the ice formed melts almost immediately due to residual heat from the exhaust manifold, it is highly desired to avoid any stalling due to carburetor icing because of the attendant inconvenience. For example, stalling due to carburetor icing of a car, equipped with automatic transmission, frequently does not occur until the driver is ready to accelerate so that at this most inconvenient time it is necessary to shift the car to neutral, restart the engine and shift back into gear, all of which magnifies the inconvenience of frequent stalls.

In addition, it is well known that commercial gasolines themselves contain small amounts of dissolved water. Some additional moisture tends to accumulate in the fuel tanks of cars, hence water is always present in the fuel passing through the engine's fuel supply system. When exposed to temperatures below 32° F., and particularly at temperatures below 20° F., the water content of a fuel freezes and tends to form ice crystals in the supply system. These ice crystals can restrict and even block the small diameter fuel line or the small openings present in the fuel filter, thus impairing and ultimately disrupting engine operation.

THE FOULING PROBLEM

In the course of operation of an internal combustion engine, deposits build up in the throat of a carburetor, particularly in the area adjacent to the throttle plate. These deposits have a choking effect on the engine, thereby causing rough idling, and in many cases, the occurrence of frequent stalling.

It is generally accepted theory that these deposits form from solid particulate matter borne by the copious quantities of intake air an operating carburetor breathes. This solid matter is fed to the air by industrial stacks, and by exhaust pipes and crankcase breathers of motor vehicles, and other sources of fumes and smoke. It is, therefore, desirable to provide novel fuels which are effective in preventing deposits from forming in the carburetor of an internal combustion engine. The agents so employed are also known as carburetor detergents.

THE CORROSION PROBLEM

Since water is almost invariably present in the bottom of gasoline storage facilities, the possibilities of rusting and rust contamination of the fuel are excellent, and these are matters of great concern. The sloshing of fuel in storage tanks can slough rust scale off the tank walls, leading to the suspension of rust particles in the fuel itself. The larger of these particles can clog fuel filters, while smaller particles can wend their way into the combustion chambers of an engine and score cylinder walls and valves. The inhibition of rusting is therefore an important desideratum, and one which can be realized by using the novel fuels of this invention.

I have now prepared novel compositions comprising naphthenic acid-acylated cyclic amidine-forming polyamines having hydroxy, amino, carboxyl-containing, or other polar groups on the N-bonded side chain. These

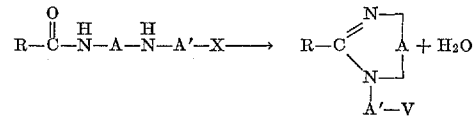
compositions are amides, cyclic amidines, salts, and mixtures thereof.

I have also found that hydrocarbons of the gasoline boiling range containing these compositions are multifunctional additives which possess anti-icing, anti-fouling, and corrosion inhibiting properties, as well as other properties.

The cyclic amidines and amides of this invention are prepared by well known methods amply described in the literature. In essence, the preparation involves reacting the naphthenic acid with the polyamine with the elimination of water. Where only one mole of water is removed the amide is formed.

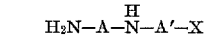


which can be further reacted with the removal of a second mole of water to yield the cyclic amidine, i.e., the imidazoline or tetrahydropyrimidine

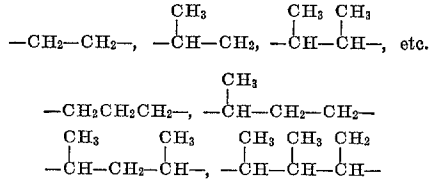


The product used may be either the amide, the cyclic amidine or mixtures thereof.

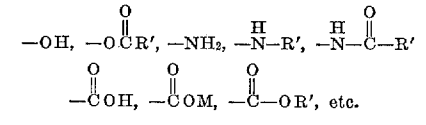
The polyamine reacted is of the formula



where A and A¹ which need not be the same are for example



etc., and X is for example



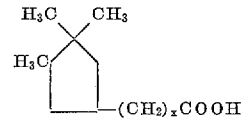
where R' is for example a hydrocarbon group, i.e. alkyl, aryl, cycloalkyl, etc., and M is a salt moiety. In the preferred embodiment X is —OH.

In certain instances where A is cyclic amidine-forming, A' need not necessarily be cyclic amidine-forming.

In addition the —A'OH side chain may be oxyalkylated to yield with alkylene oxides such as ethylene oxide, propylene oxide, butylene oxide, styrene oxide, or more than one type of oxide to yield $—(A'O)_nH$ units where n is a whole number such as 1, 2, 3, 4, 5, etc.

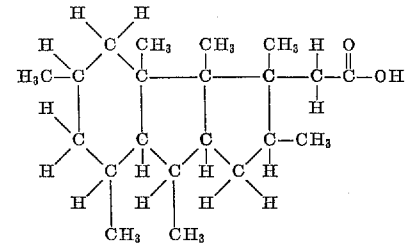
Naphthenic acids are employed in the present invention. As to the description of naphthenic acids reference is made to Industrial & Engineering Chemistry, vol. 41, No. 10, October 1949, pp. 2080–2090, as follows:

"The most widely used is naphthenic acid, a petroleum refining by-product obtained when the alkali liquor from the caustic treatment of gas oil is acidified with sulfuric acid. This treatment produces a dark brown about 12 on the Gardner color scale (when cut 1 to 9 with mineral spirits) oily liquid which separates to the top of the aqueous liquor. The mixed acids can be divided roughly into three groups having the general formulas: $C_nH_{2n}O_2$, $C_nH_{2n-2}O_2$, and $C_nH_{2n-4}O_2$. The first group occurs largely in the lower boiling fraction of the mixture. They usually contain 6 or 7 carbon atoms and are colorless. The second group, usually the largest, contains acids of 8 to 12 carbon atoms having the structure:



The third group contains the heaviest molecules which are polycyclic and have from 12 to 23 carbon atoms. All fractions from a carefully distilled napthenic acid (24) contain some color which, so far, has proved impossible to remove. Tarry residues account for the dark color of the crude, but these are laregly removed by distillation. Since napthenic acids are saturated and primarily cyclic, their soaps have much greater stability than those of other common liquid acids. The crude acid as delivered has a density of 8.04 to 8.44 pounds per gallon and a viscosity of 1.25 poises at 77° F. The acid values range from 160 to 270, but napthenic acid used for soap manufacture usually has an acid value between 220 and 230. pH of the water extract is about 5.5 and the iodine value between 8 and 11. Unsaponoifiables are held below 12%. The initial boiling points vary widely from shipment to shipment. Individual batches have boiled below 200° F. and up to almost 400° F. at 3.5 inches of mercury."

A typical formula in connection with some of the commercially available napthenic acids is the following:

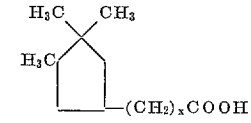


These particular acids are available in at least three different grades; Grade 1 having an average molecular weight of 290–300. Generally speaking, there is present about 6% of non-saponifiables and this type is perhaps characteristic of the most common commercially available naphtenic acid.

Grade 2 has a somewhat higher molecular weight, for instance 320–330 and contains about 8% of non-saponifiable matter. Grade 3, which finds considerable utility, has a molecular weight range of 410–420 and contains about 10% nonsaponifiable matter.

Any napthenic acid may be used but preference is to use the commercial grades above described, or in some instances, mixtures of two different grades so as to give, for example, an average molecular weight of 360 to 370 in some instance, and in others, a molecular weight of about 310, or thereabouts.

In examining the formula immediately preceding, with the formula preceding the above formula, and ignoring difference in the cyclic structure of the naphthenic acids, it is apparent that in at least some napthenic acids which are available commercially the cyclic structure is part of the beta carbon atom. On the other hand, as far as is known, and referring to the formula



there are available napthenic acids in which apparently x in the formula represents a small whole number, for instance, 3 or 4 or the like.

In practicing the present invention preference is given to the higher molecular weight napthenic acids, for example those having an average molecular weight of at least about 2000, such as about 250 to 500, or greater, for

example from about 290 to 420 but preferably from about 325–375.

Since commercial grades of napthenic acids are employed, these contain many individual species over a molecular weight range.

The most preferred napthenic acid those known as "Sunaptic" acids which are high-molecular-weight naphthenic acids prepared by the caustic extraction of selected base stocks. They range in acid number from 120 to 180, in molecular weight from 300 to 415, and are available in three grades, A, B, and C.

Specifications and typical analyses for the three Sunaptic acids are given in the table below. They are monocarboxylic acids and, having no olefinic unsaturation, are highly resistant to oxidative rancidity. They have low pour points and contain relatively low amounts of unsaponifiable matter. Sunaptic acids are soluble in most hydrocarbons.

SPECIFICATIONS

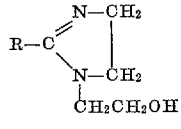
	Sunaptic Acids A		Sunaptic Acids B		Sunaptic Acids C	
	Specification	Typical Analysis	Specification	Typical Analysis	Specification	Typical Analysis
Acid number, mg. KOH/g	170–180	172	150–160	157	120–130	12
Unsaponifiables, percent by wt.[1]	7 max.	6.3	7 max.	5.0	11 max.	9.1
Density, 20/4		0.987		0.987		0.992
Specific gravity at 60° F		0.9902		0.9909		0.9930
API gravity at 60° F	11–13	11.4	11–13	11.3	10–12	11.0
Viscosity, SUS at 210° F	100–120	113	150–200	159	350–650	430
Bromine number [2]		9.0		10.0		12.1
Refractive index, n_D^{20}		1.498		1.507		1.516
Pour point, deg F		+30		+45		+75
Flash point, deg F	335 min.	380	370 min.	445	425 min.	445
Sulfur content, percent by weight	0.4 max.		0.4 max.		0.4 max.	
Average molecular weight [3]		310		340		415
Distillation Range, deg F. at 2 mm. Hg:						
Initial		326		336		408
5%		336		354		427
10%		346		370		446
50%		378		423		509
90%		452		490		580
95%		470		516		
End Point		486		526		596
Percent Recovery		98		98		95

[1] AOCS C_a6_a–40
[2] ASTM D–1158–52T
[3] Calculated from Acid Number and Percent Unsaponifiable.

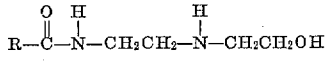
The following example is presented for purposes of illustration and not of limitation.

EXAMPLE 1

Equimolar amounts of a commercial naphthenic acid, Sunaptic Acid B, (1 mole, 365 parts by weight) and aminoethylethanolamine (1 mole, 104 parts by weight) were charged to a reactor and heated to 170° C. for 30 minutes at which time a vacuum of about 28 inches was applied for an aditional 3.5 hours. The product which was predominantly the imidazoline,



with a small amount of amide,



after cooling was dissolved in a hydrocarbon solvent to yield a solution which was 75% active.

The additive used in this invention may be dissolved directly in gasoline. As an alternative procedure a liquid concentrate of the additive may be prepared using as a solvent a hydrocarbon which is either compatible with, or a conventional component of, gasoline compositions. Suitable solvents include toluene, catalytic reformate, neutral oil and the like. The liquid concentrate may then be added to gasoline.

Gasoline base stocks which may be used in the practice of this invention include any of those conventionally used in preparing a motor fuel for a spark-ignited internal combustion engine, such as catalytic distillate, motor polymer, alkylate, catalytic reformate, isomerate, naphthas, etc. The gasoline will preferably contain an anti-knock agent of the tetra-alkyl lead type, such as tetraethyl lead, tetramethyl lead or chemical or physical mixtures thereof, and a scavenger agent such as ethylene dichloride and/or ethylene dibromide. The amount of anti-knock agent will usually be at a level of approximately 3 ml./gal., but may range from ½ ml./gal. to 6 ml./gal. The gasoline may also include other conventional additives such as solvent oils, dyes and the like.

These additives are employed in any suitable concentration capable of achieving its multiple functions such as anti-icer, a carburetor anti-foulant, and a corrosion inhibitor. In general, one employs at least about 5 p.p.m. such as about 5 to 500 p.p.m., for example from about 10 to 100 p.p.m., but preferably about 25 to 75 p.p.m. In practice, from economic considerations, the least amount of additive capable of effecting the desired results is employed.

The product prepared in Example 1 was evaluated according to the following tests.

It is to be noted that the solution of the additive employed was 75% active.

TEST I.—CARBURETOR ICING EVALUATION

Test conditions: 40° F. intake air; 90%±5% humidity; continuous air circulation.

Test procedure:

(1) Start cold engine.
(2) Accelerate to 1500 r.p.m. and maintain for one minute.
(3) Decelerate to idle r.p.m. and idle engine for one-half minute. Observe and record engine stalling characteristics.
(4) If engine stalls, immediately restart and rerun the cycles described by item (1) through (3) above.

TEST RESULTS

Fuel Sample	Number of Stalls	Total Test Cycles	Percent Reduction in Stalls
Base Gasoline	12	17	
Additive Example 1 (75% octane) (50 p.p.m.)	7	13	24

TEST II.—DYNAMIC RUST TEST FOR PETROLEUM FUELS

Apparatus: As specified in ASTM method D665–60

Procedure:

(1) Insert polished spindle into 300 ml. of test fuel.
(2) Allow spindle 10 minutes static and 20 minutes dynamic wetting time.

(3) Add 30 ml. of distilled water and stir for 4 hours.
(4) Remove spindle, wash with isopropyl alcohol, then isooctane, air dry and grade immediately.

RATING

Appearance of Spindle	Rating	Designation
Free of rust	Passes	R-1
Few spots	do	R-2
Less than 5% rusted	Borderline pass	R-3
5% to 50% rusted	Does not pass	R-4

RESULTS: TEST FUEL—PREMIUM GASOLINE

Additive	Concentration, p.p.m.	Rating
None		R-4
Additive Example 1 (75% octane)	15	R-2
Do	25	R-1

TEST III.—STATIC RUST TEST FOR PETROLEUM FUELS

Procedure:
(1) Presoak a polished spindle (spindle prepared as prescribed in ASTM Method D665–60) for 15 minutes in 300 ml. of the fuel sample in a pint container.
(2) Remove spindle and add 3 ml. of distilled water.
(3) Hand shake vigorously for 30 seconds, then replace spindle immediately.
(4) Take daily readings for 6 days.
(5) Rate by standard spindle method; R–1 to R–4. With readings of R–4 and higher, an estimate of the percent of rusted area should be made to the nearest 10 percent.

RESULTS: TEST FUEL—PREMIUM GASOLINE

Additive	Concentration, p.p.m.	Rating in degrees 1	2	3	4	5	6
None		R-3	R-3	R-3	R-3	R-3	R-9
Additive Example 1 (75% octane)	25	R-1	R-1	R-1	R-1	R-1	R-1

TEST IV.—EVALUATION OF GASOLINE ADDITIME FOR CARBURETOR DETERGENCY EFFECTIVENESS

Equipment—1954 Model 6 cylinder Plymouth engine. Displacement 217.8 cubic inch.

The metallic throttle body section of the carburetor is replaced by a specially machined clear plastic throttle body. This section contains all of the fuel and air passages including the adjustments as well as the butterfly valve.

During the "dirty-up" sequence of the evaluation, the engine is operated with the full crankcase blowby returned to the carburetor inlet. An air cleaner is also used during this sequence. A base fuel containing no detergent is used. The duration of "dirty-up" time is controlled by the percentage of area where deposits adhere to the throttle body throat through visual observation. When deposits appear to be at the desired level the engine is shut down. The throttle body is removed and rated for deposits. Rating is accomplished by means of inserting a thin cylindrical plastic template into the throttle body throat. The template has 100 equally divided spaces. Coverage by deposit of one space is 1% area. The deposits are classified as black (opaque) and light black (translucent).

For the "clean-up" sequence the blowby is not returned to the carburetor inlet. The throttle body is installed with the deposits intact. The engine is operated for five hours under identical conditions without changing any settings. The same base fuel is used containing the detergent added according to instructions. At the end of five hours the throttle body is again removed for rating of the deposits.

The throttle control is by means of an automatic control which suddenly accelerates from low idle (400 r.p.m.) to high idle (1500 r.p.m.) for an instant (approximately one second) then decelerates to the norm. This action occurs six times in rapid succession at eight minute intervals during the fuel evaluation.

Appropriate instrumentation is provided to insure uniformity of negine conditions. The crankcase blowby is also measured before and after the evaluation to establish that the test severity does not change from one run to the next.

A premium grade base fuel is used for reference runs and the additive is added to this same fuel for evaluation.

The rating method is normally reported by the percentage of the black deposit "clean-up" and the light black deposit "clean-up."

EVALUATION OF GASOLINE ADDITIVE FOR CARBEURETOR DETERGENCY EFFECTIVENESS—STANDARD TWO SEQUENCE TEST

	Black Clean-up, percent	Light Black Clean-up, percent	Total Clean-up, percent
Additive Example, 150 p.p.m. (75% octane)	24	−2	22
	30	−4	26
	4	6	10
Average	19	0	19

The above additive is particularly effective in removing the Black Clean-up which represents the denser black deposits. In this respect it is superior to an equal amount of a commercial additive—acylated oleic acid

$$NH_2CH_2CH_2\overset{H}{N}—CH_2CH_2OH$$

reaction product.

TEST V.—WATER TOLERANCE TEST

Procedure:
(1) Add 80 cc. of inhibited isooctane and 20 cc. of distilled water to a 100 cc. graduate.
(2) Hand shake 200 times.
(3) Allow to settle for five minutes.
(4) Observe interface and emulsion that occur in either phase.

The additive of Example 1 (75% octane), 30 p.p.m., yielded a clear, one phase system. In contrast a commercial additive, 30 p.p.m., formed by acylating

$$NH_2CH_2CH_2\overset{H}{N}—CH_2CH_2OH$$

with oleic acid yielded a two phase system, i.e. the lower layer of which was cloudy.

Solutions of the additive of Example 1 have improved low temperature handling properties (pour point——50° F.) as compared to a commercial additive formed from reacting oleic acid with

$$NH_2CH_2CH_2\overset{H}{N}—CH_2CH_2OH$$

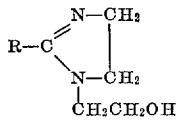
in the same solvent concentration. This affords an important commercial advantage during the winter season.

Salts of the acylated polyamines may be salts of organic or inorganic acids such as mineral acids-HCl, sulfuric acid, phosphoric, etc. and naphthenic acid, acetic acid, dimeric acids, maleic acids, phthalic acids, benzoic acid, etc., i.e. aliphatic, arylic, saturated, unsaturated, monocarboxylic, polycarboxylic, etc. acids and mixtures thereof.

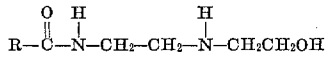
Having thus described my invention what I claim as new and desire to obtain by Letters Patent is:

1. A hydrocarbon motor fuel of the gasoline boiling range characterized by the presence of a composition, in an amount capable of achieving multiple anti-icing, anti-fouling and corrosion inhiibting functions, sad composi-

tion being a mixture of predominantly an imidazoline of the formula



with a small amount of an amide of the formula



wherein R is naphthenyl derived from naphthenic acid having a molecular weight of about 200 to 500, said mixture being prepared by reacting one mole of said naphthenic acid and one mole of aminoethylethanolamine at 170° C.

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U.S. Cl. X.R.

44—71; 252—392