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HYDROCARBON FUEL ADDITIVE AND HYDROCARBON FUEL

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1 Claim. (Cl. 252—428)

This invention relates to an improved additive and catalyst for hydrocarbon fuels and improved hydrocarbon fuel.

An object of the present invention is the provision of an improved catalytic additive which may be added to any hydrocarbon fuel to produce a fuel having improved characteristics whether it is burned in a confined space, such as in a cylinder of an internal combustion engine, or in the open, such as in heating furnaces or boilers. The additive in the fuel results in more complete combustion, and a greater output of power, heat, light, etc. per unit of hydrocarbon than has heretofore been attained. In addition to this, the combustion of the treated fuel results in substantially less than in the past of the noxious and undesirable combustion products, e.g. hydrogen, unburned hydrocarbons, unburned contaminants of hydrocarbons, carbon monoxide, soot, carbon, smoke, etc. per unit of hydrocarbon.

Another object is the provision of an addition having a relatively high flash-point for the sake of safety.

Another object is the provision of a non-corrosive stable and low cost additive for improving hydrocarbon fuels.

A further object is the provision of a simple and non-hazardous process of manufacturing a fuel additive of potentially hazardous ingredients.

This invention is an improvement of that disclosed in United States Patent 2,506,539, dated May 2, 1950. The additive of the patent comprises an aromatic metal-free nitro compound such as picric acid, and an iron salt of an aromatic nitro acid such as ferrous picrate, dissolved in a solvent set out as methylated spirits and benzene. The patented additive has a dangerously low flash-point, is highly corrosive and unstable, and is costly and hazardous to produce. According to United States Federal Regulations, the hazardous additive could not be transported in glass containers, and yet its corrosive nature is such as to preclude storing it in steel containers. The fact that the flash-point of the additive disclosed by the said patent ranges from below 20° F. to around 40° F. precluded the use of the additive in United States ships.

Additives have been developed according to the present invention having a high enough flash point to be used in hydrocarbon fuels in these ships, and it has been found that the resulting fuel is particularly advantageous for use in diesel engines and oil-fired boilers which constitute the principal power sources for commercial marine shipping.

It has been found that the mere substitution of higher flash-point solvents does not successfully produce satisfactory additives. The causes of this phenomenon lie in the highly unstable nature of ferrous picrate, and in the peculiar solubility pattern of picric acid in organic solvents.

Referring to the instability of ferrous picrate, the effective combustion catalysis in the earlier invention depends upon the decomposition of this salt in the combustion chamber. Molecularly dispersed in the fuel, the ferrous picrate, upon decomposition, gives rise to extremely finely dispersed particles of iron which rapidly resonate between native iron and iron oxide as they enter reducing or oxidizing zones of the combustion. If the soluble ferrous picrate is oxidized during preparation or storage of the additive or its mixture with the fuel to any of the several oxides of iron, these precipitate as a coarse amorphous sludge. Even if these sludge particles were carried into the combustion chamber with the fuel flow, the amount of catalytic surface of these gross particles is negligible by comparison with the molecular dispersion described above.

A catalyst or additive according to the present invention comprises an aromatic metal-free nitro compound and an iron salt of an aromatic nitro acid dissolved in a compatible solvent which does not contain oxidizing materials. The product may be further improved after the mixing by the addition of a suitable anti-oxidant or reducing substance. The additive is preferably a mixture of an aromatic nitro acid and a ferrous salt of an aromatic nitro acid, the ratio of salt to acid by weight in the mixture being within the range of from 1 to 10 down to 1 to 100, and a suitable mixture of solvents selected from the group comprising toluene, xylene, isopropyl alcohol, butanol, mineral oil, fusel oil, and aromatic petroleum fractions. In the preferred form of the invention, ferrous picrate and picric acid are used. The ratio of solvents to the catalytic mixture ranges from 30 to 1 up to 27 to 1. The anti-oxidant or reducing substance for protecting the product may be hydroquinone, nordihydroglutaric acid, N-butyl paraminophenol, N,N'-di-secondary butyl-paraphenylenediamine, or any other compound or mixture which meets the requirements of protecting the active ingredients from oxidation for the same or longer period, is stable, is soluble in the solvent mixture, and has no other objectionable qualities as corrosiveness, toxicity, etc.

When from 0.01 to 0.08% by weight of the above mixture is added to a hydrocarbon fuel, the characteristics and quality of that fuel are greatly improved, as are the results attained by the use of such fuel.

A good additive comprises a mixture of 1 part by weight of ferrous picrate and 32 parts by weight of picric acid dissolved in from 930 parts to 980 parts of a non-oxidizing solvent mixture.

The following examples illustrate the extent and advantages of this invention.

EXAMPLE I

A series of embodiments of ferrous picrate-picric acid mixtures (1:32 ratio) were made with various solvent mixtures. Table 1 shows the results. In all cases there were added 1.03 grams of the catalytic mixture to 29.6 milliliters of the solvent mixture. The components of the solvent mixtures are described as percentages by volume of the particular mixture. After each component is shown its flash-point in parentheses. Column 4 is the flash-point of the final mixture. Column 5 shows the stability of the ferrous picrate in the mixture (as the percentage of added ferrous iron remaining in solution after 24 hours); while Column 6 reports the solubility of picric acid in the mixture as percentage dissolved.

Table I

Col. 1 Aromatic Solvent	Col. 2 Aliphatic Solvent	Col. 3 Alcohol	Col. 4 Flash Point, ° F.	Col. 5 Percent of Ferrous Picrate	Col. 6 Percent of Picric Acid
Toluene 80% (40° F.)		Isopropyl 20% (53° F.)	40	100	100
Xylene 80% (88° F.)		do	53	100	100
Xylene 40% (88° F.)	Mineral Oil 40% (200° F.)	do	50	90	100
Xylene 45% (88° F.)	Mineral Oil 45% (200° F.)	Isopropyl 10% (53° F.)	54	90	50
Solvent A 90% (114° F.)[1]		do	60	40	100
Solvent A 80% (114° F.)[1]		Butanol 20% (90° F.)	90	40	100
Solvent B 87.5% (290° F.)[2]		Fusel Oil 12.5% (112° F.)	114	100	100
Solvent B 94%[2]		Butanol 6% (90° F.)	140	100	100

[1] Solvent A is an aromatic solvent of Kauri-Butanol value of 73.
[2] Solvent B is a 92% aromatic base oil distilling over the range from 502° F. to 700° F.

Thus in order to meet the three requirements of solubility, non-oxidizing properties and suitable flash point, it is apparent that the solvent system must contain an alcohol of high flash point, either 20% of an alcoholic component or greater than 60% of an aromatic component, and that the hydrocarbon solvents selected must contain no oxidizing material. Solvent A, for example, oxidizes the ferrous picrate. Line 4 of Table I shows the need for more than 10% alcohol.

EXAMPLE II

1.03 grams of a mixture of ferrous picrate and picric acid were dissolved in 6 ml. of warm denatured alcohol (methylated spirits). This solution was added to 23.6 ml. of benzene. The resultant mixture was poured into a tin-plated 4-ounce rectangular can, the cap screwed on, and the can maintained at 80° F. After three days the can was badly corroded and the product leaked through the seams.

EXAMPLE III

2.06 grams of a mixture of ferrous picrate and picric acid were dissolved in 12 ml. of warm anhydrous isopropyl alcohol and this solution added to 47.2 ml. of toluene. The resultant mixture was divided into two equal portions. The first of these (A) was run into a can as in Example II. The second portion (B) was dried by shaking it with dry silica gel. After drying, this portion was also sealed into a can. After two weeks' storage the first can was corroded and leaking, while the second can showed no evidence of corrosion.

EXAMPLE IV

32 grams of wet picric acid (10% water content) were mixed with 840 ml. of Pacific base oil (Solvent B of Table I). With vigorous stirring, the picric acid was dissolved, and the water dropped out as a heavy separate phase. 120 ml. of fusel oil, containing 8% water, were used to dissolve 1 gram of ferrous picrate. This mixture was stirred into the solution of picric acid in the base oil. Because of the water repellency of the base oil and the hydrocarbon polarity of the fusel oil, the water dissolved in the fusel oil was coacerbated out of the resultant mixture. 11.6 ml. of water were recovered after the mixture was decanted off. A minimal treatment with silica gel completed the dehydration of the mixture, and it was found to be non-corrosive.

EXAMPLE V

In view of the highly hazardous nature of dry ferrous picrate, a novel process of preparation and safe handling of this salt has been devised. According to an example of this process, 3,300 grams of ferrous sulfate (copperas) are dissolved in 4 liters of hot water (70° C.). 1,240 grams of anhydrous sodium carbonate are dissolved in 4 liters of hot water, and the two solutions mixed. The mixture is stirred and the precipitated ferrous carbonate is settled out. The relatively clear aqueous layer is decanted off and the precipitate is washed with four more 4-liter portions of hot water. After washing with water, the precipitate is washed with three 3-liter portions of denatured alcohol. The final volume after the last wash is made up to 12 liters with alcohol and the mixture is treated with 10 grams of hydroquinone. The suspension is warmed on a water bath to 70° C. and 5,400 grams of picric acid are added. The whole is stirred and allowed to react for several hours until the evolution of carbon dioxide is completed. It is then cooled. The alcohol is poured off the crystals of ferrous picrate, and these are taken up in 188 gallons of fusel oil. Meanwhile, 212 kg. of wet picric acid have been dissolved in 1,320 gallons of Pacific base oil. The fusel oil solution of ferrous picrate is pumped into this solution, which is agitated for one hour. Following an over-night settling, the water is drawn off the bottom of the mixing tank, one hundred pounds of coarse silica gel are stirred into the mixture and allowed to settle. The final product is ready for packaging in drums or cans.

EXAMPLE VI

A furnace used to heat the boiler of a large hot water heating system was placed under test. The furnace, using bunker fuel oil, was checked for maximum efficiency, and readings taken regarding its operation and condition. Product B of Example III was then introduced into the fuel system at the rate of one gallon of catalyst solution to 1,600 gallons of fuel, and the furnace again tested and examined at intervals. The following comparative data were obtained. No adjustments were made on the furnace during the test period.

	Before Catalyst (cleaned one week before test)	Catalyst Used		Burner Adjusted
		1 week	2 weeks	
Maximum Stack Temperature	470° F	480° F	510° F	460° F.
Flue Gas Carbon Dioxide	8.1%		9.2%	11.0%.
Carbon Monoxide	NIL		NIL	NIL.
Oxygen	8.9%		8.6%	
Soot removed after 1 week	14 lbs			
Soot removed after 2 weeks			10 lbs	
Soot on heat exchanger	¼ inch		Under ⅛ inch	

Higher stack temperatures normally indicate dirty heat exchanger surfaces. The increase in stack temperature accompanied by cleaner conditions in the heat exchanger areas indicates more heat was obtained from the fuel. In addition, use of the catalyst in the fuel permitted further furnace adjustments after the tests were completed which gave an additional increase in efficiency. The operator stated that the burner started more quickly and more quietly. The burner flame tested brighter and showed much larger.

EXAMPLE VII

A furnace in a boiler used mainly to heat water for industrial processes was placed under test and examined. Product B of Example III was then added at the rate of one gallon to 1,500 gallons of fuel, which was bunker fuel, and the furnace tested and examined periodically, with data and observations as below. No furnace adjustments were made during the test period.

and combustion chamber examined; results below; 150,000 miles on engine at this overhaul.

	Carbon Dioxide, Percent	Oxygen, Percent	Carbon Monoxide p.p.m.	Miles per U.S. Gal. Fuel this period
4. Catalyst Not used 19 days:				
Idle	0.8	18.8	200	----------
Half throttle	1.2	18.8	400	----------
Full load, Uphill	2.4	15.8	300	4.81
5. Catalyst Used 7 Days:				
Idle	0.6	19.1	100	----------
Half throttle	1.0	18.7	100	----------
Full load, Uphill	3.6	14.6	80	----------
6. Catalyst Used 17 days:				
Idle	0.8	19.2	100	----------
Half throttle	1.2	19.0	80	----------
Full load, Uphill	3.2	14.4	80	5.10

Without the catalyst, the exhaust pipe showed a buildup of carbon deposits. With the catalyst these were reduced to the verge of disappearance within the time of this test.

	Before Catalyst	2 days	Catalyst Used 8 days	14 days
Deposits	Heavy soot and gummy deposits at front end of firebox. Heavy white deposits on firebox surfaces and boiler metal.	No soot or gummy matter. White deposits same.	Clear of soot, etc. White deposits clearing.	Clear of soot, etc., nearly clear of white deposits.
Firebox front during burning.	Too hot for hand	Hot	Cool enough for hand	Cool enough for hand.
Ignition by diesel igniter	3-4 seconds and noisy	1 second, quiet	At once, quiet	At once, quiet.
Burner Nozzle	Cleaned every 2-3 hours of carbon.	Small amount of carbon	No cleaning	No cleaning.
Flue	Heavy soot	Half soot loose	No soot	Clean.
Smoke	Light, grey	Light, white	Light, white	Light, white.
Flue gas:				
CO_2%	5.6	5.8	10.0	10.0.
O_2%	1.08	12.4	6.4	6.3.
CO p.p.m.	200	200	10	5.
Exposure meter reading at firebox.	6.7	6.7	7.0	7 Plus.
Frequency of blowing soot from tubes.	Twice/week			No blowing. No soot. Some soft scale, half metal bare.

EXAMPLE VIII

A diesel engine, used as the prime mover in a logging truck operating on nearly constant load and at constant speed, was tested for thirty days without catalyst. Product B of Example III was then introduced into the diesel fuel in the ratio of 1 gallon catalyst mixture of 1,600 gallons of fuel, and the engine operated with periodic tests and observations. Test results showed:

	Carbon Dioxide, Percent	Oxygen, Percent	Carbon Monoxide p.p.m.	Miles per U.S. Gal. Fuel this period
1. Before Catalyst:				
Idle	0.8	19.4	1,500	----------
Half Throttle	2.0	17.8	1,200	----------
Full Load, Uphill	9.2	7.2	1,000	4.67
2. Catalyst Used 18 days:				
Idle	1.8	18.4	250	----------
Half Throttle	2.0	18.0	250	----------
Full Load, Uphill	6.0	12.6	250	4.13
3. Catalyst Used 27 days:				
Idle	1.4	18.6	200	----------
Half Throttle	2.4	17.8	150	----------
Full Load, Uphill	3.4	15.8	100	4.75

At this point one head removed, pistons removed, injectors

The exhaust gave off substantial dark smoke and unpleasant fumes without the catalyst in the fuel. With the catalyst the exhaust smoke became light and the fumes mild.

At the time of engine examination noted above, the injectors were clean, piston domes bright on exhaust port side and a small amount of carbon on intake side, ring grooves clean, valves showed slight crescent-shaped deposits of hard carbon which were clearly the small residue from larger pre-existing coatings.

The improved combustion resulting from use of the catalyst was noted just before an engine overhaul and just after an engine overhaul, as evidenced in each case by the reduced carbon monoxide content of the exhaust gases, by the increased mileage per unit of fuel, by the amount and appearance of the exhaust smoke and by the removal of carbon deposits in the exhaust pipes which were laid there while no catalyst was in use. These improvements are evidenced under all work loads and engine speeds.

EXAMPLE IX

A gasoline engine, used as the prime mover in a 1957 Ford Fairlane 500 (8 cylinder engine) was given exhaust gas analysis without use of the catalyst in the fuel. The catalyst, Product B of Example III was added to the fuel in the ratio of 1 gallon of catalyst mixture to 1,600 gallons of fuel, and the exhaust gases were again analyzed after about 2,000 miles of operation using fuel containing

the catalyst. No adjustments were made to the engine during this period. A further partial analysis was made after 22 weeks of operation with the catalyst in the fuel, again with no adjustment.

The test results are summarized below.

	Carbon Dioxide, Percent	Oxygen, Percent	Carbon Monoxide, Percent
Before Catalyst:			
Idle	10.9	5.1	3.0
Accelerating	12.6	12.8	1.6
Decelerating	8.9	15.2	2.1
Half Throttle	13.4	1.6	5.2
With Catalyst 2,000 Miles:			
Idle	9.8	4.2	0.15
Accelerating	9.8	3.2	0.2
Decelerating	7.0	7.0	0.1
Half Throttle	11.0	3.0	0.25
With Catalyst 22 weeks: Idle	11.6	3.4	0.7

The considerable reduction of carbon monoxide under all engine speeds while using the calalyst mixture is very marked, and continues to show in large degree even after a period when the engine could be expected to have drifted off the optimum adjustments found at the start of the tests.

EXAMPLE X

A wick lantern burning kerosene was cleaned thoroughly, and the glass globe graduated to permit measurement of flame height. With a new wick, carefully trimmed, and a measured volume of clean kerosene fuel, the lamp was lighted and permitted to burn for one hour. A light meter was located a fixed distance from the lamp, all other light sources excluded, and the light intensity measured in foot-candles. Product B of Example III was then introduced into the fuel, in the ratio of one gallon of catalyst mixture to 1,500 gallons of fuel. The flame height was maintained at the same height, and with no other change, other light sources excluded and the light meter read again at intervals of one-quarter hour for one hour.

With a constant flame height above the metal wick-holder edge of 28 millimeters, at a distance of six inches from the lamp edge, the light meter read 11-foot candles without catalyst. Under the same conditions, but using catalyst, the meter read 13½ foot-candles during the test period. This indicates an increase in flame brightness of

22% under these conditions of operation and measurement.

EXAMPLE XI

The same wick lantern used in Example X was operated using domestic furnace fuel, heavier and much less highly refined than kerosene, and much cheaper. Without the catalyst, the flame was low and very smoky. Addition of the catalyst mixture in the ratio of one gallon of catalyst mixture to 1,500 gallons of fuel gave burning conditions which permitted much higher flame height with no increase in smoking, and consequently much improved light production. Flame height increase was of the order of 100% over the untreated fuel.

What we claim as our invention is:

An improved process for the manufacture of a liquid hydrocarbon fuel catalyst comprising the steps of dissolving one part of copperas in water, adding a solution of 0.35 part of sodium carbonate in water, mixing, washing the precipitated solids in water and in alcohol, treating the resultant alcoholic suspenion with hydroquinone (0.1 part) and 1.69 parts of wet picric acid, crystallizing the reaction product, dissolving it in 179 parts of fusel oil, mixing this solution with 1,280 parts of a non-oxidizing hydrocarbon solvent whose flash point exceeds 80° F. and whose aromatic content exceeds 70% and in which 60.5 parts of wet picric acid have been dissolved, drawing off the water which drops out, and treating the mixture with 13 parts of silica gel.

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