

UNITED STATES PATENT OFFICE

2,474,183

ROCKET PROPULSION BY REACTING ALKYL-SUBSTITUTED MONONUCLEAR AROMATIC AMINES AND NITRIC ACID

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No Drawing. Application August 9, 1943,
Serial No. 497,999

4 Claims. (Cl. 60—35.6)

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This invention relates to a reaction propulsion method, and more particularly to a method for generating power by ejecting a stream of combustion products at high velocities. Rocket motors of the type used for propelling airplanes are the most important field in which this method of propulsion is employed at the present time, although the invention in its broader aspects is not limited to this field.

Modern rocket motors of the type now in use to give an accelerated take-off or accelerated speeds in airplanes consist of a suitable housing provided with pairs of jets adapted to inject a fuel and an oxidant, respectively. The combustion of these two materials creates a mass of hot, burning gases which are ejected at high velocity through a suitable orifice, the reaction from this ejection providing the propulsive force. Such motors are of great potential value in assisting the take-off of seaplanes, since additional power is needed to overcome the skin friction of the water against the hulls of such planes. They are also of great value in assisting the take-off of heavily loaded land planes, since it is well-known that only a fraction of the power in a modern airplane is used in flight, as compared with that necessary to lift the plane from the ground under ordinary take-off conditions.

In order to assist the take-off of airplanes it is of utmost importance to have a rocket fuel which will ignite immediately and with certainty, as the plane would be almost certain to crash if the rocket motor failed to fire. For this reason a self-igniting fuel mixture is greatly preferred to one which must be ignited by a spark or by compression, as in ordinary internal combustion engines. It is a principal object of the present invention to provide a reaction propulsion method which is both instantaneous in action and certain in character, so that power failure is reduced to a minimum.

I have found that the alkyl-substituted mononuclear aromatic amines containing one or more alkyl substituents will ignite spontaneously upon admixture with strong nitric acid to produce a stream of combustion products capable of developing high velocities in a rocket motor. I have also discovered that this class of compounds possesses a number of other extremely important properties which cause the members thereof to be well-suited for use in propulsive fuels. The compounds of this class have very low freezing points and will therefore remain fluid at the low temperatures encountered in severe winter weather and during high altitude flights. More-

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over they are soluble in low-boiling hydrocarbon fuels such as gasoline and light fuel oil and will form solutions therein that do not freeze or thicken at low temperatures. Solutions of this type containing at least 20% by volume of alkyl-substituted mononuclear aromatic amines will ignite spontaneously upon admixture with strong nitric acid, and are therefore suitable for use as a rocket fuel instead of the pure aromatic compounds themselves.

The class of alkyl-substituted mononuclear aromatic amines includes those compounds containing one or more alkyl substituents on the amino nitrogen and those containing one or more alkyl substituents on the aromatic nucleus as well as those in which both an amino nitrogen and the aryl nucleus are substituted by aliphatic radicals. Typical compounds possessing the advantages enumerated above are the lower N-aliphatic mononuclear aromatic amines such as mono- and dimethylaniline and mono- and diethylaniline. These compounds may be employed in the pure state, but the crude mixtures obtained by their ordinary methods of preparation may be used with equally good results. Thus, for example, crude monoethylaniline as prepared by the autoclave process has the following composition:

	Per cent
30 N-monoethylaniline	55
Aniline	30-35
Residue	10-15

The residue is a high-boiling mixture containing N,N-diethylaniline, p-amino-ethylbenzene and mixed aminodiethylbenzenes.

35 Crude monoethylaniline prepared by passing the mixed vapors of aniline and ethanol over a bauxite catalyst at about 300-350° C. has the composition

	Per cent
40 N-monoethylaniline	60
Aniline	30
Residue	10

45 The residue consists principally of N,N-diethylaniline, but contains small quantities of nuclear-substituted anilines.

Crude monomethylaniline prepared by the autoclave process contains about 40% N-monomethylaniline, about 20% N,N-dimethylaniline and about 40% aniline. All three of these mixtures are soluble in gasoline and light fuel oils and will ignite and generate power upon admixture with the proper quantities of strong nitric acid.

Another preferred class of igniting and com-

bustion agents are the lower nuclear-substituted alkyl anilines such as the toluidines and the mixed xylidines obtained by the reduction of nitrated toluene and xylene mixtures. Other typical compounds are the N-alkyl xylidines and toluidines such as N-mono- and dimethyl meta- and para-toluidines and alkyl-substituted phenylene diamines, such as N,N'-dipropyl, dibutyl and diamyl para-phenylene diamines. These compounds may be used as such, or in admixture with each other, or in admixture with other igniting and combustion agents such as aniline, gasoline, Diesel fuel oil, #2 fuel oil, benzene, or mixtures thereof.

II. order to obtain rapid and positive spontaneous ignition of the aromatic amines it is necessary to use strong nitric acid, and this term is intended to designate nitric acid containing not more than about 10% of water. As is illustrated in detail in Example 5, bleached nitric acid having a strength of about 95% HNO_3 is about the weakest acid that will give reliable results, but the quenching effect of larger amounts of water can be compensated to a limited extent by the presence of NO_2 . Accordingly, nitric acid of about 96-99.5% HNO_3 content or fuming nitric acid containing not more than 8-10% of water are the proper types of acid to use in conjunction with the igniting agents of the present invention, and these are the materials designated by the term "strong nitric acid."

From the foregoing it will be seen that the process of the present invention consists in the generation of rocket propulsion by impinging a jet of strong nitric acid upon a similar jet of a fuel containing an aliphatic-substituted mononuclear aromatic amine, or by commingling the oxidizing agent and fuel by any other suitable means. The ratio of strong nitric acid to fuel will depend upon the type of fuel and upon the strength of the acid used, but in general the ratios should be such as to provide sufficient nitric acid to oxidize at least 70-80% of the fuel. The alkaryl amine may be used as a fuel or it may be dissolved in a hydrocarbon fuel to function as an igniting agent therefor, with or without the addition of aniline or other additional combustion agents. In this case the amount of alkaryl amine may vary from 10% to 50% by volume of the total quantity of fuel, the higher concentrations being used when the rocket motor is first fired and a somewhat leaner mixture being employed during continued operation. Alternatively, the motor may be started by the use of a straight alkaryl amine or mixture thereof with aniline or other aromatic amines as the sole igniting agent and carburant and then operated with a straight hydrocarbon fuel or with a similar fuel containing a relatively small quantity of alkaryl amine as an igniting agent.

The rapidity of ignition and flame formation of the aliphatic-substituted mononuclear aromatic amines can be demonstrated by a cup test in which a strong nitric acid is poured into a dish containing the amine or solution thereof under test. A large number of such tests have shown that the results obtained thereby are reproducible and will give a reliable indication of the operation of similar mixtures in a rocket motor. Accordingly, cup tests of mixtures illustrative of the present invention are described in the following examples, it being understood that similar results are obtained when the same ingredients are supplied to the jets of a rocket motor as described above.

The invention will be illustrated in greater detail by the following specific examples. It should be understood, however, that although these examples may describe some of the more specific features of the invention, they are given primarily for purposes of illustration and the invention in its broader aspects is not limited thereto.

Example 1

The efficacy of N-ethyl aniline, both alone and in admixture with low-boiling hydrocarbon fuels, was tested by a cup test in which suitable quantities of strong nitric acid were poured into a 4-inch porcelain evaporating dish containing the igniting agent.

(a) 15 cc. of red fuming nitric acid (sp. gr. 1.60) were poured into 10 cc. of the N-ethyl aniline. There was an immediate bright flash followed by violent combustion with evolution of heavy white fumes.

(b) 10 cc. of the same acid were poured into a solution of 3 cc. of N-ethyl aniline in 7 cc. of #2 fuel oil. An immediate bright flash was followed by rapid burning.

(c) 10 cc. of red nitric acid analyzing 81.4% HNO_3 , 4.1% H_2O and 15.5% dissolved NO_2 were poured into 7 cc. of the monoethyl aniline. An audible flash resulted, followed by a hissing flame.

(d) 10 cc. of 99.5% nitric acid were poured into 7 cc. of the fuel oil solution described in (b). There was a large bright flame after about 0.25 second or less, and the mixture burned vigorously.

Example 2

15 cc. of 99.5% nitric acid were poured into 10 cc. of N-methyl aniline as described in Example 1. There was an instant bright, audible flame which burned with evolution of brown fumes. The same result was obtained with N-isopropyl aniline and with N,N-dimethylaniline.

Example 3

15 cc. of 99.5% nitric acid were poured into 10 cc. of o-toluidine. The mixture ignited immediately and burned with a large, bright flame. The same result was obtained upon substituting 2-cymidine or p-tertiary amyl aniline. A solution containing 30% by volume of p-tertiary-amyl aniline in 70% of #2 fuel oil ignited in less than 1 second with an audible flash and burned with a smoky yellow flame. 10 cc. of 3,5-dimethylaniline ignited immediately upon addition of 15 cc. of 99.5% nitric acid, and the same result was obtained with a technical mixture of xylidines obtained by the reduction of a nitro-xylene mixture.

Example 4

Aniline itself is a good igniting and combustion agent for propulsive fuel mixtures, but its freezing point (-6°C.) is too high for use. I have discovered, however, that the addition to aniline of aliphatic-substituted mononuclear aromatic amines such as 2-cymidine, mixed xylidines, N-methyl aniline, N-ethyl aniline and the like will produce combustion agents of much lower freezing points having as good or better igniting properties than aniline itself.

Another very serious disadvantage of aniline is its relatively low solubility in hydrocarbon fuels such as diesel fuel, gasoline and fuel oil. Thus, for example, a mixture of 10 parts by volume of aniline with 90 parts by volume of light fuel oil forms two immiscible layers. A 10% aniline-90% by volume gasoline solution separates into two

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layers at 20° C.; a 15%–85% at 25° C. and a 20%–80% at 30° C. The alkyl-substituted anilines, on the other hand, are very soluble in hydrocarbon fuels and do not separate out at low temperatures. Thus, for example, the solubilities of representative compounds of this series in gasoline are as follows:

Percent by volume	Gasoline	Effect on Cooling
N-Methyl Aniline:		
33.3	66.7	Turbid at -35° C., Freezes at -40° C.
50	50	Turbid at -35° C., Two layers at -39° C.
25	75	Turbid at -35° C., Does not freeze at -48° C.
10	90	Turbid at -50° C., but does not freeze.
N-Ethyl Aniline:		
50	50	Does not separate at -50° C.
33.3	66.7	Do.
25	75	Do.
10	90	Do.
Mixed Xylidines:		
20	60	Does not freeze at -48° C.

The freezing points of representative mixtures containing aniline are as follows:

Percent by volume Aniline	Other Component	Freezing Point, °C.	Remarks
95	5 Mixed xylidines	-9	
90	10 Mixed xylidines	-11.5	
85	15 Mixed xylidines	-13	
70	30 Mixed xylidines	-28	
60	40 Mixed xylidines	-40.5	
50	50 Mixed xylidines	<-48	
85	15 2-cymidine	-13	
65	35 2-cymidine	-30	
50	50 2-cymidine	-42	
80	20 N-ethyl aniline	-14.5 to -18.5	No definite F. P.
60	40 N-ethyl aniline	-25 to -28	Do.
80	20 N-methyl aniline	-13.5 to -14	Do.
60	40 N-methyl aniline	-23	Sharp F. P.
90	10	-10.5	Do.
85	15	-13.2	Do.
80	20 Equal Volumes of N-Ethyl Aniline, Mixed Xylidines and 2-Cymidine	-15	Do.
70	30	-20	Do.
50	50	-36	Do.

It is evident from these figures that the alkyl-substituted anilines may be used as such or in admixture with aniline as igniting and combustion agents in gasoline, diesel fuel, light fuel oils, benzene and other low-boiling hydrocarbons even in severe winter weather and at the low temperatures encountered in high-altitude flights. Typical results are shown by the following tests, which were made by pouring 2 parts by volume of 97% HNO₃ into 1 part of the composition under test, as described in Example 1, the parts being by volume:

(a) Aniline ignited vigorously with copious flame formation

(b) Aniline 60%, mixed xylidines 40%. More vigorous than aniline.

(c) Aniline 50%, N,N-dimethylaniline 25%, nitrobenzene 25%. Results equal to aniline.

(d) Aniline 50%, mixed xylidines 25%, nitrobenzene 25%. Better than (b).

(e) Gasoline 80%, benzene 10%, aniline 5%, nitrobenzene 5%. Most vigorous of all.

Example 5

Strong nitric acid should be used to obtain reliable and rapid ignition of the mononuclear aromatic amines and their mixtures with low-boiling hydrocarbons. Bleached nitric acid having a strength of 94–95% HNO₃ is about the weakest

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acid that will give reliable results. However, NO₂ and N₂O₄ may also be used, and the quenching effect of water in acids weaker than 95% may be compensated to a limited extent by the presence of NO₂. This was shown by testing the following compositions:

No.	HNO ₃ , percent	H ₂ O, percent	NO ₂ , percent
1	99.5		
2	98	2	
3	96	4	
4	95	4.65	
5	93	3.3	3.6
6	89.6	3.5	7.0
7	88.2	5.9	.60
8	77.6	7.8	14.4
9	74.6	12.7	13.6

¹ Commercial bleached 95—nitric acid, plant production.

These acids were tested in the cup test against a crude vapor-phase aniline having the composition previously described and also against mixtures of this material with hydrocarbon fuels. In all cases 10 cc. of the acid were poured into

7 cc. of the igniting agent The results are shown in the following table:

Acid No.	Igniting Agent	Time lag
1	Crude N-ethyl aniline	Instantaneous
2	do	Do.
3	do	Do.
4	do	0.5 sec.
55	50% MEA, 50% #2 Fuel Oil	Instantaneous.
2	do	Do.
4	40% MEA, 60% #2 Fuel	1.2 Sec.
4	30% MEA, 70% #2 Fuel	2.0 Sec.
4	40% MEA, 60% #1 Octane gasoline	0.5 Sec.
5	50% MEA, 50% #2 Fuel Oil	0.25 Sec.
6	do	0.75 Sec.
7	do	1 Sec.
60	do	1 Sec.
8	do	1 Sec.
9	do	No flame.

Example 6

65 Nuclear substituted anilines containing a number of alkyl radicals are very effective igniting agents. Thus, for example, 7 cc. of a mixture of pseudocumidine (2,4,5-trimethylaniline) and mesidine (2,4,6-trimethylaniline) ignited upon

70 addition of 10 cc. of ordinary 95% nitric acid with a time lag of only 0.4 seconds and burned with a bright flame.

Example 7

75 A pair of rocket motor jets having internal

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diameters of $\frac{3}{4}$ " and set at an angle of 60° were fed with 99.5% nitric acid and with N-monoethyl-aniline, respectively, under pressures of 7 lbs. per square inch. The mixture ignited immediately at the jets and burned with a big flame that was propelled violently against a metal shield five feet distant.

What I claim is:

1. A rocket propulsion method which comprises generating an ignited propulsive charge by combining with strong nitric acid a volatile hydrocarbon having dissolved therein 10-50% of an alkyl-substituted mononuclear aromatic amine and ejecting the burning charge at high velocity.
2. A rocket propulsion method which comprises generating an ignited propulsive charge by combining with strong nitric acid a volatile hydrocarbon having dissolved therein 10-50% of an N-aliphatic mononuclear aromatic amine and ejecting the burning charge at high velocity.
3. A rocket propulsion method which comprises generating an ignited propulsive charge by combining with strong nitric acid a volatile hydrocarbon having dissolved therein 10-50% of an N-alkyl aniline and ejecting the burning charge at high velocity.
4. A rocket propulsion method which comprises generating an ignited propulsive charge by com-

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mingling with strong nitric acid a volatile hydrocarbon having dissolved therein about 10-50% of a mixture of aniline and N-ethylaniline and ejecting the burning charge at high velocity.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
914,624	Winand	Mar. 9, 1909
1,571,862	Midgley	Feb. 2, 1926
2,080,928	Rogers et al.	May 18, 1937
2,217,649	Goddard	Oct. 8, 1940
2,230,844	Miller	Feb. 4, 1941
2,398,201	Young et al.	Apr. 9, 1946

FOREIGN PATENTS

Number	Country	Date
17,696	Great Britain	Dec. 17, 1915
863,928	France	Jan. 6, 1941
157,231	Switzerland	Dec. 1, 1932

OTHER REFERENCES

Journal of the Chemical Society, London, 1942, pages 584-585.