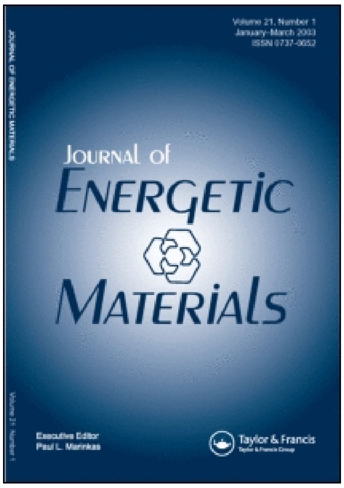

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S. A. Barton[a]; J. L. Halpin[a]; P. Tomar[a]
[a] Defence Research Establishment Valcartier, Courcelette, Quebec, Canada

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SELF-IGNITION LIMITS OF ALUMINUM ALKYLS IN HYDROCARBON SOLVENTS

S.A. Barton, J.L. Halpin and P. Tomar

Defence Research Establishment Valcartier
P.O. Box 8800, Courcelette, Quebec G0A 1R0, Canada

ABSTRACT

The self-ignition (SI) limit is the lowest concentration of a pyrophoric compound in solution with a hydrocarbon solvent that will ignite spontaneously when brought into contact with air. A simple quantitative method for measuring the SI limits of pyrophoric compounds is described. The SI limits are given for the aluminum alkyls triethylaluminum (TEA), diethylaluminum hydride (DEAH) and trimethylaluminum (TMA) in a series of *n*-hydrocarbons at 20°C. The results indicate pyrophoric reactivity increases in the order TEA, DEAH, TMA. The hexane SI limits of TMA/TEA mixtures are also given, and are shown to vary nonlinearly with pyrophoric composition.

INTRODUCTION

Aluminum alkyl compounds are termed pyrophoric because they ignite rapidly on contact with ambient air. They also react violently with many compounds, notably water. At room temperature and pressure, aluminum alkyls are usually colourless, free-flowing liquids.

The miscibility of aluminum alkyls in all proportions with saturated aliphatic and aromatic hydrocarbons such as hexane and toluene is an important factor in their safe handling and storage. Dilution with a compatible hydrocarbon solvent reduces the pyrophoric reactivity.

Two parameters that can be used to characterize the reactivity of a pyrophoric liquid are the self-ignition (SI) limit and the pyrophoric limit.

The SI limit of a metal alkyl has been defined [1] as the minimum concentration of the compound in hydrocarbon solution that will ignite spontaneously in air. This limit should not be confused with the pyrophoric limit which is generally defined as the minimum concentration of a metal alkyl in solution which, when brought into contact with a cellulosic material (eg. sawdust, paper) will cause the cellulosic material to spontaneously ignite or char. The non-pyrophoric limit (NPL) test devised by Mudry et al. [1] measures the highest metal alkyl concentration in solution that will *not* cause filter paper to char. However, their results show little difference between the NPL of TMA (11 wt%) and that of TEA (12 wt%) with hexane as the solvent. As a method for comparing the reactivity of aluminum alkyls, the

NPL test is therefore unsatisfactory.

While the pyrophoricity of aluminum alkyls has been studied, we have found no published data on their SI limits. This study describes a simple test method for defining and determining the SI limits of metal alkyl solutions. The following three aluminum alkyls were tested in a series of n-hydrocarbons: trimethylaluminum (TMA), triethylaluminum (TEA) and diethylaluminum hydride (DEAH). We also studied mixtures of TMA and TEA because they can provide low freezing point liquids of high reactivity, e.g. a 50:50 (by volume) mixture freezes near -70°C.

THE SELF-IGNITION LIMIT TEST

The SI limit test measures the point at which dilution of a pyrophoric liquid by a hydrocarbon solvent prevents spontaneous ignition. The SI limit is a measure of the pyrophoric reactivity of a compound.

We define the ***hydrocarbon number*** H_n to be the minimum volume percent (vol. %) of hydrocarbon required to prevent ignition. The subscript n refers to the number of carbon atoms in the n-hydrocarbon chain; e.g. $n = 6$ for n-hexane. The hydrocarbon number is related to the self-ignition limit S_n (g/mL) by:

$$S_n = \frac{(100 - H_n)\rho}{100} \tag{1}$$

where ρ is the density of the pyrophoric liquid in g/mL. The quantities

S_n, H_n and ρ are temperature dependent. The work reported here was performed at 20°C.

Test Equipment

During a series of preliminary tests in which the sample was ejected manually from a syringe, it was found that the ejection force had a major effect on the results. If the sample was introduced slowly into the atmosphere, the amount of dust and smoke increased and the probability of a flame appearing decreased. When the fuel was forcefully ejected, a flame was more likely to appear.

To ensure consistent results we used the sample ejection apparatus shown in Fig. 1. It consists of a syringe holder, a slider-mass assembly and a latching mechanism mounted on a stand. The slider unit has a mass of 770 g to which a weight of 1200 g is added. This total mass is great enough to ensure that the ejection force does not influence the appearance or absence of a flame. During each test, the arm of the slider-mass assembly is raised and latched by the core of the solenoid. The syringe is clamped into the holder, and the holder height is adjusted so that the syringe plunger is in contact with the slider unit. The solenoid switch is depressed to eject the sample.

Preparation of Test Solutions

The mixtures of pyrophoric liquid and hydrocarbon were made inside a standard glove box under a blanket of dry nitrogen. The oxygen level in the box was continuously monitored using a portable gas analyzer (Neutronics model PCO 961) and a dessicant was used to minimize the moisture content. Following standard handling and safety procedures [2], each sample of pure pyrophoric liquid was transferred to a 10 mL serum bottle and the required volume of hydrocarbon was added to make the total mixture volume 10 mL. Each serum bottle was closed with a rubber stopper, covered with an aluminum seal, and shaken to ensure complete mixing. All mixture compositions were recorded in terms of volume percent and were considered to be accurate to ±1 vol. %. The mixtures of TMA/TEA were prepared in the same manner. Pure TEA and TMA were used as supplied by Texas Alkyls Inc. DEAH was used as a 75% (by weight) mixture with 25% TEA, again supplied by Texas Alkyls Inc. The hydrocarbons, which were high-purity research grade (at least 99.99% pure), were dried over molecular sieve before use.

Experimental Procedure

Each test was performed using a new 1 mL syringe (Becton-Dickenson # 5602) fitted with a 20 gauge, one-inch long hypodermic needle, which had been previously dried at 110°C and flushed with dry nitrogen. A 0.2 mL sample of pyrophoric mixture was withdrawn from its sealed bottle, the syringe was then clamped into its holder (Fig. 1) and the fuel was ejected by depression of the solenoid switch. Ignition was indicated by a visible flame and each result was recorded as either positive (ignition) or negative (non-ignition). The jet of liquid ejected would normally strike the baseplate before ignition occured. The baseplate was therefore covered with a new sheet of aluminum foil before each test to ensure that the result was not affected by the surface property.

For every hydrocarbon solution, tests were repeated at least ten times. The vol. % of hydrocarbon in a mixture that produced a flame in less than or equal to 10% of the tests was taken to be the hydrocarbon number (H_n) for that pyrophoric composition.

The results obtained were weakly dependent on the volume of solution used; e.g. the hexane number obtained for TEA was 39 using 0.1 mL and 41 using 0.2 mL of solution. Provided that a sufficiently large volume (0.2 mL) of solution is ejected with a great enough force onto a standard surface (clean, dry aluminum foil), the results are not apparatus dependent.

RESULTS AND DISCUSSION

For the results presented in this section, we neglect the effects of variation in the atmospheric pressure and humidity. Therefore the estimated error in the hydrocarbon numbers, ±1, is obtained only from the maximum absolute error involved in our volume measurements.

Relative Pyrophoricity of TEA, DEAH and TMA

In order to compare the pyrophoric reactivity of the three pure aluminum alkyls, we give in Table 1 the hydrocarbon numbers (H_6) and SI limits (S_6) for TEA, DEAH and TMA with n-hexane as the solvent.

TABLE 1
Hexane Numbers (vol. %) and SI Limits (g/mL) of Pure Aluminum Alkyls at 20°C

	H_6	S_6
TEA	41	0.50
DEAH	49	0.41
TMA	57	0.33

The SI limits were calculated from the H_6 values using Eq. 1 and the densities [3] of the alkyls given in Table 2.

TABLE 2
Physical Properties of DEAH, TEA and TMA at 20°C [3]

	DEAH	TEA	TMA
molecular formula	$Al(C_2H_5)_2H$	$Al(C_2H_5)_3$	$Al(CH_3)_3$
molecular weight	86.11	114.17	72.09
density (g/mL)	0.813	0.840	0.765
vap. press. (mm Hg)	0.013	0.016	8.7

The H_6 value for pure DEAH given in Table 1 is derived from that obtained for our 75:25 DEAH:TEA mixture (which had a hexane number of 47), assuming a linear relationship between composition and H_6. That is, if we let X be the pure DEAH hexane number, we assume:

$$(0.75 \mathrm{x} X) + (0.25 \mathrm{x} 41) = 47 \qquad (2)$$

Although we have found that over the whole range of TEA:TMA mixtures (see below) there is in fact a nonlinear relationship between hexane number and pyrophoric mixture composition, over the range 75-100% the relation is essentially linear. We are therefore confident that the value derived for pure DEAH is accurate.

The results given in Table 1 indicate pyrophoricity increasing in the order TEA, DEAH, TMA. This order of reactivity follows the order of increasing weight % of aluminum in the compounds, which is 24, 31 and 38 for TEA, DEAH and TMA respectively.

SI Limits of TEA and TMA in *n*-Hydrocarbon Solvents

Table 3 gives the values we obtained for H_n and the SI limits of TEA and TMA in *n*-hydrocarbons ranging from hexane to dodecane.

TABLE 3
Hydrocarbon Numbers (vol. %) and SI Limits (g/mL) of TEA and TMA at 20°C

Hydrocarbon	*n*	TEA		TMA	
		H_n	S_n	H_n	S_n
Hexane	6	41.0	0.50	57.0	0.33
Heptane	7	47.0	0.45	64.0	0.28
Octane	8	47.5	0.44	69.0	0.24
Nonane	9	48.0	0.44	71.0	0.22
Decane	10	47.0	0.45	72.0	0.21
Dodecane	12	45.0	0.46	74.0	0.20

Figure 2 shows the H_n values graphically. The upper curve shows that for TMA the volume of solvent required to prevent self-ignition increases as the number of carbons in the *n*-hydrocarbon chain increases. TEA exhibits a different behaviour, as seen in the lower curve of Fig. 2. After an initial sharp increase from hexane to heptane, H_n increases only slightly to nonane, and then decreases out to dodecane. The curves in Fig. 2 can be used to rapidly determine if a solution of TEA or TMA in a hydrocarbon will ignite spontaneously. Any solution with a vol. % hydrocarbon above the curve for the given pyrophore will not ignite spontaneously in air at 20°C, whereas those solutions below the curve will.

By considering the mole fractions of pyrophoric liquid in each hydrocarbon solvent at the SI limit, the behaviour of TEA and TMA can be shown to be similar. These mole fractions, calculated using the densities and molecular weights given in Tables 2 and 4, are shown graphically in Fig. 3. For both TEA and TMA, the mole fraction at the SI limit is observed to decrease from the hexane value and then to increase eventually for longer chain hydrocarbons. It is interesting to note that for both TEA and TMA, the mole fraction of pyrophore is not constant at the SI limits for the series of hydrocarbons. This means either that the vapour pressure of pyrophore above the solutions is not constant at the SI limits, or that the solutions are nonideal, i.e. they do not obey Raoult's law.

TABLE 4
Physical Properties of n-Hydrocarbons at 20°C [4]

Name	Formula	M. Wt.	Vap. Press. (mm Hg)	Density (g/mL)
Hexane	C_6H_{14}	86.18	107.7	0.660
Heptane	C_7H_{16}	100.21	33.0	0.684
Octane	C_8H_{18}	114.23	10.5	0.703
Nonane	C_9H_{20}	128.26	3.5	0.718
Decane	$C_{10}H_{22}$	142.29	1.3	0.730
Dodecane	$C_{12}H_{26}$	170.34	0.2	0.749

SI Limits of TMA/TEA Mixtures in n-Hexane

The hexane numbers (H_6) and SI limits for a series of TMA/TEA mixtures are found in Table 5 and are illustrated graphically in Fig. 4. The hexane number increases rapidly and nonlinearly with volume percent of TMA in the first portion of the graph, but the increase is roughly linear in the region 40-100% TMA. A straight line joining the points at 40 and 100% is drawn in Fig. 4.

The curve in Fig. 4 can be used to determine if a solution of a TMA/TEA mixture in hexane will ignite spontaneously. Any solution with a vol. % hexane significantly above the curve will not normally ignite spontaneously in air at 20°C, whereas those solutions below the curve will.

TABLE 5
Hexane Numbers (vol. %) and SI limits (g/mL)
of TMA/TEA mixtures at 20°C

Vol. % TMA	H_6	S_6
0	41	0.50
10	47	0.44
20	49	0.42
40	52	0.39
60	54	0.37
80	55	0.35
100	57	0.33

The SI limits given in Table 5 were calculated from the H_6 values using Eq. 1, and assuming each pyrophoric mixture density to be a weighted sum of the individual pure pyrophoric liquid densities.

CONCLUSIONS

A simple laboratory test method for measuring the SI limits of pyrophoric liquids in hydrocarbon solvents has been established, and a useful parameter related to the SI limit, the hydrocarbon number, has been defined.

The measured hydrocarbon numbers and SI limits of TEA, DEAH and TMA in hexane indicate pyrophoric reactivity increasing in that order. The behaviour of the hydrocarbon numbers for TEA and TMA in a series of *n*-hydrocarbons indicates that the solutions may behave nonideally, and for TEA/TMA mixtures, the pyrophoric reactivity initially increases rapidly and nonlinearly when TMA is added to TEA.

Our results give the quantity of hydrocarbon solvent required to prevent the spontaneous ignition of the pyrophoric liquids TEA, DEAH and TMA at 20°C. This has important implications in their handling, transportation, storage and use in combustion applications. Our data should be used with caution, however. To effectively neutralize the pyrophoricity of an aluminum alkyl, the volume percent of hydrocarbon solvent should certainly exceed the values given in Tables 3 and 5, particularly when storing or transporting large volumes of liquid. Although we have not measured the effect of temperature, we expect that pyrophoricity will increase rapidly as the temperature is raised.

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REFERENCES

1. D.B. Malpass, W.L. Mudry, D.C. Burleson, and S.C. Watson, *J. Fire and Flammability*, **6**: 478–487 (1975).
2. J.E. Knap, R.E. Leech, A.J. Reid, and W.S. Tamplin, *Ind. Eng. Chem.*, **49**: 874–879 (1957).
3. E.J. Mezey, R.W. Coutant, E.R. Zamjec, and P.S. Mohler, *Physical Properties and Combustion Kinetics of TMA/TEA/DEAH mixtures. Phase I: Key Physical Property Measurements*, Battelle Columbus Laboratories, Columbus, Ohio, AEDC-TR-82-18, March 1983.
4. CRC Handbook of Chemistry and Physics, 54th Edition, Ed. R.C. Weast, CRC Press, Cleveland, Ohio, 1973.

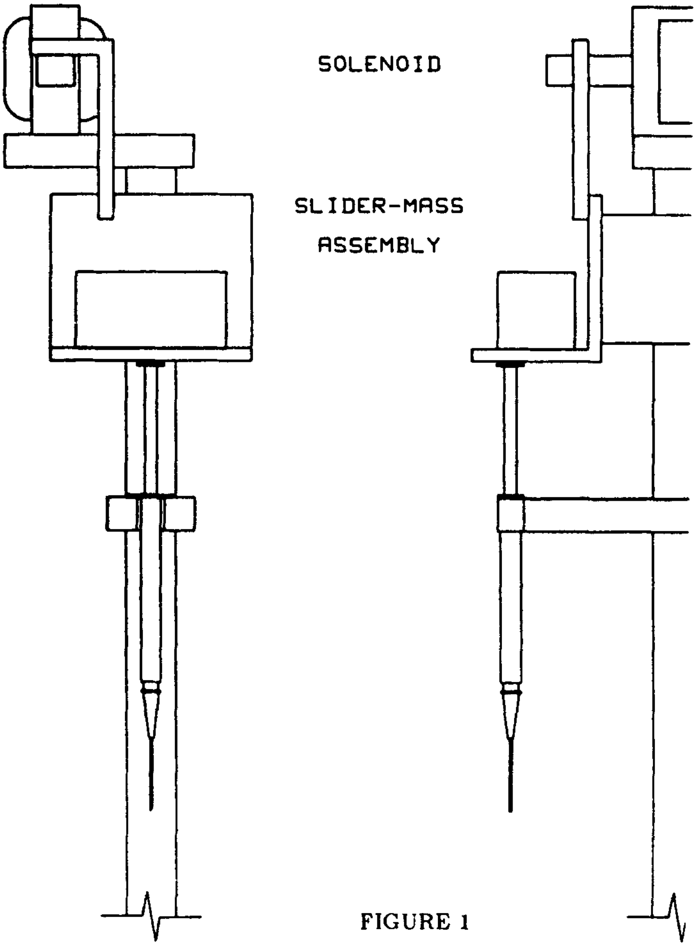

FIGURE 1
Apparatus for controlled sample ejection.

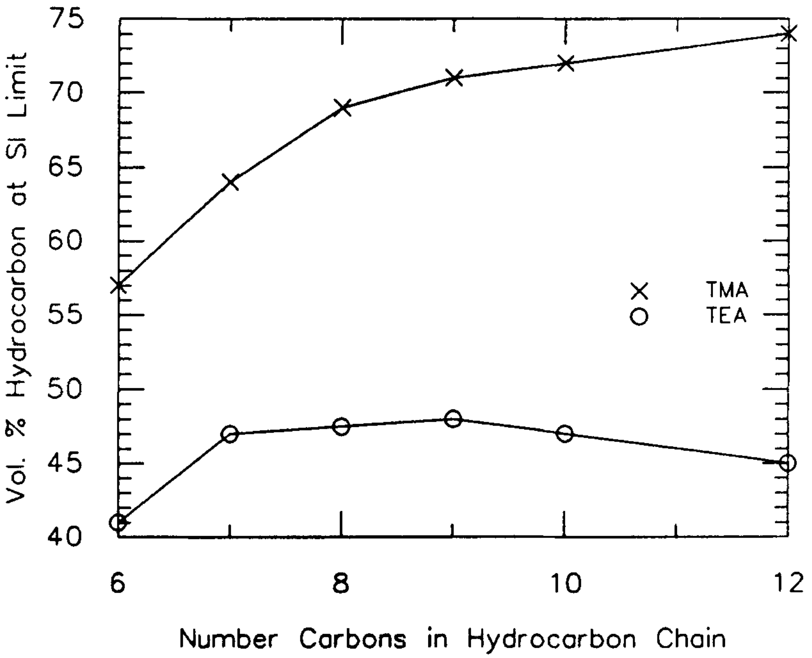

FIGURE 2
Hydrocarbon numbers (vol. %) for TEA (lower) and TMA (upper) at 20°C.

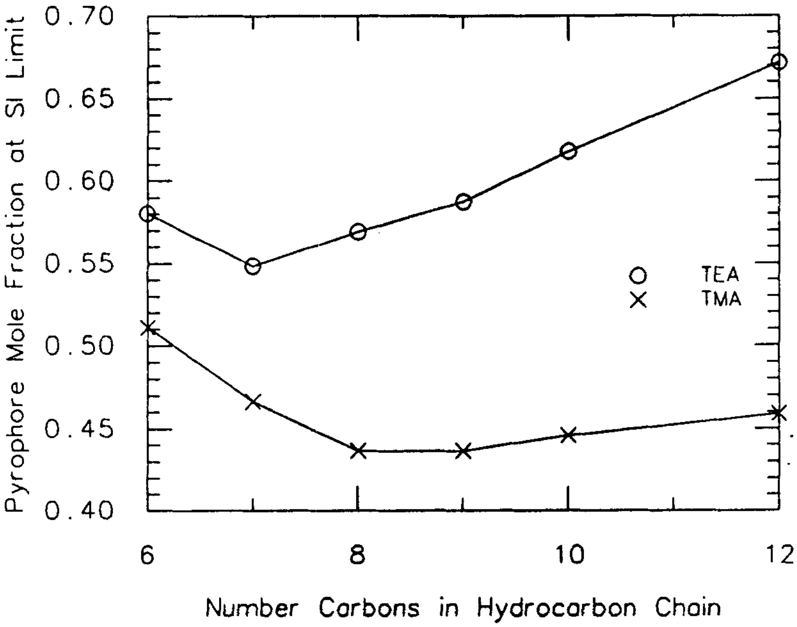

FIGURE 3

Pyrophoric mole fractions at SI limits for TEA (upper) and TMA (lower) in hydrocarbons at 20°C.

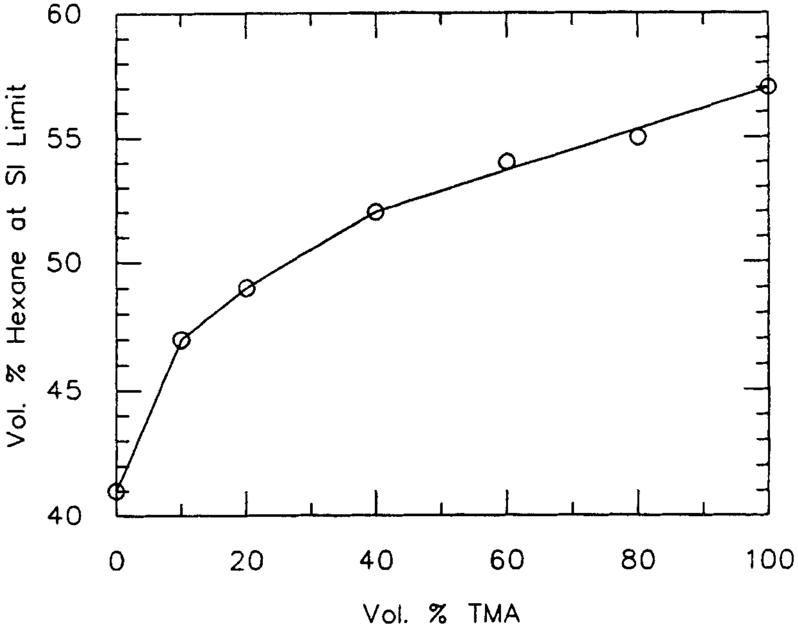

FIGURE 4
Hexane numbers of TMA/TEA mixtures at 20°C.