



ELSEVIER

Journal of Hazardous Materials 59 (1998) 145–157

**JOURNAL OF
HAZARDOUS
MATERIALS**

Alternative cooling fluids for use in nitration vessels

Anthony J. Bellamy^{*}, Lik-Kwang Chung¹, Andrew E. Talbot

Environmental and Chemical Systems Department, School of Engineering and Applied Science, Royal Military College of Science, Cranfield University, Shrivenham, Swindon, Wilts SN6 8LA, UK

Received 10 July 1997; received in revised form 6 August 1997; accepted 22 September 1997

Abstract

Accident reports have shown that some secondary cooling fluids are extremely dangerous if they accidentally come into contact with mixed-acid nitrating acids. A selection of water-based potential heat exchange fluids has been tested by mixing with typical nitrating acids and compared with the effects produced by adding water alone. In contrast with the explosive effects produced when methanol/water and ethanediol/water are allowed to mix with mixed acids, three aqueous inorganic solutions—magnesium nitrate, iron(III) nitrate and phosphoric acid—were found to interact much less exothermically, even less than is observed on adding the same amount of water that these solutions contain. In addition, they do not generate unstable by-products, cf. the nitrate esters formed from alcohol-based fluids, and possess the other properties required for a good secondary cooling fluid. The replacement of the currently used, hazardous cooling fluids by these alternatives is advocated. © 1998 Elsevier Science B.V.

Keywords: Nitrating acid; Cooling fluid; Accidental mixing

1. Introduction

The cause of several serious accidents encountered in the manufacture of nitroglycerine has been attributed [1] to accidental mixing of the nitrating acid with the secondary cooling fluid in the heat exchanger. The cooling fluids in use in these cases were either

^{*} Corresponding author.

¹ Present address: ASD/DMO, 1 Depot Road, #18-05, Defence Technology Towers, Tower A, Singapore 109679.

water, 'brine', or methanol/water, all of which are expected to react violently with a nitrating acid. Apart from heat generated by dilution of the acids, the other components in the cooling fluid may react chemically with the nitrating acid to produce other hazards, e.g. oxidation of chloride ion to chlorine gas in a 'brine', or nitration of methanol in a methanol/water system. Since the potential for damage in such an accidental mixing should be minimised as far as possible, we have investigated and identified some possible replacement cooling fluids. Our results indicate that these would exhibit a much less vigorous reaction on accidental mixing with nitrating acids, while at the same time retaining many of the favourable properties of the presently used cooling fluids.

2. Experimental

The selection of suitable systems for study was made in reference to the International Critical Tables [2,3], choosing those aqueous solutions of inorganic and organic compounds that had freezing points at or below -20°C (see Table 1). Nitrate salts appeared to be attractive since their use would not introduce an additional anion into the mixture formed by accidental mixing of the cooling fluid with a mixed acid nitrating mixture; the use of sulphates was ruled out by their low solubility.

The potential cooling fluids were first screened for their interaction with typical nitrating acids, viz. 50 wt.% HNO_3 , 50 wt.% H_2SO_4 (nitrating acid A) representing the nitrating acid used in the nitration of glycerine by the Biazzini process [4], and 30 wt.% HNO_3 , 60 wt.% H_2SO_4 , 10 wt.% H_2O (nitrating acid B) representing the nitrating acid used in the nitration of glycerine by the Nilssen and Brunnberg injector process [5]. The acids were prepared by mixing appropriate quantities of 99.5% HNO_3 , 98% H_2SO_4 and

Table 1
Freezing points of some potential cooling fluids [2]

Solution composition (wt.%)	m^a (mol kg^{-1})	K_f^b (K kg mol^{-1})	Freezing point ^c ($^{\circ}\text{C}$)
$\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (25/75)	10.4	2.0	-20.8
$\text{HOCH}_2\text{CH}_2\text{OH}/\text{H}_2\text{O}$ (40/60)	10.75	2.23	-24.5
$\text{Mg}(\text{NO}_3)_2/\text{H}_2\text{O}$ (31/69)	3.0	7.85	-23.6
$\text{Ca}(\text{NO}_3)_2/\text{H}_2\text{O}$ (40/60)	4.1	5.73	-23.5
$\text{Fe}(\text{NO}_3)_3/\text{H}_2\text{O}$ (29/71)	1.71	13.0	-22.2
$\text{NaCl}/\text{H}_2\text{O}$ (23/77)	5.1	4.06	-20.7
$\text{MgCl}_2/\text{H}_2\text{O}$ (16/84)	2.0	8.8	-17.6
$\text{CaCl}_2/\text{H}_2\text{O}$ (25/75)	3.0	9.33	-28.0
$\text{CH}_3\text{COOK}/\text{H}_2\text{O}$ (30/70)	4.37	5.15	-22.5
$\text{CH}_3\text{COOH}/\text{H}_2\text{O}$ (52/48)	18.0	1.2	-21.6
$\text{H}_3\text{PO}_4/\text{H}_2\text{O}$ (41/59)	7.1	3.5	-24.9

^a m = molality (g mol kg^{-1} water) e.g., $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (25/75) \equiv 333 g methanol/1000 g water = 333/32 g mol kg^{-1} water = 10.4m.

^b Cryoscopic constant (molal freezing point depression constant).

^c Freezing point = $0 - (m \times K_f)^{\circ}\text{C}$.

30% oleum. A known weight of fluid to be tested (20 g in the preliminary study; this was extended to include 5, 10, 15 and 25 g for the extended study of promising fluids) was added rapidly (< 5 s) from a dropping funnel to 100 g of stirred nitrating acid contained in an insulated 250 ml round-bottomed flask. Before mixing, both liquids

Table 2
Addition of potential cooling fluid to nitrating acid A (100 g)

Solution composition (wt.%)	Weight added (g)	Weight H ₂ O added (g)	Temperature rise (°C)	Observations
H ₂ O (100)	5.0	5.0	22.0	
H ₂ O (100)	10.0	10.0	39.5	
H ₂ O (100)	12.5	12.5	45.0	
H ₂ O (100)	15.0	15.0	57.0	
H ₂ O (100)	20.0	20.0	66.0	
CH ₃ OH/H ₂ O (25/75)	5.0	3.8	22.5	
CH ₃ OH/H ₂ O (25/75)	10.0	7.5	39.5	
CH ₃ OH/H ₂ O (25/75)	15.0	11.3	52.5	Vigorous boiling
CH ₃ OH/H ₂ O (25/75)	20.0	15.0	54.0	Vigorous boiling; upper product phase formed
HOCH ₂ CH ₂ OH/H ₂ O (40/60)	5.0	3.0	22.0	Lower product phase formed
HOCH ₂ CH ₂ OH/H ₂ O (40/60)	10.0	6.0	42.0	Lower product phase formed
HOCH ₂ CH ₂ OH/H ₂ O (40/60)	15.0	9.0	61.5	Lower product phase formed
HOCH ₂ CH ₂ OH/H ₂ O (40/60)	20.0	12.0	80+	Extremely vigorous reaction
Mg(NO ₃) ₂ /H ₂ O (31/69)	5.0	3.5	13.5	White precipitate
Mg(NO ₃) ₂ /H ₂ O (31/69)	10.0	6.9	26.0	White precipitate
Mg(NO ₃) ₂ /H ₂ O (31/69)	15.0	10.4	39.0	White precipitate
Mg(NO ₃) ₂ /H ₂ O (31/69)	20.0	13.8	48.5	White precipitate
Mg(NO ₃) ₂ /H ₂ O (31/69)	25.0	17.3	57.5	White precipitate
Ca(NO ₃) ₂ /H ₂ O (40/60)	20.0	12.1	44.5	White precipitate
Ca(NO ₃) ₂ /NaNO ₃ /H ₂ O (40/10/50)	20.0	10.0	37.0	White precipitate
Fe(NO ₃) ₃ /H ₂ O (29/71)	5.0	3.6	13.0	Cream precipitate (mechanical stirring required)
Fe(NO ₃) ₃ /H ₂ O (29/71)	10.0	7.2	28.5	Cream precipitate (mechanical stirring required)
Fe(NO ₃) ₃ /H ₂ O (29/71)	15.0	10.7	36.5, 37.0	Cream precipitate (mechanical stirring required)
Fe(NO ₃) ₃ /H ₂ O (29/71)	20.0	14.3	44.0	Cream precipitate (mechanical stirring required)
Fe(NO ₃) ₃ /H ₂ O (29/71)	25.0	17.9	56.5	Cream precipitate (mechanical stirring required)
CH ₃ COOK/H ₂ O (30/70)	20.0	14.0	68.0	
CH ₃ COOH/H ₂ O (52/48)	20.0	9.6	46.5	
H ₃ PO ₄ /H ₂ O (41/59)	5.0	3.0	11.0	
H ₃ PO ₄ /H ₂ O (41/59)	10.0	5.9	21.0	
H ₃ PO ₄ /H ₂ O (41/59)	15.0	8.9	31.5	
H ₃ PO ₄ /H ₂ O (41/59)	20.0	11.9	39.0	
H ₃ PO ₄ /H ₂ O (41/59)	25.0	14.8	46.0	

were at room temperature. The flask was fitted with a condenser, a temperature sensor, and a magnetic stirring bar. The temperature rise on mixing was recorded automatically. In all cases, red fumes were liberated on mixing. Pertinent observations, e.g. gas evolution, solids formation, etc. were recorded (see Tables 2 and 3). In those experiments, where a thick precipitate was formed on mixing [e.g. with $\text{Fe}(\text{NO}_3)_3$], a mechanical stirrer was used. When the experiment was complete, the contents of the

Table 3
Addition of potential cooling fluid to nitrating acid B (100 g)

Solution composition (wt.%)	Weight added (g)	Weight H_2O added (g)	Temperature rise ($^\circ\text{C}$)	Observations
H_2O (100)	5.0	5.0	18.0	
H_2O (100)	10.0	10.0	32.5	
H_2O (100)	12.1	12.1	38.0	
H_2O (100)	15.0	15.0	43.5	
H_2O (100)	20.0	20.0	48.5	
$\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (25/75)	20.0	15.1	46.5	Vigorous boiling; upper product phase formed
$\text{HOCH}_2\text{CH}_2\text{OH}/\text{H}_2\text{O}$ (40/60)	5.0	3.0	22.5	Lower product phase formed
$\text{HOCH}_2\text{CH}_2\text{OH}/\text{H}_2\text{O}$ (40/60)	10.0	6.0	39.5	Lower product phase formed
$\text{HOCH}_2\text{CH}_2\text{OH}/\text{H}_2\text{O}$ (40/60)	15.0	9.0	80+	Apparatus blown apart
$\text{HOCH}_2\text{CH}_2\text{OH}/\text{H}_2\text{O}$ (40/60)	20.0	12.0	80+	Apparatus blown apart
$\text{Mg}(\text{NO}_3)_2/\text{H}_2\text{O}$ (31/69)	5.0	3.5	9.5	White precipitate
$\text{Mg}(\text{NO}_3)_2/\text{H}_2\text{O}$ (31/69)	10.0	6.9	21.5	White precipitate
$\text{Mg}(\text{NO}_3)_2/\text{H}_2\text{O}$ (31/69)	15.0	10.4	29.0	White precipitate
$\text{Mg}(\text{NO}_3)_2/\text{H}_2\text{O}$ (31/69)	20.0	13.8	36.0	White precipitate
$\text{Mg}(\text{NO}_3)_2/\text{H}_2\text{O}$ (31/69)	25.0	17.3	38.0	White precipitate
$\text{Ca}(\text{NO}_3)_2/\text{H}_2\text{O}$ (40/60)	20.0	12.1	34.5	White gelatinous precipitate
$\text{Ca}(\text{NO}_3)_2/\text{NaNO}_3/\text{H}_2\text{O}$ (40/10/50)	20.0	10.0	31.5	White precipitate; less vigorous than $\text{Ca}(\text{NO}_3)_2$ alone
$\text{Fe}(\text{NO}_3)_3/\text{H}_2\text{O}$ (29/71)	20.0	14.3	37.0	Cream precipitate (mechanical stirring required); brown gas
$\text{NaCl}/\text{H}_2\text{O}$ (23/77)	20.0	15.4	39.0	Chlorine evolution
$\text{MgCl}_2/\text{H}_2\text{O}$ (16/84)	20.0	16.8	44.5	Chlorine evolution, but less vigorous than NaCl and CaCl_2
$\text{CaCl}_2/\text{H}_2\text{O}$ (25/75)	20.0	15.0	41.5	Cream precipitate; chlorine evolution
$\text{CH}_3\text{COOK}/\text{H}_2\text{O}$ (30/70)	20.0	14.0	52.5	
$\text{CH}_3\text{COOK}/\text{H}_2\text{O}$ (50/50)	20.0	10.0	58.5	
$\text{CH}_3\text{COOH}/\text{H}_2\text{O}$ (52/48)	20.0	9.6	36.0	
$\text{H}_3\text{PO}_4/\text{H}_2\text{O}$ (41/59)	10.0	5.9	19.0	
$\text{H}_3\text{PO}_4/\text{H}_2\text{O}$ (41/59)	15.0	8.9	26.0	
$\text{H}_3\text{PO}_4/\text{H}_2\text{O}$ (41/59)	20.0	11.9	30.5, 30.0, 30.0	
$\text{H}_3\text{PO}_4/\text{H}_2\text{O}$ (41/59)	22.5	13.3	34.0	
$\text{H}_3\text{PO}_4/\text{H}_2\text{O}$ (41/59)	25.0	14.8	34.0	

flask were poured onto ice and disposed of; in the experiments with methanol and ethanediol, when an alkyl nitrate was formed, the product layer was dissolved in dichloromethane and hydrolysed with aqueous sodium carbonate before disposal. For comparison, water (5–25 g), methanol/water (25/75), and ethanediol/water (40/60), were also mixed with the nitrating acids.

To assess the adequacy of the flask's insulation, control experiments were performed in which water (20 g) was added to nitration mixture A (100 g) at different rates. Addition times of 2.5 s, 22.3 s and 335 s gave maximum temperature rises of 66, 65 and 62°C, respectively, indicating that heat losses from the mixing flask during the timescale of a normal addition (< 5 s addition time) did not affect the measurement of the maximum temperature.

Calorimetric, viscosity and corrosion measurements are outlined in Appendix A.

3. Results and discussion

The preliminary results are best analysed with reference to the control curves (Fig. 1) showing temperature rise plotted against weight of water added, when pure water is added to the nitrating acid. If the temperature rise for each of the potential cooling fluids is then plotted with the corresponding control curve (Figs. 2 and 3) using the weight of water in the sample added (Tables 4 and 5), one can readily see how a given fluid sample compares with an equivalent weight of water. Any deviation from the 'water line' must be due to the non-aqueous components of the fluid, and reflects the interaction of those components with the nitrating acid (see column 5, Tables 4 and 5).

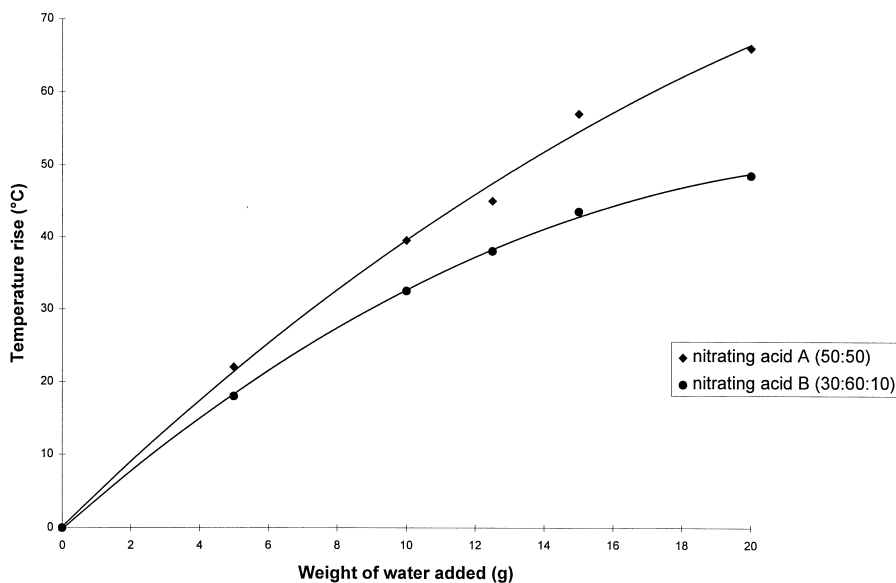


Fig. 1. Water control curves.

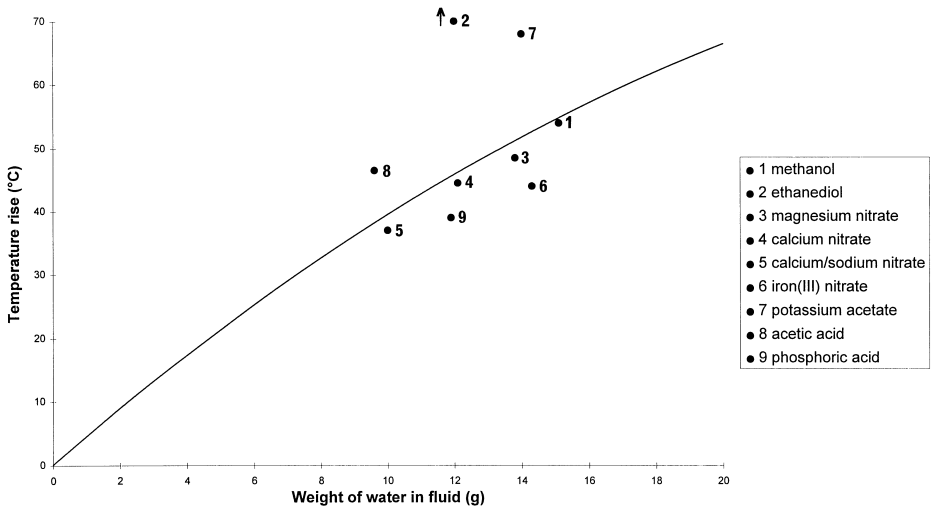


Fig. 2. Temperature rise on addition of 20 g fluid to nitrating acid A (100 g).

Some of the points lie close to the ‘water line’, and therefore represent ‘thermally-neutral’ solutes, viz. calcium nitrate, calcium nitrate/sodium nitrate, calcium chloride and magnesium chloride. Other points lie above the ‘water line’ and represent exothermically reacting solutes, viz. methanol (acid B only), ethanediol, acetic acid and potassium acetate, while others lie below the ‘water line’ and represent endothermically reacting solutes, viz. iron(III) nitrate, magnesium nitrate, phosphoric acid and sodium chloride. Clearly, fluids that produce points lying above the ‘water line’ should be avoided as coolant fluids, while those that produce points lying below the ‘water line’ appear more

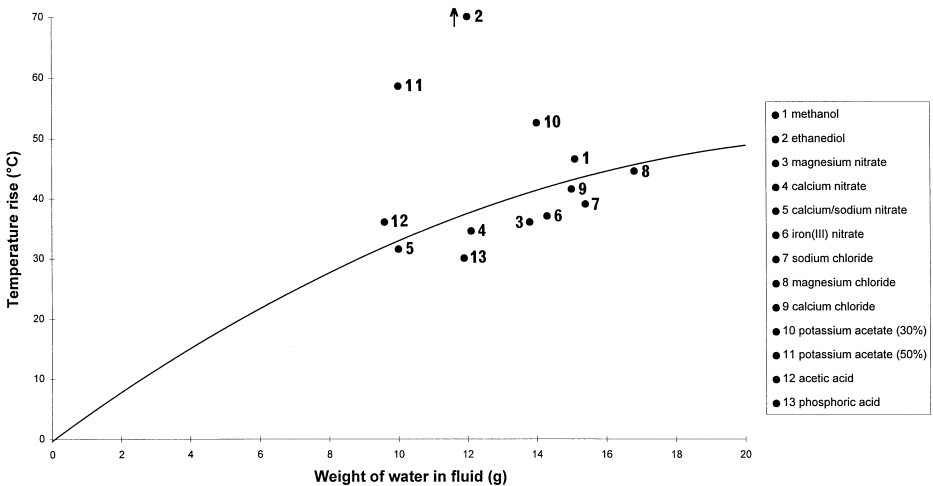


Fig. 3. Temperature rise on addition of 20 g fluid to nitrating acid B (100 g).

Table 4

Relative heating (vs. water) on addition of potential cooling fluid (20 g) to nitrating acid A (100 g)

Solution composition (wt.%)	Weight H ₂ O added (g)	Temperature rise observed (°C)	Equivalent temperature rise based on water content (°C)	Difference (°C) in temperature rise
H ₂ O (100)	20.0	66.0	66.0	–
CH ₃ OH/H ₂ O (25/75)	15.1	54.0	54.8	–0.8
HOCH ₂ CH ₂ OH/H ₂ O (40/60)	12.0	80+	45.9	> +34.1
Mg(NO ₃) ₂ /H ₂ O (31/69)	13.8	48.5	51.2	–2.7
Ca(NO ₃) ₂ /H ₂ O (40/60)	12.1	44.5	46.2	–1.7
Ca(NO ₃) ₂ /NaNO ₃ /H ₂ O (40/10/50)	10.0	37.0	39.5	–2.5
Fe(NO ₃) ₃ /H ₂ O (29/71)	14.3	44.0	52.6	–8.6
CH ₃ COOK/H ₂ O (30/70)	14.0	68.0	51.8	+16.2
CH ₃ COOH/H ₂ O (52/48)	9.6	46.5	38.2	+8.3
H ₃ PO ₄ /H ₂ O (41/59)	11.9	39.0	45.6	–6.6

attractive as coolant fluids since they are likely to minimise the effects of accidental mixing with a nitrating acid. Interestingly, ethanediol/water, a commonly used cooling fluid, gave a point above the ‘water line’. All fluids containing chloride ions exhibited chlorine evolution, an added hazard. The experiments with salts of calcium, iron(III) and magnesium gave precipitates, presumably of the corresponding sulphates.

Table 5

Relative heating (vs. water) on addition of potential cooling fluid (20 g) to nitrating acid B (100 g)

Solution composition (wt.%)	Weight H ₂ O added (g)	Temperature rise observed (°C)	Equivalent temperature rise based on water content (°C)	Difference (°C) in temperature rise
H ₂ O (100)	20.0	48.5	48.5	–
CH ₃ OH/H ₂ O (25/75)	15.1	46.5	43.5	+3.0
HOCH ₂ CH ₂ OH/H ₂ O (40/60)	12.0	80+	37.2	> +42.8
Mg(NO ₃) ₂ /H ₂ O (31/69)	13.8	36.0	41.6	–5.6
Ca(NO ₃) ₂ /H ₂ O (40/60)	12.1	34.5	35.9	–1.4
Ca(NO ₃) ₂ /NaNO ₃ /H ₂ O (40/10/50)	10.0	31.5	32.8	–1.3
Fe(NO ₃) ₃ /H ₂ O (29/71)	14.3	37.0	42.4	–5.4
NaCl/H ₂ O (23/77)	15.4	39.0	44.1	–5.1
MgCl ₂ /H ₂ O (16/84)	16.8	44.5	45.6	–1.1
CaCl ₂ /H ₂ O (25/75)	15.0	41.5	43.5	–2.0
CH ₃ COOK/H ₂ O (30/70)	14.0	52.5	41.9	+10.6
CH ₃ COOK/H ₂ O (50/50)	10.0	58.5	32.5	+26.0
CH ₃ COOH/H ₂ O (52/48)	9.6	36.0	31.1	+4.9
H ₃ PO ₄ /H ₂ O (41/59)	11.9	30.5, 30.0, 30.0	36.9	–6.4

The causes of the deviations from the 'water line' are assumed to be associated with the particular chemistry of the species involved. An exothermic interaction is probably associated with the heat of nitration in cases of methanol and ethanediol, and with the heat of protonation of the conjugate base of a weak acid in the case of potassium acetate, while an endothermic interaction is probably associated with the heat of protonation of the conjugate base of a moderately strong acid in the case of phosphoric acid, and with the heat of precipitation of sulphates in cases of calcium, magnesium, and iron(III) salts.

3.1. Extended study of promising cooling fluids

The adverse effects observed with a number of the potential cooling fluids, viz. exothermic interaction and chlorine generation, caused these solutions to be excluded from further investigation. Those selected for further study were the nitrates of magnesium and iron(III), and phosphoric acid. Water, methanol/water, and ethanediol/water, were also included for comparison. The temperature rise observed on mixing the selected fluids with the nitrating acids was measured over the range 5–25 g fluid, and the rise was plotted against the weight of water present in the added fluid (see Figs. 4 and 5; data from Tables 2 and 3).

The curves for aqueous magnesium nitrate, iron(III) nitrate (acid A only) and phosphoric acid, all lay below the water curves over the complete range of weights added. The curves for ethanediol/water lay considerably above the water curves, with the 20 and 25 g additions causing an extremely exothermic reaction. In the case of nitrating acid B, the apparatus was blown apart on adding these quantities by the gas/vapour generation. On adding 20 g of ethanediol/water to nitrating acid A, the temperature rose rapidly from 19 to 97°C, remained at this temperature for approxi-

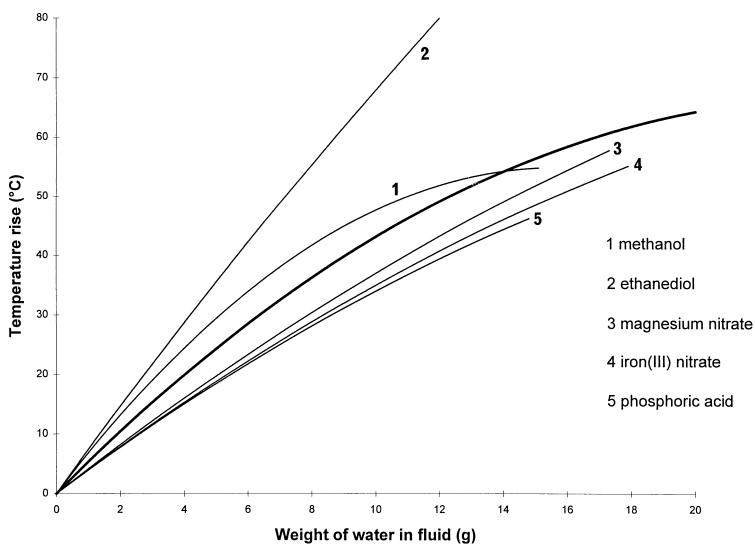


Fig. 4. Temperature rise on addition of 5–25 g fluid to nitrating acid A (100 g).

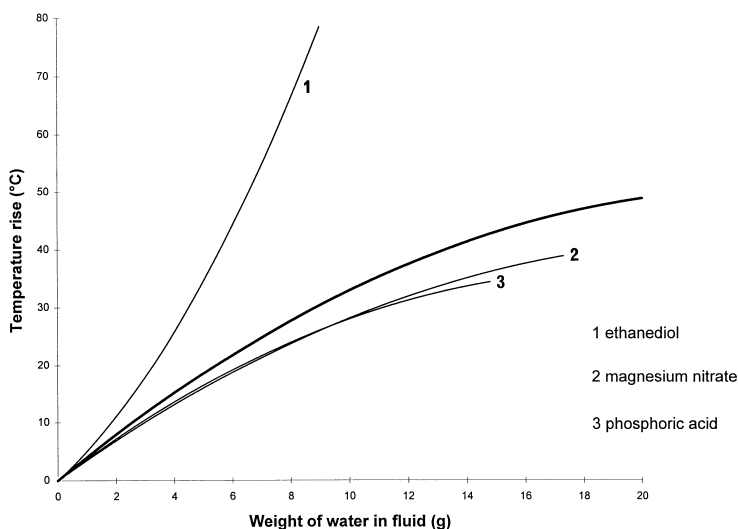


Fig. 5. Temperature rise on addition of 5–25 g fluid to nitrating acid B (100 g).

mately 30 s and then, with more vigorous reaction, rose to 137°C. With 5–15 g additions, a lower product layer, identified by GC–MS as the dinitrate of ethanediol, was formed.

Addition of methanol/water was only studied in detail for nitrating acid A. The curve lay well above the water curve for additions 5–15 g but then dropped below the water curve for the 20 g addition. In fact, the temperature rises observed for the 15 and 20 g additions were almost the same, suggesting that the boiling point of methanol was holding the temperature down. An upper product layer was only observed with the 20 g addition (also with nitrating acid B).

3.2. Relating the heat evolved to the temperature rise

Heat of dilution data for mixtures of HNO_3 , H_2SO_4 and H_2O were available from Ref. [6] and these were used to relate the heat evolved to the temperature rise. While data for compositions in which the HNO_3 : H_2SO_4 ratio was 1.0 (relating to nitrating acid A and additions of water to it) are given in Ref. [6], the data closest to nitrating acid B ($\text{HNO}_3/\text{H}_2\text{SO}_4 = 30/60 = 0.5$) was for $\text{HNO}_3/\text{H}_2\text{SO}_4 = 34.7/65.3 = 0.53$. However, this was considered to be sufficiently close for the present purpose.

Using curves constructed from the published data [6], the heats of dilution for the various $\text{HNO}_3/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ mixtures formed by adding 5–25 g H_2O to nitrating acids A and B were calculated. The differences between the heats of dilution for each resultant mixture and those of the original nitrating acid were then used to calculate the heat evolved on adding a given amount of water to 100 g of nitrating acid (A or B), leading to Fig. 6 that shows heat evolved on water addition plotted against the weight of water added for the two nitrating acids. Finally, the heat evolved was plotted against the

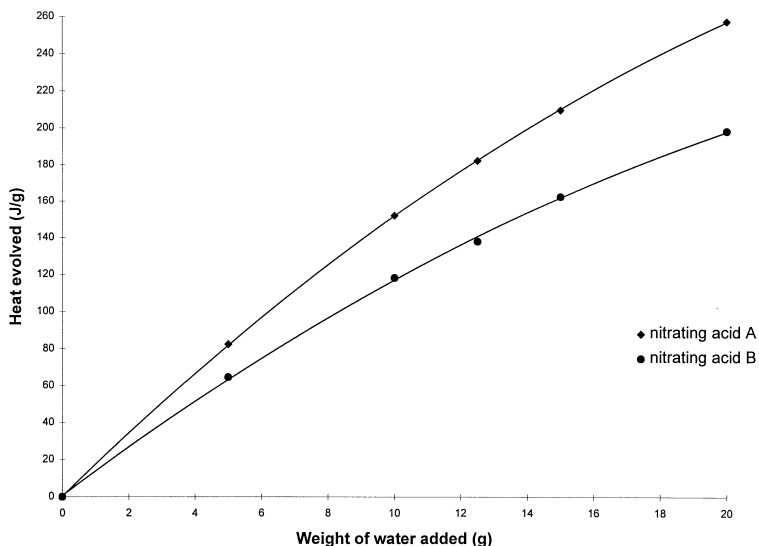


Fig. 6. Calculated heat evolved on adding water to nitrating acids A and B (100 g).

observed temperature rises. Both nitrating acids gave linear correlations that were almost coincident (slopes within 1%, see Fig. 7). The slope of the correlation indicates that 3.85 J g^{-1} nitrating acid is evolved for each temperature rise of 1°C , regardless of the composition of the nitrating acid.

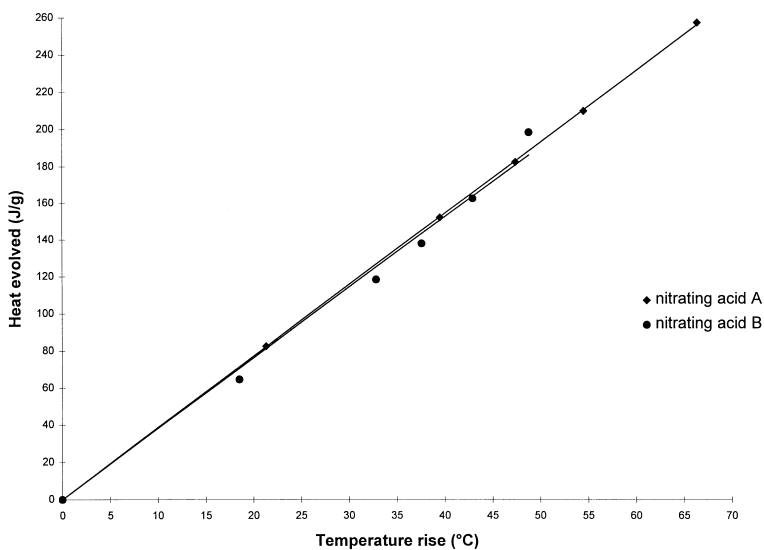


Fig. 7. Heat evolved vs. temperature rise on adding water to nitrating acids A and B.

Table 6
Melting point and specific heat of potential cooling fluids

Solution composition (wt.%)	Melting onset (°C) (lit. ref. freezing point)	Specific heat ($\text{J g}^{-1} \text{K}^{-1}$) in the range -17 to 0°C
H_2O (100)	0.0	4.21 (liquid at 0°C)
$\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (25/75)	-28.0 (-20.0)	3.73–3.97
$\text{HOCH}_2\text{CH}_2\text{OH}/\text{H}_2\text{O}$ (40/60)	-34.0 (-14.8)	2.80–3.13
$\text{Mg}(\text{NO}_3)_2/\text{H}_2\text{O}$ (31/69)	-32.1 (-23.5)	2.65–2.94
$\text{Fe}(\text{NO}_3)_3/\text{H}_2\text{O}$ (29/71)	-24.0 (-21.5)	2.64–2.85
$\text{H}_3\text{PO}_4/\text{H}_2\text{O}$ (41/59)	-34.0 (-27.9)	2.52–2.67

3.3. Other relevant properties of potential cooling fluids

Other important properties required of a potential cooling fluid are low freezing point, high specific heat, low viscosity at low temperature, and corrosion free use. These properties were measured (see Appendix A) for the three most promising potential cooling fluids, aqueous iron(III) nitrate, magnesium nitrate and phosphoric acid, as well as for methanol/water and ethanediol/water.

To avoid supercooling effects that might be encountered in measuring the freezing point, the onset of melting of the frozen fluids was measured by differential scanning calorimetry (DSC). The results are tabulated, along with reported freezing points, in Table 6. Due to the changes in composition of the liquid phase that occur during freezing of aqueous solutions, the onset of melting is expected to be lower than the freezing point. The onset of melting and the freezing point for the three fluids were all below -20°C . The specific heats of the fluids in the range -17 to 0°C were also measured by DSC and are also given in Table 6. Their values were in the range 2.5–2.95, compared to 4.21 for water at 0°C , 3.73–3.97 for methanol/water (25/75), and 2.8–3.13 for ethanediol/water (40/60). In this respect, the three fluids are slightly inferior to the commonly used cooling fluids.

The viscosity of these fluids was measured, for convenience, at 0°C rather than at lower temperatures. The results are tabulated in Table 7. All three fluids had viscosities at 0°C , which were comparable to that of ethanediol/water (40/60), and slightly higher

Table 7
Viscosity of potential cooling fluids

Solution composition (wt.%)	Density (g cm^{-3})	Mean fall time (s)	Relative viscosity vs. water	Viscosity at 0°C (cP)
H_2O (100)	1.00	278	—	1.8
$\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (25/75)	0.96	584	2.0	3.6
$\text{HOCH}_2\text{CH}_2\text{OH}/\text{H}_2\text{O}$ (40/60)	1.05	792	3.0	5.4
$\text{Mg}(\text{NO}_3)_2/\text{H}_2\text{O}$ (31/69)	1.28	578	2.7	4.8
$\text{Fe}(\text{NO}_3)_3/\text{H}_2\text{O}$ (29/71)	1.26	712	3.2	5.8
$\text{H}_3\text{PO}_4/\text{H}_2\text{O}$ (41/59)	1.28	882	4.1	7.3

than methanol/water (25/75). In corrosion tests with 316 stainless steel, none of the three fluids appeared (visibly or by weight loss) to have corroded the surface of the metal after 3 months in the presence of air.

4. Conclusions

Experimental mixing results and accident reports [1] have shown that the currently used secondary cooling fluids methanol/water and ethanediol/water are extremely dangerous if they accidentally come into contact with mixed acid nitrating acids. In contrast, three aqueous inorganic solutions, magnesium nitrate, iron(III) nitrate and phosphoric acid, have been shown to interact with mixed acids significantly less exothermically, even less than is observed for the amount of water that these solutions contain. In addition, on mixing with nitrating acids, they do not generate unstable by-products such as the nitrate esters formed from alcohol-based cooling fluids. Furthermore, these new potential cooling fluids also possess the other properties required for a good secondary cooling fluid. While the use of these fluids instead of, for example, methanol/water, would be 25–40 times more expensive (per kg fluid), their use could drastically reduce the damage caused should accidental mixing with nitrating acids occur.

Acknowledgements

We thank Cranfield University for financial support.

Appendix Specific heat, viscosity and corrosion measurements

1. DSC measurements

A Mettler TA 4000 DSC system, incorporating a DSC 30 calorimeter and TC11 processor, was used. The fluid (about 20 mg) was sealed in an aluminium pan and cooled to -20°C (i.e. above the freezing point). The temperature was then increased at $5^{\circ}\text{C min}^{-1}$ to $+10^{\circ}\text{C}$. The specific heat over the range -17°C to 0°C was computed from the slope of the heat flow vs. temperature curve. The same sample was also cooled to below the temperature where complete freezing occurred, and then heated at $5^{\circ}\text{C min}^{-1}$ until melting had occurred. The onset temperature for melting was computed from the DSC curve.

2. Viscosity measurements

A suspended level (Ubbelohde) No. 1 viscometer was used in a water/ice bath at 0°C . The filled viscometer was allowed to equilibrate for at least 30 min before measurements were commenced. An average of at least three measurements was taken.

3. Corrosion experiments

316 Stainless steel in the form of 3.0×5.0 cm plates was used. Each plate was cleaned by washing with toluene, acetone and distilled water, and then dried in an oven. After weighing, the plate was immersed in the test liquid contained in a plastic bottle, which was then sealed. After 3 months, the plate was removed, washed with distilled water, dried and re-weighed.

References

- [1] G.S. Biasutti, *History of Accidents in the Explosives Industry*, 1985.
- [2] E.W. Washburn (Ed.), *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*, Natl. Res. Council of USA, Freezing Points, Vol. 4, 1928.
- [3] E.W. Washburn (Ed.), *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*, Natl. Res. Council of USA, Viscosity, Vol. 5, 1929.
- [4] T. Urbanski, *Chemistry and Technology of Explosives*, Vol. 2, Pergamon, 1964, p. 107.
- [5] T. Urbanski, *Chemistry and Technology of Explosives*, Vol. 2, Pergamon, 1964, p. 114.
- [6] F.E. Rhodes, C.C. Nelson, *Ind. Eng. Chem.* 30 (1938) 648.